Ralph Thorpe

GEOLOGICAL
SURVEY
OF
CANADA

DEPARTMENT OF ENERGY,
MINES AND RESOURCES

BULLETIN 160

# THE GEOCHEMISTRY OF SILVER AND ITS DEPOSITS

## with notes on geochemical prospecting for the element

R. W. Boyle

Price, $6.50

1968

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1,450—1967—5586

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Set in Times Roman with
20th Century captions by
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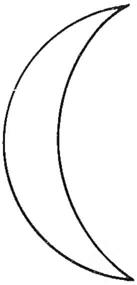
Artwork by CARTOGRAPHIC UNIT, GSC



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**Upper:** Silver medallion struck to commemorate the 400th anniversary of the discovery of silver by Juan de Tolosa at Zacatecas, Mexico, in the year 1546.

**Lower:** Silver medallion struck to commemorate the 60th anniversary of the discovery of silver at Cobalt, Ontario, in the year 1903. According to legend Fred LaRose, a blacksmith employed by the Temiskaming and Northern Ontario Railway, threw his hammer at an inquisitive fox, missed it, but broke off a piece of native silver from the vein that bears his name.

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By
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Available by mail from the Queen's Printer, Ottawa,
from Geological Survey of Canada,
601 Booth St., Ottawa,
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Price $6.50 Catalogue No. M42-160

*Price subject to change without notice*

ROGER DUHAMEL, F.R.S.C.
Queen's Printer and Controller of Stationery
Ottawa, Canada
1968

# PREFACE

Silver, one of the noble metals, has been utilized by man for more than five thousand years, first in artistic objects, jewellery, and coinage, and more recently in industry and the arts. Despite the great commercial and artistic value of silver little is actually known about the geochemistry of the element.

The author here presents a comprehensive compilation of the geochemistry of silver, partly from his own research, which has extended over ten years, and partly from the literature. He describes the principal types of silver deposits and discusses their origin. The data here presented, in addition to being a fundamental contribution to the geochemistry of silver, will be found useful to those interested in geochemical prospecting for the element.

Y. O. FORTIER,
*Director, Geological Survey of Canada*

OTTAWA, March 15, 1966

## BULLETIN 160 — Die Geochemie des Silbers und seiner Ablagerungen.

Von R. W. Boyle

Diese umfassende Zusammenstellung über die Geochemie des Silbers enthält auch eine Beschreibung der sechs Hauptarten der Silberablagerungen, eine Erörterung ihrer Herkunft und Angaben über die geochemische Suche nach Silber.

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## БЮЛЛЕТЕНЬ 160 — Геохимия серебра и его залежей.

Р. В. Бойл

Эта работа является исчерпывающей сводкой данных по геохимии серебра. Она включает описание шести главных типов залежей серебра, анализ их происхождения и справку о геохимической разведке серебра.

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# THE GEOCHEMISTRY OF SILVER AND ITS DEPOSITS

## with notes on geochemical prospecting for the element

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### *Abstract*

Silver is a member of Group IB of the periodic table, which includes copper, silver, and gold. In its chemical reactions silver resembles copper in some respects and gold in others. The principal oxidation state of silver is +1, and its stable ion in natural aqueous environments is $Ag^+$. The naturally occurring isotopes of the element are $Ag^{107}$ and $Ag^{109}$. No substantiated variation in the $Ag^{107}/Ag^{109}$ ratio has been observed in nature.

Silver occurs in the native state, as a constituent of various natural alloys, and in a great variety of minerals combined with sulphur, antimony, arsenic, tellurium, and selenium. The element also forms a number of halides and a basic sulphate in nature. The principal silver minerals are native silver, argentite, acanthite, argentian tetrahedrite and tennantite, proustite, pyrargyrite, chlorargyrite, and argentojarosite. All these minerals constitute ore minerals of the element, but the largest amount of silver is obtained from argentiferous galena.

The abundance of silver in the upper lithosphere is about 0.10 ppm. The average silver content of igneous type rocks in parts per million is ultrabasic rocks (0.08), gabbro (0.12), diabase (0.12), diorite (0.10), and granite (0.05). The average silver content of sedimentary rocks in parts per million is sandstone (0.08), normal shale (0.10), limestone (0.07), and anhydrite and gypsum (0.05). Certain varieties of graphitic shales, sulphide schists, phosphorites, and some types of sandstone, dolomites, and limestones may contain up to 1 ppm Ag or more.

The average silver content of soils is about 0.10 ppm, and the average for natural fresh waters is about 0.0002 ppm. Sea water contains 0.00025 ppm Ag. Silver is a trace constituent of many plants and animals. Certain coals are enriched in silver with 2 to 10 ppm Ag in the ash.

Silver is won mainly as a by-product from various types of gold, lead-zinc, and copper deposits. The native silver deposits are mined principally for the element. The following types of deposits can be distinguished:

1. Copper-silver shale deposits (Kupferschiefer type).
2. Disseminations in sandstones ('red bed' type).
3. Silver-bearing skarn type deposits.
4. Lodes, veins, etc. dominantly in sedimentary rocks.
5. Silver-gold and gold-silver veins in or associated with volcanic flows, tuffs, etc.
6. Silver deposits in a complex geological environment comprising sedimentary rocks, volcanic rocks, etc.

The oxidation processes in silver deposits are complex and depend essentially on the Eh and pH. Colloidal and coprecipitation phenomena also play a large part. Iron and manganese minerals and carbonates in the gangue and ore greatly influence the reactions that lead to the secondary enrichment of silver.

Practically all the geochemical methods of prospecting are applicable in the search for silver deposits. The most effective methods appear to be those based on the sampling of stream sediments and soils.

# *Résumé*

L'argent fait partie du groupe IB du tableau périodique, qui comprend le cuivre, l'argent et l'or. Dans ses réactions chimiques, l'argent est semblable au cuivre sous certains aspects et à l'or sous d'autres. Le principal état d'oxydation de l'argent est +1 et son ion stable dans les milieux aqueux naturels est $Ag^+$. Les isotopes naturels de cet élément sont $Ag^{107}$ et $Ag^{109}$. Aucune variation du rapport $Ag^{107}/Ag^{109}$ n'a été observée dans la nature.

L'argent se présente à l'état naturel comme élément constitutif de divers alliages naturels et, dans une grande variété de minéraux, il est combiné au soufre, à l'antimoine, à l'arsenic, au tellure et au sélénium. Il forme aussi un certain nombre de composés halogénés et de sulfates basiques dans la nature. Les principaux minéraux argentifères sont l'argent natif, l'argentite, l'acanthite, la tétraédrite et la tennantite argentifères, la proustite, la pyrargyrite, la chlorargyrite, et l'argentojarosite. Tous ces minéraux sont des minerais d'argent, mais la plus grande partie de l'argent est extraite de la galène argentifère.

La proportion d'argent dans la haute lithosphère est d'environ 0.11 ppm. La teneur moyenne en argent des roches ignées en ppm est de 0.08 pour les roches ultrabasiques, 0.12 pour le gabbro, 0.12 pour la diabase, 0.10 pour la diorite et 0.05 pour le granite. La teneur moyenne en argent des roches sédimentaires est de 0.08 ppm pour le grès, 0.10 pour le schiste normal, 0.07 pour le calcaire, 0.05 pour l'anhydrite et le gypse. Certaines variétés de schistes graphitiques, les schistes sulfureux, les phosphorites et quelques variétés de grès, de dolomies et de calcaires peuvent avoir une teneur en argent de 1 ppm ou plus.

La teneur moyenne en argent des sols est d'environ 0.10 ppm, celle des eaux douces naturelles, 0.0002 ppm et celle de l'eau de mer, 0.00025 ppm. L'argent existe à l'état de traces dans plusieurs plantes et animaux. Certaines cendres de charbon contiennent de 2 à 10 ppm d'argent.

L'argent est obtenu principalement comme sous-produit de l'exploitation de divers types de gîtes d'or, de plomb-zinc et de cuivre. Les gîtes d'argent natif sont exploités avant tout pour récupérer l'argent. On peut distinguer les types suivants de gîtes d'argent:

1. Gîtes de schistes cupro-argentifères (du type Kupferschiefer).
2. Dispersion dans les grès (du type «couche rouge»).
3. Gîtes argentifères du type skarn.
4. Veines, filons, etc., surtout dans les roches sédimentaires.
5. Veines d'argent-or et d'or-argent, associées aux coulées volcaniques, aux tufs, etc., ou en faisant partie intégrante.
6. Gîtes argentifères dans des milieux géologiques complexes, comprenant des roches sédimentaires, volcaniques, etc.

Les processus d'oxydation des gîtes d'argent sont complexes et dépendent essentiellement du pH et du Eh. L'action des colloïdes et le phénomène de coprécipitation jouent aussi un rôle important. Le fer, le manganèse et les carbonates, lorsqu'ils sont présents dans la gangue et le minerai, influencent fortement les réactions qui conduisent à l'enrichissement secondaire de l'argent.

On peut utiliser presque toutes les méthodes de prospection géochimique pour la recherche de gîtes d'argent. Les méthodes les plus efficaces semblent être celles qui sont fondées sur l'échantillonnage des sols et des sédiments fluviaux.

*"Surely there is a vein for the silver, and*
*a place for gold where they fine it"*
Job 28:1

## *Chapter I*

# INTRODUCTION

Research on the geochemistry of silver was begun by the writer some ten years ago and has continued at intermittent intervals in the field and laboratory since that time. The work is not yet complete, but it was thought that the present interest in the metal merited a report at this time.

## Historical Notes on Silver

The discovery of silver is lost in antiquity. Reference to the metal can be found in most ancient manuscripts, and silver ornaments and decorations have been found on the site of the Great Chaldean temple at Ur on the Euphrates, and in the tombs of the Pharaohs dating back as far as 4000 B.C. In the Code of Menes, who reigned in Egypt about 3500 B.C., it was decreed that "one part of gold is equal to two and one-half parts of silver in value." The metal was apparently common in Solomon's time for he says it was "nothing accounted of." The Phoenicians were familiar with silver and are supposed to have obtained it from mines in Armenia, Siphnos, Crete, Sardinia, and Spain. By 1000 B.C. it is probable that both silver and gold were used as coinage metals in all countries between the Indus and the Nile. Other uses mentioned in old manuscripts include the fabrication of idols, shrines, bowls, vases, flasks, and jewellery. The art and trade of the silversmith and minter have, therefore, come down to us from antiquity.

Native silver is a relatively rare mineral in the countries of the Middle East, and it seems probable that the bulk of the ancient silver was won by reduction of lead-silver sulphides followed by desilverization of the crude lead. Perhaps some silver may have come from the native metal in oxidized lead-silver deposits or from the

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reduction of the chloride. Some may also have been won from placers in the form of electrum. The river Pactolus in Lydia (the present Gediz), which flowed through the centre of Sardis into the Hermus, was rich in electrum and seems to have supplied much gold and silver to the ancient metal workers. Whatever its source and mode of production by the ancients, it is certain that by the time of the Greek civilization the process of desilverization of lead was well understood, since research in the old mining region of Laurion in Greece leaves little doubt that cupellation was extensively employed in the separation of silver from lead. The inhabitants of Troy II also knew of the cupellation process and could reduce the silver content of their lead down to 0.02 per cent.

The extraction of silver (and gold) from copper sulphides, arsenopyrite, etc., by the process of liquation[1] was probably also known to the ancients, as the Greeks seem to have been familiar with it and the Romans are known to have practised the art.

The Romans mined silver ores extensively in the metalliferous regions of their empire and advanced the art and science of the metallurgy of silver as well as that of other metals (Davies, 1935). According to Strabo in his *Geographia* written shortly before the Christian Era, "the (silver) ore (of Carthagena) was washed and sieved five times, fused with lead, and then cupelled for pure silver." Pliny the Elder in his *Historia naturalis*[2], written in the early years of our era, also mentions the cupellation of silver. The Romans were more adept at the cupellation of silver from lead than were the Greeks. Research on some of the Roman pigs shows that they could extract down to 0.01 and even to 0.002 per cent silver.

The process of 'parting' gold and silver by cementation with salt, whereby the silver is converted to chloride and the gold is run off, was apparently known in the sixth century B.C. Despite this knowledge, it is doubtful if much of the silver mentioned in old manuscripts came from the refining of native gold, since the gold of ancient placers and oxidized zones was probably very fine and would yield only a little silver when parted. Parting by means of acids was unknown to the Romans. As far as can be determined, the first reference to the parting of gold and silver by means of nitric acid is to be found in the treatises of the Moslem alchemists of the thirteenth century.

Later it was discovered that silver could be extracted from its ores by treatment with mercury in the presence of common salt and iron or copper salts, a method that evolved into the Patio process. Today silver is won from its ores by a number of processes, including cyanidation, smelting followed by desilverization of lead, and electrolysis.

The purity of ancient silver artifacts and coins varies widely, but there are certain systematic changes of composition with time that are of interest from an archaeological viewpoint (Caley, 1964). The silver from present day refineries is of

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[1] In the process of liquation the copper, arsenic, etc., ores were first smelted, often with a siliceous flux, to yield an impure ingot. This ingot was then alloyed with lead if there was insufficient lead in the ores, and the alloy was heated to a temperature between the melting point of lead and copper, during which the lead would liquate out, carrying the silver (and gold) with it. The lead was then cupelled on bone ash.

[2] *Historia naturalis*, Book XXXIII.

high purity, and the content of silver in modern coins, silverware, and jewellery is rigidly controlled.

Ancient silver mines are known in China, India, Iran, Sudan (Nubia), and Ethiopia. Those in Spain are mentioned in the Apocrypha, and the Grecian silver mines such as those at Laurion have had a long and interesting history, influencing in part the economics and politics of the Greek and Roman Empires. Silver was won from deposits in Armenia in Phoenician times, and it is said that the Celts mined silver from the famous Terezia vein in the Banská Štiavnica district of Central Slovakia, Czechoslovakia. In the famous silver belt of Central Europe silver mining began at Freiberg in Saxony in the twelfth century and at Příbram, Czechoslovakia, in the fourteenth century. The silver mines of Jáchymov (Joachimsthal), Czechoslovakia, were discovered in 1516. It was from the silver of these deposits that the *Joachimsthaler* was minted, from which comes our word 'dollar'.

Silver has played an important part in the history, politics, and economics of the Americas. It seems certain that the Incas and Aztecs mined silver long before the coming of the Spaniards. The silver mines of Charcas, Peru, were discovered by the Spaniards in 1535, those of Potosí, Bolivia, in 1544, those of Taxco, Mexico, in 1522, those of Zacatecas, Mexico, in 1546, and those of Guanajuato, Mexico, in 1550. In New Mexico, Arizona, and probably California, the Spaniards operated mines from which they obtained silver at least as far back as 1620. By contrast the silver mines in the northern part of the western United States, in western Canada, and at Cobalt, Ontario, are relatively young, having been discovered only in the last part of the last century and the early part of the present.

It seems probable that the Indians of the United States and Canada had little knowledge of silver beyond its use as ornaments. Rickard (1932) recorded the presence of native silver embedded in the copper knives and spearheads of the pre-Columbian Indians of the Ohio valley, and stated that copper beads and other ornaments were wrapped in native silver by the Indians of the Mississippi and Ohio valleys. Early explorers also record the fact that native silver was used as ornaments by the natives of Virginia. One can only speculate on the source of the silver used by the Indians of the eastern United States. As native silver is generally found with artifacts and ornaments of native copper, it seems probable that the source was the copper deposits of Michigan, where some native silver does occur. Rickard (quoting Grenville) said that in Virginia "the mountains and rivers yielded also white grains of metal, which is deemed silver."

placer Ag

The first reference to the occurrence of silver in Canada is in Jacques Cartier's account of his second voyage (1534-1536). At Hochelaga (Montreal) Cartier was told by the Indians that silver occurred up the Ottawa River. The source of this silver is unknown; it could have been the Cobalt area. Another early reference to silver in Canada is in Champlain's journal dated 1613 where mention is made of a Master Simon, a mining engineer, who discovered silver on St. Mary's Bay, Nova Scotia. The exact site of this discovery is not known, but it may have been the galena-calcite vein mentioned by Bailey at Mink Cove on Digby Neck (*Proc. N.S. Inst. Sci.*, vol. 2, 2nd ser. 1894-98, p. 76). A much later but accurate description of a silver-bearing vein in Canada is that in the diary of Sieur de Troyes, dated 1686, and on a map published in France in 1744. The location (Anse à la mine) is an argentiferous galena vein on the east shore of Lake Timiskaming some 8 miles southeast of Cobalt. This vein was rediscovered in 1850 and developed as the Wright mine, but produced only a few tons of ore (Barlow, 1899; Miller, 1913; Knight, 1924).

The name silver comes from the Anglo-Saxon *soelfor*, which is probably a corruption of the Germanic name *silber*. The etymology of silber is in doubt, but is thought to be a loanword from the Assyrian, *sarpu*. The ancient names for silver refer to its bright white colour—the Hebrew term is derived from the verb "to be white", and the Greek term from *argos* "to be shining", which seems to have come from the Aryan root *arg* or more specifically from the Sanskrit word *argenos*—clear. The Latin name *argentum* derives from the Greek and is still preserved in the symbol for the element, Ag, and in the name of its most common ion, viz., argentous. The alchemists, on account of its pure splendent lustre, early connected silver with the moon, giving it the crescent symbol of Diana. The most common salt of silver, the nitrate, is still sometimes referred to as lunar caustic (Latin, *luna*, the moon).

## Acknowledgments

Colleagues in the Geological Survey and students in Carleton University contributed various field and laboratory data on the geochemistry of silver. In particular, thanks are due W. H. Champ and W. F. White for the numerous spectrographic analyses they provided; J. Lynch, M. A. Jardine, and J. A. Maxwell for a variety of ancillary analytical data; and H. Steacy for the selection and preparation of pure minerals from the National Mineral Collection in which silver was determined. Critical field and analytical data were also provided by T. Presant on soils, by A. Y. Smith on sandstones and coal, and by S. S. Rajah on gossans.

Mrs. P. Grove and my wife did an excellent job of extracting from world literature the significant papers concerned with the chemistry and geochemistry of the element. S. C. Robinson and J. L. Jambor also provided data and discussion on the mineralogy of the silver minerals for which the writer is grateful. Thanks are also due to C. de Leuchtenberg who assisted greatly in the translation of a large number of foreign papers, and repeatedly brought to the writer's attention valuable information which otherwise would have gone unnoticed. Finally, the writer wishes to record his appreciation to all those geologists at various mines in many countries who kindly showed him the deposits with which they are so familiar.

A. G. Johnston prepared the metallogenic map for silver in Canada and also assisted in many other ways.

## Chapter II

# CHEMISTRY, MINERALOGY, AND GEOCHEMISTRY OF SILVER

## General Chemistry

Silver, Ag; at. no. 47; at. wt. 107.870; sp. gr. 10.49 (20°C); m.p. 960.8°C; Valence 1, 2, (3)

Silver is a member of Group IB of the periodic table, which includes copper (Cu), silver (Ag), and gold (Au). Except that the so-called "coinage metals" exhibit monovalency, there is little resemblance to the alkali metals of Group IA. As might be expected from electron orbital considerations, there is a similarity between Ni, Pd, and Pt and the corresponding elements of Group IB, namely Cu, Ag, and Au. Thus, palladium has only one electron less than silver, and since the energy differences are small in the electronic constitution of the two elements, the differences in the chemical behaviour of the two elements in some respects are slight. In natural environments, however, there appear to be no relationships between silver and palladium. ? There are certain similarities between silver and cadmium, the corresponding element in Group IIB of the periodic system. These are also indicated in nature, as silver and cadmium are associated in a variety of deposits, and a number of silver minerals often have higher than average contents of cadmium.

The energetic properties of silver, together with those of copper and gold, the two elements with which it is so often associated in nature, are given in Table 1. The thermodynamic properties of the element, its ions, and compounds are given in Table 2. Additional data can be found in the publications by Kelley (1960), and Wicks and Block (1963).

Silver is considered by some to be a transition element, although it does not fulfill the necessary electronic conditions[1] that characterize transition elements. Silver has a moderately high melting point (960.8°C) and the highest electrical and thermal conductivity of any metal. In the metallic form it is unaffected by water or by oxygen, but is blackened by ozone with the formation of the oxide AgO, and also by sulphur, hydrogen sulphide, and other sulphur compounds with the formation of

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[1] Strictly speaking, the transition elements are characterized by an inner *d* level, which is not filled to capacity, e.g., nickel. In silver the 4*d* orbital is completely filled.

TABLE 1 | *Energetic Properties of Copper, Silver, and Gold*

| Property | Copper | Silver | Gold |
|---|---|---|---|
| Outer electron configuration | $3d^{10}\,4s^1$ | $4d^{10}\,5s^1$ | $5d^{10}\,6s^1$ |
| Oxidation states (valence) | 1, 2, (3) | 1, 2, (3) | 1, 3. |
| Electronegativity Kilo-calories/gram-atom | $Cu^{+1}$ 177<br>$Cu^{+2}$ 235 | $Ag^{+1}$ 175 | $Au^{+1}$ 212 |
| Ionization potential (in volts) | $Cu^{+1}$ 7.723<br>$Cu^{+2}$ 20.28 | $Ag^{+1}$ 7.574<br>$Ag^{+2}$ 21.4 | $Au^{+1}$ 9.223<br>$Au^{+3}$ ~ 31.0 |
| Lattice energy coefficient | $Cu^{+1}$ 215<br>$Cu^{+2}$ 630 | $Ag^{+1}$ 180 | $Au^{+1}$ ~ 183 |
| Atomic radius, Å (Co-ordination in brackets) | 1.24 (8)<br>1.28 (12) | 1.40 (8)<br>1.44 (12) | 1.40 (8)<br>1.44 (12) |
| Ionic radius, Å (Co-ordination in brackets) | $Cu^{+1}$ 0.96 (6)<br>$Cu^{+1}$ 1.00 (8)<br>$Cu^{+2}$ 0.72 (6) | $Ag^{+1}$ 1.31 (8)<br>$Ag^{+1}$ 1.34 (10)<br>$Ag^{+2}$ 0.89 (6) | $Au^{+1}$ 1.46 (10)<br>$Au^{+1}$ 1.49 (12)<br>$Au^{+3}$ 0.85 (6) |
| Miscellaneous radii, Å | $Cu^{+1}$ (in fluorides) 1.00<br>$Cu^{+1}$ (in oxides) 1.05<br>$Cu^{+2}$ (in fluorides) 0.87<br>$Cu^{+2}$ (in oxides) 0.97<br>Cu (tetrahedral covalent) 1.35<br>$Cu^{+1}$ (hydrated) 1.7<br>$Cu^{+2}$ (hydrated) 3.5 | $Ag^{+1}$ (in fluoride) 1.33<br>$Ag^{+1}$ (in oxides) 1.35<br>Ag (tetrahedral covalent) 1.53<br>$Ag^{+1}$ (hydrated) 1.7 | $Au^{+1}$ (hydrated) 1.4 |
| Ionic potential, $\frac{Z}{r}$ | $Cu^{+1}$ 1.00<br>$Cu^{+2}$ 2.78 | $Ag^{+1}$ 0.76 | $Au^{+1}$ 0.68<br>$Au^{+3}$ 3.53 |

Sources: Szádeczky-Kardoss (1958); Green (1959)

$Ag_2S$. Nitric acid, fused alkalies, and potassium cyanide dissolve silver readily in the presence of air.

In its bivalent compounds, silver has the electronic configuration of $d^9$ - type (i.e., similar to bivalent copper) and shows a considerable degree of covalent character because of its relatively high ionization potential. In other compounds where it exhibits a monovalent character, e.g., AgCl, AgBr, and where its ionization potential is much lower, silver is moderately ionized in the crystals. In the +1 oxidation state silver ordinarily forms linear complexions with one *s* and one *p* orbital or tetrahedral arrangements with $sp^3$ orbitals; in the +2 and +3 oxidation states co-ordination complexes with $dsp^2$ orbitals, giving a square planar geometry, are stable.

Silver forms compounds in which it exhibits oxidation (valence) states, +1, +2, +3. The +1 valence state results from the removal of the single 5*s* electron. This is the most stable ionized state and in aqueous environments in nature is the only one possible. Ordinarily the 18 electron configuration (N shell, 4th quantum

TABLE 2 | *Thermodynamic Data on Silver*[1]

| Formula | Description | State | ΔH° | ΔF° | S° |
|---|---|---|---|---|---|
| Ag | Metal | c | 0.0 | 0.0 | 10.206 |
| $Ag^+$ | | aq | 25.31 | 18.430 | 17.67 |
| $Ag^{++}$ | | aq | | 64.1 | |
| $AgO^+$ | | aq | | 53.9 | |
| $AgO^-$ | | aq | | −5.49 | |
| $Ag_2O$ | | c | −7.306 | −2.586 | 29.09 |
| AgO | | c | −6.0 | 2.6 | |
| $Ag_2O_3$ | | c | | 20.8 | |
| AgF | | c | −48.5 | −44.2 | 20. |
| $AgF \cdot H_2O$ | | c | −120.4 | −101.8 | (27.4) |
| $AgF \cdot 4H_2O$ | | c | −331.5 | −268.6 | (45.9) |
| AgCl | | c | −30.362 | −26.224 | 22.97 |
| AgBr | | c | −23.78 | −22.930 | 25.60 |
| AgI | | c | −14.91 | −15.85 | 27.3 |
| $Ag_2S$ | α | c | −7.60 | −9.62 | 34.8 |
| $Ag_2S$ | β | c | −7.01 | −9.36 | 35.9 |
| $Ag_2SO_4$ | | c | −170.50 | −147.17 | 47.8 |
| $[Ag(S_2O_3)_2]^{3-}$ | | aq | −285.5 | −247.6 | |
| $Ag_2SeO_4$ | | c | −94.7 | −68.5 | 48.3 |
| $AgNO_3$ | | c | −29.43 | −7.69 | 33.68 |
| $Ag_2CO_3$ | | c | −120.97 | −104.48 | 40.0 |
| $Ag_2MoO_4$ | | c | | −196.4 | |
| $Ag_2WO_4$ | | c | | −206.0 | |
| $Ag_2CrO_4$ | | c | −176.2 | −154.7 | 51.8 |
| $[Ag(NH_3)_2]^+$ | | aq | −26.724 | −4.16 | 57.8 |

Source: Latimer (1952)

ΔH°—the standard heat of formation in kilo-calories of the substance or ion from its elements at 25°C

ΔF°—the standard free energy of formation in kilo-calories of the substance from its elements at 25°C

S°—the entropy of the substance or ion in cal/deg. in its thermodynamic reference state at the reference temperature of 25°C

c—crystalline

aq—in aqueous solutions

[1] Values in parentheses are estimated.

level) underlying the valence (i.e., 5*s*) orbital in an atom like silver is never broken into by the formation of chemical bonds; the *d* orbitals once completely filled, as in silver, are inert. However, in silver it is apparent that either the 18 electron configuration is not really complete, or it can lose electrons to the *s* and *p* orbitals of the 5th quantum level to form bonds. This is apparently what happens when silver exhibits valence states of +2 and +3 and when a mechanism of stabilizing these particular ions is present. In nature the +2 and +3 states are unstable in an aqueous medium, especially above 100°C, since they have oxidation potentials in excess of that required for the oxidation of water and hence are reduced to the monovalent state by water. The higher oxidation states are, however, stable in certain complex compounds and in very strong oxidizing solutions.

The potentials relating the oxidation states of silver as given by Latimer (1952) are:

*Acid solution*

$$\mathrm{Ag} \underset{-0.799}{\overline{\qquad\qquad}} \mathrm{Ag^{+}} \underset{-1.98}{\overline{\qquad\qquad}} \mathrm{Ag^{++}} \underset{\sim -2.1}{\overline{\qquad\qquad}} \mathrm{AgO^{+}}$$

*Basic solution*

$$\mathrm{Ag} \underset{-0.344}{\overline{\qquad\qquad}} \mathrm{Ag_2O} \underset{-0.57}{\overline{\qquad\qquad}} \mathrm{AgO} \underset{-0.74}{\overline{\qquad\qquad}} \mathrm{Ag_2O_3}$$

Crystallographically silver belongs to the gold group, which comprises gold, silver, copper, and lead. All of these metals are isometric, hexoctahedral—$4/m\ \bar{3}\ 2/m$, and have the copper-type structure with the atoms lying at the points of a face-centred cubic lattice. This structure conforms to the space group $Fm\ 3m$, and the unit cell contains 4 atoms. The cell edges for the four metals are as follows:

| | Cu | Au | Ag | Pb |
|---|---|---|---|---|
| $a_0$Å | 3.61496(18°C) | 4.07825(25°C) | 4.0862 | 4.9505 |

The atomic radius of silver is identical to that of gold (1.44 Å), a feature that permits a continuous alloy series with a minimum cell edge at about 20 per cent silver. There is much less similarity in the atomic radii of silver (1.44 Å) and copper (1.28 Å), and as a consequence relatively little solution of silver in native copper takes place. At 700°C, 5.5 per cent silver by weight dissolves in copper; at 500°C, 1.4 per cent; at 200°C, 0.1 per cent; and at 0°C, the two metals are nearly mutually insoluble (Owen and Rogers, 1935). Silver (and gold) form continuous alloy series with palladium, again because of the close similarity in their atomic radii, Ag (1.44 Å), Pd (1.37 Å).

The solubility of silver in lead is well known. The two metals form a simple eutectic at 304°C (2.5 per cent silver). The radii of the two metals, Ag (1.44 Å), Pb (1.74 Å), are significantly different, but there is apparently sufficient potential elasticity in the metallic lattice of the lead to allow the entry of the silver. This particular feature, with modifications, extends to certain lead minerals and results in a general coherence of lead and silver in nature. Further discussion of this particular aspect of the geochemistry of silver is given in a later section.

Silver dissolves up to 45 per cent or more mercury and will take up about 5 per cent antimony and about 7 per cent arsenic.

As noted above, silver in the +1 oxidation state is moderately ionized in its compounds whereas in the +2 state it is mainly covalent. According to the best estimates based on crystal measurements, AgCl (chlorargyrite) and AgBr (bromargyrite), which have sodium chloride lattices, have a fair proportion of ionic bonding (~ 30 per cent), but they are perhaps better characterized as intermediate, that is, they possess an ionic-covalent bond and in addition have some marked semi-metallic properties, as witnessed by their plastic, sectile, and ductile nature. Silver iodide, AgI, is even more complex since it exists in a number of modifications that are discussed later in the section on mineralogy. It is largely covalent with about 11 per cent ionic character and some semi-metallic character. Silver monoxide, $Ag_2O$, is largely covalent. Silver sulphide, $Ag_2S$ (argentite and acanthite), is apparently largely covalent with some ionic character and in addition has some metallic bonding as betrayed by its metallic lustre and very sectile nature. Silver +2 compounds, which are rare and of little importance geochemically, are covalent. These examples are sufficient to make it clear that the bonding properties of silver compounds and minerals are exceedingly complex. Before applying any specific radius or other energetic factor to explain the substitutional phenomena of silver in natural minerals, ~~a knowledge of~~ the mineral structure and other parameters must be relatively well known. In addition it is apparent that in minerals such as galena, multiple substitution of silver in consort with some other element such as bismuth or antimony takes place. This is discussed in the section on mineralogy.

In the +1 state silver forms the ion $Ag^+$, sometimes called the argentous ion. This ion does not hydrolyze appreciably in aqueous solution, is a mild oxidizing agent, and forms many soluble complex ions, e.g., $[AgCl_2]^-$, $[AgCl_3]^{2-}$, $[AgCl_4]^{3-}$, $[Ag(CN)_2]^-$, $[AgSO_4]^-$, $[Ag(S_2O_3)_2]^{3-}$. The chloride complexes are apparently stable both in an acid and mildly alkaline medium, and some are probably stable at elevated temperatures. The thiosulphate complex is stable in alkaline and neutral solutions. On addition of acid the thiosulphate complex decomposes to give S, $Ag_2S$, and some $Ag_2SO_4$. It can also be reduced by strong reducing agents to $Ag_2S$. Both the chloride and thiosulphate complexes endow silver with considerable mobility in natural aqueous environments, since the element is not readily precipitated by such common anionic complexes as $CO_3^{2-}$, $PO_4^{3-}$, etc.

Addition of a base to solutions of a silver salt gives a covalent white to brown oxide, which exhibits no marked amphoteric properties.

$$2\,Ag^+ + 2OH^- \rightarrow Ag_2O + H_2O$$

The oxide is, however, soluble in a solution of ammonia with the formation of a colourless complex ion, $[Ag(NH_3)_2]^+$.

$$Ag_2O + 4NH_3 + H_2O \rightarrow 2[Ag(NH_3)_2]^+ + 2OH^-$$

Argentic oxide, AgO, is precipitated by alkaline oxidation of aqueous solutions of argentous non-reducing salts. It is isomorphous with CuO. In acid media argentic oxide dissolves at normal temperatures to give argentic ion.

$$AgO + 2H^+ \rightleftharpoons Ag^{2+} + H_2O$$

Argentic ion is relatively unstable in water, especially at higher temperatures, since oxygen is liberated and $Ag^{2+}$ is reduced to $Ag^+$.

$$4Ag^{2+} + 2H_2O \rightarrow 4Ag^+ + 4H^+ + O_2$$

Argentic oxide is stable in water at least up to 100°C since the reaction

$$4AgO + 2H_2O \rightarrow 4Ag^+ + 4OH^- + O_2$$

is not thermodynamically spontaneous (McMillan, 1962).

Neither the argentous nor argentic oxides are known in nature.

There are claims for the existence of silver hydroxide, but it is more probable that the brownish substance formed when solutions of silver salts are treated with strong hydroxides, is hydrous silver oxide, $Ag_2O \cdot nH_2O$.

The silver halides, AgCl, AgBr, and AgI, are readily precipitated when silver solutions are mixed with solutions of the corresponding halide. All are relatively insoluble in water, but are soluble in suitable complexing reagents such as solutions of ammonia, NaCl, KCl, HCl, etc., with the formation of complex ions of the type $[Ag(NH_3)_2]^+$, $[AgCl_2]^-$. The three halides are photo-sensitive, a phenomenon that is utilized in photography. Silver fluoride, AgF, can be prepared. It is remarkable in that it is hygroscopic, dissolves readily in water, and is not photo-sensitive. Bivalent silver halides are unknown except $AgF_2$. It is a strong oxidizing agent. The chloride, bromide, and iodide of silver are known as natural minerals; the fluorides are unknown in nature.

Silver carbonate, $Ag_2CO_3$, is precipitated when alkaline carbonate solutions are added to silver solutions. It is relatively insoluble, but probably occurs in certain natural waters in small amounts.

Silver sulphate, $Ag_2SO_4$, is only slightly soluble in water. It is unknown as a natural mineral, but is probably present in certain natural waters in small amounts. A basic sulphate of ferric iron and silver, argentojarosite, occurs in certain oxidized zones of silver deposits.

Silver nitrate, $AgNO_3$, or "lunar caustic" is the most common salt of silver. It is unknown as a natural mineral but may be present in certain natural waters where sources of soluble nitrates are present.

Silver phosphate, $Ag_3PO_4$, is formed by mixing solutions of silver and a phosphate. It is yellow and only sparingly soluble in water. Silver phosphate has not been recorded as a natural mineral, but should be looked for since it would seem to be a relatively stable substance under most natural conditions.

Silver arsenate, $Ag_3AsO_4$, is isotypic (isostructural) with silver phosphate. It is a reddish salt that is only slightly soluble in water. It has not been recorded as a mineral, but would seem to be stable enough under certain natural conditions.

Silver chromate, $Ag_2CrO_4$, is an insoluble reddish brown to orange to green to greenish black compound, formed when silver solutions are mixed with those containing $CrO_4^{2-}$ ion. The compound would seem to be stable in natural settings and should be looked for as a mineral.

Silver molybdate, $Ag_2MoO_4$, a white to yellowish white compound, and silver tungstate, $Ag_2WO_4$, can both be prepared and would seem to be stable enough in natural environments to form minerals, although neither has been recorded as such.

Silver sulphide, $Ag_2S$, is known in nature as the minerals argentite and acanthite. It is formed when silver solutions are mixed with those containing sulphide ion or hydrogen sulphide under slightly acid, neutral, or alkaline conditions. Silver sulphide is soluble in solutions of alkali sulphides, with the formation of complex alkali silver sulphide ions.

-Sb-
-Te

Silver also combines readily with both sulphur and arsenic or antimony and with selenium and tellurium to form a number of complex compounds. Many of these are natural minerals and are discussed in the section on mineralogy.

A number of silver silicates have been prepared by treating silicates of alkali and alkaline earth metals with fused silver nitrate at the temperatures of about 300°C (Thilo and Wodtcke, 1958). They include a red silver orthosilicate, $AgSiO_4$; a yellow chain-like silicate, $(Ag_2SiO_3)_n$; a yellow layer-like silicate, $(Ag_2Si_2O_5)_n$; and a colourless silver mica, $AgAl_2[AlSi_3O_{10}](OH)_2$. None of these silicates has been identified in natural settings.

A large number of organic silver compounds are known, but probably few of these are of importance in geochemistry. Chelate complexes of silver seem to be few, and these are mainly co-ordinated through oxygen or sulphur or both, rather than through nitrogen. The importance of silver chelates in nature remains to be worked out.

Table 3 gives a résumé of the solubility of some of the common salts and other compounds of silver likely to be encountered in nature.

TABLE 3 *Solubility of Some Silver Compounds*

| Compound | Solubility in water, g/100cc (25°C) | Solubility product (Ksp) at temperature (°C) noted | Solubility in other reagents |
|---|---|---|---|
| $Ag_2O$ | $2.1 \times 10^{-3}$ | $2.0 \times 10^{-8}$(25°) | Sol. in $NH_4OH$, KCN, and $HNO_3$ solutions |
| AgCl | $1.8 \times 10^{-4}$ | $1.56 \times 10^{-10}$(25°) | Sol. in $NH_4OH$, KCN, and $Na_2S_2O_3$ solutions |
| AgBr | $1.3 \times 10^{-5}$ | $7.7 \times 10^{-13}$(25°) | Slightly sol. in $NH_4OH$<br>Sol. in $Na_2S_2O_3$ or KCN solution |
| AgI | $2.8 \times 10^{-7}$ | $1.5 \times 10^{-16}$(25°) | Sol. in $Na_2S_2O_3$ or KCN solution |
| $Ag_2CO_3$ | $3.2 \times 10^{-3}$ | $6.15 \times 10^{-12}$(25°) | Sol. in excess $NH_4CO_3$<br>Sol. in $NH_4OH$ or $Na_2S_2O_3$ solutions |
| $Ag_2SO_4$ | 0.78 | $1.24 \times 10^{-5}$(25°) | |
| $Ag_2S_2O_3$ | Slightly soluble | | Sol. in $Na_2S_2O_3$ |
| $Ag_3PO_4$ | $6.5 \times 10^{-4}$ | | Sol. in $NH_4OH$ |
| $Ag_3AsO_4$ | $8.5 \times 10^{-4}$ | | Sol. in $HNO_3$<br>Sol. in acetic acid, $NH_4OH$ |
| $Ag_2CrO_4$ | $2.5 \times 10^{-3}$ | $1.9 \times 10^{-12}$(25°) | Slightly sol. in $NH_4OH$<br>Sol. in $HNO_3$ |
| $AgNO_3$ | 329 | $1.2 \times 10^{-4}$(25°) | |
| $Ag_2S(\beta)$ | $1 \times 10^{-16}$ | $1.1 \times 10^{-49}$(25°) | Insol. in $NH_4OH$ |
| $Ag_2S(\alpha)$ | | $6.8 \times 10^{-50}$(25°) | Sol. in hot, dilute $HNO_3$<br>Sol. in alkali sulphide solutions |

Sources: Latimer (1952); Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., 1963; Waggoner, W.H., J. Chem. Ed., vol. 35, pp. 339–342, 1958

Silver forms a colloid only with difficulty, and the pure sols are unstable unless they are quite dilute or protected by a suitable electrolyte or colloid. The occurrence of elemental silver colloids in nature may be possible, however, particularly in the oxidizing waters of sulphide deposits.

Many of the compounds of silver also form colloids. The halide colloids can be easily prepared, and sulphide, arsenide, and other colloidal complexes are also known. The presence and significance of all of these types of colloids in nature are relatively unknown. The silver halide colloids may carry either a positive or a negative charge depending on the nature and composition of the dispersion medium. In the case of the positive colloid, an excess of silver ions in solution results in the adsorption of positive silver ions at the surface of the halide colloid, giving it a net positive charge. An excess of halide ions in solution yields a net negative charge due to the adsorption of negative halide ions at the surface of the silver halide colloid.

## Isotopes

Silver has two stable isotopes whose characterization and abundance[1] are:

| | |
|---|---|
| ${}_{47}Ag^{107}$ | 51.35% |
| ${}_{47}Ag^{109}$ | 48.65% |

In addition to these, radioisotopes with mass numbers 102, 103, 104, 105, 106, $107^m$, 108, $109^m$, 110, $110^m$, 111, $111^m$, 112, 113, $113^m$, 114, 115, $115^m$, 116, and 117 are known. These have short half lives measured in days, hours, minutes, or seconds, and none is known to occur in natural settings. The longest lived of the radioisotopes, $Ag110^m$, has a half life of approximately 253 days and decays by $\beta^-$ emission. It is the most suitable for use as a tracer in experiments involving the chemistry of silver.

Aston (1935) found the ratio $Ag^{107}/Ag^{109}$ to be 1.10 and gave the atomic weight of silver as 107.87 ± 0.02. Paul (1943) determined the ratio of the two isotopes as 1.080 ± 0.006 and gave the atomic weight of silver as 107.881 ± 0.002.

Hess, Marshall, and Urey (1957) determined the isotopic composition of a sample of terrestrial silver and of silver extracted from the troilite phase of the Xiquipilco (Toluca), Mexico, meteorite. The $Ag^{107}/Ag^{109}$ ratios obtained for the terrestrial sample ranged from 1.079 to 1.084, with an average of 1.082 ± 0.020. In the meteorite sample the corresponding ratio was 1.067 ± 0.028, a value in agreement with the terrestrial ratio, within the experimental error.

Murthy (1962) investigated the isotopic composition of silver in the metal (iron) phases of the Sikhote Alin and Canyon Diablo meteorites and in the troilite of the Toluca iron meteorite, and found that the ratio $Ag^{107}/Ag^{109}$ was approximately 2 to 3 per cent higher than that for terrestrial silver. Murthy's values are:

| Sample | $Ag^{107}/Ag^{109}$ | Std. Dev. |
|---|---|---|
| Toluca troilite | 1.087 | ±0.004 |
| Sikhote Alin iron phase | 1.091 | ±0.005 |
| Canyon Diablo iron phase | 1.107 | ±0.003 |

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[1] Strominger, D., Hollander, J.M., and Seaborg, G.T.; Table of Isotopes, *Reviews of Modern Physics*, 30, No. 2, Pt. II, 1958.

As an unreasonably short interval of time is indicated between the end of nucleosynthesis and the formation of iron meteorites, if the excess $Ag^{107}$ is attributed to the decay of the extinct radionuclide $Pd^{107}$ (*see* below), Murthy thinks that the isotopic anomaly may have to be interpreted in terms of a last-minute contribution of some amounts of short-lived radioactivities to the solar nebula, or by postulating that some $Pd^{107}$ was produced in the solar system in its early stages, after its separation from the galactic nucleosynthesis.

Chakraburtty, *et al.* (1964) redetermined the isotopic ratios of silver in the Canyon Diablo, Toluca, and other meteorites. They found no enrichment of $Ag^{107}$ in any of the meteorites, and no significant difference from terrestrial silver, data not in agreement with that obtained by Murthy. Before the issue rests, further data would seem to be necessary.

TABLE 4 *$Ag^{107}/Ag^{109}$ Ratios in Various Silver Minerals*[1]

| Mineral | Locality | $Ag^{107}/Ag^{109}$ |
|---|---|---|
| Silver nitrate | Commercial | 1.0755 |
| Native silver | Silver King mine, Pinal co., Arizona | 1.0734 |
| Native silver | Ontonagon, Lake Superior district, Mich. | 1.0766 |
| Native silver | Gagnon mine, Butte, Mont. | 1.0744 |
| Native silver | El Mochito mine, Honduras | 1.0746 |
| Native silver | Chihuahua, Mexico | 1.0755 |
| Native silver | Kongsberg, Norway | 1.0744 |
| Silver nitrate | Commercial | 1.0763 |
| Native silver | Cobalt, Ontario | 1.0783 |
| Native silver | Cobalt, Ontario | 1.0758 |
| Native silver | Cobalt, Ontario | 1.0753 |
| Native silver | Silver Miller mine, Cobalt, Ontario | 1.0746 |
| Native silver | Nova Scotia mine, Cobalt, Ontario | 1.0743 |
| Native silver | Silver Banner mine, Cobalt, Ontario | 1.0736 |
| Native silver | Great Bear Lake, N.W.T., Canada | 1.0745 |
| Silver nitrate | Commercial | 1.0758 |
| Bromargyrite | Australia | 1.0752 |
| Chlorargyrite | Arizona | 1.0750 |
| Embolite | Australia | 1.0756 |
| Freibergite | Bolivia | 1.0754 |
| Naumannite | Idaho | 1.0751 |
| Hessite | Transylvania | 1.0754 |
| Argentite | Germany | 1.0752 |
| Polybasite | Mexico | 1.0743 |
| Stephanite | Germany | 1.0757 |
| Pyrargyrite | Germany | 1.0750 |
| Proustite | Chile | 1.0746 |

[1] From Shields, W.R. *et al.* (1962)

Shields, *et al.* (1962) investigated the $Ag^{107}/Ag^{109}$ ratio in a number of samples of native silver and other silver minerals and found no significant variation from the normal abundance of the isotopes. They give the $Ag^{107}/Ag^{109}$ ratio of terrestrial silver as 1.07597. The data for individual samples are given in Table 4.

The absolute isotopic abundance ratio, $Ag^{107}/Ag^{109}$, and the atomic weight of natural silver have recently been determined by Crouch and Turnbull (1962). They give the ratio $Ag^{107}/Ag^{109}$ as $1.0733 \pm 0.0043$ and the atomic weights as: chemical scale ($O=16$) $107.8740 \pm 0.0033$; physical scale ($O^{16}=16$) $107.9037 \pm 0.0026$; unified scale ($C^{12}=12$) $107.8694 \pm 0.0026$.

Both $Ag^{107}$ and $Ag^{109}$ are stable fission products of $U^{235}$. The former derives ultimately from $Pd^{107}$ with a half-life of $7.5 \times 10^6$ years, and the latter from $Pd^{109}$ with a half-life of 13.6 hours. Uranium deposits, and as a matter of fact all rocks containing uranium, should have some fissiogenic silver. It is, however, doubtful that the bulk of the silver in ores such as those of Great Bear Lake is derived directly by this process since a consideration of the fission yields (0.19 per cent for the chain yielding $Pd^{107}$ and 0.030 per cent for $Pd^{109}$) and the isotopic composition of the native silver in the ore as found by Shields, *et al.* (1962) (Table 4), does not lend support to such an origin.

The ultimate origin of the two stable silver isotopes is a matter of speculation. They may be primordial in large part and not directly derived from fission processes. On the other hand they may be fissiogenic with $U^{235}$ as their parent, and they may have originated deep within the earth during its long history. It seems certain that they have been well mixed in the crustal part that is exposed to observation, but this is not unexpected considering the processes that silver has passed through prior to its concentration in veins and other types of deposits.

## Abundance and Geochemical Character

The cosmic abundance of silver as given by Green (1959) from the data of Suess and Urey (1956) is 0.00052 ppm or 0.26 atom of Ag per $10^6$ Si atoms.

Silver is a trace constituent of meteorites. Its abundance in the various types of meteorites is given in Table 5. It is evident that silver is enriched in the sulphide phase of meteorites as a consequence of the chalcophile character of the element. Its presence in the irons and nickel-irons is evidence of its siderophile nature.

The content of silver in the silicate phase of meteorites is very low, indicating that the element exhibits practically no oxyphile character in cosmic processes.

There is considerable uncertainty in the value of the terrestrial abundance of silver. Goldschmidt (1954) gives 0.02 ppm for the lithosphere; Rankama and Sahama (1950) give 0.10 ppm as the average for igneous rocks; and Green (1959) gives 0.2 ppm as the average for igneous rocks. More recently Taylor (1964) has given 0.07 ppm as the continental crustal abundance of the element, a mean of the basalt (0.1 ppm) and granite (0.04) averages. The writer estimates the terrestrial abundance of silver to be 0.10 from several hundred analyses of all types of common Canadian rocks, done in the laboratories of the Geological Survey by spectrographic and assay methods.

TABLE 5 *Abundance of Silver in Meteorites*

| Type | Source of Information | Abundance, ppm |
|---|---|---|
| Nickel–iron | Goldschmidt (1954) | 3.2 – 5.0 |
| Nickel–iron | Rankama and Sahama (1950) | 4 |
| Irons | Green (1959) | 3.3 |
| Iron–nickel | Chakraburtty, *et al.* (1964) | 0.011 – 0.197 |
| Troilite | Goldschmidt (1954) | 10 – 38 |
| Troilite | Rankama and Sahama (1950) | 18 |
| Sulphide | Green (1959) | 18 |
| Silicate | Rankama and Sahama (1950) | (0) |
| Chrondrites | Onishi and Sandell (1957) | 0.4 |
| Chrondrites | Schindewolf and Wahlgren (1960) | 0.04 – 0.13 |
| Tektites | Cohen (1959) | < 1 |
| Tektites (Australites) | Taylor and Sachs (1960) | < 0.5 |

In the upper lithosphere silver occurs in the native state and as a constituent of a few natural alloys. It is also a trace element in various native metals and semimetals such as iron, copper, and arsenic. These features indicate the siderophile nature of the element. The metal also combines readily with sulphur, tellurium, and selenium as a consequence of its strong chalcophile character, and in addition combines with sulphur, arsenic, antimony, and bismuth to form a complex series of natural compounds. Silver forms a number of halides in the zone of oxidation, but the only evidence of its oxyphile character in nature is to be found in a sole compound, argentojarosite, a basic sulphate. No silicates of silver are known in nature.

Silver combines with a large number of artificial organic compounds, but the occurrence of these in nature is unknown. The element is a trace constituent of various terrestrial and marine organisms, but its biological role, if any, is largely unknown. Silver is also a trace constituent of some coals and is found in some petroleum residues.

## Mineralogy of Silver

### Silver Minerals

The minerals of silver are given in Table 6. Of those listed the most common are native silver, acanthite, pyrargyrite, proustite, tetrahedrite-tennantite, chlorargyrite, and argentojarosite. For the details of the silver minerals the reader should consult Palache, Berman, and Frondel (1944, 1951), Ramdohr (1960), Chukhrov, *et al.* (1960–1965), and Berry and Thompson (1962).

*Native silver* crystallizes in a great variety of forms, the most common being groups of parallel cubic or octahedral individuals, arborescent and wiry forms, irregular masses, and scales or spangles. In some deposits native silver is relatively

**TABLE 6** *Silver Minerals*

| | |
|---|---|
| *Native element and alloys* | |
| Argentian gold (electrum) | (Au,Ag) |
| Silver | Ag |
| Moschellandsbergite | $Ag_2Hg_3$ |
| Silver amalgam | (Ag,Hg) |
| *Sulphides, antimonides, arsenides, tellurides, etc.* | |
| Dyscrasite | $Ag_3Sb$ |
| Novakite | $(Cu,Ag)_4As_3$ |
| Argentite | $\alpha\ Ag_2S$ |
| Acanthite | $\beta\ Ag_2S$ |
| Aguilarite | $Ag_4SeS$ |
| Naumannite | $Ag_2Se$ |
| Crookesite | $(Cu,Tl,Ag)_2Se$ |
| Eucairite | CuAgSe |
| Hessite | $Ag_2Te$ |
| Petzite | $Ag_3AuTe_2$ |
| Stromeyerite | $Ag_{1-x}CuS$ |
| Mckinstryite | $Cu_{0.8}Ag_{1.2}S$ |
| Sternbergite | $AgFe_2S_3$ |
| Argentopyrite | $AgFe_2S_3$ |
| Empressite | AgTe |
| Stuetzite | $Ag_{5-x}Te_3$ |
| Muthmannite | (Ag,Au)Te |
| Sylvanite | $(Au,Ag)Te_4$ |
| *Sulphosalts* | |
| Polybasite | $(Ag,Cu)_{16}Sb_2S_{11}$ |
| Pearceite | $(Ag,Cu)_{16}As_2S_{11}$ |
| Polyargyrite(?) | $Ag_{24}Sb_2S_{15}$ |
| Argyrodite | $Ag_8GeS_6$ |
| Canfieldite | $Ag_8SnS_6$ |
| Stephanite | $Ag_5SbS_4$ |
| Pyrargyrite | $Ag_3SbS_3$ |
| Proustite | $Ag_3AsS_3$ |
| Pyrostilpnite | $Ag_3SbS_3$ |
| Stylotypite | $(Ag,Cu,Fe)_3SbS_3$ |
| Xanthoconite | $Ag_3AsS_3$ |
| Tetrahedrite-tennantite | $(Cu,Fe,Ag)_{12}(Sb,As)_4S_{13}$ |
| Samsonite | $Ag_4MnSb_2S_6$ |
| Lengenbachite | $Pb_6(Ag,Cu)_2As_4S_{13}$ |
| Diaphorite | $Pb_2Ag_3Sb_3S_8$ |
| Freieslebenite | $Pb_3Ag_5Sb_5S_{12}$ |
| Owyheeite | $Pb_5Ag_2Sb_6S_{15}$ |
| Schirmerite | $PbAg_4Bi_4S_9$ |
| Miargyrite | $AgSbS_2$ |
| Aramayoite | $Ag(Bi,Sb)S_2$ |
| Matildite | $AgBiS_2$ |
| Pavonite | $AgBi_3S_5$ |

| | |
|---|---|
| *Sulphosalts (cont'd)* | |
| Smithite | $AgAsS_2$ |
| Trechmannite | $AgAsS_2$(?) |
| Benjaminite | $Pb(Cu,Ag)Bi_2S_4$ |
| Fizelyite | $Pb_5Ag_2Sb_8S_{18}$ |
| Ramdohrite | $Pb_3Ag_2Sb_6S_{13}$ |
| Andorite | $PbAgSb_3S_6$ |
| Hutchinsonite | $(Pb,Tl)_2(Cu,Ag)As_5S_{10}$ |
| Betechtinite | $(Cu,Fe)_{11}(Pb,Ag)S_7$(?) |
| Marrite | $AgPbAsS_3$ |
| *Halides* | |
| Chlorargyrite[1] (cerargyrite) | $AgCl$ |
| Huantajayite | $(Na,Ag)Cl$ |
| Ostwaldite | Colloidal-like $AgCl$ |
| Bromargyrite[1] (bromyrite) | $AgBr$ |
| Miersite | $(Ag,Cu)I$ |
| Iodargyrite[1] (iodyrite) | $AgI$ |
| Boleite | $Pb(Cu,Ag)Cl_2(OH)_2 \cdot H_2O$ |
| *Basic sulphates* | |
| Argentojarosite | $AgFe_3(SO_4)_2(OH)_6$ |
| Argentian plumbojarosite | $(Pb,Ag)Fe_{3-6}(SO_4)_{2-4}(OH)_{6-12}$ |

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[1] The Commission on New Minerals and Mineral Names of the International Mineralogical Association at its 1960 and 1962 meetings agreed to these new names for the silver halides

pure, but more generally it contains some gold or mercury and traces to minor amounts of As, Sb, Bi, Te, Cu, Fe, Zn, Pb, Co, Ni, Pt, and Ir in solid solution.

Mercurian silver containing from 2 to 30 per cent Hg and higher has been described from British Columbia; Cobalt, Ontario; Silver Islet, Ontario; Kongsberg, Norway; Northern Chile; Arizona and Montana, U.S.A.; and elsewhere. According to Newhouse (1933) mercurian silver with relatively high amounts of Hg is characteristic of silver deposits in which cinnabar is present, or in those containing nickel and cobalt sulphides and arsenides. The present writer's research further shows that mercurian silver is mostly of hypogene origin. Silver of supergene origin rarely contains mercury. This fact seems also to be borne out by numerous isolated references in the literature.

Antimonian silver is common at Cobalt, Ontario, where it is associated with dyscrasite. Homogeneous material from the Timiskaming mine gave Ag–92.19 per cent, Sb–6.78 per cent, As–0.45 per cent (Peacock, 1940). Other analyses of antimonian silver from various silver deposits throughout the world generally show less than 0.5 per cent Sb. Antimonian silver and dyscrasite seem to be characteristic of deposits relatively low in antimony and copper, especially the latter. If these elements had been abundant in the primary solutions or diffusion currents, argentian tetrahedrite would have been precipitated.

Arsenian silver is not as common as antimonian silver. In general the arsenic contents are less than 0.5 per cent As.

Some semi-quantitative spectrographic analyses of native silver from deposits in Canada and elsewhere are given in Table 7. The main points of interest are the nearly universal presence of mercury and bismuth in deposits of the Cobalt type with a Ni-Co arsenide mineral assemblage and the general absence of these elements in supergene native silver. Antimony is a common trace constituent in a number of the samples, and traces of barium, aluminum, zinc, copper, lead, nickel, cobalt, bismuth, manganese, and iron are frequently encountered.

Native silver is widely diffused in several types of deposits. In some, e.g., Cobalt, Ontario, the metal is of hypogene origin and is commonly associated with Ni-Co arsenides and sulphides and in some places with pitchblende e.g., Great Bear Lake,

TABLE 7 | *Spectrographic Analyses of Native Silver*

| Description and Location | 1%–10% | 0.1–1.0% | 0.01–0.1% | 0.001–0.01% |
|---|---|---|---|---|
| Wire silver: No. 1. Mine, Ainsworth area, British Columbia | | Zn | Al, Cu, Fe, Hg, Pb, Mg, Mn, Si | Ca |
| Massive: No. 1. Vein, Eldorado mine, Great Bear Lake, N.W.T. | | Fe, Mg, Si, As, Ca, Co, Mn, Ni, Al, Cu. | Bi, Hg, Sb, Zn | Ba, Sr, V, Ti |
| Foil in ice lens (supergene), Elsa mine, Galena Hill, Yukon | | Al, Fe, Si, Mn | Cu, Pb, Sb | Ba, Ca, Mg |
| Silver Mountain mine, Thunder Bay District, Ontario | Si | Al, Ca | Ba, Fe, Ti | Cu, Pb, Mg, Mn, Sr |
| Wire: Silver Islet, Lake Superior, Ontario | | Hg | Ca, Sb, Zn | Al, Cu, Fe, Pb, Mn, Mg, Si |
| Wire: Cobalt Lake Mining Co., Cobalt, Ontario | | | Al | Bi, Ca, Co, Cu, Fe, Mg, Ni, Si |
| Coniagas mine, Cobalt, Ontario | Sb | Hg, Ni | Al, Bi, Co, Pb, Si | Ca, Cu, Fe, Mg, Mn, Zn |
| Castle Trethewey mine, Gowganda district, Ontario | | Bi | Al, Ca, Cu, Fe, Hg, Sb, Si | Co, Mg, Mn, Ti |
| Mann mine, Gowganda, Ontario | | Al, Hg, Sb, Si | As, Bi, Co, Fe, Mg, Ni | Ba, Ca, Cu, Pb, Mn, Ti |
| Little Silver mine, Coleman twp., Ontario | Sb | Hg | Ca | Al, Bi, Cu, Fe, Mg, Mn, Ni, Si |
| Broken Hill, N.S.W., Australia (supergene?) | | | Al, Fe, Pb, Si | Ba, Ca, Cu, Mg, Mn, Ti |
| Wire: Batopilis, Mexico | | Fe, Si | Al, Cu, Mg, Mn, Pb | Ba, Ca, Zn |

Semi-quantitative spectrographic analyses by W. H. Champ

N.W.T.; also with various silver sulphides, pyrite, etc. The common gangue minerals are calcite, barite, fluorite, and quartz. In other deposits native silver is of supergene origin derived from the oxidation of various silver sulphides, sulphosalts, etc. Native silver occurs only rarely as nuggets and flakes in placers, examples being recorded from Alaska and from Burwash and Arch Creeks (Kluane and Donjek River area), Yukon.

Silver is nearly always present in *native gold*, the colour of which ranges from deep gold-yellow to pale yellow and yellowish white with increase in the silver content. The name *electrum* has been applied to gold with 20 per cent or more of silver. Silver substitutes for gold, and there is apparently a complete solid solution series from gold through argentian gold (electrum) and aurian silver to silver.

*Moschellandsbergite*, $Ag_2Hg_3$, is a rare mineral. It is silver white with a bright metallic lustre and crystallizes in dodecahedrons or in massive and granular aggregates.

*Arquerite*, a variety of silver amalgam or mercurian silver, occurs as small grains and nuggets up to several ounces in weight in the placers of Silver, Vital, Kenny, Tom, and Kwanika Creeks in the Fort St. James area, British Columbia (Armstrong, 1949); also in Burwash Creek in the Kluane Lake district, Yukon, and probably elsewhere in the placers of the Cordillera. The arquerite from the Fort St. James area contains up to 15 per cent mercury, minor amounts of Au, Cu, and Si, and traces of Mg, Fe, Al, Ti, Ca, Sr, Sb, Mn, Ni, Ba, Sn, Ba, Cr, Pb, Co, and B. Samples of the amalgam from Burwash Creek contain up to 20 per cent mercury and minor amounts of Pb and Sb, and traces of Zn, Si, Ca, Mn, Fe, Mg, Ni, and Bi. The arquerite in the Canadian Cordillera seems to occur mainly in the mercuriferous belts; it accompanies cinnabar in some creeks.

*Dyscrasite*, the silver antimonide, $Ag_3Sb$, is a silver-white mineral, usually tarnished to a lead-grey. It has been found at St. Andreasberg in the Harz Mountains; at Wolfach on the Kinzig, Baden, Germany; Broken Hill, Australia; Reese River district, Nevada; in Alsace at Ste. Marie aux Mines; and at Cobalt, Ontario. The material from Cobalt contains small amounts of mercury and arsenic.

*Argentite* and *acanthite* are the most common sulphides of silver. Argentite, $\alpha Ag_2S$, is isometric and is stable above 175°C. Below this temperature it inverts to acanthite, $\beta Ag_2S$, the orthorhombic form. All natural $Ag_2S$ is, therefore, acanthite and gives the X-ray pattern for this mineral. According to Frueh (1958) both acanthite and argentite have a body-centred cubic arrangement of S atoms, but the arrangement of the Ag atoms in the two polymorphs is very different.

Acanthite and argentite generally contain small amounts of copper. The variety with about 14 per cent copper is called *jalpaite*. Acanthite is one of the most persistent minerals in all types of silver deposits and is one of the most important ore minerals of the element. It is generally of hypogene origin, but in certain deposits it may be an abundant supergene mineral.

The selenides, *aguilarite*, *naumannite*, *crookesite*, and *eucairite* are comparatively rare minerals, occurring in various types of silver deposits with acanthite, native silver, clausthalite, tiemannite, and other selenides. The minerals are of hypogene origin in all deposits. Naumannite was present in some quantity in the De Lamar mine, Silver City district, Idaho, and the mineral is one of the principal silver-bearing minerals in the late Tertiary Kushikino gold-silver deposit in Japan. In the latter deposit naumannite is associated with electrum, polybasite, pyrite, chalcopyrite, tetrahedrite, pyrargyrite, sphalerite, and galena in a quartz-calcite gangue (Mukaiyama and Izawa, 1964). Early (1950) has described the mineralogy and synthesis of the silver selenides in detail.

As stated, argentite, $\alpha Ag_2S$, is stable above 175°C and acanthite, $\beta Ag_2S$ is stable below this temperature. Naumannite also has two polymorphs: $\alpha Ag_2Se$ is stable above approximately 125°C and $\beta Ag_2Se$, below this temperature. Roy, *et al.* (1959) have investigated these two transitions as geological thermometers. They find that the transition temperatures are quite insensitive to pressures up to 1,200 atmospheres and suggest that the presence of ions, such as $Cu^+$ and $Se^{2-}$ substituting for $Ag^+$ and $S^{2-}$, respectively, do not have a drastic effect on the transitions. They conclude that the presence of argentite or "cubic habit" naumannite in ores—where analysis shows these minerals to be relatively pure—can be taken to indicate minimum temperatures of formation of approximately 180°C and 130°C, respectively.

The silver tellurides, *hessite*, *petzite*, *empressite*, *stuetzite*, *muthmannite*, and *sylvanite* are comparatively rare minerals, but in some types of deposits they may be abundant and are the principal source of gold and silver. In all deposits the tellurides are of hypogene origin.

*Hessite*, $Ag_2Te$, occurs in two polymorphs, an isometric one above 149.5°C and a monoclinic one below this temperature. The mineral has a metallic lustre and is steel-grey to lead-grey. It generally contains some gold and traces of Fe, Pb, Hg, and other metals. Notable localities for the occurrence of hessite are: the Zavodinsk mine, near Ziryanovsk, in Kazak S.S.R.; Nagyág, Roumania; Kalgoorlie, Western Australia; Goldhill, Colorado; and Nevada City, California. In Canada the mineral has been identified in the gold-silver ores of the Horne mine, Noranda, Quebec; in the gold-quartz veins of the McWatters mine, Rouyn township, Quebec; in the lead-rich ores of the Frood mine, Sudbury; and in numerous other localities (Thompson, 1949).

*Petzite*, $Ag_3AuTe_2$, is similar to hessite and may be a high gold-bearing variety of the latter mineral. It has been noted in many of the localities where hessite occurs. Petzite occurs in small quantities in some of the gold-quartz veins in the Red Lake area, Ontario; in the gold-quartz veins at Kirkland Lake, Ontario; in similar veins at the Hollinger and McIntyre mines, Timmins, Ontario; in the gold-silver ores of the Horne mine, Noranda, Quebec; in the gold-quartz veins of the Stadacona mine, near Rouyn, Quebec; in the gold ores of the Sladen Malartic mine, Fournière township, Abitibi county, Quebec; and in numerous other localities (Thompson, 1949).

*Empressite*,[1] AgTe, and *muthmannite* (Ag,Au)Te, are similar in appearance, both being a pale to yellow-bronze. *Stuetzite*,[1] $Ag_{5-x}Te_3$, is lead-grey on fresh

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[1] The chemical definition of these two minerals is controversial. See, for instance, the paper by Honea (1964) and the discussions by Cabri (1965a) and Honea (1965). The terminology used here is that suggested by Honea.

surfaces and bronze on tarnished surfaces. Empressite occurs in some quantity with galena and native tellurium at the Empress Josephine mine, Kerber Creek district, Colorado; muthmannite is a common mineral in the telluride assemblage at Nagyág, Roumania. Stuetzite appears to be more common than was formerly thought (Honea, 1964). It occurs at several places in Colorado; in the Kalgoorlie district, Australia; at Vatukoula, Fiji Islands; and elsewhere. It is generally associated with native tellurium and other tellurides such as sylvanite, hessite, etc. Stuetzite occurs in a gold-quartz vein on the Grotto Group on Hardscrabble Creek, near Pitman, Skeena mining district, British Columbia (Thompson, 1954). Muthmannite has not been recorded in Canadian deposits.

*Sylvanite*, $(Ag,Au)Te_4$, is a metallic mineral with a steel-grey to silver-white colour. In composition its Au:Ag ratio is close to 1:1, but in some analyses Au greatly exceeds Ag, and the mineral passes into krennerite, $AuTe_2$, and calaverite, $AuTe_2$. The three minerals are not, however, isomorphous. Sylvanite is associated with other tellurides at Nagyág, Roumania; Kalgoorlie and Mulgabbie, Western Australia; and at Cripple Creek, Colorado; and in numerous other places in the U.S.A. In Canada, sylvanite occurs in the sulphide ores of the Flin Flon mine, Manitoba-Saskatchewan; at the Gold Eagle, Howie, and Hasaga mines, Red Lake district, Ontario; at Bigstone Bay, Lake of the Woods; in the gold-silver ores of the Horne mine, Noranda, Quebec; at the Bevcon gold mine, Abitibi county, Quebec; in the gold ores of the Sladen Malartic mine, Fournière township, Abitibi county, Quebec; and in several other localities (Thompson, 1949).

Markham (1960) has discussed the synthetic and natural phases in the system Au-Ag-Te and also his findings with respect to the occurrence of tellurides at Kalgoorlie, Western Australia, and Vatukoula, Fiji Islands. He finds that the experimental data are insufficient to indicate a meaningful range of depositional temperatures for any given telluride, but thinks that when the calaverite-krennerite transition is experimentally determined, it should provide a useful geological thermometer. Cloke (1963a) and Petersen (1964) have commented on some of the physico-chemical features of Markham's paper.

Cabri (1965b) recently carried out a systematic investigation of the phase relations in the Au-Ag-Te system and found that krennerite, rather than being a polymorph of $AuTe_2$, should be interpreted as a single mineral entity with the approximate formula $Au_4AgTe_{10}$. It is stable up to its incongruent melting point of 382±5°C, and hence its presence in deposits is not necessarily indicative of low temperatures of formation. The incongruent melting temperature of sylvanite (354±5°C) indicates a maximum temperature for its formation. Cabri also found that hessite and petzite are each characterized by three polymorphs. Continuous solid solution exists between the highest polymorphs and extends to a composition about 7 weight per cent more gold-rich than stoichiometric petzite. A new phase, termed the "x" phase, was found to be stable along the petzite-hessite join from about 2.5 to 14.5 weight per cent gold within temperature limits of 50° to 415°C.

The phase relations in the silver-tellurium system have been described by Kracek, Ksanda, and Cabri (1965).

Some of the facts concerning the occurrence of silver (and gold) tellurides may be noted here. The tellurides seldom if ever are associated with the selenides; for some reason they seem to be mutually exclusive. The tellurides generally occur in deposits in volcanic assemblages, particularly Precambrian greenstones, as for example, their occurrence in the Kirkland Lake-Noranda-Malartic areas of Ontario and Quebec; Porcupine area, Ontario; Red Lake area, Ontario; Flin Flon, Manitoba; and the famous telluride-gold lodes of Kalgoorlie, Western Australia. In younger (generally Tertiary) volcanic rocks, notable occurrences of gold and silver tellurides are known at Cripple Creek, Colorado; Brád and Nagyág, Roumania (Transylvania); Vatukoula, Fiji Islands, and elsewhere. Another interesting feature of the occurrence of tellurides in volcanic rocks is the fact that they tend to occur in mineralized belts that are associated with one specific period of fracturing. This is exemplified by their occurrence in all of the areas noted above.

*Stromeyerite*, $Ag_{1-x}CuS$, is a fairly common silver mineral, especially in deposits that contain relatively high contents of copper. It is a dark steel-grey mineral that is bluish on exposed surfaces. Some varieties contain traces to small amounts of Fe, Zn, Pb, and Cd. Stromeyerite may be either hypogene or supergene in deposits. In the latter situation it is often associated with chalcocite. The crystal structure of stromeyerite has been discussed by Frueh (1956).

Notable foreign occurrences of stromeyerite are at Zmeyewskaya-Goro, Siberia; Rudelstadt and Kupferberg, Silesia; Prince Leopold mine, Congo; Telemarken, Norway; Mount Lyell, Tasmania; Copiapó, Chile; Zacatecas, Mexico; Butte, Montana; and Silverton and various other places in Colorado. In Canada the mineral has been identified in the lead-zinc-copper-silver ores at Walton, Nova Scotia; in the native silver ores at Cobalt and Gowganda, Ontario; and at the Silver King mine, Nelson Mining district, British Columbia.

*Sternbergite*, $AgFe_2S_3$, is rare in most silver-bearing deposits. It has a metallic lustre and is pinchbeck-brown in colour. It is reported to occur in some quantity in the silver ores of Jáchymov and Přibram, Bohemia, Czechoslovakia. In most occurrences it is probably of hypogene origin.

Sternbergite belongs to a group of minerals loosely termed "the silver pyrite group." The other members are *argyropyrite*, $Ag_3Fe_7S_{11}$, *argentopyrite*, $AgFe_2S_3$, and *frieseite*, $Ag_2Fe_5S_8$. Only sternbergite and argentopyrite have been adequately differentiated and described; the others may be dimorphous with sternbergite or they may be mixtures. Further work, especially by X-ray methods, is required on the indefinite members.

The silver sulphosalts are a varied and complex group of minerals; some occur in abundance in silver deposits and are ore minerals of silver, others are only mineral curiosities. The most common silver sulphosalts are tetrahedrite-tennantite, pyrargyrite-proustite, polybasite, pearceite, and stephanite, in about that order of frequency.

*Tetrahedrite-tennantite*, $(Cu,Fe,Zn,Ag)_{12}(Sb,As)_4S_{13}$, is widely dispersed in practically all types of silver, gold, copper, lead, and zinc deposits. The high silver-bearing varieties have been variously named argentian tetrahedrite, argentian tennantite, and freibergite. Freibergite is actually argentian tetrahedrite, but the term is a good field one for differentiating the silver-bearing varieties of both tetrahedrite and tennantite.

The lattice of tetrahedrite-tennantite is remarkably tolerant to the substitution of various elements for copper and for antimony and arsenic, and it seems probable that a great variety of isomorphous series exists between the various elemental species of the mineral. Data in the literature combined with that obtained by the writer on tetrahedrite-tennantite from various localities in Canada and elsewhere show that the following substitutions may take place:

1. For Cu: Fe, Mn, Zn, Cd, Ag, Au, Hg, Pb, Ni, Co, Ge, Ba, Sn, V, In
2. For As: Sb, Bi
3. For S: Se, Te

With the exception of mercury, there seems to be no apparent relationship between the content of silver and the various substituting elements in tetrahedrite-tennantite. Mercurian tetrahedrite is generally very low in silver, and the reverse is true that argentian tetrahedrite-tennantite is low in mercury. The reason for this is not readily apparent, but the fact suggests either that mercury and silver cannot be carried together in the solutions or diffusion currents that deposit tetrahedrite, or that the incorporation of one of the elements in the tetrahedrite-tennantite lattice mutually excludes the other.

The state of silver in the tetrahedrite-tennantite lattice is not known definitely because of the complexity of the mineral. The structure of tetrahedrite-tennantite is somewhat similar to that of sphalerite. The copper atoms are of two kinds: one has ligancy 4 and the other ligancy 3 with sulphur. The mineral is largely covalent and the tetrahedral covalent radius of silver should apply in a rough qualitative way to its substitution for copper. The difference in the covalent radii of the two elements, Ag (1.53 Å), Cu (1.35 Å), is, however, significant and approaches the limit permitted for extensive substitution, according to the Goldschmidt rule. The metallic lustre of tetrahedrite-tennantite also suggests some metallic binding in the mineral and the atomic radius of silver might be applied. The difference between the atomic radii of the two elements, Ag (1.40 Å), Cu (1.24 Å), is, however, again significant. Despite these difficulties in energetic properties, it is apparent that silver may substitute for copper in the tetrahedrite-tennantite lattice up to 25 per cent or more (Staples and Warren, 1946). With increase in silver content there is a progressive increase in the cell edge (Bernard, 1962), indicating a considerable degree of elasticity in the lattice.

The composition of tetrahedrite with respect to regional zonation of deposits and internal zoning within deposits, has been investigated in the Spišsko-Gemerské Rudohorie Mountains of Czechoslovakia by Bernard (1957, 1958, 1963). He found that the veins at the extreme border of the mineralized area contain tetrahedrite with high Hg contents (5–10 per cent and mostly $>10$ per cent), whereas in those of the central part of the ore mountains the mercury content of the tetrahedrite seldom exceeds one per cent. Bernard also found that within individual deposits, viz. Rudňany, the silver content of the tetrahedrite and its cell edge decreased markedly with depth.

Tetrahedrite-tennantite is generally a hypogene mineral in most silver deposits, although there are numerous references in the older literature suggesting that it may be of supergene origin in some deposits. It is generally late in the paragenetic sequence, and this has probably led some investigators to think that it may be supergene. Individual deposits are generally marked by the occurrence of either tetrahedrite, the antimony member, or tennantite, the arsenic member. While there are references to both end members of the series occurring in single deposits, this appears to be rare.

Many of the silver deposits of Canada contain either argentian tetrahedrite or tennantite as the chief ore mineral of silver. In this respect we may mention the lead-zinc-silver deposits of the Keno Hill area, Yukon (argentian tetrahedrite); the lead-zinc-silver deposits of the Slocan area, British Columbia (argentian tetrahedrite); the silver-lead-zinc veins of the Beaverdell camp, British Columbia (argentian tetrahedrite); and the lead-zinc-silver deposit at Walton, Nova Scotia (tennantite).

*Proustite*, $Ag_3AsS_3$, and *pyrargyrite*, $Ag_3SbS_3$, the ruby silver minerals, form a complete solid-solution series from solidus temperatures down at least to 300°C (Toulmin, 1963). Both proustite and pyrargyrite are relatively pure containing only minor to trace amounts (generally less than 500 ppm) of Cu, Pb, Zn, Cd, Sn, Fe, Ni, Co, and Ge. This indicates that the lattices of the two minerals are relatively intolerant to substitution in the silver sites.

Proustite and pyrargyrite are generally hypogene minerals, but in some deposits there is abundant evidence that pyrargyrite is of supergene origin. In the Keno Hill deposits, Yukon, it is both hypogene and supergene. In his study of the proustite-pyrargyrite solid-solution series, Toulmin (1963) found no examples of coexisting pyrargyrite and proustite in the same specimens, although he noted that different samples from the same mine or district commonly have different ruby silvers. The present writer has noted that it is general to find only one abundant ruby silver in single ore shoots and generally only one in the same district. Only rarely has he observed two abundant ruby silvers in the same deposit or in the same district. Furthermore, he has noted that where tetrahedrite occurs the abundant ruby silver is invariably pyrargyrite, the antimonian variety, and where tennantite is present, proustite, the arsenian variety, is dominant.

Proustite and pyrargyrite are important silver ore minerals in a number of Canadian silver deposits. Here we may mention the lead-zinc-silver deposits of the Keno Hill area, Yukon (pyrargyrite); the silver-lead-zinc veins of the Slocan district, British Columbia (pyrargyrite); the lead-zinc-silver veins of the Ainsworth area, British Columbia; the silver-lead-zinc veins of the Beaverdell camp, British Columbia (pyrargyrite); the native silver veins of Cobalt, Ontario (pyrargyrite and proustite); and the lead-zinc-silver deposit at Walton, Nova Scotia (proustite).

The rare silver sulphosalts, *pyrostilpnite*, $Ag_3SbS_3$, and *xanthoconite*, $Ag_3AsS_3$, have only been recorded from a few silver deposits. They have been synthesized in aqueous and other media by Béland (1946, 1948), Peacock (1947), and Weil and Hocart (1953). Toulmin (1963), however, did not find them in the study referred to above and concluded that if the minerals are truly stable at all, their stability fields must lie at low temperatures (below 300°C), or that their structures are stabilized by foreign elements. Chang (1963) also failed to synthesize pyrostilpnite, but found that the natural mineral inverted to pyrargyrite at temperatures as low as 197°C. He concluded that the two minerals are polymorphs and that pyrostilpnite is the low temperature stable form. Xanthoconite may, therefore, be the low temperature stable form of proustite.

Natural occurrences of pyrostilpnite are reported from Andreasberg in the Harz, Germany; Přibram, Czechoslovakia; and Silver City district, Idaho. Xanthoconite has been found at Jáchymov, Czechoslovakia; Freiberg, Germany; Chañarcillo, Chile; and Ouray, Colorado. It occurs in a number of mines in the Cobalt silver camp, Ontario, especially in the La Rose and Keeley mines. In all of their occurrences pyrostilpnite and xanthoconite are generally closely associated with argentian tetrahedrite, tennantite, and the ruby silvers.

*Polybasite*, $(Ag,Cu)_{16}Sb_2S_{11}$, and *pearceite*, $(Ag,Cu)_{16}As_2S_{11}$, are two closely related silver sulphosalts. In polybasite Cu may substitute for Ag up to about 30 atomic per cent and As may substitute for Sb up to about 60 atomic per cent. In pearceite Cu substitutes for Ag to about 30 atomic per cent and Sb for As to only about 4 atomic per cent (Palache, *et al.*, 1944). A hiatus appears, therefore, to exist between a complete solid solution series involving pearceite and polybasite. Recent investigations by Frondel (1963), however, showed that the arsenic analogue of polybasite (*arsenpolybasite*) and the antimony analogue of pearceite (*antimonpearceite*) occur in nature, and that polybasite-arsenpolybasite and pearceite-antimonpearceite probably form an isodimorphous, complete solid-solution series, $(Ag,Cu)_{16}(Sb,As)_2S_{11}-(Ag,Cu)_{16}(As,Sb)_2S_{11}$. Harris, Nuffield, and Frohberg (1965) questioned the validity of Frondel's classification and preferred to regard pearceite and polybasite as the arsenic and antimony end members of a continuous series having fundamental unit cell dimensions of $a \sim 13$, $b \sim 7.5$, $C \sim 12$Å, $\beta = 90°$, and composition $(Ag,Cu)_{32}(As,Sb)_4S_{22}$. Their study showed that in certain specimens, some or all of the axial dimensions are doubled. Hence, pearceite having the fundamental cell should be called pearceite (1-1-1), and pearceite with all axes doubled should be (2-2-2), etc.[1]

Polybasite and pearceite may both contain small amounts of Fe, Zn, and Pb substituting for Ag; Bi may replace either As or Sb.

Polybasite and pearceite are hypogene in some deposits and apparently supergene in others. Polybasite is common in many of the classic silver deposits in Europe, in Mexico, and in Colorado, U.S.A. Pearceite is much less common than polybasite. Both minerals accompany native silver, acanthite, freibergite, and the ruby silvers in deposits. In Canada polybasite occurs in small amounts in a number of the silver deposits in the Western Cordillera, including Keno Hill, Beaverdell, and Torbrit Silver mines. The mineral has also been recorded in the gold-quartz veins of the Howey and Hasaga mines, Red Lake district, Ontario, and in the native silver ores of the Cobalt camp, Ontario. Pearceite occurs in the barite-silver-lead-zinc-copper deposit at Walton, Nova Scotia and in the Golden Manitou mine, Val d'Or, Quebec.

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[1] Hall (*Am. Mineralogist*, vol. 52, pp. 1311–1321) has recently presented data showing that the traditional polybasite and pearceite are members of two separate solid-solution series in which antimony and arsenic substitute mutually. The parallel series are, however, not dimorphous as suggested by Frondel, and copper is a necessary component in the series.

*Stephanite*, $Ag_5SbS_4$, is generally relatively pure, but may contain traces of Fe, Cu, and As. It is a relatively rare mineral occurring with other silver sulphosalts, acanthite, tetrahedrite, and native silver in a number of classic silver deposits in Europe, Mexico, and U.S.A. In Canada it occurs in the silver-lead-zinc ores of the Slocan area, British Columbia, and in the native silver deposits of Cobalt and South Lorrain, Ontario. In most deposits stephanite is of hypogene origin, but there are a few references in the older literature to its supergene occurrence.

*Argyrodite*, $Ag_8GeS_6$, and *canfieldite*, $Ag_8SnS_6$ form a solid-solution series with Sn replacing Ge. Both minerals may contain traces to small amounts of Fe, Zn, Cu, Hg, As, and Sb. Both argyrodite and canfieldite are reported from Freiberg, Saxony, and from various silver-lead and silver-tin mines in Bolivia. Argyrodite occurs in the Dolly Varden mine, Alice Arm, Skeena mining district, British Columbia (Thompson, 1953). There appear to be no reported occurrences of canfieldite in Canada. In most deposits argyrodite and canfieldite are apparently hypogene in origin.

The rest of the sulphosalts are rare and generally occur within single deposits or districts. All appear to be of hypogene origin and are associated with the common silver sulphosalts, acanthite, native silver, and freibergite. *Miargyrite*, $AgSbS_2$, was an abundant silver ore mineral in the bonanzas of the Randsburg district of California. The details of its structure and the coordination of its constituent Ag, Sb, and S atoms have been recently discussed by Knowles (1964). *Matildite*, $AgBiS_2$, and occasionally *aramayoite*, $Ag(Bi,Sb)S_2$, are common in some deposits, generally as microscopic intergrowths with galena.

Some of the less common silver sulphosalts in Canada occur as follows: *Andorite*, $PbAgSb_3S_6$, has been found on the Kay group, about 20 miles east of Takla Landing on Stuart Lake, Omineca mining division, British Columbia (Warren, 1947); *Owyheeite*, $Pb_5Ag_2Sb_6S_{15}$, has been recorded from the Alma group near the head of Memphis Creek and in the Alamo lode near the head of Howson Creek, both in the Slocan mining district, British Columbia (Warren, 1948); also in the Rambler mine, Slocan, in the Sherwood mine, Della Lake, Alberni mining district, Vancouver Island (Thompson, 1950); and in Rossland mines, near Rossland, Trail Creek, British Columbia (Thompson, 1953). *Matildite* occurs in the veins of the How Group, Camsell River, Northwest Territories (Thompson, 1953) and in some of the native silver deposits of Cobalt, Ontario.

The silver halides include *chlorargyrite* (cerargyrite), *bromargyrite* (bromyrite), *miersite*, and *iodargyrite* (iodyrite). They are comparatively common supergene minerals in arid regions or where aridity prevailed in the past.

*Chlorargyrite*, AgCl, and *bromargyrite*, AgBr, have a halite structure but are characterized by an intermediate ionic-covalent bond, which also shows some semimetallic properties as witnessed by the plastic, sectile, and ductile nature of the minerals. Chlorargyrite and bromargyrite form a complete solid-solution series with the boundary between the two species being drawn at $Cl:Br = 1:1$. Both minerals may contain considerable amounts of iodine (up to 15 per cent in some analyses), and mercury has been reported in a few samples. Bromian chlorargyrite has been called *embolite*, and iodian chlorargyrite has been given the name *iodembolite* by some authors. Chlorian bromargyrite has been referred to as *megabromite*, *embolite*, and *orthobromite*, and iodian bromargyrite has been variously called *iodobromite* and *iodembolite*. All of these names are confusing and have been confused by several writers. They should be discontinued, and the main mineral names should be used with the appropriate elemental adjectives applied, thus—bromian iodian chlorargyrite, chlorian iodian bromargyrite, etc.

Chlorargyrite is a common mineral in the oxidized zones of silver deposits where it is associated with native silver, bromargyrite, iodargyrite, jarosite, wad, limonite, cerussite, malachite, and other supergene minerals. It has been found in many of the classic silver deposits of Europe, including Johanngeorgenstadt, Freiberg, Schneeberg, Andreasberg in the Harz, and Jáchymov; in U.S.S.R. in the polymetallic deposits of Kazakhstan, in the Altai Mountains, and elsewhere; in Chile in large amounts, especially at Caracoles and Chañarcillo; in Bolivia at Potosí; in Mexico at Zacatecas and in numerous other silver districts; in Australia in the Broken Hill district, New South Wales; and in the United States in many of the western mining districts, especially at Treasure Hill, Nevada, in the Bullfrog district, Nevada, at Leadville, Colorado, Silver City area, New Mexico, Tombstone, Arizona, and in the Poorman mine, Silver City district, Idaho. Chlorargyrite seems to be very rare in Canada; the writer has not found the mineral in his examination of the oxidized zones of silver deposits in western or eastern Canada. The mineral did occur in the Silver Islet vein, Lake Superior, in small amounts and seems to have resulted from the action of underground salt waters on acanthite. Small amounts of chlorargyrite are also reported from the deposits in the Slocan area of British Columbia.

*Huantajayite* is supposedly an argentian halite, but evidence of its homogeneity is lacking. It occurs at several mines in the Huantajaya district, Tarapacá, Chile, where it is associated with calcite, chlorargyrite, bromargyrite, atacamite, etc. in the oxidized zones of the silver deposits. The mineral dissolves in water giving a milky-white suspension of AgCl.

*Ostwaldite* is a colloidal form of AgCl originally described by Klaproth from the oxidized zones at Andreasberg in the Harz (Cornu, 1909). The name should probably be discarded, since the mineral appears to be a microcrystalline variety of chlorargyrite.

Bromargyrite is not as common as chlorargyrite, mainly because of the lower abundance of bromine in natural waters. It has the same mineral associations as chlorargyrite. Bromargyrite has been reported from deposits near Dernbach, Germany; in the Ukraine, U.S.S.R.; in the oxidized zones of the Broken Hill deposit, New South Wales, Australia; abundantly at Chañarcillo, Chile; in the deposits at Zacatecas, Mexico; and at Tombstone, Arizona. There are no reported occurrences of bromargyrite in Canada.

Silver iodide, AgI, can exist in a number of polymorphs— a $\gamma$ or sphalerite-type low temperature isometric polymorph[1], called *miersite*, metastable up to 147°C;

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[1] See, however, the paper by Majumdar and Roy (1959), who from experimental data doubt the existence of a true sphalerite form of AgI.

a $\beta$ or wurtzite-type hexagonal polymorph, *iodargyrite,* stable up to 147°C; an $\alpha$ or high temperature polymorph, stable above 147°C, having a disordered body-centred cubic structure of iodine with silver atoms randomly distributed through the interstices; and a high pressure form with the NaCl structure. Other polytypes have been suggested. Schneer and Whiting (1963), Burley (1963), and Bassett and Takahashi (1965) have discussed in detail the various phase transformations and thermal hysteresis in the AgI system.

Miersite AgI, and *marshite,* CuI, are isostructural and probably form a complete solid-solution series. Miersite generally contains some copper.

Miersite and iodargyrite occur in the oxidized zones of the Broken Hill deposit, New South Wales, Australia. Iodargyrite has also been reported from Dernbach, Germany; abundantly at Chañarcillo, Atacama, Chile; in Mexico from the Zacatecas region; in the oxidized zones of the polymetallic deposits, Kazakhstan, U.S.S.R.; in the United States in the oxidized zones at Tonopah and Goldfield, Nevada, at Lake Valley, Sierra County, New Mexico, and at the Commonwealth mine, Pearce Hills, Cochise County, Arizona. There are no reported occurrences of iodargyrite or miersite in Canada.

All of the silver halides, except the fluoride, are photosensitive, a feature that has received much attention by numerous investigators. On exposure to light they slowly turn pink, then violet, brown, and finally black, a feature that has been explained in many ways. While the process is not yet fully understood it is now generally agreed that defect structures and mobile photoconductivity electrons are involved. The primary photolytic reaction for silver chloride can be represented as follows:

$$Ag^{+} + Cl^{-} \underset{h\nu}{\rightleftharpoons} Ag^{\circ} + Cl^{\circ}$$

On exposure to light photoconductivity electrons are freed from the $Cl^{-}$ ions. These electrons apparently move freely in the silver chloride crystals and by chance come into contact with silver ions that exist interstitially in the lattice or are associated in some manner or other with minute specks of silver sulphide in the crystals. These silver ions form the nuclei of colour centres in the crystals. The electrons, on reaching the sites of the silver ions, neutralize the latter, forming neutral silver atoms, and these absorb the visible light giving a dark colour to the crystals. During this process the $Cl^{\circ}$ atoms diffuse, combine to form $Cl_2$, and escape as chlorine. This makes the process irreversible.

*Argentojarosite,* $AgFe_3(SO_4)_2(OH)_6$, is a supergene silver mineral formed where mildly acid conditions prevailed during the oxidation of silver deposits containing pyrite. It is generally accompanied by anglesite, limonite, cerussite, secondary quartz, etc. The mineral was originally discovered at the Tintic Standard mine, Dividend, Utah (Schempp, 1923), and seems to have been rather common in the ores of the Tintic district. A closely allied mineral, argentian plumbojarosite, occurs in some of the oxidized ore shoots of the Keno Hill-Galena Hill district, Yukon. Both argentojarosite and argentian plumbojarosite may be more common in the oxidized lead-silver deposits of the Western Cordillera and elsewhere than the occurrences described would lead one to expect. Both minerals are yellowish to brownish, generally pulverulent or very fine grained and micaceous, and hence tend to be obscured by limonite, anglesite, beudantite, and other secondary minerals in the oxidized zones.

The conditions for the synthesis of argentojarosite have been described by Fairchild (1933). The mineral precipitates from acidic ferric sulphate and silver sulphate solutions during the hydrolysis of the ferric iron. The mineral is closely related to the other jarosites, which include jarosite proper, ammoniojarosite, natrojarosite, and plumbojarosite.

## Silver in Other Minerals

Silver is a minor and trace constituent of a great variety of minerals, a feature of the geochemistry of the element that was investigated many years ago (Malaguti and Durocher, 1850; Hartley and Ramage, 1897).

### *Silver in Silicates*

Data obtained from a spectrographic investigation of a variety of pure silicate minerals for silver in the laboratories of the Geological Survey are given in Table 8.

TABLE 8 | *Silver Content of the Common Silicate Minerals*[1]

| Mineral | Locality | Ag, ppm |
|---|---|---|
| Quartz | Various, Yellowknife, Keno Hill, etc. | $< 0.05$ |
| Orthoclase | Herschell township, Hastings county, Ontario | $< 0.05$ |
| Orthoclase | Itrongay, Madagascar | $< 0.05$ |
| Microcline | Derry Mine, Derry township, Quebec (13.25% $K_2O$, 1.25% $Na_2O$) | $< 0.05$ |
| Albite, var. cleavelandite | Quebec Beryllium property, Lacorne township, Quebec | 0.47 |
| Albite, var. cleavelandite | Lacorne township, Quebec | 1.0 |
| Albite, var. cleavelandite | Branchville, Conn., U.S.A. | 0.07 |
| Albite, var. cleavelandite | Portland, Conn., U.S.A. | 0.08 |
| Albite, var. peristerite | Villeneuve Mine, Villeneuve township, Quebec | 0.26 |
| Albite, var. peristerite | Buckingham, Labelle county, Quebec | 0.35 |
| Albite, var. peristerite | Cardiff township, Haliburton county, Ontario | 0.2 |
| Albite | Mont St. Hilaire, Quebec | 0.09 |
| Albite | North Burgess township, Lanark county, Ontario | 0.13 |
| Labradorite | Tabor Island, Labrador | 0.05 |
| Bytownite | Brome Mountain, Quebec | $< 0.05$ |
| Muscovite | Eau Claire, Ontario | $< 0.05$ |
| Muscovite | Jonquière, Chicoutimi county, Quebec | $< 0.05$ |

| Mineral | Locality | Ag, ppm |
|---|---|---|
| Muscovite | Methuen township, Peterborough county, Ontario | 0.05 |
| Biotite | Douglas, Renfrew county, Ontario | < 0.05 |
| Biotite | Lot 32, range 12, Sebastopol township, Ontario | < 1 |
| Biotite | Monteagle township, Hastings county, Ontario | < 1 |
| Tourmaline | Derry township, Quebec | < 1 |
| Tourmaline | Villeneuve Mine, Villeneuve township, Quebec | < 1 |
| Tourmaline | Lot 25, range VII, Wakefield township, Ottawa county, Quebec | < 1 |
| Tourmaline | Yellowknife area, N.W.T. | 1–10 |
| Olivine | Daun, Eifel district, Germany | < 1 |
| Olivine | Mount Albert, Gaspé county, Quebec | < 1 |
| Olivine | Timothy Mountain, Cariboo district, British Columbia | < 1 |
| Garnet | Dana township, Ontario | < 1 |
| Garnet, var. grossularite | Wakefield township, Quebec | < 1 |
| Garnet, var. andradite | Cawood, Pontiac county, Quebec | < 1 |
| Zircon | Saranac property, Monteagle township, Ontario | 0.08 |
| Zircon | Lake Donaldson, Buckingham township, Quebec | < 1 |
| Zircon | Lot 10, range 5, Grenville township, Argenteuil county, Quebec | < 1 |
| Sodalite | Bancroft area, Ontario | 0.07 |
| Sodalite | Ice River, British Columbia | 0.10 |
| Nepheline | Bancroft, Ontario | 0.05 |
| Nepheline | Blue Mountain, Ontario<br>Hastings county, Ontario | < 0.05 |
| Amphibole, var. edenite | Grenville township, Quebec | 0.08 |
| Hornblende | Bancroft, Ontario | 0.05 |
| Hornblende | Cardiff township, Ontario | 0.05 |
| Hornblende | Lot 18, range 2, Wakefield township, Quebec | 0.07 |
| Aegerine | Mont St. Hilaire, Quebec | < 1 |
| Acmite | Gatineau district, Quebec | < 0.05 |
| Acmite | Mont St. Hilaire, Quebec | 0.07 |
| Augite | Prague, Czechoslovakia | < 1 |

[1] Analyses by spectrographic laboratories, Geological Survey of Canada

Silver is present in nearly all silicates, but the content is generally very low, seldom exceeding 0.5 ppm. On the available data there are no obvious relationships between silver and any of the other elements in the common silicates.

Pure quartz from practically all settings is very low in its silver content according to our investigations. Others, however, have reported up to 100 ppm or more in samples of natural and synthetic material (Cohen and Sumner, 1958; Chukhrov, *et al.* 1965)

Devore (1955) determined the silver content of a large number of samples of hornblende, biotite, garnet, and chlorite. The ranges he found for silver were: hornblende, 0.3–1.7 ppm; biotite, 0.1–1.0 ppm; garnet, 0.2–15.0 ppm; and chlorite, trace–6.0 ppm.

Biehl (1957) noted that the silver contents of some of the micas of the grey Freiberg gneisses were peculiar, but gave no specific data. De Barros (1957) also found up to 0.3 ppm silver in some Spanish and Portuguese muscovites and D. D. Hogarth (pers. com.) has informed the writer that some phlogopites from the Gatineau area, Quebec, contain silver. These isolated data suggest the possibility of an association of silver with potassium. However, the writer has often observed that micas, particularly biotite, contain some admixed sulphides, and the silver may be in these minerals rather than in the structure of the muscovite, biotite, etc. The whole problem of silver in micas requires a thorough investigation.

The close relationship between the ionic radii and electronic properties of sodium, potassium, and silver, and the known tendency for silver to replace sodium in glasses (Eitel, 1954) and zeolites (Hey, 1962) would lead one to suspect that silver might be enriched in the alkali silicates. During the writer's research he has found that certain albites, sodalites, and other sodium-rich silicates contain higher than normal amounts of silver, suggesting a replacement of sodium by silver. However, not all sodium-rich silicates are enriched in silver, and hence few definite statements are warranted.

There is no evidence from our data to suggest that $Ag^{2+}$ (0.89Å) enters the $Fe^{2+}$, $Ca^{2+}$, and $Na^{+}$ positions of silicate minerals as postulated by Taylor (1965b).

### *Silver in Native Elements*

Silver is a frequent microconstituent in the native elements as shown in Table 9.

TABLE 9 *Silver Content of Native Elements*

| Native Element | Recorded range in % |
|---|---|
| Iron | 0.0001 – 0.001 |
| Copper | 0.1 – 4.0 |
| Gold | 0.1 – 20.00 ($>$ 20.00% = electrum) |
| Lead | traces to minor amounts |
| Palladium | traces |
| Osmiridium | traces |
| Zinc | traces |
| Mercury | traces to minor amounts |
| Carbon (diamond) | traces |
| Arsenic | traces |
| Antimony | 0.01 – 1.00% |
| Bismuth | traces to 0.01; pure material from O'Brien mine, Ontario, and Altenberg, Germany, gave $<$ 5 and 70 ppm Ag, respectively. |
| Tellurium | 0.20 – 1.69 |

Sources: Hintze (1889–1939); Doelter, *et al.* (1911–1931); Palache, *et al.* (1944); Chukhrov, *et al.* (1960–1965); Laboratories, Geological Survey of Canada

The element prefers the gold group of which it is a member. Native antimony, bismuth, and tellurium may also be enriched in silver, a feature that is readily understood, since the affinity of silver for the three elements is particularly marked.

TABLE 10 | *Silver Content of Common Tellurides and Selenides*

| Mineral | Range recorded in % |
|---|---|
| *Tellurides* | |
| Altaite, $PbTe$ | 0.43 – 1.28 |
| Wehrlite, $Bi_{2+x}Te_{3-x}$ (?) | 0.48 – 4.37 |
| Melonite, $NiTe_2$ | 0.077– 0.86 |
| Calaverite, $AuTe_2$ | 0.40 –3.23 |
| Krennerite, $AuTe_2$ | 0.46 – 5.87 |
| Montbrayite, $Au_2Te_3$ | 0.22 – 0.55 |
| Nagyagite, $Pb_5Au(Te,Sb)_4S_{5\text{-}8}$ | up to 1.12 |
| *Selenides* | |
| Berzelianite, $Cu_2Se$ | 3.51 – 8.50 |
| Umangite, $Cu_3Se_2$ | 0.45 – 0.55 |
| Penroseite, $(Ni,Cu,Pb)Se_2$ | 0.59 – 7.78 |
| Clausthalite, $PbSe$ | traces to small amounts |
| Klockmannite, $CuSe$ | up to 0.73 |
| Wittite, $Bi_6Pb_5(Se,S)_{14}$ | up to 0.19 |
| Selenokobellite, $Pb_2(Bi,Sb)_2(S,Se)_5$ | 0.36 – 0.44 (Ödman, 1941) |

Sources: Hintze (1889–1939); Doelter, *et al.* (1911–1931); Palache, *et al.* (1944); Chukhrov, *et al.* (1960–1965); Laboratories, Geological Survey of Canada

### *Silver in Tellurides and Selenides*

Silver is a common trace element in practically all tellurides and selenides, and in some it occurs in considerable quantities (Table 10). It is particularly abundant in the gold tellurides in which it replaces gold. It also occurs in relatively high amounts in some of the lead and bismuth tellurides and in the copper and lead selenides. In these minerals silver appears to replace Pb, Bi, and Cu.

### *Silver in Sulphides, Arsenides, Antimonides, Sulphosalts, etc.*

There is a vast literature on the silver content of arsenides, antimonides, sulphides, sulphide-arsenides, and sulphosalts, much of which is summarized by Fleischer (1955). The data in Table 11 have been compiled up to the end of 1965 from all material in the literature available to the writer and from the numerous analyses done in the laboratories of the Geological Survey. It is recognized that the data are incomplete, but the ranges shown give an idea of the silver content to be expected in arsenides, sulphides, etc.

One of the great problems in ascertaining the role that silver plays in arsenides, sulphides, and allied minerals is the matter of purity of the samples. In a great many

TABLE 11 | *Silver Content of Some Common Sulphides, Antimonides, Bismuthides, Arsenides, and Sulphosalts*

| Mineral | Range in ppm |
|---|---|
| *Arsenides and antimonides* | |
| Niccolite, NiAs | 10 – 100 (higher values recorded probably due to impurities) |
| Breithauptite, NiSb | No data on pure material ? |
| Loellingite, $FeAs_2$ | No data on pure material |
| Safflorite, $(Co,Fe)As_2$ | 0.5 – 100 (higher values recorded probably due to impurities) |
| Skutterudite, $(Co,Ni)As_3$ | Up to 4% Ag but probably due to impurities |
| Smaltite-chloanthite $(Co,Ni)As_{3-x}$ | 1 – 1,000 (values up to 4% recorded but probably due to impurities) |
| Rammelsbergite, $NiAs_2$ | 1 – 10 |
| Aurostibite, $AuSb_2$ | Up to 1% Ag or greater ? Ag in yellowknife samples |
| *Sulphides and sulphide-arsenides* | |
| Digenite, $Cu_{2-x}S$ | 10 – > 1,000 |
| Chalcocite, $Cu_2S$ | < 1 – > 1,000 (contents up to 1% Ag recorded but purity uncertain) |
| Bornite, $Cu_5FeS_4$ | < 1 – 1,000 |
| Galena, PbS | < 1 – 8,000 (values up to 6.4% Ag recorded but probably due to impurities) |
| Sphalerite, ZnS | 3 – 3,500 (values up to 1.5% Ag recorded but probably due to impurities) |
| Hawleyite, $\beta$ CdS | ~ 50 |
| Chalcopyrite, $CuFeS_2$ | 5 – 3,300 |
| Stannite, $Cu_2FeSnS_4$ | Isolated values up to 1% Ag recorded. High values probably due to impurities |
| Pyrrhotite, $Fe_{1-x}S$ | 1 – 210 (values up to 5,500 ppm recorded but probably due to impurities) |
| Pentlandite, $(Fe,Ni)_9S_8$ | 1 – 50 (average for Sudbury ores—3.4 ppm) (Hawley, 1962) |
| Covellite, CuS | Traces to 500 ppm |
| Cinnabar, HgS | < 1 – 10 |
| Stibnite, $Sb_2S_3$ | Traces to 500 ppm |
| Molybdenite, $MoS_2$ | < 1 – > 100 |
| Bismuthinite, $Bi_2S_3$ | Traces to 3,000 ppm. Pure material from Quebec and Bolivia show only < 5 – 70 ppm Ag |
| Pyrite, $FeS_2$ | < 1 – 500 (values up to 1,500 ppm have been recorded on isolated samples) |
| Cobaltite, (Co,Fe)AsS | 1 – 100 |
| Gersdorffite, NiAsS | 1 – 100 |
| Ullmannite, NiSbS | 10 – 1,000 |
| Arsenopyrite, FeAsS | < 1 – 400 |
| Molybdenite, $MoS_2$ | 0.1 – 100 (Goldschmidt and Peters, 1932) |
| *Sulphosalts* | |
| Wittichenite, $Cu_3BiS_3$ | 100 – 1,500 |
| Germanite, (Cu,Ge)(S,As) | 50 – 100 |

| Mineral | Range in ppm |
|---|---|
| *Sulphosalts (cont'd)* | |
| Famatinite, $Cu_3(Sb,As)S_4$ | Up to 1,900 |
| Geocronite, $Pb_5(Sb,As)_2S_8$ | 0.5 to 1.5% (Kuznetsov, 1957) |
| Enargite, $Cu_3(As,Sb)S_4$ | Traces to minor amounts |
| Beegerite, $Pb_6Bi_2S_9$ | Up to 15.40%, but purity uncertain |
| Teallite, $PbSnS_2$ | Traces |
| Jordanite, $Pb_{14}As_7S_{24}$ | No data |
| Bournonite, $PbCuSbS_3$ | Up to 1.69% |
| Meneghinite, $CuPb_{13}Sb_7S_{24}$ | Up to 1,100 ppm |
| Boulangerite, $Pb_{2\text{-}5}Sb_{2\text{-}4}S_{5\text{-}11}$ | Traces – 600; 4,000 – 5,000 (Kuznetsov, 1959) |
| Chalcostibite, $CuSbS_2$ | Traces to 1,000 |
| Cosalite, $Pb_2Bi_2S_5$ | 3,200 – 7,500 (contents up to 1.67% reported) |
| Selenocosalite, $Pb_2Bi_2(S,Se)_5$ | 1.02 to 1.20% (Ödman, 1941), values up to 3.74% reported |
| Kobellite, $Pb_2(Bi,Sb)_2S_5$ | Up to 3.58% |
| Selenokobellite, $Pb_2(Bi,Sb)_2(S,Se)_5$ | 3,600 – 4,400 (Ödman, 1941) |
| Franckeite, $Pb_5Sn_3Sb_2S_{14}$ | Up to 1% |
| Cylindrite, $Pb_3Sn_4Sb_2S_{14}$ | 3,900 – 6,200 |
| Jamesonite, $Pb_4FeSb_6S_{14}$ | 40 – 13,400 |
| Semseyite, $Pb_9Sb_8S_{21}$ | 1,300 – 5,600 |
| Galenobismutite, $PbBi_2S_4$ | No data |
| Cuprobismutite, $CuBiS_2$ (?) | Up to 1% |
| Zinkenite, $Pb_6Sb_{14}S_{27}$ | 2,300 – 5,200 |
| Plagionite, $Pb_5Sb_8S_{17}$ | Traces to 1,800 |
| Berthierite, $FeSb_2S_4$ | Traces to 100 |
| Livingstonite, $HgSb_4S_7$ | No data |

Sources: Hintze (1889–1939); Doelter, *et al.* (1911–1931); Palache, *et al.* (1944); Fleischer (1955); Chukhrov, *et al.* (1960–1965); Laboratories, Geological Survey of Canada; Numerous other papers (*see* Bibliography)

occurrences the sulphides, etc. are highly intergrown with silver minerals or contain silver minerals as blebs, rods, and specks. In many cases the investigators do not state whether the minerals are homogeneous or not, and it is nearly impossible to tell whether the silver is in the lattices of the minerals or present in one or more admixed silver minerals. Geochemists doing spectrographic work on sulphides, arsenides, and similar minerals should examine their specimens for homogeneity by microscopic methods or better still by means of the electron probe. The data would then be of much more significance in obtaining an idea of the extent of the replacements of one element by another.

The common nickel and cobalt arsenides and antimonides may contain considerable quantities of silver, but since these minerals often accompany native silver and other silver minerals the element is probably largely present in admixtures of these minerals. The values given by Goldschmidt and Peters (1932) seem to be on relatively pure material. Their values rarely exceed 1,000 ppm Ag.

The gold mineral, aurostibite, generally contains silver substituting for gold in its lattice. The amounts may be difficult to determine, however, since the mineral is commonly associated with native gold, which also contains silver (Sobotka, 1954; Boyle, 1961).

In the three common sulphides, pyrite, pyrrhotite, and chalcopyrite, silver is decidedly concentrated in the chalcopyrite, where it probably replaces copper in the lattice. Hawley and Nichol (1961) noted no marked variation in the Ag content of the chalcopyrites they studied from the Sudbury, McIntyre, Noranda, Manitouwadge, and Normetal mines. Auger (1941) found that the silver content of chalcopyrite increased slightly from the top of the 2,500-foot level of the "Lower H" orebody at Noranda after which there was a slight decrease to the 3,100-foot level.

Pyrrhotite is generally low in its silver content. Hawley and Nichol (1961) found that the pyrrhotites from the Sudbury ores were poor in silver whereas those from the Manitouwadge, Flin Flon, and Normetal copper mines were decidedly richer in the element. The pyrrhotite from the McIntyre gold mine was markedly low in silver, having about one-quarter the amount found in pyrite from the same orebodies. Auger (1941) noted an increase in the Ag content in pyrrhotite in the "Lower H" orebody at Noranda.

Silver is nearly a universal microconstituent of pyrite. Hawley and Nichol (1961) found that the pyrite from the copper deposits they studied (Flin Flon, Chibougamau, Quemont, Noranda, Normetal, and Manitouwadge) consistently showed a higher Ag content than pyrite from the Sudbury district or from the McIntyre gold mine. No variation in depth was observed in the Ag content of the pyrite from the McIntyre orebodies. Auger (1941), however, found a slight increase in the silver content of pyrites with depth in the "Upper H" and "Lower H" orebodies at Noranda. In another study Hawley (1952) and Auger (1941) met with mixed results in the determination of the change of Ag content in pyrite with depth, in Canadian gold mines. In some deposits they noted increases, in others decreases. At Keno Hill, Boyle (1965) found that the Ag content of pyrite was extremely erratic, varying widely from deposit to deposit. Depthwise in the deposits there also appeared to be no apparent correlations.

The data on the silver content of arsenopyrite are much fewer than those for pyrite, but it is evident that this arsenide-sulphide may contain as much or more silver than the iron sulphide. At Keno Hill the arsenopyrite may contain up to 400 ppm Ag as well as some gold. At Yellowknife both gold and silver are constituents of arsenopyrite, and roasting methods are employed to liberate the elements prior to cyanidation.

Investigations on the nature of gold in pyrite and arsenopyrite have been carried out by a number of investigators and their findings have been summarized by Boyle (1961). The research on gold applies with equal force to silver. Some investigators hold that most of the gold (and silver) occurs in native gold or other Au-Ag minerals as microscopic or submicroscopic particles dispersed through the pyrite or in fractures, etc.; others maintain that some of the gold and silver is held in the lattice of the pyrite. Both views are probably correct, as will be shown presently.

Under the microscope one often observes native gold (Au-Ag) and other silver-bearing minerals such as freibergite, acanthite, etc. in pyrite and arsenopyrite, and it is certain that the spectrographic analyses and assays are simply reporting the Ag present in these minerals. On the other hand some pyrite and arsenopyrite containing high contents of gold and silver contain no observable particles of gold and silver-bearing minerals. In this case it is generally necessary to liberate the gold and silver by roasting methods prior to cyanidation. Such an extreme treatment suggests that the gold and silver are a part of the sulphide and not held as a mechanical mixture.

Pyrite and arsenopyrite, as well as many other compounds of the transition metals with non-metallic elements or metalloids, although largely bonded in a covalent manner, nevertheless have a moderate degree of metallic bonding, which increases with increase in the metallic or electropositive character of the constituent elements. Because of their partly metallic character, it would be expected that pyrite and arsenopyrite would accommodate small amounts of nearly all metals in their structures, gold and silver being no exception. In other words these two sulphides behave in part as alloys. Furthermore silver has a marked chalcophile character, which means that it would readily bind with the sulphur atoms in a covalent manner. It would seem, therefore, that there may be some substitution of silver for iron in the pyrite and arsenopyrite lattice and perhaps some interstitial substitution of the element as well. The amount cannot be great, however, because of the significant differences in the covalent radii of the two elements (Ag = 1.53 Å; Fe = 1.24 Å) and the atomic radii (Ag = 1.40 Å; Fe = 1.24 Å). The lattices of the two minerals, however, are probably elastic enough to accommodate the normal amounts of silver (1 – 200 ppm) recorded by spectrographic and other methods of analyses.

Many of the less common copper sulphides contain small amounts of silver, probably substituting for copper in their lattices. Chalcocite, covellite, and bornite are often argentiferous and their deposits may be a source of by-product silver. The silver values in these minerals seem to vary widely.[1] The fine-grained and sooty varieties seem to be relatively high in silver whereas the more crystallized types are lower. No general rules can be applied, however, on the basis of grain size. Secondary (supergene) chalcocite and covellite also seem to be higher in silver than some apparent hypogene varieties. In the 'red bed' sedimentary deposits chalcocite may be greatly enriched in silver.

Note need to check

Stannite may contain relatively high contents of silver, according to the literature, but the purity of the samples is in doubt. They may be contaminated with silver sulphosalts. The silver content of cinnabar, stibnite, and molybdenite is generally low. In some stibnites the writer has found relatively high amounts of the element, but the samples were impure, containing sulphosalts and native gold. According to the literature some bismuthinite samples may contain up to 3,000 ppm Ag. Pure samples of bismuthinite from Quebec and Bolivia spectrographically analyzed in the laboratories of the Geological Survey contained only from <5 to 70 ppm Ag.

Sphalerite, wurtzite, and schalenblende, ZnS, nearly always contain silver as a microconstituent, a feature recorded by numerous investigators (Oftedal 1940; Warren and Thompson 1945; Schroll 1950; di Brito 1955a; Shima and Shima 1956; Haranczyk 1957; Moiseeva 1959; Litvinovich and Loginova 1960; Boyle 1965; and numerous others). The values given by these investigators vary widely from nil up to 3,500 ppm or more. For instance the sphalerite in the Keno Hill-Galena Hill deposits may contain from 5 to 5,000 ppm Ag. Oftedal (1940) early observed that

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[1] According to Skinner (1966) the solubility of $Ag_2S$ in chalcocite is 1.87 mol % at 63°C

samples, in which he found more than 50 ppm Ag, contained argentiferous galena, tetrahedrite, and other silver minerals. This observation is certainly true for the sphalerite from Keno Hill and may be the case for other higher than normal silver-bearing sphalerites recorded in the literature.

On the other hand some relatively homogeneous sphalerites, wurtzites, and schalenblendes appear to contain silver in their lattices, where it apparently substitutes in the zinc sites or in interstitial spaces. Riehl and Ortmann (1941) showed that silver diffuses into the zinc sulphide lattice via the interstices, and Gaudin, *et al.* (1951) found that silver ion is strongly absorbed by sphalerite. The latter investigators thought that the process proceeded by rapid ion exchange (Ag for Zn) at first, followed by slow reaction controlled perhaps by solid-state diffusion. These experiments suggest that the ZnS lattice is a relatively open one, and that silver may enter by a diffusion mechanism and replace zinc or reside in the interspaces. This is perhaps not unexpected since the ZnS lattice is rather elastic, permitting the substitution in the zinc sites of several elements with somewhat different energetic properties. Silver with a covalent radius of 1.53 Å should, therefore, substitute for zinc whose radius is 1.31 Å, but the amount of substitution is perhaps never great (up to 100 ppm?) because of the marked difference in the bond orbital configurations of the two elements, oxidation numbers, etc. That this is the case is suggested by the results obtained by Wright, *et al.* (1963), who found that less than 5 ppm Ag was incorporated in synthetic sphalerite at temperatures up to 500°C and pressures at 4,000 to 10,000 psi.

Colwell (1963) in his study of the trace elements in some eastern Canadian sphalerites observed that the low temperature Grenville deposits (Frontenac, Kingdon mines, etc.) contained more silver than the high temperature deposits (New Calumet, Tetreault, etc.).

Silver-bearing galena has received much attention by numerous investigators. Some of the more recent studies include those by Oftedal (1940), Frondel, *et al.* (1942), Nesterova (1958), Ontoiev, *et al.* (1960), Van Hook (1960), Marshall and Joensuu (1961), and Boyle (1965).

The content of silver in galena varies widely and seems to be correlative with the type of deposit in which it occurs. Thus the galena in many polymetallic veins and other types of deposits is generally rich in silver, whereas the galena from deposits of the so-called "Mississippi Valley type" tends to have low contents of silver.

Colwell (1963) in his study of the trace elements in some eastern Canadian galenas found silver in nearly all of the samples investigated. The amounts present ranged from 1 to 1,390 ppm. He concluded that in general the silver content appeared to depend on local abundance, a feature that obscured any definite correlation with the temperature of formation of the deposits. He did, however, observe an increase in the average silver content of galena with increasing temperature in the Grenville deposits. The galena from the low temperature types (Frontenac, Kingdon mines, etc.) averaged about 47 ppm Ag whereas the high temperature deposits (New Calumet, Tetreault, etc.) averaged 109 ppm Ag. Colwell further found that galenas from the Keeley and Silver Islet deposits (Cobalt type native silver deposits) contained very little silver, and he thought that this indicated a distinct silver-poor period of sulphide mineralization.

The writer has further observed that the crystallinity and structure of the galena has a bearing on its silver content. At Keno Hill the large crystals of galena tend to have lower contents of silver than small crystals, and galena crystals in general tend to have less silver than massive varieties, although there are exceptions to this. Schistose and dense microcrystalline (steel) varieties of galena are often enriched in silver, and ore shoots containing significant amounts of these varieties of galena tend to be silver-rich.

The nature of silver, antimony, bismuth, and other elements in galena has received much investigation and comment, most of which is aptly summarized by Ramdohr (1938, 1960), Edwards (1954), and more recently by those mentioned in the references given in the discussion that follows. There is no doubt that much of the silver in most galena samples is present in admixed silver minerals, including acanthite, freibergite, matildite, beegerite, bismuthinite, and a host of other sulphides and sulphosalts. These minerals, as seen in polished sections, may be randomly distributed through the galena or they may occur along crystallographic directions such as the octahedral planes. Recent synthetic investigations and detailed studies on natural galena suggest, however, that some silver, and probably other elements, may occur in the galena lattice, although the amount is probably low in most occurrences.

The reasons why silver minerals tend to concentrate in galena are of great interest, and although not all are known, some generalizations can be discerned.

Galena is face-centred cubic with a sodium chloride lattice and contains 8 atoms per unit cell. Each Pb atom is bonded to 6 S atoms and each S atom in turn to 6 Pb atoms. The bonding is largely covalent with a marked semi-metallic character, as evidenced by the high metallic lustre, specific conductivity, diode, and thermoelectric properties of the mineral. Because of the semi-metallic character, diffusion of metallic and semi-metallic elements within the galena crystal should be relatively rapid, probably of the order of $5 \times 10^{-5}$ cm$^2$/sec. at 250°C.

The high temperature forms of several silver, antimony, and bismuth minerals are isostructural or nearly so with galena and may enter into solid solution with the lead sulphide at elevated temperatures (above 200°C). Among these the most common are argentite, $Ag_2S$, miargyrite, $AgSbS_2$, matildite, $\alpha AgBiS_2$, and aramayoite, $Ag(Bi,Sb)S_2$. The limits of solid solution of the four common silver species in PbS are relatively well known from experimental data. The three sulphides, $Ag_2S$, $Bi_2S_3$, and PbS melt congruently at the pressure of the system, and the following features have been observed by Van Hook (1960).

The miscibility of $Ag_2S$ in PbS is limited to 0.4 mol % $Ag_2S$ in the binary system PbS-$Ag_2S$, whereas much higher amounts of $Bi_2S_3$ (9 mol % at 800°C) are soluble in galena in the system PbS-$Bi_2S_3$. A continuous series of solid solutions appears in the ternary system PbS-$Bi_2S_3$-$Ag_2S$ at relatively high temperatures, and although considerable amounts of $AgBiS_2$ unmix at 195°C (the $\alpha \rightleftharpoons \beta$ inversion point of matildite), much of this component remains dissolved in galena at low temperatures (10 mol % $AgBiS_2$ at 170°C in the presence of excess $AgBiS_2$). These observations have led Van Hook to conclude that the solubility of Ag in PbS may be extensive, even at low temperatures when Bi is present, and that similar relationships probably prevail when Sb is present in the system.

The solubility of silver sulphide in galena has also been substantiated by other workers. Wright, *et al.* (1963) found that silver sulphide is soluble in galena in amounts from 0.03 mol per cent at 300°C to 0.52 mol per cent at 600°C at pressures of 4,000 to 10,000 psi. Recently, Hutta and Wright (1964) found experimentally a systematic increase in the silver content of galena crystals with increase in temperature of crystallization. At 300°C, 0.03 mol per cent of $Ag_2S$ was dissolved homogeneously in galena and at 600° the mol percentage was 0.52 $Ag_2S$.

It thus seems to be well established that at elevated temperatures Ag, Bi, and Sb partake of the galena structure without any marked distortion of the lattice or any great increase in the free energy of the crystal. From energetic considerations it seems probable that at relatively high temperatures Ag, Bi, and Sb would occupy some of the lead positions in the expanded PbS lattice and that the charge distribution would be equalized where necessary by multiple substitutions of the type ($Ag^+ + Bi^{3+} = 2\,Pb^{2+}$), ($Ag^+ + Sb^{3+} = 2Pb^{2+}$), ($2Bi^{3+} = 3\,Pb^{2+}$), ($2Ag^+ = Pb^{2+}$) or by substitution of Sb in interstitial positions or perhaps even in the S positions. In considering the latter type it should be remembered that Sb and also Bi may be electron acceptors, taking up three electrons ($-3$ oxidation state) in their valency orbitals to attain the noble gas configuration. Arrangements such as those suggested above appear to be a feature of some semi-metallic lattices, and in this respect they simulate certain alloys.

At lower temperatures the presence of foreign constituents with marked size differences and charge distributions (e.g., $Ag^+$—1.31Å, $Pb^{2+}$—1.24Å; $Ag^\circ$—1.44Å, $Pb^\circ$—1.74Å) distort the galena lattice, with a consequent rise in the free energy of the crystals. In order to reduce the free energy of the system to a minimum, components such as Ag, Sb, and Bi migrate by diffusion to 111 or 100 planes or other suitable low chemical potential sites, where they crystallize as freibergite, argentite (acanthite), matildite, etc. It is also probable that some of the silver and other elements are trapped in interstitial sites in the galena lattice. The diffusion processes leading to all these phenomena are probably greatly enhanced by the large number of crystal imperfections, which seem to be a feature of natural galena (Greig 1960).

It is evident from experimental work and from the data on relatively homogeneous galena that some silver may be retained within the lattice. The amounts appear in some cases to be dependent on the content of bismuth (or antimony) as shown by Ontoiev, *et al.* (1960). These investigators found that the cell edge of the high bismuth-silver galena they investigated decreased in a systematic manner, leaving little doubt that both Ag and Bi are component parts of the galena lattice.

The amount of silver retained by the galena lattice seems to depend on several factors, among which the most important are the thermal history of the mineral, the amounts of compensating elements such as bismuth and antimony, and the amount of structural distortion the galena has undergone.

A number of investigations have been carried out to determine the relationship between the lead isotopic composition of galena and the silver content of the mineral. The results are inconclusive to say the least. Cahen, *et al.* (1958) investigated a number of galenas from the Alps and from deposits in North Africa. They found that practically all galenas with model ages comparable to the age of the host formation are silver rich and are found in veins, often with more or less obvious magmatic connections. On the other hand, the galenas in sedimentary rocks, and apparently independent of igneous activity, are poor in silver and have model ages that are older than the host formation. The galenas that have model ages of the right order of magnitude as compared with their host formation are considered to be composed of "primary" lead, apparently derived from magmas. The galenas that have model ages older than their host formations are considered to be composed of "rejuvenated" lead from an older source of lead ore. Surely this view of the origin of lead deposits is oversimplified. One wonders why the silver accompanied the lead in the first situation and not in the second, since presumably the old source of lead ore was initially magmatic and enriched in silver.

Furthermore the data on the lead isotopes and the silver content of the galena in the Keno Hill deposits are not in agreement with the findings of Cahen, *et al.* (1958). The silver contents of the galena are some of the highest recorded in the world (up to 8,000 ppm) yet all of the lead isotopic analyses on 200 samples or more are anomalous, that is they give ages in the future.

Russell, *et al.* (1957) investigated the galena from the Broken Hill deposits, New South Wales, Australia, and found that the great massive lenses of the main lode had ordinary leads whereas the lead in galena from fractures (Thackaringa type) in the rocks near the main lode had anomalous isotopic ratios. They further noted that the ordinary lead-bearing galena from the massive lenses contained more bismuth, tin, cadmium, and other elements than the anomalous lead-bearing galena in the fractures. From qualitative spectrographic analyses the silver content of the two types of galena was about the same in the two types of deposits. More recently Bounsall (1961) has confirmed that there is no significant difference in the silver content of the two types of lead deposits in the Broken Hill area that can be correlated with differences in the isotopic composition of the galena.

Silver is a major constituent of a number of the common sulphosalts and in addition is found in trace and minor amounts in a number of the less abundant lead and copper sulphosalts in which it probably replaces lead and copper. Some varieties of geocronite, beegerite, boulangerite, and jamesonite seem to be greatly enriched in silver. The data on the silver content of the other sulphosalts are given in Table 11.

### *Silver in Halides, Carbonates, Oxides, Sulphates, etc.*

Data on the silver content of carbonates, halides, oxides, sulphates, etc. are sparse, scattered in the literature, and mainly qualitative. That available is compiled in Table 12. Most of the values given are from the writer's research on various ore deposits in Canada.

The common halides contain very little silver. Marshite is isomorphous with AgI, and silver can replace copper in all proportions. The mineral percylite is a secondary mineral formed in the oxidized zones of lead-zinc-silver and other types of veins. The silver in the mineral evidently replaces the copper or lead in the lattice. Percylite is closely akin to a number of other lead-copper hydroxide-chloride minerals,

TABLE 12 *Silver Content of Some Halides, Carbonates, Sulphates, Oxides, etc.*

| Mineral | Location | Ag, ppm (range) |
|---|---|---|
| *Halides* | | |
| Halite, NaCl | Various | $<$ 0.5 ppm |
| | Sudharz district, Germany (Herrmann, 1958) | 0 – 0.001 |
| Sylvite and carnallite | Sudharz district, Germany (Herrmann, 1958) | 0 – 0.02 |
| Marshite, CuI | Broken Hill, N.S.W. (Palache, *et al.* 1951) | Up to 1.19% recorded |
| Calomel, HgCl | Various | Traces |
| Fluorite, $CaF_2$ | Various | $<$ 1 |
| Percylite, $PbCuCl_2(OH)_2$? | Various | 0.90 to 8.98% recorded |
| Phosgenite, $Pb_2(CO_3)Cl_2$ | Monteponi, Italy (Palache, *et al.* 1951) | 100 |
| Atacamite, $Cu_2(OH)_3Cl$ | Walton, N.S. | $<$ 3 |
| *Carbonates* | | |
| Calcite, $CaCO_3$ | Veins, Yellowknife, N.W.T. | $<$ 1 |
| | Veins, Keno Hill, Y.T. | $<$ 1 |
| | Veins, Walton, N.S. | $<$ 1 |
| Siderite, $FeCO_3$ | Veins, Keno Hill, Y.T. | $<$ 1 |
| | Veins, Keno Hill, oxidized | Up to 50 |
| | Replacement deposits, Walton, N.S. | $<$ 10 |
| Smithsonite, $ZnCO_3$ | Keno Hill, zones of reduction | 1 – 50 |
| Cerussite, $PbCO_3$ | Keno Hill, oxidized zones | 1 – 50 |
| Malachite, $Cu_2(CO_3)(OH)_2$ | Keno Hill, oxidized zones | 100 – 1,000 (pure) |
| | Whitehorse, oxidized zones | 70 |
| | New Brunswick, Dorchester mine area | 50 – 500 (impure) |
| Azurite, $Cu_3(CO_3)_2(OH)_2$ | Australia, Bisbee Arizona | $<$ 5 |
| Bismutite, $(BiO)_2(CO_3)$ | Arizona, Outpost mine, White Picacho, Yavapai co. | $<$ 5 – 50 |
| *Sulphates* | | |
| Barite, $BaSO_4$ | Keno Hill, Y.T., vein | $<$ 1 – 5 |
| | Walton, N.S., veins and replacement deposit | $<$ 0.05 – 0.5 |
| | Rudňany, Czech. (Bernard, 1961) | 10 – 50 |
| Anglesite, $PbSO_4$ | Keno Hill, oxidized zone | $>$ 1,000 |
| Anhydrite, $CaSO_4$ | Walton, N.S., (sedimentary) | $<$ 0.05 – 0.4 |
| Gypsum, $CaSO_4 \cdot 2H_2O$ | Keno Hill, Y.T., in veins | $<$ 1 |
| | Walton, N.S., (sedimentary) | $<$ 0.05 – 0.4 |

| Mineral | Location | Ag, ppm (range) |
|---|---|---|
| *Sulphates (cont'd)* | | |
| Plumbojarosite, $PbFe_6(SO_4)_4(OH)_{12}$ | Keno Hill, Y.T., oxidized zones | $> 1\%$ |
| Rozenite, $FeSO_4 \cdot 4H_2O$ | Keno Hill, Y.T., oxidized zones | $< 5$ |
| Various sulphates: chalcanthite, epsomite, copiapite, etc. | Tintic district, Utah (Morris and Lovering, 1952) | 0.00 – 1,160 |
| *Phosphates, arsenates* | | |
| Erythrite, $Co_3(AsO_4)_2 \cdot 8H_2O$ | Coleman twp., Ontario; Gowganda; Cobalt | $< 5$ |
| Annabergite, $Ni_3(AsO_4)_2 8H_2O$ | Churchill co., Nevada; Keweenaw co., Michigan | $< 5$ |
| Scorodite, $Fe(AsO_4) \cdot 2H_2O$ | Keno Hill, oxidized zones | 1 – 50 |
| Apatite, $Ca_5(PO_4)_3F \cdot Cl$ | Various | $< 0.1$ |
| | Various, (Cruft, 1962) | 0.0 |
| Pyromorphite, $Pb_5(PO_4)_3Cl$ | Keno Hill, oxidized zones | 100 – 1,000 |
| Beudantite, $PbFe_3(AsO_4)(SO_4)(OH)_6$ | Keno Hill, oxidized zones | 100 – 1,000 |
| *Antimonates* | | |
| Bindheimite, $Pb_2Sb_2O_6(O,OH)$ | Keno Hill, oxidized zones | 100 – 1,000 |
| *Tungstates* | | |
| Wolframite, $(Fe,Mn)(WO_4)$ | Dublin Gulch, Y.T. | $< 1$ |
| Scheelite, $CaWO_4$ | Yellowknife, in veins | 1 – 10 |
| | Dublin Gulch, Y.T. | $< 1$ |
| *Oxides* | | |
| Tenorite, CuO | Vesuvius, Italy | Not found |
| | Algoma mine, Ontonagan, Michigan | Trace |
| Cuprite, $Cu_2O$ | Chile, Arizona, Mexico | $< 1$ – 300 |
| Hematite, $Fe_2O_3$ | Walton, N.S., in faults | $< 5$ |
| | Various, (Hartley and Ramage, 1897) | Detected |
| | Rudňany, Czech. (Bernard, 1961) | Up to 100 |
| Limonite | Keno Hill, in oxidized zones | 100 – 1,000 |
| | Keno Hill, precipitated from springs | $< 0.5$ |
| | Walton, N.S., in oxidized zones | 0 – 22 |
| | Various, (Hartley and Ramage, 1897) | Detected |
| Pyrolusite | Thüringen, Germany (Fischer, 1958–59) | 3 |
| Wad and various manganese oxides | Keno Hill, in oxidized zones | 100 – 1,000 |
| | Keno Hill, precipitated from springs | 0.5 |
| | Walton, N.S., bog | 0.7 |
| | Walton, N.S., in nodules in limestone | 0 – 1.4 |

| Mineral | Location | Ag. ppm (range) |
|---|---|---|
| *Oxides (cont'd)* | | |
| Wad and various manganese oxides (*cont'd*) | Various, (Hartley and Ramage, 1897) | Detected |
| | U.S.A. (Hewett, *et al.* 1963) | 30 – 300 |
| | Ramsdellite, Lake Valley, New Mexico (Fleischer, *et al.* 1962) | 150 |
| | Polk co., Arkansas; manganese ore, (Foley, 1960) | 23 |
| | Various manganese–silver ores, U.S.A., Mexico, Sumatra, etc. (Clevenger and Caron, 1925) | Up to 1,000 or more |
| Cassiterite, $SnO_2$ | Dublin Gulch, Y.T., in impregnation zone | 1 – 5 |
| | Various, (Goldschmidt and Peters, 1932) | 1 – 10 |
| | Various, (Hartley and Ramage, 1897) | Detected |
| Uraninite, $UO_2$ | Parry Sound, Ontario | $<5$ |
| | Wilberforce, Ontario | $<5$ |
| Pitchblende, $UO_2$ | Great Bear Lake, N.W.T. | 1 – 5 |
| Thorianite | Galle, Ceylon | $<5$ |
| Samarskite | Norway (Lunde, 1927) | 4.0 – 4.4 |
| Tantalite | Finland (Lunde, 1927) | 0.6 |
| Ilmenorutile | Norway (Lunde, 1927) | 0.1 – 0.2 |
| Magnetite, $FeFe_2O_4$ | Various | 1 – 5 |
| Chromite, $FeCr_2O_4$ | Various | $<1$ – 5 |

Sources: Laboratories, Geological Survey of Canada, unless otherwise stated

including boleite, cumengite, pseudoboleite, diaboleite, chloroxiphite, etc. Probably all contain some silver, although analyses are available for only a few of these minerals. The same applies to phosgenite and other copper, lead, and zinc carbonate-hydroxide halide minerals.

Halite, NaCl, chlorargyrite, AgCl, and bromargyrite, AgBr, are isostructural, and halite and chlorargyrite form an isomorphous series according to Cipriani (1953). One would expect, therefore, some substitution of silver in the sodium sites of halite, if silver were present in the solutions or vapours from which the halite crystallized. Cipriani, in fact, found up to 59 ppm Ag in the sylvite-halite crusts at Vesuvius and concluded that most of the silver was mainly present in the halite. In this respect the mineral huantajayite, described many years ago from the Huantajaya district, Tarapacá, Chile, is of interest. This mineral is supposedly argentian halite, (Na,Ag)Cl, but evidence of its homogeneity is apparently lacking. It occurred at several mines and was associated with calcite, chlorargyrite, bromargyrite, iodargyrite, and atacamite. Huantajayite should be re-examined carefully by modern X-ray and chemical methods to determine its authenticity.

All of the common carbonates have a very low silver content, generally much less than 1 ppm. Smithsonite can apparently absorb small amounts of silver as can also cerussite. Malachite and azurite seem to be capable of carrying up to several hundred parts per million of silver, probably in their lattices as a substitution for copper.

Among the sulphates investigated the largest amounts of silver have been noted in anglesite and plumbojarosite. In these minerals the silver apparently substitutes for lead, although in some varieties of anglesite the silver may be in admixed secondary native silver or in argentojarosite or argentian plumbojarosite.

Lovering (Morris and Lovering, 1952) found silver in a number of hydrous sulphates in the efflorescences of the Tintic Standard mine openings, Tintic district, Utah. The largest amount (1,160 ppm Ag) was found in chalcanthite; smaller amounts (up to 170 ppm Ag) were determined in epsomite, pisanite, alumian, and melanterite.

There is relatively little silver in most apatites, and the content of the element in pure crystalline erythrite, annabergite, and scorodite is generally very small. Some varieties of scorodite, however, may be enriched in silver, especially those derived from gold-bearing arsenopyrite lodes. In most cases this scorodite contains the silver as a constituent of the wires and spangles of admixed native gold. Pyromorphite-mimetite and beudantite appear to concentrate some silver where these minerals occur in the oxidized zones of lead-silver deposits. Whether the silver is present in the lattice of these minerals substituting for lead or not is difficult to say because of the possible contamination by plumbojarosite, argentian anglesite, etc. Relatively pure specimens of beudantite and pyromorphite from Keno Hill, however, always contain silver and it appears that the element substitutes for lead in the lattice of the minerals.

Muta (1956) investigated the pyromorphite-mimetite series in Japan and observed that the pyromorphite minerals in ore deposits associated with volcanic rocks are richer in silver and copper than those associated with granitic rocks. The same trends were also found in galena.

Bindheimite carries some silver in all occurrences investigated by the writer. In this mineral the silver appears to replace lead.

Among the tungstates, silver appears to be slightly enriched in the scheelite of some gold deposits. The nature of the silver is unknown. Perhaps it resides in microscopic particles of native gold. It is worth mentioning that there is a general association of tungsten, gold, and silver in many types of gold deposits.

Of the various oxides, limonite and wad, particularly the latter, tend to be the most common carriers of silver, especially where they occur either in or near silver deposits. The presence of silver in quantity in wad (up to 100 ounces Ag/ton or more) is an old problem discussed in detail in the years past by Coghill (1912), Clevenger and Caron (1925), and numerous others. The reasons for the extended study were mainly metallurgical since the manganiferous silver ores are highly refractory and only yield their silver after intensive reduction.

After much study Clevenger and Caron and others concluded that much of the silver in wad is held as silver manganite of uncertain composition. Silver silicate was also thought to be present in certain types of oxidized ores.

In a recent contribution to the problem of silver in manganese oxides, Hewett, Radtke, and Taylor (1965) have investigated the black calcite (or aragonite) that occurs in a number of silver deposits in the western United States. The colour of this black calcite is due to the presence of a manganese oxide which may contain up to 5 per cent silver. Examination of a high grade specimen with an electron microprobe indicated that the silver is bound as a crystalline silver manganate in the manganese oxide. Hewett, Radtke, and Taylor think that the silver manganate was deposited from hypogene solutions and was not a product of weathering processes. They further think that much of the chlorargyrite in the argentiferous black calcite veins in the White Pine district, Nevada, may have developed from the hypogene silver manganate.[1]

In recent years the writer has investigated the nature of silver in wad and limonite from Keno Hill, Yukon; Walton, Nova Scotia; and elsewhere with the following results:

1. Some samples of wad and limonite appear to have the silver uniformly distributed throughout the mineral complexes; in other samples the silver is erratically distributed.
2. Many of the silver-bearing wads and limonites carry considerable quantities of silica, alumina, titanium, phosphorus, arsenic, and antimony (*see*, for instance, Tables 42, 56, and 60 in Boyle, 1965).
3. In samples of wad and limonite where the silver is uniformly distributed the element is tightly bonded to the manganese and iron complexes and is not soluble in potassium cyanide, dilute nitric acid, sulphuric acid, acetic acid, etc. This silver may well be present as a silver manganate, manganite, or ferrite although its constitution is apparently amorphous (colloidal) since no distinct X-ray patterns can be discerned from those of the wad and limonite minerals. In certain samples with a relatively high organic content, the silver may be bound in organic (humic) complexes of manganese and iron. In still other samples the silver may be present as an integral part of a variety of indefinite silico-aluminate complexes and ferro-arsenate complexes as silver phosphate, as silver arsenate, etc.
4. Samples of wad and limonite containing silver with a marked erratic distribution contain the element in a variety of ways: as the native metal in the form of specks, minute wires, etc.; as a constituent of admixed argentian plumbojarosite or argentojarosite; as a constituent of admixed argentian beudantite and/or bindheimite; and as a trace constituent of numerous admixed secondary minerals such as anglesite, cerussite, malachite, etc.

The reason for the enrichment of silver in wad and limonite is probably due to the colloidal behaviour of hydrous manganese dioxide and hydrous ferric oxide. Hydrous manganese dioxide sols and gels carry a negative charge and strongly adsorb the positive silver ions to their surface. With aging the silver may partake

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[1] More recent research by Hewett and Radtke (*Econ. Geol.*, vol. 62, pp. 1–21) and Radtke, Taylor, and Hewett (*Econ. Geol.*, vol. 62, pp. 186–206) on the black calcite has shown the presence of three silver-bearing manganese oxides which they have named aurorite, argentian todorokite, and hydrous silver-bearing lead manganese oxide. Although these authors still maintain that the manganese oxides that form the pigment in many specimens of black calcite are hypogene, they have found that the high silver-bearing manganese oxides are of supergene origin and developed later than chlorargyrite.

of the structure of the manganese dioxide complex, giving a silver manganite or some such compound. Alternatively the silver may simply remain in an adsorbed state either at the grain boundaries of the microcrystals of the complex or perhaps in interstitial positions. On recrystallization, after long periods of aging, some of the silver may also be split out of the complex giving nuclei of native silver. Silica sols and gels and humic colloids, likewise, carry negative charges and tend to adsorb the positive silver ions to their surfaces. Hence, the presence of these colloids in wad would also tend to increase the amount of silver precipitated in the wad-silica-humic complex. Some silver thus precipitated could conceivably be bound as silver silicate as suggested by some early investigators, as a silver mica, or as a silver mangano-organic complex.

Ferric oxide hydrosols and gels tend to carry a positive charge and theoretically should not adsorb positive silver ions. However, it is known experimentally that ferric oxide gels and sols do adsorb silver ions to some extent, especially when arsenate and phosphate are present in the solutions. Probably the reason is that these anions impart a net negative charge to the ferric oxide complex, and this in turn attracts the positive silver ions. Whatever the cause it is common to find silver somewhat enriched in limonites that contain appreciable amounts of arsenic and phosphorus. How the silver is held in the aged gel is not known, but it could be as the insoluble silver arsenate or phosphate.

In a milieu where manganese, iron, lead, silica, alumina, sulphate, phosphate, arsenate, antimonate, etc. are present in solution in oxidizing zones the colloidal reactions must be very complex indeed. There, normal adsorption phenomena undoubtedly play a part, but hydrolytic reactions, especially those involved in the hydrolysis of iron and manganese sulphates, soluble arsenates, antimonates, and phosphates, etc., also come into play. During these reactions silver is precipitated as argentojarosite, in plumbojarosite, beudantite, bindheimite, and other hydrolytic products, all of which may be intimately associated with the wad and limonite gels. On aging the wad-limonite complex tends to segregate out these silver-bearing minerals.

Silver is a microconstituent of a number of other oxides. Cuprite and $Ag_2O$ and tenorite and AgO are isostructural, and hence one would expect the substitution of some silver in the copper sites of these minerals if silver were available. Most samples appear to be low in silver ($<300$ ppm), however, judging from analyses done in the laboratories of the Geological Survey of Canada. The common lead oxides such as litharge and minium probably also tend to incorporate some silver in their lattices, although there are no data.

## Silver in Igneous-Type[1] Rocks

The silver content of igneous-type rocks is given in Tables 13 and 14. The published analyses are limited and generally restricted to one district or in some cases a few districts. The older analyses are probably a little high because most were

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[1] The term igneous-type is used to avoid the controversy on the origin of granites, ultrabasic rocks, and various types of porphyries.

done by assay methods. The more recent analyses are generally done by optical spectrographic methods and are probably a little low judging from the writer's experience with both methods.

In most igneous rocks the bulk of the silver is present either in sulphides or in the ferromagnesian minerals. Separations carried out by the writer show that up to 5 ppm Ag may be present in the pyrite and pyrrhotite from igneous rocks and up to several hundred parts per million in chalcopyrite if this mineral is present. The ferromagnesian minerals generally contain much lower amounts of silver ($<0.5$ ppm), some of which may be in pyroxene, amphibole, biotite, or magnetite, etc. Since good separations of these minerals can rarely be made from rocks the amount in each mineral is difficult to ascertain. Some biotites appear to be relatively rich in silver, but this is not always the case. Quartz and feldspar are generally poor in silver in most rocks, but albite and muscovite may contain small quantities of the element.

TABLE 13 | *Silver Content of Igneous-Type Rocks*

| Rock Type | Location | Literature reference | Ag, ppm average and/or range |
|---|---|---|---|
| Ultramafic rocks | Japan | Hamaguchi and Kuroda (1959) | 0.060 |
| Ultramafic rocks | Various | Vinogradov (1962) | 0.05 |
| Ultrabasic rocks | Scotland | Morris and Killick (1960) | 0.028 – 0.086 |
| Ultrabasic rocks | Norway | Goldschmidt (1954) | 0.01 – 0.10 |
| Ultrabasic rocks | Various | Turekian and Wedepohl (1961) | 0.06 |
| Dunite | Norway | Lunde (1927), Lunde and Johnson (1928) | 0.03 – 2.1 |
| Peridotite | Norway | " " | 0.0 – 9.4 |
| Pyroxenites | Norway | " " | 0.0 – 1.3 |
| Picrites | Thüringen, Germany | Fischer 1958–59 | 0.2 |
| Mafic rocks (gabbros, etc.) | Various | Vinogradov (1962) | 0.1 |
| Basaltic rocks | Various | Turekian and Wedepohl (1961) | 0.11 |
| Gabbros | Japan | Hamaguchi and Kuroda (1959) | 0.11 |
| Gabbro | Norway | Goldschmidt (1954) | 0.03 |
| Syenogabbro | Scotland | Morris and Killick (1960) | 0.43 – 0.47 |
| Dolerite | England | Brammall and Dowie (1936) | 2.4 |
| Pyritic gabbro | Belgium | Wéry (1948) | 2.0 |
| Norite | Merensky Reef, South Africa | Goldschmidt and Peters (1932) | 0.5 |
| Diabases | Japan | Hamaguchi and Kuroda (1959) | 0.12 |
| Diabase (W–1) | Virginia | Morris and Killick (1960) | 0.057 |
| | | Taylor (1965a) | 0.030 |
| Diabase | California | Wagoner (1901) | 7.44 |
| Quartz diabase | England | Brammall and Dowie (1936) | 2.1 – 2.3 |

| Rock Type | Location | Literature reference | Ag, ppm average and/or range |
|---|---|---|---|
| Basalts | Japan | Hamaguchi and Kuroda (1959) | 0.11 |
| Basalt | California | Wagoner (1901) | 0.55 |
| Intermediate rocks (diorites, andesites, etc.) | | Vinogradov (1962) | 0.07 |
| Andesites | Japan | Hamaguchi and Kuroda (1959) | 0.08 |
| Diorites | Japan | " " " | 0.053 |
| Liparites | Japan | " " " | 0.049 |
| Syenites | Various | Turekian and Wedepohl (1961) | 0.0X |
| Syenite | Scotland | Morris and Killick (1960) | 0.032 – 0.040 |
| Syenite | Nevada | Wagoner (1901) | 15.43 |
| Quartz monzonite, diorite, and granite | Arizona | Putnam and Burnham (1963) | < 0.4 – 4.0 |
| Nepheline syenite | Norway | Goldschmidt (1954) | ~ 0.03 |
| Felsic rocks (granites, granodiorites, etc.) | | Vinogradov (1962) | 0.05 |
| Granodiorites | Japan | Hamaguchi and Kuroda (1959) | 0.050 |
| Granitic rocks (high calcium) | Various | Turekian and Wedepohl (1961) | 0.051 |
| Granitic rocks (low calcium) | Various | " " (1961) | 0.037 |
| Granites | Japan | Hamaguchi and Kuroda (1959) | 0.037 |
| Granite (G–1) | Rhode Island | Morris and Killick (1960) | 0.042 |
| | | Taylor (1965a) | 0.040 |
| Granites–grey, pink | England | Brammall and Dowie (1936) | 0.76 – 4.6 |
| Granites–strongly reddened | England | " " " (1936) | 14.4 – 64.9 |
| Granites | California | Wagoner (1901) | 0.94 – 7.66 |
| Granite | Nevada | " " | 5.59 |
| Granites, etc. | Norway | Goldschmidt (1954) | ~ 0.02 |

There appears to be no striking correlation between the acidity (silica content) of an igneous rock and the silver content. Since most of the silver is contained in sulphides and ferromagnesian minerals it would seem that basic rocks should be the richest in silver, and there should be a decrease in content in the more acid rocks. The data of Hamaguchi and Kuroda (1959) suggest such a trend, but the data from the Yellowknife and Keno Hill areas in Canada show that if there is a trend toward less silver in acidic rocks it is not marked. In the recent investigation of the differentiation succession of the rocks of the Insch Mass (mostly gabbro), Aberdeenshire, Morris and Killick (1960) likewise found no systematic relationship between the silver content of basic and more acidic phases. They did, however, encounter increased amounts of silver in the syeno-gabbro samples they investigated. Higazy (1952b) found that silver was present in the greatest amounts (up to 10 ppm) in the

TABLE 14 | *Silver Content of Some Canadian Igneous-Type Rocks*

| Rock Type | Location | Literature reference | Ag, ppm range and/or average (in brackets) |
|---|---|---|---|
| Pyroxenite | Muskox intrusion, N.W.T. | Smith (1962) | $<$ 0.10 – 0.22 |
| Picrite | " " | " | (0.21) |
| Gabbro | " " | " | 0.10 – 0.29 |
| Sulphide and chromite layer (Merensky type) | " " | " | 0.15 – 1.8 |
| Diabase | Yellowknife, N.W.T. | Boyle (1961) | (1.4) |
| Nipissing diabase | (*see* Table 46) | | (0.11) |
| Nipissing diabase | Ontario | Fairbairn, *et al.* (1953) | 0.9 – 7.6 (4.0) |
| Nipissing diabase | Cobalt–South Lorrain district, Ontario | Moore (1934) | 0.8 – 1.2 |
| Nipissing diabase | Gowganda, Ontario | Moore (1956) | 1.0 – 6.0 |
| Granophyre in Nipissing diabase | Gowganda, Ontario | Moore (1956) | 1.0 – 500 |
| Nipigon diabase | Ontario | Fairbairn, *et al.* (1953) | ($<$ 1) |
| Diabase | Walton, Nova Scotia | Boyle (1963a) | (0.33) |
| Basalt | North Mountain, Nova Scotia | Boyle (1963a) | (0.11) |
| Syenite Rock–1 | Bancroft area, Ontario | Applied Spectroscopy, vol. 15, p. 159, (1961) | 0.5 – 1.9 (1.3) |
| Granodiorite | Yellowknife, N.W.T. | Boyle (1961) | 0.4 – 1.4 |
| Granite | Yellowknife, N.W.T. | Boyle (1961) | 0.3 – 1.4 |
| Quartz-feldspar porphyry | Yellowknife, N.W.T. | Boyle (1961) | 0.6 – 2.0 |
| Diorite | Keno Hill, Y.T. | Boyle (1965) | (0.32) |
| Biotite lamprophyre | Keno Hill, Y.T. | Boyle (1965) | (0.16) |
| Quartz–feldspar porphyry | Keno Hill, Y.T. | Boyle (1965) | (0.24) |
| Granodiorite | Keno Hill, Y.T. | Boyle (1965) | $<$ 0.10 – 0.17 |
| Diorite–granodiorite | Whitehorse, Y.T. | Boyle (unpubl.) | (0.2) |

early differentiates (picroteschenite, etc.) of the Braefoot Outer Sill, Fife, Scotland. The high contents of silver in the picroteschenite (10 ppm) are probably present in minute granules of sulphides. In the Muskox intrusion, N.W.T., Canada (Smith, 1962), the Merensky type sulphide and chromite layer is greatly enriched in silver (average 1.1 ppm Ag) compared with the pyroxenites, picrites, gabbros, etc. that average about 0.16 ppm Ag.

Certain types of quartz-feldspar porphyries in the Yellowknife Greenstone Belt, N.W.T., are enriched in both silver and gold. These porphyries contain considerable quantities of pyrite that seems to be syngenetic. Nearly all the gold and silver is present in this pyrite.

Note

Brammall and Dowie (1936) noted that strongly reddened granites in the Malvern Hills, England were higher in silver and gold than the normal grey, pink, and reddish granites. They attributed the enrichment to hematite disseminations

Ag
with
hematite

caused by pneumatolytic processes related to the latest phase of granite intrusion.

Note

Because of the possible replacement of silver for sodium and potassium suggested by similar ionic radii, other chemical properties, and the experimental data on glasses (Eitel, 1954), it might be worth while to investigate the sodium, potassium, and silver contents of igneous rocks for a possible correlation. In this respect the data provided by Cipriani (1953) is of interest. He found that the high soda-bearing magmas from Vesuvius were associated with increased contents of silver in the fumarolic products.

Note

Fairbairn, *et al.* (1953) made the interesting observation that the silver content of the Nipissing diabase, in which many silver deposits in Ontario occur, is higher than the other diabases they investigated in Ontario. Moore (1934, 1956) also found this diabase to be enriched in silver in the Cobalt, South Lorrain, and Gowganda areas. In the granophyre of the diabase he found 1 to 500 ppm Ag with an average of 62 ppm Ag for ten samples. The origin of this granophyre is somewhat controversial, some investigators considering it to be a differentiate of the diabase, others holding that it is a phase of the wall-rock alteration associated with the silver mineralization at Gowganda and elsewhere. The writer found the Nipissing diabase in the Cobalt area to contain an average of 0.11 ppm Ag, a content much lower than that reported by Fairbairn, *et al.* (1953) and Moore (1934, 1956).

Note

There is no clear-cut relationship between the silver content of the granitic rocks in the silver-poor Yellowknife area and those in the silver-rich Keno Hill area. If there is a trend, those in the Yellowknife area appear to be the highest in the element.

The data on the silver and gold contents of igneous rocks are far too few to give an accurate idea of the ratio of these two closely associated elements. From the work in the Yellowknife area the ratio Ag:Au in the normal igneous type rocks appears to vary from about 100:1 to 140:1. In the quartz-feldspar porphyry the ratio Ag:Au is about 15:1.

Goldschmidt (1954) estimated the abundance of silver in igneous rocks to be 0.02 ppm. Hamaguchi and Kuroda (1959) give an average of 0.08 ppm. Calculations based on the data on Canadian rocks give an abundance of 0.10 ppm Ag. Like all abundance calculations this figure should be taken as a rough estimate until more accurate figures are available on the quantity of each igneous rock type in the earth.

## Silver in Sedimentary Rocks

Note

The available data on the silver content of sedimentary rocks is given in Tables 15 and 16. The highest amounts of silver unquestionably occur in the black shales, black schists, sulphide schists, alum shales, and phosphorites. Only small amounts of silver occur in normal sandstones, quartzites, limestones, and evaporites.

Leutwein (1951) found that in the alum shales of Thüringen, the silver was largely associated with the carbonaceous substance. Marmo (1960), on the other hand, indicated that the silver is bound to the pyrrhotite of the sulphide-graphite schists of Pohjanmaa, Finland, rather than to the carbon. The present writer also finds that most of the silver in the black schists that he has investigated is bound in

## TABLE 15 | *Silver Content of Sedimentary Rocks*

| Rock Type | Locality | Reference | Ag, ppm average or range |
|---|---|---|---|
| Sandstone | California | Wagoner (1901) | 0.32 – 0.54 |
| Sandstone | Germany | Hartmann (1963) | 0.1 – 2.6 |
| Sandstones | Various | Turekian and Wedepohl (1961) | 0.0X |
| Shales | Various | Turekian and Wedepohl (1961) | 0.07 |
| Shales and clays | Various (average) | Vinogradov (1962) | 0.1 |
| Black shale | Various | Goldschmidt (1954) | 0.6 – 1.7 |
| Bituminous marl | | Goldschmidt (1954) | 5 – 10 |
| Carbonaceous clay | | Goldschmidt (1954) | 0.5 – 1.0 |
| Black schists (sulphide schists) | Finland | Marmo (1960) | 0. – 7.6 |
| Black schists | Outokumpu region, Finland | Peltola (1960) | 0 – 7 |
| Alum schist | Thüringen, Germany | Leutwein (1951) | 1 – 30 |
| Black shale and phosphorites | Phosphoria Formation, U.S.A. | U.S.G.S. Prof. Paper 424A, p. 3 | 10 |
| Shale | Volga and Baltic basins U.S.S.R. | Tikhomirova (1960) | 0.7 |
| Pierre shale | Great Plains region, U.S.A. | Tourtelot (1962) | < 0.5 |
| Black shales | Woodford–Chattanooga shales, central midcontinent area, U.S.A. | Landis (1962) | < 0.5 – 10 |
| Black shales | Oklahoma, Kansas, Missouri | Hyden and Danilchik (1962) | 0.1 – 3.0 |
| Black shales | Various, western U.S.A. | Davidson and Lakin (1961) | < 1 – 30 |
| Black shales | Various, western U.S.A. | Davidson and Lakin (1962) | < 1 – 15 |
| Deep sea clays, etc. | Atlantic Ocean | Wagoner (1907) | 0.30 – 1.9 |
| Deep sea clay | | Turekian and Wedepohl (1961) | 0.11 |
| Recent sapropel sediment | Baltic Sea | Manheim (1961) | < 1 |
| Modern sediments (sands, clays, etc.) | Gulf of Paria | Hirst (1962) | 0.1 – 1.0 |
| Deep sea carbonate | | Turekian and Wedepohl (1961) | 0.0X |
| Limestone | Kansas | Runnels and Schleicher (1956) | 0.34<br>0.1 – 20 |
| Limestone–dolomite | U.S.S.R. | Lurye (1957) | < 5 – ∼ 10 |
| Manganese oxides (sedimentary) | Arizona | Hewett, *et al.* (1963) | 0 – detected |
| Manganese oxides (sedimentary) | Nevada | Hewett, *et al.* (1963) | 30 |
| Manganese nodule | | Goldschmidt and Peters (1932) | 1.0 |
| Deep sea manganese nodules | Pacific Ocean | Hewett, *et al.* (1963) | Not found |
| Deep sea manganese nodules | Pacific Ocean | Mero (1962) | 3 |
| Recent volcanic ash | Ecuador | Mallet (1887, 1890) | 10 – 12 |

Note

See

TABLE 16 *Silver Content of Some Canadian Sedimentary Rocks*

| Rock Type | Locality | Reference | Ag, ppm range | Ag, ppm average |
|---|---|---|---|---|
| Graphitic argillites, schists, and phyllites | Keno Hill, Y.T. | Boyle (1965) | 0.17 – 1.60 | 0.50 |
| Quartz–sericite schist | Keno Hill, Y.T. | " " | 0.12 – 1.1 | 0.44 |
| Thick- and thin-bedded grey quartzites | Keno Hill, Y.T. | " " | 0.13 – 1.30 | 0.31 |
| Siliceous white quartzites | Keno Hill, Y.T. | " " | 0.17 – 0.37 | 0.25 |
| Calcareous quartzites | Keno Hill, Y.T. | " " | 0.24 – 0.54 | 0.36 |
| Limestones | Keno Hill, Y.T. | " " | 0.10 – 0.27 | 0.15 |
| Graphitic tuff, slate, and schist | Yellowknife, N.W.T. | Boyle (1961) | 0.33 – 3.4 | 1.14 |
| Black shale and argillite | Walton area, N.S. (Horton Bluff Formation) | Boyle (1963a) | < 0.03 – 4.0 | 0.32 |
| Carbonaceous and phosphatic shale | " " " | " " | 0.19 – 1.2 | 0.43 |
| Quartzite and sandstone | " " " | " " | < 0.05 – 1.4 | 0.22 |
| Dolomite, arenaceous and argillaceous dolomite | " " " | " " | 0.04 – 0.5 | 0.17 |
| Calcareous concretions | " " " | " " |  | < 0.05 |
| Grey and green shale | Walton area, N.S. (Cheverie Formation) | " " | 0.05 – 0.90 | 0.19 |
| Red shale and argillite | " " | " " | 0.05 – 0.29 | 0.11 |
| Sandstone | " " | " " | 0.03 – 0.90 | 0.25 |
| Limestone | Walton area, N.S. (Macumber Formation) | " " | < 0.1 – 0.3 | 0.1 |
| Limestone conglomerate | " " | " " | < 0.1 – 0.3 | 0.1 |
| Anhydrite | Walton area, N.S. (Windsor evaporites) | " " | < 0.05 – 0.4 | < 0.1 |
| Calcareous anhydrite | " " | " " | < 0.05 | < 0.05 |
| Gypsum | " " | " " | < 0.05 – 0.4 | < 0.1 |
| Red and buff shale | Walton area, N.S. (Windsor Group, Tennycape Formation) | " " | 0.23 – 0.15 | 0.19 |
| Sandstone and conglomerate | Walton area, N.S. (Triassic) | " " | < 0.10 – 0.18 | 0.05 |
| Albert bituminous shale | Albert mines, New Brunswick | Boyle (unpubl.) |  | 0.07 |
| Pyritiferous and arseno-pyritiferous slate | Ovens area, Nova Scotia (Halifax slate) | Boyle (unpubl.) | – | 2.2 |
| Pyritiferous shale | Kettle Point Formation, Kettle Point and Florence, Ontario | Boyle (unpubl.) | – | 0.12 |
| Pyritiferous slate and schist | Cobalt district | (*see* Table 46) | – | 0.83 |

pyrite (Table 17), more specifically often in small amounts of chalcopyrite or galena in the pyrite. He further finds that the degree of diagenesis and metamorphism of the black schists more or less determines the location of the silver. In black shales that have undergone little metamorphism the silver appears to be associated with both the carbonaceous substance and fine-grained nearly colloidal sulphide. With increase of metamorphism and the migration of the sulphides into knots or crystals, the bulk of the silver tends to collect either in the iron sulphides or in chalcopyrite and galena that occur in blebs or in small fractures in the pyrite or pyrrhotite.

TABLE 17 | *Silver and Gold Content of Pyrite from Rocks*

| Rock Type | Locality | Ag, ppm (range or average) | Au, ppm (range or average) |
|---|---|---|---|
| Graphitic schist and phyllite | Keno Hill area, Y.T. | 5 – 50 | – |
| Graphitic quartzite and siliceous quartzite | Keno Hill area, Y.T. | 50 – 100 | – |
| Black shale and argillite | Walton area, N.S. (Horton Bluff Formation) | 0.34 – 4.0 | $<$ 0.02 – 0.17 |
| Dolomite and argillaceous dolomite | Walton area, N.S. (Horton Bluff Formation) | ~ 4 | – |
| Calcareous anhydrite | Walton area, N.S. (Windsor evaporites) | $<$ 0.5 | – |
| Pyritized coal in sandstone | Walton area, N.S. (Cheverie Formation) | 5 – 300 | – |
| Slate | Ovens, N.S.: | | |
| | Pyrite | 1.2 | 0.15 |
| | Arsenopyrite | 0.5 | 2.05 |
| Coal | Port Hood, N.S. | 0.2 | 0.04 |
| Shale | Kettle Point Formation, Florence, Ont. | 0.2 | 0.02 |
| Diabase | Walton area, N.S. | $<$ 0.5 | – |

Porphyrin complexes with various metals are known in petroliferous shales, and it seems probable that silver may occur in such compounds in certain carbonaceous shales, limestones, etc. Arrhenius and Bramlette (1957) found that silver, as well as other heavy metals, is concentrated in the organic phase of skeletal fish debris in pelagic sediments of late Pleistocene to Recent age.

check this

It is of interest to note that in rocks containing coexisting sedimentary pyrite and arsenopyrite silver prefers the pyrite whereas gold prefers the arsenopyrite. This feature appears to be a general one judging from the writer's data on the Meguma slates in Nova Scotia (Ovens, N.S., Table 17). Another interesting feature, which requires confirmation, is that the pyrite in the country rocks of silver-rich areas seems to have higher than average amounts of silver. This circumstance has been noted both at Keno Hill and Walton and is being investigated further by the writer in other silver belts and barren areas.

Results of further checkin

Many of the marine phosphorites contain small amounts of silver over large areas. A. I. Smirnov reported that the Cambrian phosphorites of Karatau, U.S.S.R., are slightly enriched in silver. Gulbrandsen (1960a, 1960b) found that the silver in the rocks of the Phosphoria Formation is enriched in the organic component. In the thin phosphorites of the Carboniferous basin of the Walton-Cheverie area, Nova

Note

Scotia, the writer found that some of the silver was associated with the colloidal collophane (apatite) part of the rock and some with the carbonaceous substance and sulphides. The association with the collophane may be due to the precipitation of silver by phosphate ion as the insoluble silver orthophosphate.

Black shales, sulphide schists, etc. are formed under reducing conditions where the sulphide ion concentration has been relatively high, due in large part to the action of bacteria, which reduce sulphates to $H_2S$ or act on the protein complexes of dead organisms liberating $H_2S$. This $H_2S$ then precipitates much of the available silver as well as a number of other chalcophile elements. Some adsorption by carbonaceous substances probably also takes place, and some of the silver may be precipitated by phosphate ion in certain environments.

Note

The presence of relatively large amounts (10–12 ppm) of silver (in the form of chloride) in the recent volcanic ash of two volcanoes in Ecuador (Mallet, 1887, 1890) is of interest considering the frequent occurrence of silver-gold deposits in or associated with tuffs (sedimented volcanic ash) or porphyries (crystallized volcanic material) in the Canadian Shield, Tertiary terrains, etc. These data also agree with the general findings of the writer that certain tuffs and porphyries in the Shield are enriched in silver (Tables 14 and 16). Certainly such rocks would seem to be an adequate source for the derivation of silver-bearing veins by a metamorphic secretion mechanism.

Normal shales, sandstones, quartzites and limestones are relatively low in their silver content. Commonly the amount of silver appears to depend on the content of sulphides present, although in some cases it is evident that other constituents such as sodium- and potassium-rich clay minerals and hydrated iron and manganese oxides are responsible for much of the silver. Runnels and Schleicher (1956) observed that the silver content of the limestones in Kansas tended to increase with the purity of the limestone. In the sedimentary sequence of the Northern Bayaldyr district in Central Karatau, U.S.S.R., Lurye (1957) found that silver was enriched in the same limestone-dolomite part of the stratigraphic section as lead, zinc, barium, manganese, and iron. He felt that the enrichment was due to a primary sedimentary process since the elements were restricted stratigraphically, were connected with lithological and facies changes, and were developed over a large area. Other than these observations little is known about the geochemistry of silver in calcareous rocks.

Note - check with Roy

There appear to be no extensive modern data on the silver content of oxidate sediments, a gap in our knowledge that should be filled by suitable research. Malaguti and Durocher (1850) and Hartley and Ramage (1897) found traces of silver in practically all the sedimentary iron ores, manganese ores, and bauxites they investigated. Goldschmidt and Peters (1932) found 1 ppm Ag in a manganese nodule, Riley and Sinhaseni (1958) found an average of 14 ppm Ag in the acid soluble part of three manganese nodules from the Pacific, and there are a number of more recent references in the literature to the occurrence of silver in various sedimentary iron and manganese ores. Research by the present writer, not yet complete, suggests that some manganese bog ores may be enriched in silver in certain areas whereas in others they are relatively poor in the element.

The presence of silver in sedimentary manganese and iron ores can be explained mainly as the result of colloidal adsorption processes. Hydrated manganese oxide colloids and gels carry a negative charge on their surfaces, a feature that leads to the strong adsorption of silver ion, $Ag^+$, as well as all other cations. During aging of the gels the silver is largely incorporated in the hydrated manganese oxide minerals. Hydrated iron oxide colloids and gels, on the other hand, generally carry a positive charge that repels the silver ion and little concentration of silver should take place in relatively pure sedimentary iron deposits. However, $PO_4^{3-}$, $AsO_4^{3-}$, and other complex anions may be strongly chemisorbed to the iron colloids and gels, imparting a net negative charge to the colloids. This, then, will permit the adsorption of $Ag^+$ ion especially since silver phosphate and arsenate are only sparingly soluble. One would expect, therefore, that the silver content of sedimentary iron deposits would show some relationship to the phosphate, arsenate, or perhaps the silica content of the ores. Since many sedimentary iron deposits also contain some pyrite, this mineral would also tend to concentrate any available silver.

An interesting occurrence of traces of silver (and gold) is that in the salt-dome calcitic and gypsiferous cap rocks of Texas and Louisiana mentioned by Hanna and Wolf (1941). In these rocks the noble metals appear to be associated with sulphides, including pyrite, hauerite ($MnS_2$), galena, and sphalerite and in some places with barite, celestite, and native sulphur. The origin of the sulphides and their contained silver seems to be best explained by the hypothesis that as $H_2S$ rose from underlying petroliferous layers it came into contact with groundwaters (or connate waters in some cases) carrying lead, zinc, iron, manganese, silver, etc., in the region of the cap rocks and deposited the sulphides in the available porous zones.

Note

Mention should be made here of the concentration of silver in the Permian Kupferschiefer of the Mansfeld area, Germany, and elsewhere in Europe, including its equivalent the Marl Slate in northeast England; the copper shales of the Boléo district in Baja California, Mexico; the White Pine copper shales in Michigan; the Witwatersrand, Blind River, and Jacobina pyritiferous conglomerates and sandstones, and the so-called 'red bed' cupriferous and plumbiferous sandstones in various parts of the world. The origin of the metals in all of these sediments is controversial to say the least. Some investigators contend forcefully that the metals are syngenetic; others argue just as strongly that the metals are epigenetic and were deposited either from groundwaters, metamorphic waters, diffusion currents, or magmatic hydrothermal solutions; and still others think that the metals were originally syngenetic and have been redistributed by epigenetic agents.

Since many argentiferous sediments are low-grade silver deposits we shall reserve discussion on their origin until a later section. At this point it is interesting to record their silver content (Table 18) and compare it with those of normal sediments (*see also* the data in Tables 37 and 42). The data in Table 18 have been compiled mainly from the literature and from analyses done in the laboratories of the Geological Survey. Since the silver content of the sediments varies widely from area to area and from bed to bed the data must be considered only as general approximations. It is evident, however, that silver tends to be concentrated in the cupriferous deposits. The enrichment factor for silver in these deposits is generally many times

TABLE 18 | *Silver Content of Some Argentiferous Sediments*

| Rock Type | Locality | Ag, ppm (range) | Remarks |
|---|---|---|---|
| Kupferschiefer shales | Mansfeld, Germany; and elsewhere in Europe | 5 – 8,800 | Ore averages about 180 ppm Ag (∼ 5 oz/ton) |
| Marl Slate | Northeast England | < 0.2 | Deans (1950) |
| Cupriferous tuffs | Boléo district, Mexico | 7 – 12 | Wilson (1955) gives average as 9 ppm (∼ 0.26 oz/ton) |
| | | 125 | Average given by Touwaide (1930) (∼ 3.6 oz/ton) |
| Cupriferous shale and siltstone | White Pine, Michigan, U.S.A. | 1 – 160 | High Ag contents occur in beds containing native Cu (Carpenter, 1963) |
| Cupriferous shales and arkose, etc. | Zambia (Northern Rhodesia) | < 0.5 – 9.0 | Average estimated Ag content about 5 ppm (∼ 0.15 oz/ton) |
| Pyritiferous conglomerates and sandstones | Blind River region, Ontario | 0.13 – 6.5 | Average about 2.8 ppm Ag (∼ 0.084 oz/ton). Pyrite averages about 7.5 ppm Ag |
| Witwatersrand gold-bearing, pyritiferous conglomerate and associated sediments | South Africa | 0.5 – 1.0 | Ore averages about 0.8 ppm Ag (∼ 0.025 oz/ton) (For variations *see* Hargraves, 1963) |
| Pyritiferous conglomerates | Jacobina, Brazil | 0.5 – 1.5 (estimated) | Gold-bearing |
| Cupriferous sandstones (Red-bed copper type) | Nova Scotia, New Brunswick, Canada | < 0.5 – 2.0 | Ag erratically distributed. Concentrations in coaly fragments |
| Permian cupriferous sandstones | Western Urals, U.S.S.R. | 10 – 100 | Ag is enriched 10 times that of normal sandstones (Kashirtseva, 1962) |
| Silver Reef sandstone | Utah, U.S.A. | ∼ 3 | Local concentrations of silver ore |
| Cupriferous sandstones and shales | Corocoro, Bolivia | 7 – 16 | Local concentrations of native silver (Singewald, 1933) |
| Copper conglomerates and sandstones | Keweenaw Peninsula, Mich. | 0.5 – 1.0 (very low at depth, ∼ 0.02) | Estimated. Amygdaloidal basalts in same area carry similar amounts of silver. Some sandstones were mined for silver. (*See* Rominger 1876, and Nishio, 1919) |
| Sandstone | Kaller Stollen, Germany | ∼ 3.5 (estimated) | Galena concentrate ranges from 80–180 ppm Ag and averages about 150 ppm Ag. (Behrend, 1950). |

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| Rock Type | Locality | Ag, ppm range | Remarks |
|---|---|---|---|
| Sandstone (*cont'd*) | Silver Mine, Salmon River area, Cape Breton Island, N.S. | ~ 1.5 | Galena concentrate averages about 30 ppm Ag (analyses by GSC laboratories) |
| Sandstone and quartzite | Laisvall, Sweden | 10 | Lead ore averages about 4% Pb. (Grip, 1960) |
| Dolomite, limestone etc. impregnated with galena and sphalerite | Pine Point, N.W.T. | 6 | Mississippi valley type deposits. Silver concentrated mainly in galena. Value given is average for high grade ore (Jeffs, 1955) |

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that of normal sandstones and shales. Few gold analyses of the cupriferous and argentiferous sandstones and shales are available, and it is difficult to obtain a reliable estimate of the Ag/Au ratio. From the published data and from analyses of sandstones in the Maritime Provinces of Canada the ratio Ag/Au appears to be about 100:1. The pyritiferous gold- and uranium-bearing conglomerates and sandstones are not particularly enriched in silver but, as is well known, are generally enriched in gold. The Witwatersrand and Jacobina reefs have a silver:gold ratio of about 1:10. The ratio Ag/Au in the Blind River conglomerates is difficult to determine because of the erratic distribution of gold, but it would appear to be about 30:1 judging from assays of typical ore.

Note

In the various argentiferous sediments silver is bound in a number of ways. Native gold probably carries the bulk of the silver in deposits such as the Witwatersrand, Blind River, and Jacobina, and small amounts occur in the pyrite. In the Kupferschiefer most of the silver is intimately associated with the copper minerals, principally bornite, chalcocite, and tetrahedrite, and with galena and sphalerite. It occurs both in the native form and as a constituent of the sulphide minerals. Silver occurs most abundantly in the beds containing native copper in the White Pine deposit (up to 150 ppm); smaller amounts (~1 ppm) are present in the beds where chalcocite predominates. In the Zambian (Northern Rhodesian) deposits most of the silver appears to be present in chalcopyrite, bornite, and chalcocite, with perhaps minor quantities in the various cobalt sulphides. The silver in the Boléo deposits is in the copper concentrates, principally in chalcocite, chalcopyrite, bornite, covellite, native copper, and probably also in galena. In most of the copper-sandstone deposits the bulk of the silver is in chalcocite and bornite, less commonly in chalcopyrite and native copper. The last two tend to be rarer constituents in the copper-sandstone deposits. Some silver is also present as the native metal and as a constituent of the minor amounts of galena that accompany the copper minerals; also in a number of secondary minerals particularly malachite, azurite, pyromorphite, etc. in the zones of oxidation. At Corocoro the silver occurs in native copper, in chalcocite and domeykite, and as native silver in local shoots. The ores at Silver Reef in Utah were cerargyrite above the water-table and mainly argentite and native silver below. In deposits of the Pine Point and Mississippi valley type most of the silver occurs in galena, with infinitesimally small amounts in the sphalerite. In some of the southeast Missouri deposits, however, the sphalerite may carry appreciable contents of silver. Chalcopyrite probably carries a little silver in a few of the Mississippi valley type deposits, but this mineral is generally present in only small amounts in any of the ores.

Palmer (1935) has described an interesting occurrence of gold and silver in petrified logs in the Aspen district of Nevada. One log assayed 18.26 ounces of gold and 10.8 ounces of silver to the ton, and native gold, presumably containing the silver values, was readily observed under the microscope. Palmer thought that the carbonized wood produced the reducing environment that precipitated the gold and silver from circulating solutions that came into contact with the logs.

How much Ag & Au with U deposits

## Silver in Metamorphic Rocks

The available data on the silver content of metamorphic rocks are given in Tables 19 and 20. The analyses are too few to draw sound conclusions, but the following indications are noted.

TABLE 19 *Silver Content of Metamorphic Rocks*

| Rock Type | Locality | Reference | Ag (ppm) range | Ag (ppm) average |
|---|---|---|---|---|
| Serpentinites | Norway | Lunde and Johnson (1928) | 0.3 – 0.9 | |
| Serpentine | Leka, Norway | Goldschmidt (1954) | | 0.03 |
| Epidiorite | Co. Donegal, Ireland | Higazy (1952a) | | < 1.0 |
| Biotite–epidiorite | " " " | " | | 0.93 |
| Biotite–skarn | " " " | " | | 3.7 |
| Lepidomelane–skarn | " " " | " | | < 1.0 |
| Chlorite–skarn | " " " | " | | < 1.0 |
| Quartzite | " " " | " | | 6.5 |
| Mica schist | " " " | " | | 1.86 |
| Eclogite | Norway | Lunde and Johnson (1928) | 0.0 – 0.3 | |
| Various crystalline schists | Malvern Hills, England | Brammall and Dowie (1936) | | 0.6 |
| Banded schist and gneiss (reddened) | " " " | " " " | 0.6 – 33.0 | 7.3 |
| Granitized sandstone (in contact with red granite) | " " " | " " " | 3 – 16 | 10 |
| Amphibolites and hornblende schists and derivatives (some reddened) | " " " | " " " | < 1.0 – 7.0 | 2.75 |
| Pyroxenite–hornblendite | " " " | " " " | < 1.0 – 2.6 | 1.35 |
| ? Granodiorite derived from above rock | " " " | " " " | | 20.1 ? |
| Clay schists and quartzite | Schwarzburger saddle, Thüringen, Germany | Fischer (1958–59) | 0.01 – 0.3 | 0.11 |
| Marble | Carrara, Italy | Wagoner (1901) | | 0.2 |

TABLE 20 | *Silver Content of Some Canadian Metamorphic Rocks*

| Rock Type | Locality | Reference | Ag (ppm) range | Ag (ppm) average |
|---|---|---|---|---|
| Amphibolite (amphibolite facies) | Yellowknife greenstone belt, N.W.T. | Boyle (1961) | 0.6 – 1.4 | ~ 1.0 |
| Amphibolite (epidote amphibolite facies) | Yellowknife greenstone belt, N.W.T. | Boyle (1961) | 0.3 – 1.2 | ~ 0.7 |
| Chlorite schist (greenschist facies) | Yellowknife greenstone belt, N.W.T. | Boyle (1961) | | ~ 0.3 |
| Keewatin greenstones | Cobalt district | (*see* Table 46) | 0.19 – 0.30 | 0.25 |
| Argillites and slates | Sedimentary area, Yellowknife | Boyle (1961) | 0.3 – 2.0 | ~ 1.0 |
| Greywacke | Sedimentary area, Yellowknife | Boyle (1961) | 0.3 – 1.2 | ~ 0.75 |
| Quartz-mica schists | Sedimentary area, Yellowknife | Boyle (1961) | 0.9 – 1.2 | ~ 1.0 |
| Conglomerate and greywacke | Cobalt district | (*see* Table 46) | | < 0.05 |
| Skarn | Keno Hill area, Y.T. | Boyle (1965) | 0.1 – 0.15 | 0.1 |
| Skarn | Whitehorse area, Y.T. | Boyle (unpubl.) | 0.10 – 0.45 | 0.20 |
| Crystalline limestone | Whitehorse area, Y.T. | Boyle (unpubl.) | – | ~ 0.05 |

In metamorphic rocks silver appears to occur in the same minerals as noted for igneous and sedimentary rocks. Much of the silver occurs in pyrite, pyrrhotite, chalcopyrite, etc. and in the ferromagnesian minerals, principally biotite, pyroxene, amphibole, and magnetite. Some silver may be present in muscovite and feldspar, substituting in the sodium and potassium sites of these minerals.

Regionally metamorphosed rocks do not appear to have silver contents much different from the sediments or igneous rocks from which they were derived. Certain skarns and other contact rocks, on the other hand, seem to be somewhat enriched in silver. This is perhaps normal since such rocks often contain copper deposits and a few gold deposits, and silver generally accompanies these two elements. Brammall and Dowie (1936) concluded that the higher silver values in the reddened metamorphic rocks (migmatites) of the Malvern Hills were due to disseminations of hematite introduced as a result of pneumatolytic processes during the latest stage of granite intrusion.

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There is insufficient data to establish unequivocally the migration trend of silver during metamorphic processes. Nevertheless certain trends seem to be indicated. During granitization silver is not concentrated during the period of formation of pegmatites, but is strongly enriched in various types of veins and other types of deposits that appear to form during the late stages of the metamorphic and granitization events.

Silver, being a chalcophile element, probably follows sulphur, arsenic, and antimony during regional and contact metamorphic processes. There is also considerable evidence to suggest that the migration characteristics and diffusion rate of

Note

silver are about the same as those of gold, lead, zinc, cadmium, bismuth, and copper, since these elements are commonly associated in deposits. Higazy (1952a) has also suggested that silver probably follows and substitutes for potassium during the formation of skarn. The association of silver and potassium is also evident from the fact that the latter element is often strongly enriched in the wall-rock alteration zones of certain gold-silver veins and lead-zinc-silver deposits. An association with sodium may also prevail in zones of soda-metasomatism.

Some recent work carried out along traverses across contact skarn bodies in the Whitehorse copper belt, Yukon, indicates that silver tends to follow copper during the formation of the magnetite-bornite ores (Table 21). The skarns are slightly enriched in silver compared with the crystalline limestone from which they

TABLE 21 *Silver Content of Skarn, Whitehorse Copper Belt, Yukon*

| Rock Type | Ag (ppm) | Cu (ppm) | $K_2O$ (%) | $Na_2O$ (%) |
|---|---|---|---|---|
| Diorite–granodiorite | 0.2 | 15 | 1.2 | 2.8 |
| Skarn adjacent to above | 0.45 | 22 | 1.2 | 4.4 |
| Normal skarn | 0.2 | 12 | 0.1 | 0.2 |
| Skarn adjacent to magnetite–bornite deposit | 1.5 | 3,900 | ~ 0.1 | ~ 0.2 |
| Magnetite–bornite deposit | 60 | 6.4% | ~ 0.1 | ~ 0.1 |
| Crystalline limestone adjacent to above | 0.1 | 135 | < 0.1 | < 0.1 |
| Crystalline limestone | ~ 0.05 | ~ 5 | < 0.1 | < 0.1 |

Note: Traverses across granodiorite, skarn, copper deposit, and limestone at Arctic Chief mine. For geology see Kindle (1964)

TABLE 22 *Distribution of Silver in Country Rocks, Shear Zones and Deposits, Yellowknife Greenstone Belt, N.W.T.*

| Rock Type | Average Ag content, ppm |
|---|---|
| Greenstones (Amphibolite and epidote amphibolite facies) | ~ 0.7 |
| Graphitic tuffs and other sediments | 1.14 |
| Quartz–feldspar porphyry | ~ 1.5 |
| Chlorite–schist phase of shear zones (Rock is derived mainly from greenstone and from porphyry in places) | 0.25 |
| Carbonate–sericite schist phase of shear zones (Rock is derived mainly from greenstone and from porphyry in places) | 1.13 |
| Average of gold–quartz lenses | 4.77 |

were derived. There is also a general increase in the silver content of the skarn adjacent to the orebodies. There is no apparent correlation of silver with potassium or sodium in the rocks, except perhaps in the skarns adjacent to the granodiorite. In these an increased content in soda is marked by an increased amount of silver.

The great chlorite schist zones containing the gold-silver deposits at Yellowknife seem on limited data to be depleted in silver compared to the metavolcanic rocks in which they occur (Table 22). The silver lost during the conversion of the andesites and basalts to chlorite schist probably migrated into dilatant zones where it was concentrated in the gold-quartz veins and lenses. It would be interesting to examine this feature in detail in a number of gold and silver areas to see if this is a general characteristic of rocks that have been extensively chloritized or otherwise altered.

There appears to be no change in the silver content with increasing metamorphism in the sediments of the Yellowknife Group, Yellowknife, N.W.T. (Table 20).

## Silver in Soils and Other Products of Weathering

### Soils

Data on the silver content of soils are limited and the calculation of an average value seems unwarranted at the present state of our knowledge. Swaine (1955) listed a number of investigations in which silver was determined in various types of

TABLE 23 *Silver Content of Different Rocks and Soils in Finland* (*From* Lounamaa, 1956)

| Rock Type | | | Ag, ppm |
|---|---|---|---|
| SILICIC ROCKS | Rock: | | |
| | | mean | 0.58 ± 0.056 |
| | | range | <1 – 6 |
| | Soil: | | |
| | | mean | 0.41 ± 0.051 |
| | | range | <1 – 3 |
| ULTRABASIC ROCKS | Rock: | | |
| | | mean | 0.30 ± 0 |
| | | range | <1 |
| | Soil: | | |
| | | mean | 0.45 ± 0.12 |
| | | range | <1 – 3 |
| CALCAREOUS ROCKS | Rock: | | |
| | | mean | 0.30 ± 0 |
| | | range | <1 |
| | Soil: | | |
| | | mean | 0.30 ± 0 |
| | | range | <1 |

soils. The values quoted for normal soils range from <0.01 to 5 ppm Ag. Vinogradov (1959) made only a brief reference to a few investigations of the silver content of soils. Rogers, *et al.* (1939) found from 1 to 10 ppm Ag in some of the Florida soils they investigated. In most of the soils, however, the silver was below the detection limit. The higher values in silver occurred in the subsoils. Ahrens (1945) detected silver in a number of South African clays, and Salmi (1955) found up to 30 ppm Ag in the ash from a few samples of the Vuorokas and Malmisuo peat bogs in Finland. The general run of peat samples, however, contained less than 10 ppm Ag in the ash. McLaughlin (1955) found up to 15 ppm Ag in podzols developed on arkose in New Zealand. In general the clay fractions were richer in silver (<0.5–7 ppm) than the normal silt fractions (<0.5–2 ppm). Lounamaa (1956) found from less than 1 up to 3 ppm Ag in the different soils of Finland he investigated. The mean values ranged from 0.30 to 0.45 ppm (Table 23). Other investigations of the silver content of soils are mentioned in the section on geochemical prospecting.

The writer and his colleagues have carried out a number of investigations to determine the nature and content of silver in the soils of various parts of Canada (Presant, 1963; Boyle, 1965). The generalized results are given in Tables 24, 27, and 28. Specific examples of the metal content on traverses across vein faults and with depth at Keno Hill are given in Tables 25 and 26.

TABLE 24 | *Silver Content of Soils, Keno Hill Area, Yukon*[1]

| Bed Rocks | Soil Type | Ag, ppm Range | Remarks |
|---|---|---|---|
| Schists and quartzites | Residual | ∼ 0.5 | Average silver content of rocks 0.37 ppm |
| Greenstones | Residual | ∼ 0.5 | Average silver content of rocks 0.32 ppm |
| Schists, quartzites, and greenstones | Glacial till | < 0.5 | |
| Schists, quartzites, and greenstones | Glacial sand, gravel, etc. | ∼ 0.2 | |
| Schists, quartzites, and greenstones | Muck, peat, and other organic soils | 0.4 | Mainly overlie glacial tills |
| Schists and quartzites | Residual | Up to 10 | Over lead–zinc–silver lodes |
| Greenstones | Residual | Up to 20 | Over lead–zinc–silver lodes |
| Schists, quartzites, and greenstones | Glacial till, etc. | < 0.5 | Over lead–zinc–silver lodes |
| Schists, quartzites, and greenstones | Muck, peat, and other organic soils | 1.5 | Over residual soils in vicinity of lead–zinc–silver lodes |
| Schists, quartzites, and greenstones | Muck, peat, and other organic soils | 0.4 | Over glacial tills in vicinity of lead–zinc–silver lodes |
| Schists, quartzites, and greenstones | Glacial till, gravel, etc. | Up to 200 | Samples taken 1 foot to 6 inches above veins |

[1] For geology of the area *see* Boyle (1965)

TABLE 25 *Typical Traverse Showing Metal Content of Soils Across a Vein Fault, Keno Hill*[2]

| Sample interval in feet | Elemental concentration in ppm[1] | | | | | | | Remarks |
|---|---|---|---|---|---|---|---|---|
| | Ag | Pb | Cu | Zn | As | Sb | Mn | |
| 0–30 | <1 | 50 | 40 | 100 | 20 | 2.0 | 500 | Residual soil on greenstone. Horizon B |
| 30–60 | <1 | 30 | 40 | 110 | 35 | 2.5 | 500 | ” ” ” ” ” ” |
| 60–90 | <1 | 50 | 50 | 80 | 25 | 2.5 | 500 | ” ” ” ” ” ” |
| 90–120 | <1 | 30 | 60 | 70 | 25 | 2.5 | 500 | Residual soil on graphitic schist and phyllite. Horizon B |
| 120–150 | <1 | 20 | 60 | 40 | 20 | 2.0 | 200 | ” ” ” ” ” ” ” ” ” |
| 150–180 | <1 | 40 | 60 | 100 | 20 | 2.0 | 1000 | Residual soil on graphitic schist and phyllite. Horizon B<br>Projected outcrop of vein at 160′ |
| 180–210 | 2 | 100 | 60 | 200 | 100 | 8.5 | 1000 | Residual soil on graphitic schist and phyllite. Horizon B |
| 210–240 | 10 | 150 | 60 | 200 | 1000 | 44.0 | 1000 | ” ” ” ” ” ” ” ” ” |
| 240–270 | 10 | 80 | 40 | 800 | 920 | 50.0 | 1000 | ” ” ” ” ” ” ” ” ” |
| 270–300 | 10 | 1000 | 50 | 300 | 590 | 40.0 | 1000 | ” ” ” ” ” ” ” ” ” |
| 300–325 | 9 | 600 | 40 | 100 | 400 | 31.0 | 1000 | ” ” ” ” ” ” ” ” ” |
| 325–350 | 9 | 800 | 40 | 200 | 760 | 30.0 | 1000 | ” ” ” ” ” ” ” ” ” |
| 350–375 | 4 | 400 | 40 | 200 | 270 | 18.5 | 300 | ” ” ” ” ” ” ” ” ” |
| 375–400 | 5 | 500 | 40 | 200 | 410 | 25.0 | 300 | ” ” ” ” ” ” ” ” ” |

[1] Ag, Pb, Cu, Zn, and Mn analyses by W.H. Champ and W.F. White
As and Sb analyses by M.A. Jardine

[2] For geology of the area *see* Boyle (1965)

TABLE 26 *Variation in Metal Content of Soils With Depth, Onek Vein, Keno Hill*[3]

| Sample interval in feet | Elemental concentration in ppm[1] | | | | | | | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ag | Pb | Cu | Zn | As | Sb | Mn | Sn | Cd | |
| 0–6″ | 9 | 480 | 21 | 280 | 27 | 18 | 200 | 50 | 2 | Humus layer. Horizon A |
| 1′–3′ | 3 | 700 | 30 | 200 | 50 | 20 | 500 | 50 | 17 | Reddish brown residual soil: Heavy concentrates contain a few small galena cubes encrusted with cerussite and anglesite, cerussite, anglesite, limonite, and wad. Horizon B |
| 3′–6′ | 70 | 4000 | 60 | 300 | 160 | 430 | 500 | 150 | 17 | Reddish brown residual soil: Heavy concentrates contain some cerussite, anglesite, small galena cubes, pyrite, limonite, and wad. Horizon B |
| 6′–7′ | 120 | 5000 | 150 | 1000 | 500 | 2000 | 500 | 300 | 40 | Reddish brown residual soil mixed with oxidized vein debris. Heavy concentrates contain much galena coated with cerussite and anglesite, cerussite, anglesite, limonite, bindheimite, and some wad. Horizons B and C |
| Vein (average assay) oxidized ore—surface to 50-foot level | 88.12 oz/ton | 42.0% | 0.87% | 0.67% | 0.38% | 0.18% | 4% | 0.046% | 0.027% | Average assay[2] of oxidized ore: surface to 50-foot level. Ore contains galena, cerussite, anglesite, freibergite residuals, pyrite, minor sphalerite, and much limonite and wad |

[1] Ag, Pb, Cu, Zn, Sn and Cd analyses by W.H. Champ and W.F. White
As and Sb analyses by M.A. Jardine

[2] Assay of ore by Mines Branch, Ottawa

[3] For geology of the area *see* Boyle (1965)

TABLE 27 *Silver Content of Soils, Bathurst–Newcastle Area, New Brunswick*[1]

| Horizon[2] | Ag (ppm) range | Ag (ppm) Mean of all horizons (26 profiles) | Ag (ppm) Mean of normal horizons (14 profiles) | Ag (ppm) Mean of horizons over Brunswick No. 6 Deposit[3] (2 profiles) | Ag (ppm) Mean of horizons over Nigadoo Deposit[4] (5 profiles) | Ag (ppm) Mean of horizons over Middle River Deposit[5] (2 profiles) |
|---|---|---|---|---|---|---|
| $A_0$ | 0.2 – 90.0 | 5.7 | 1.6 | 45.6 | 5.2 | 3.4 |
| $A_2$ | 0.1 – 36.0 | 2.4 | 0.4 | 18.6 | 0.4 | 1.8 |
| $B_1$ | 0.2 – 6.7 | 1.8 | 0.3 | 3.9 | 4.6 | 4.1 |
| $B_2$ | 0.1 – 24.0 | 3.5 | 0.3 | 19.5 | 4.1 | 6.1 |
| C | 0.1 – 16.0 | 2.7 | 0.3 | 5.3 | 9.0 | Not detected |

[1] Data from Presant (1963)
[2] Soils are podzols developed mainly on glacial till
[3] Brunswick No. 6 deposit is a massive sulphide body containing essentially Pb, Zn, Cu, Fe, Ag, S
[4] Nigadoo deposit is a sulphide vein deposit containing essentially Pb, Zn, Cu, Fe, As, Ag, S
[5] Middle River deposit is a massive sulphide body containing essentially Pb, Zn, Cu, Fe, Ag, S

TABLE 28 *Silver Content of Soils, Walton–Cheverie Area, Nova Scotia*

| Description | | Ag range (average values in ppm in brackets) | | Ag, average content in ppm in underlying rocks |
|---|---|---|---|---|
| Bog soils, bogs, organic debris in marshes, beaver ponds, etc. | | < 0.10 – 0.89 | (0.32) | 0.23 |
| Bank soils along creeks, all rock types, B horizon | | < 0.10 – 0.97 | (0.27) | 0.23 |
| Soil profiles over Horton Bluff and Cheverie Formation, consisting of shales, sandstones, minor limestone, etc. | $A_{0+1}$ | < 0.05 – 0.96 | (0.47) | |
| | $A_2$ | < 0.05 – 0.38 | (0.28) | 0.23 |
| | B | 0.17 – 0.57 | (0.31) | |
| | C | 0.05 – 0.62 | (0.27) | |
| Soil profiles over gypsum and anhydrite of Windsor Series | $A_{0+1}$ | | (0.2) | ∼0.1 |
| | $A_2$ | | (0.2) | |
| | B | | (0.2) | |
| | C | | (∼0.1) | |
| Soils over mineralized zones; samples from B horizon | | 0.36 – 1.90 | (0.84) | Highly variable. Some mineralized zones have less than 5 ppm Ag, others such as the Magnet Cove deposit are greatly enriched in silver, containing up to 500 ppm or more |

The soils at the higher elevations in the Keno Hill area are residual in part or developed from an ancient till. Those at the lower elevations are developed mainly on glacial till and allied deposits. Over much of the area the soils are permanently frozen and are severely disturbed by repeated freezing and thawing, solifluction, etc. They have, therefore, poorly developed profiles and little can be said about the silver contents in the different horizons.

The average silver content of residual soils developed on schists and quartzites is about the same as that on greenstones (metadiorites, metagabbros etc.), although locally the soils on the latter rocks may have a slightly higher content of silver than those developed on adjacent schists and quartzites. The silver content of glacial till and other glacial materials is always low and is seldom greater than 0.5 ppm. Similarly the silver content of muck and other organic soils is generally low except locally where the lead-silver lodes have an influence in raising the silver content.

Near the lead-zinc-silver lodes the silver content of most residual soils is considerably enriched, as shown in Tables 24, 25, and 26, with values up to 10 ppm or more being common. In these soils the silver follows lead, zinc, tin, cadmium, antimony, arsenic, and manganese, all of which are many times the normal background values for the elements.

Near-surface glacial tills, sands, and gravels exhibit no enrichment of silver near the lead-zinc-silver lodes. The same is true for most mucks and other organic soils, especially those formed on terrain underlain by glacial materials. The organic layer overlying residual soils may exhibit a small enrichment of silver near certain lodes, but the distribution of the element is generally erratic. Deep samples of glacial till taken just above deposits may, however, be greatly enriched in silver.

Locally the stream sediments in the Keno Hill area are enriched in silver and have contents up to 10 ppm or more. Anomalous trains up to 2 miles long occur in some streams (Gleeson, *et al.*, 1966).

The soils in the Bathurst-Newcastle area of New Brunswick are podzols developed mainly from glacial till, glacio-fluvial material, and glacio-lacustrine material. The profile development is good and the horizons are generally clearly marked.

Presant (1963), and Presant and Tupper (1965) found that high amounts of silver in the bedrock and mineral deposits are generally matched by higher than normal concentrations of silver in the surface horizons of the overlying soils. Silver tends to concentrate in the surface $A_0$ horizon, suggesting that it is combined with organic material in some way. This tendency is especially marked in the normal horizons as shown in Table 27.

Presant (1963) also found a good positive correlation between silver and pH in the $A_0$, $B_1$, and C horizons, a feature suggesting that increased acidity facilitates the removal of silver from these horizons. Silver also shows a fairly good positive correlation with iron in the B and C horizons, no correlation with iron in the $A_2$ horizons, and a significant negative correlation with iron in the $A_0$ horizon.

The soils of the Walton-Cheverie area, Nova Scotia, are podzols developed from glacial tills that overlie most of the region. In these tills there may be some local mixing with residual soils. The profile development is good in most places, and the horizons are generally clearly marked.

The average silver content of all types of soils, excepting those over mineralized zones, is about 0.30 ppm. Bog soils, bogs, and the decomposed organic debris in marshes, beaver ponds, etc. are in general higher in silver than the normal soils (Table 28). This is also true for the organic horizons of most of the soil profiles, a feature which was also noted by Presant (1963) in New Brunswick. The reasons for this enrichment are obviously biochemical and are probably in part related to the strong adsorption of silver by humic colloids. The leached $A_2$ horizons are on the average somewhat depleted in silver, as would perhaps be expected, and the B horizons, especially the zones where a maximum accumulation of iron oxides are present, are slightly enriched. All B horizons over or in the vicinity of mineralized zones, some of the latter containing only traces of silver, are greatly enriched in the element. Where manganese dioxides occur in these horizons, or in others in close proximity to mineralized zones, the content of silver is a maximum, indicating a strong adsorptive capacity of manganese sols for the element. In the soils overlying mineralized zones silver follows barium, strontium, lead, zinc, arsenic, and antimony, all of which show parallel enrichments.

Stream sediments near mineralized zones are also enriched in silver, particularly those containing a high content of hydrous manganese oxides. Such sediments average 0.93 ppm Ag, whereas the normal sediments average about 0.14 ppm Ag. Enrichments of silver in the stream sediments are accompanied by parallel enrichments of barium, strontium, lead, zinc, arsenic, and antimony.

The investigations carried out by the writer and his colleagues suggest that silver is bound in the following ways in soils:

1. As a minor constituent of nodules and particles of galena, anglesite, beudantite, and other silver-bearing lead minerals. These minerals occur in the disturbed residual soils in the vicinity of lead-zinc-silver deposits in the Keno Hill area and elsewhere in Yukon. Where the silver contents of the soil are greater than 5 ppm these minerals generally appear in the heavy concentrates.

2. As a constituent of flakes and small nuggets of gold. These are common in the residual soils in the vicinity of some gold-silver veins in Yukon and elsewhere. Nuggets, plates, dendrites, and flakes of native silver may occur in soils near certain native silver deposits or where lead-zinc-copper-silver deposits are deeply oxidized. Chlorargyrite nodules have been reported from the saline soils of arid silver-bearing regions.

3. As a minor constituent of various heavy minerals in the soils, particularly magnetite, pyrite, chalcopyrite, sphalerite, etc. These minerals have been found in the soils near all of the ore deposits in eastern and western Canada.

4. As a minor constituent of particles of manganese oxides and also in the coatings of these compounds on sand and silt. It has been noted that soils enriched in manganese oxides are also enriched in silver in the Keno Hill area and in the Walton-Cheverie area, Nova Scotia. The enrichment is presumably due to the coprecipitating effect of the negatively charged manganese colloids and gels on the positive silver ions available in the soil solutions.

5. As a minor constituent of the various hydrated iron oxides that occur as particulate matter or as coatings on sand, silt, etc. The iron hydroxide colloids and gels normally carry a positive charge and should repel the positive silver ions. However, in soil complexes where $PO_4^{3-}$ and other anions are available, these may shield the positive charge on the iron colloids and actually give them a combined negative charge. The colloids and gels may then adsorb silver as well as numerous other cations. This process seems to be responsible for the presence of silver in the hydrated iron oxides in some soil profiles.

6. As a minor constituent of the organic matter in soils. Presant (1963) found that the $A_0$ horizon of the soils in the Bathurst, New Brunswick, area was generally enriched in silver.[1] In the Yukon soils the organic layers are enriched in places, but this feature is not a general one, probably because of the unusual climatic conditions under which the soils have developed. It is evident from detailed studies of some of the organic layers in eastern Canada that the silver is bound in the colloidal (?) humic components. Only small amounts of silver are removed by acids, alkalis, ammonium acetate, etc. Ashing is necessary to effectively liberate the silver.

7. As a minor constituent of the clay fraction. The precise mode of binding of the silver in this fraction is uncertain. Small amounts can be liberated by acid leaches, ammonium acetate, etc. indicating that some silver may be adsorbed to the surfaces of the clay minerals. The remainder of the silver appears to be tightly bound in the clay minerals. In these the $Ag^+$ may replace $K^+$ or $Na^+$ because of the similarity in ionic radii. There are other indications that a little silver is associated with the highly aluminous constituents of the soils, but its mode of binding is unknown. Perhaps it is present as an adsorbed constituent, or it may be an integral part of the colloidal aluminum hydroxide, alumina-silica, or alumina-phosphate complexes. The experiments carried out by Kayser and Bloch (1948) with bentonite seem to suggest that silver (as the nitrate) is lightly adsorbed to the surfaces of the clay minerals, whereas the element (as the chloride, bromide, etc.) partakes of the structure of the clay minerals.

8. Probably as silver orthophosphate in some soils. This is purely supposition and is based on the fact that silver is precipitated as the insoluble orthophosphate in the presence of soluble (available) phosphates. Soluble arsenates, molybdates, tungstates, and chromates would have the same precipitating effect.

9. In jarosite and beudantite. The soils overlying some of the New Brunswick massive sulphide deposits are highly stained by yellow sulphate minerals that X-ray analysis shows to be mainly jarosite and beudantite. These minerals are relatively high in silver.

In addition to the above mechanisms, a knowledge of the chemistry of silver suggests that the element may be bound as the chloride, bromide, or iodide in the saline soils of arid regions. There is also probably a minor amount of silver in the soil solutions of all soils, and some silver is probably also present in bacteria and

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[1] The A horizon in the Cobalt silver area is, likewise, considerably enriched in silver (*see* Boyle, R.W., and Dass, A.S., *Econ. Geol.* vol. 62, pp. 274–276)

other organisms in the soil. These occurrences would seem to complete the possible modes of binding of the element in soils.

Our investigations indicate that the mobility and fixation of silver in soils is influenced by the following factors:

1. Topography. In the mountainous parts of the Yukon, and presumably also in British Columbia, the soils tend to be considerably disturbed by downhill migration. This results in poor profile development and mixing of material from different horizons. Both these features make systematic work difficult with respect to the migration and concentration tendencies of silver and other elements within the soil horizons. In our experience it is necessary to carry out the work on a local basis, and we have found that broad generalizations do not apply. On the other hand in eastern Canada, where elevations are subdued and where profile development is fair to good, certain generalizations on the geochemistry of silver in the soils are permissible.

2. Climate. Our investigations are too restricted to draw adequate conclusions on the effect that climate may have on the chemistry of silver in the soil. In the far northern regions where permafrost prevails the soils are greatly disturbed by frost-boiling, solifluction, etc. This tends to disrupt the profiles and brings particles of unweathered material to the surface. This is a favourable feature for geochemical prospecting, since particles of silver-bearing ore minerals and secondary oxidation products occur near the surface in the vicinity of deposits, a circumstance that permits relatively shallow sampling.

In the more temperate regions where podzols predominate, more normal chemical conditions prevail, and the chemistry of silver in the soils can be traced with more assurance.

3. Parent materials. No major differences have been noted in the silver content of soils developed from different rock types in Yukon. In eastern Canada, where the soils are developed on glacial tills or mixtures of tills and residual soils, we have noted no radical variations in the silver content of the normal soils.

In all of our investigations we have found that the presence of silver-bearing deposits normally influences the silver content of the soils. In Yukon, New Brunswick, and Nova Scotia the silver content of the soils is generally increased over or near mineral deposits. Where deep glacial deposits overlie silver-bearing veins, as in some parts of the Yukon, this generalization does not hold. Limited work in northern Ontario also suggests that silver veins are masked by deep glacial accumulations (Boyle, 1966).

4. Drainage conditions. Well drained soils tend to have lower contents of silver compared with poorly drained soils in the same area. This is probably due to the fact that all silver compounds are slightly soluble and are gradually removed in time from the various horizons.

5. Eh of soils. The normal range of the oxidation-reduction potentials in soils has apparently little direct effect on the mobility of silver since the element has normally only one oxidation state. Indirectly, however, the Eh is of major importance

since it plays a part in the hydrolysis of iron and manganese, precipitation of iron and manganese oxide hydrates, production of $S^{2-}$ ion, oxidation of organic material, etc., and these exert a major influence on the chemistry of the silver ion as described below.

6. pH of soils. The pH of the soils affects the mobility of silver in many ways, some of them directly and some indirectly. Normally silver salts are more soluble, and silver is more mobile in an acid environment. With decreasing acidity there is a slight hydrolysis of the argentous ion, $Ag^+$, and acid and basic salts may be precipitated under proper conditions. In an alkaline environment the oxide or hydrated oxide is precipitated. These simple reactions rarely if ever prevail in any soil, however, since iron, manganese, alumina, and organic matter modify the course of events in a number of ways.

In an environment where decreasing acidity and a relatively high Eh prevail, iron if present in the ferrous state, is oxidized to the ferric state, undergoes hydrolysis and may be precipitated as a basic salt or as the oxide hydrate, $FeO(OH) \cdot nH_2O$. In some of the profiles investigated where the pH's range from 3 to 5, jarosite, $KFe_3(SO_4)_2(OH)_6$, and beudantite, $PbFe_3(AsO_4)(SO_4)(OH)_6$, two complex basic sulphates of ferric iron, are present, and these have scavenged much silver, rendering the element immobile. In other profiles it is evident that much of the silver is tied up in the hydrated iron oxides. Normally ferric oxide hydrate is a poor carrier of silver, since its colloid bears a positive charge. Where $PO_4^{3-}$, $AsO_4^{3-}$, hydrated $MnO_2$, silica, humic colloids, etc. are present these are attracted to the ferric oxide hydrate and may give the combined colloidal complex a negative charge, which permits the adsorption or coprecipitation of $Ag^+$ as well as numerous other cations. This mechanism seems to be responsible for the association of silver with the iron oxides.

Decreasing acidity, likewise, causes the precipitation of hydrated manganese oxides and since these carry a negative charge they adsorb and coprecipitate any available silver. Alumina, also, undergoes hydrolysis with decrease in acidity, forming a most complex series of hydroxides and alumino-silicates. The latter in turn seize on the available $K^+$, forming the familiar potassium clay minerals. Because $Ag^+$ and $K^+$ are similar in their radii and adsorption characteristics it seems logical to conclude that some silver is scavenged and removed from circulation by the clay minerals.

These features serve to emphasize that silver is relatively immobile in soils where the pH is greater than 4. The mobility of the element is restricted in part by the hydrolysis of the argentous ion, but mainly by the hydrolytic and colloidal reactions that characterize the chemistry of iron, manganese, and alumina in the soils.

7. Presence of organic compounds. Organic matter, particularly the humic substances, adsorb silver strongly and apparently build the element into their structures, perhaps forming chelated complexes with the metal. Whatever the mode of binding it is evident that much silver is immobilized where abundant organic matter is present in the soil. This is shown by the marked enrichments of silver in the $A_0$ horizons of many soils and its presence in relatively increased amounts in peat and half bog soils, decomposed organic debris in marshes, etc.

The pH seems to have little effect on the mobility of silver in the organic horizons of soils or in peats, etc. The pH may be as low as 3.0 with no particular decrease in the content of silver in the humic components.

Another point of interest is the fact that as the humification processes proceed the large coordinated humic groups dissociate and pass into a soluble (colloidal) form in the soil solutions and are ultimately removed by the groundwaters. As the soluble groups appear to retain much of their silver during the disintegration process, the mobility of silver is increased in the soils.[1]

Finally, under a high oxidation potential the humic complexes may be oxidized yielding $CO_2$, $H_2O$, etc. and liberating any bound silver. This silver is then in an extremely mobile state, although in most cases it is generally seized quickly by the remaining humic complexes. This process repeated *ad infinitum* leads to the enrichment of silver noted in some of the organic layers of soils, in peats, etc.

8. Presence of complexing agents. These may act in two ways—to increase or to decrease the mobility of the element. Anions such as $SO_4^{2-}$, $NO_3^-$, $HCO_3^-$, and various organic acids render silver relatively soluble and hence increase the mobility of the element. On the other hand anions such as $PO_4^{3-}$, $Cl^-$, $Br^-$, $I^-$, $CrO_4^{2-}$, $AsO_4^{3-}$, etc. precipitate insoluble compounds and decrease the mobility. The presence of $H_2S$ or $S^{2-}$, due to the bacterial reduction of protein complexes in organic environments, would precipitate the sulphide, thus greatly reducing the mobility of silver. Complexing agents such as $(S_2O_3)^{2-}$ or an excess of $Cl^-$ give soluble silver complexes of the type $[Ag\ (S_2O_3)_2]^{3-}$, $[AgCl_2]^-$, and $[AgCl_3]^{2-}$, rendering the element more mobile.

9. Formation of colloids. Practically nothing is known about natural silver colloids in soils. AgCl and numerous other types of silver colloids are known, and if these occur in nature they would be expected to increase the mobility of the element in soils. Because the silver halide complexes may carry either a positive or negative charge the precipitation of these colloids would vary according to the types of colloids and electrolytes present in the soil solutions. Positive colloidal ferric hydroxide would precipitate the negative halide colloids, negative manganese colloids, the positive halide colloids, etc.

10. $Fe^{2+} - Fe^{3+}$ content of soil solutions. The acid reaction[2]—

$$Fe^{2+} + Ag^+ \rightleftarrows Ag + Fe^{3+}$$

is reversible, the direction depending on the $Fe^{2+}/Fe^{3+}$ ratio in solution. Where a high $Fe^{2+}$ concentration prevails, silver is precipitated, and the mobility of the ele-

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[1] This statement seems justified by analogy with gold. Freise (1931) found that humic acids dissolve and transport gold, and this view is supported by Shcherbina (1956). Fetzer (1934, 1946), however, presented experimental evidence that seems to indicate that gold (and silver) is not readily dissolved by humic substances. The whole problem requires further investigation, since there seems to be undoubted evidence that gold (and silver) is being transported in natural soil solutions and in waters charged with humic complexes.

[2] This reaction is one of the most important as regards the geochemistry of silver in near surface processes. It has been discussed in detail by Tananaeff (1925) who gives the equilibrium constants at 0°, 25°, and 45°C as follows:

$$K_{0^\circ} = 0.0019; \quad K_{25^\circ} = 0.0060; \quad K_{45^\circ} = 0.0110$$

ment is reduced. Where a high $Fe^{3+}$ concentration is present silver is kept in the soluble and hence mobile ionic state. It should be particularly noted that the reactions apply only to iron in solution; once hydrated oxides or hydroxides are precipitated these no longer play a part in the oxidation-reduction reactions. Soluble manganous salts probably also play a role similar to those of ferrous salts in neutral and mildly alkaline soils

$$2\ Ag^{+} + Mn^{2+} + 4\ OH^{-} \rightleftarrows 2\ Ag + MnO_2 + 2\ H_2O.$$

11. Influence of organisms. There are no data on the part that organisms such as bacteria and fungi play in the mobility of silver in the soil. Presumably since these organisms render nitrogen compounds in the soil soluble as nitrates this would increase the mobility of silver as the nitrate. Bacteria and other organisms also break down the various organic complexes and hence would liberate any complexed silver. The production of $H_2S$ by bacteria on the other hand would reduce the mobility of silver as mentioned above.

## Other Products of Weathering

There are only qualitative data on the occurrence of silver in weathering products such as bauxites, laterites, bog-iron deposits, bog-manganese deposits, etc.

Better ? dat 'report ?

Hartley and Ramage (1897) found silver in all of the bauxites they examined, and Chhibber (1946) mentioned the presence of the element in the bauxites of Tungar Hill, India. There are also scattered references in the literature to the presence of traces of silver in lateritic ores, bog-iron ores, and bog-manganese ores. In some of the bog-manganese deposits of Nova Scotia the writer found up to 1.8 ppm Ag.

In Canad anywhere

During the weathering of gold- and silver-bearing rocks and deposits the two metals tend to concentrate in particles of native gold in the weathered detritus. Such auriferous blankets or eluvial deposits are common in Brazil, the Guianas, Mexico, and elsewhere. They are composed principally of laterite—a mixture of ferric oxides, hydrated ferric oxides, clay, and sand. Some contain essentially gravel, sand, and clay and may be partly cemented by caliche and iron oxides. The origin of the gold-silver particles in these materials has been a long-standing problem. It is certain that some of the particles are of residual origin and represent the flakes and nuggets weathered from gold-quartz veins. Some of the gold and silver is probably also of chemical origin; that is, the particles are either enlarged or individually accreted by additions of gold and silver from solutions that derived the metals both from the weathered constituents of the rocks and from various gold- and silver-bearing sulphides in veins and other types of deposits. Mustart (1965), however, could find no evidence to support this thesis in the Yukon. He concluded that the gold accumulated in streams by mechanical processes attendant on the weathering of quartz veins.

Note

As the weathering cycle proceeds the material in eluvial deposits may be further decomposed, eroded, transported, and redeposited. This can be effected by wind, streams, rivers, or by the surf of the sea, resulting in aeolian, stream, and beach placers. During these movements the gold-silver particles may be comminuted and reduced to a flour or, as is more often the case, especially in an aqueous environment, the small particles may be recrystallized, partly dissolved, and the gold reprecipitated on the larger particles. Since silver is more mobile (more soluble) than gold the chemical processes of solution and reprecipitation generally lead to an increase in the fineness of the gold flakes and nuggets with increasing distance from the source. Furthermore, the outside parts of nuggets often have a significantly greater fineness than the inner parts, a feature that adds convincing support to the theory of accretion of gold from solutions as the particles are moved along by mechanical processes. Other evidence of the solution and precipitation of gold and silver in placers is witnessed by the occurrence of gold crystals in places, wire gold, replacement of deer horns by film gold, agate-like structures of certain nuggets, and the fact that some investigators have found increased amounts of gold and silver in stream waters in the vicinity of gold veins and polymetallic deposits (*see* below). Further details on the interesting problems of the geochemistry of the origin of gold in oxidized zones and placers are well presented by Maclaren (1908), Emmons (1937), and Mackay (1944).

See

The most frequent associates of gold-silver particles in placers, in addition to the common silicates, are magnetite, ilmenite, monazite, garnet, zircon, pyrite, native bismuth, cassiterite, and cinnabar. Nuggets of native silver are rare, although they do occur in some of the placers in Alaska and in those of Burwash and Arch Creeks (Kluane and Donjek Rivers district), Yukon. Arquerite, the silver-mercury amalgam, occurs in the placers of Silver, Vital, Kenny, and Kwanika Creeks in the Fort St. James area, British Columbia and in Burwash Creek in the Kluane Lake district, Yukon. Certain types of eluvial and alluvial fans and similar deposits in addition to gold also contain galena, anglesite, bindheimite, mimetite, and other oxidation products of lead-zinc-silver veins. Silver accompanies all these minerals as it does in the original deposits, but the grade of the gravels, clays, etc. rarely exceeds 0.5 ounce Ag/ton (17 ppm Ag). Such deposits are known in many parts of the world, particularly in the unglaciated regions. Those associated with a mineralized porphyrite granite stock near Guadalcázar in Mexico have received detailed attention (Foshag and Fries, 1942; Fries and Schmitter, 1948). Other types associated with sink-holes in limestone are known in Burma and China (Rundall, 1927-28; Searls, 1952), and have been worked in the past.

Undoubted fossil gold-silver placers have been described from several countries. They occur in conglomerates, sandstones, and arkoses of various ages. Examples are known in the Black Hills, South Dakota; at Gays River, Nova Scotia; Indian River, Yukon (Maclean, 1914); and elsewhere.

## Silver in Natural Waters and Precipitates

Silver is widely diffused in spring, stream, river, and lake waters, but generally only in small amounts. The average for all fresh waters is about 0.0002 ppm Ag. Regional variations both above and below this average appear to be normal.

Most of the silver in natural waters is derived from silver in rocks, deposits, and their weathered products. Small amounts of silver in some areas may arise from domestic and industrial sewage, Katadyn processes of sterilizing water, and from the seeding of clouds by silver iodide during rainmaking projects. Minute quantities of Ag $110^m$, with a half-life of 253 days, are also contributed to natural waters as a result of nuclear explosions.

Several investigations of the silver content of spring, stream, river, and lake waters have been carried out in a number of countries. A few of these investigations are recorded in Table 28. A study of the published investigations and others carried out by the writer and his colleagues indicates that spring waters are generally slightly higher in their silver content than stream, river, or lake waters. Acid waters tend to carry more silver than neutral and alkaline waters, although there are exceptions to this generalization in the case of hot springs. Chloride, sulphate, and bicarbonate waters are often enriched in silver, and there are indications that waters containing an abundance of dissolved iron and manganese tend to carry increased contents of silver. Some organic waters seem also to be enriched in silver, although more data are required before good correlations can be made. Silver is generally accompanied by Cu, Zn, Cd, V, and U; less commonly by Ba, Ti, Sn, Zr, Mo, As, Sb, P, Pb, Au, Bi, Ni, Co, and W. Waters leaching gold-silver and polymetallic deposits tend to carry 10 to 100 times as much silver as normal spring, stream, river, and lake waters. There are exceptions to this generalization, especially where carbonate gangue accompanies the silver minerals.

Many of the natural precipitates from cold springs, underground waters, and hot springs contain small amounts of silver (Table 29). Some precipitates are greatly enriched in the element, especially those that are associated with silver deposits.

Manganese oxides (wad) frequently concentrate silver, and certain varieties of limonite, especially if they are admixed with or contain manganese oxides, phosphate, arsenate, etc., tend to carry considerable amounts of the element. Organic compounds (humic complexes) also seem to be major concentrators of silver in some areas. Sulphate efflorescences and stalactites in the drifts and workings of gold-silver mines were found by Morris and Lovering (1952) to be silver-bearing. Contents up to 1,150 ppm were recorded in chalcanthite, with lower amounts in pisanite (170 ppm), copiapite (32 ppm), etc. Of the precipitates associated with hot springs, the siliceous sinters (usually with some sulphides) deposited from alkaline waters tend to concentrate more silver than the carbonate and limonitic sinters.

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In the natural precipitates silver is most frequently accompanied by Cu, Au, Zn, Pb, Cd, Zr, Ti, Sb, As, Ba, B, P, and S, and less frequently by Hg, V, U, Th, W, Co, Ni, Mo, Bi, Li, and Te. Judging from the data in the literature the Ag/Au ratio of hot spring deposits such as siliceous sinter, travertine, etc. is generally greater than 1. There is great variability in the Ag/Au ratios of cold spring deposits, but they commonly exceed 1. The highest contents of gold and silver generally occur in the siliceous sinters precipitated from hot alkaline saline waters. This circumstance is particularly marked at Whakarewarewa and other thermal areas in New Zealand (Grange, 1937). Such natural data suggest that some silver-gold-quartz deposits were probably precipitated from alkaline saline siliceous waters or from diffusion currents in an alkaline environment.

The mode of occurrence of silver in natural precipitates is exceedingly variable. In manganese oxides and limonite much of the silver is probably present in an

TABLE 29 | *Silver Content of Spring, Stream, River, and Lake Waters*

| Location | Type of Water (principal dissolved constituents, etc.) | pH | Reference | Ag (ppm) |
|---|---|---|---|---|
| New Guinea | Stream and spring waters: Mn, Fe, organic matter, Cl(?) | – | Blanchard (1933) | Present |
| Spain, Iberian Peninsula | Stream, spring, and well waters: Cu, V, Fe, Ca, Na, Mg, K, Si, Al, U | – | Mingarro and Catalina (1958) | Up to 2.5<br>Av.–0.98 |
| Siberia, U.S.S.R. | Stream, spring, mine waters: $SO_4$, As, Zn, Cu, Pb, Sb, (Mo), (Cd), (P) | 4.5–8.4 | Udodov and Parilov (1961) | 0–0.0438 |
| Central Kazakhstan, U.S.S.R. | Surface and underground waters: $CaHCO_3$, $NaHCO_3$, $MgHCO_3$, $SO_4$ | 5.8–7.8 | Belyakova (1958)<br>Belyakova, *et al.* (1963) | 0.00015–0.51 |
| Eastern Transbaikal, U.S.S.R. | Surface and underground waters | – | Trofimov (1961) | 0.002–0.01 |
| Transbaikal, U.S.S.R. | Surface and underground waters | – | Albul and Miller (1959) | 0.00005–0.0026 |
| Urals, Kazakhstan, etc., U.S.S.R. | Mine waters mainly from pyritic and gold deposits | Acid and neutral | Ginzburg (1960) | 0.001–20 |
| Yakutsk, U.S.S.R., Olenek River Basin | Stream, river, and spring waters | 6.8–8.6 | Kosolapova (1963) | 0.00012–0.25 |
| United States | Stream, river, and lake waters | – | Braidech and Emery (1935) | 0.01–0.20 (in residues) |
| North America and Norway | River water | – | Livingstone (1963) | Up to 0.001 |
| Keno Hill, Yukon | Spring and stream waters: $SO_4$, Ca, Mg, Mn, Zn, Al | 4.4–7.8 | Boyle (1965) | ~0.001 |
| North America | Large rivers | – | Durum and Haffty (1961, 1963) | 0–0.00094 |
| Maine, U.S.A. | Lakes | – | Kleinkopf (1955, 1960) | 0.00001–0.0035 |
| Walton, N.S. | Streams and springs: Cl, $SO_4$, $HCO_3$, Mn, Ca, Mg, Na, K | 6.5–7.5 | Boyle (unpubl.) | <0.0001–0.0005 |
| Beppu, Japan | Hot springs: acid and bicarbonate, Zn | Acid and neutral | Koga (1957) | 0.0–0.057 (av. 0.011) |
| Steamboat Springs, Nevada | Hot springs: $SiO_2$, NaCl, $HCO_3$, borate, sulphate, carbonate | 5.3–9.1 | Brannock, *et al.* (1948) (Ag not determined in water) | Up to 43 Ag in siliceous muds |
| Niland, California | Steam well: NaCl, $CaCl_2$, KCl | – | White, *et al.* (1963) | Up to 1.3% Ag in residue<br>0.1–0.3 ppm Ag in water |
| Comstock Lode, Nevada | Vadose mine waters: Acid; $SiO_2$, Mg, Fe, Al, Ca, Cu, Mn, $SO_4$ | Acid | Reid (1905) | 0.207 |

| Location | Type of Water (principal dissolved constituents, etc.) | pH | Reference | Ag (ppm) |
|---|---|---|---|---|
| Comstock Lode, Nevada | Deep mine waters; alkaline sulphate and carbonate waters with some Cl. Temperature 116–170°F. | Neutral to alkaline | Reid (1905) | 0.0033 |
| Sukayu, Japan | Hot springs: $CaSO_4$ | – | Kuroda (1942) | 0.010 |
| Japan (various localities) | Hot springs (various compositions) | – | Uzumasa (1965) | <0.005–0.057 |

adsorbed form or as an integral part of the oxide complexes. Some varieties of silver-bearing vein limonites contain the element in a number of ways: in minute specks of native silver; in a great variety of secondary silver-bearing minerals such as jarosite (plumbojarosite and argentojarosite), bindheimite, beudantite, anglesite, pyromorphite, malachite, azurite, etc.; and probably in some cases as the insoluble silver orthophosphate, silver arsenate, and silver chloride, bromide, or iodide. Limonite, intimately mixed with organic substances, probably holds the silver in complex silver humates. In the siliceous sinters silver is generally present in the associated sulphides of iron, antimony, arsenic, lead, copper, etc. Where chlorides are present in natural waters their calcareous, siliceous, limonitic, or ocherous precipitates probably contain the silver as the insoluble chloride. Barite sinters seem to hold the silver mainly in associated galena and other sulphides. In organic environments where decaying animal remains and vegetation are abundant the silver is probably precipitated mainly as a humate in most cases, or as a sulphide under strongly reducing conditions.

Silver is a trace constituent of the various products of volcanic and fumarolic activity. Cipriani (1953) found an average of 15 ppm Ag in the sodium chloride-potassium chloride-bearing sublimates of the Vesuvian fumaroles, and there are scattered references to the presence of silver (and gold) in the sublimated sulphur, chlorides, sulphates, sulphides, ammonium salts, and mixed volcanic ash of a number of volcanoes and their associated fumaroles. Data on those from Kamchatka, U.S.S.R.; Valley of Ten Thousand Smokes, Alaska; Japan; and elsewhere have been compiled by White and Waring (1963). It is evident that the silver is associated with the sulphurous vapours in a number of cases and with aqueous vapours highly charged with chlorides, hydrochloric acid, and carbon dioxide in others.

Note

The silver content of normal sea and ocean water appears to range from 0.00015 to 0.0029 ppm (Table 31). This compares with a gold content that ranges from 0.000004 to 0.000008 ppm.

Schutz and Turekian (1965) have recently investigated the geographical and vertical distribution of silver in sea water by means of neutron activation analysis. The average of all their analyses from the Atlantic, Indian, Antarctic, and Pacific Oceans and the Gulf of Mexico and Labrador Sea is 0.29 $\mu$g Ag/l (0.00029 ppm).

TABLE 30 *Silver Content of Natural Precipitates*

| Location | Type of precipitate | Reference | Ag, ppm |
|---|---|---|---|
| New Guinea | Wad, limonite, organic (humic colloids) | Blanchard (1933) | Up to 2.8% Ag and 6.8% Au |
| New Zealand (Whakarewarewa) and other areas | Siliceous sinter deposited mainly from alkaline springs (Au–2.0 ppm); Waters contain much NaCl and $H_2S$ | Grange (1937) | Up to 138 |
| New Zealand (Rotorua) | Siliceous sinter (Au–0.025 ppm) | Maclaren (1906) | 0.76 |
| | Sulphurous sinter (Au–0.06 ppm) | | 4.04 |
| Arkansas, U.S.A. | Manganese oxides in novaculite (copper content 1.4%) | Foley (1960) | Up to 23 ppm Ag and 0.7 ppm Au |
| U.S.A. | Manganese oxides (supergene and hot spring derivation) | Hewett, *et al.* (1963) | <0.3 to 300 |
| U.S.A. Tintic District, Utah; Tintic Standard mine | Various sulphates such as chalcanthite, epsomite, pisanite, etc. | Morris and Lovering (1952) | Nil–1,160 |
| Keno Hill, Yukon | Vein limonite derived from pyrite, sphalerite, etc. | Boyle (1965) | 100–1,000 |
| Keno Hill, Yukon | Limonitic precipitates from water leaching veins | Boyle (1965) | <0.5 |
| Keno Hill, Yukon | Vein wad derived from siderite, etc. | Boyle (1965) | <100–1,000 |
| Keno Hill, Yukon | Manganese oxides precipitated from water leaching veins | Boyle (1965) | Av. 0.5 |
| Walton area, N.S. | Wad (manganese oxides precipitated from springs) | Boyle (unpubl.) | Av. 0.7 |
| Walton area, N.S. | Limonite precipitated from NaCl springs, etc. | Boyle (unpubl.) | 0–22 |
| Casa-Diablo hot spring area, Mono county, California | Hot spring sinter (trace of gold) | White (1955) | Up to 17 ppm |
| Steamboat Springs, Nevada | Carbonate sinters from hot springs | Brannock, *et al.* (1948) | 4 |
| Steamboat Springs, Nevada | Siliceous muds from hot springs | Brannock, *et al.* (1948) | 10–42 |
| Niland, California | Residue from high temperature steam well | White, *et al.* (1963) | Up to 1.3% Ag in residue |
| Vesuvius, Italy | Fumarolic products | Cipriani (1953) | 2–59 (Av. 15) |

The highest average values are in the Indian Ocean—0.69 μg Ag/l, followed by the southeast Atlantic—0.64, the Antarctic—0.42, the central Pacific—0.34, the northeast Atlantic and Caribbean—0.25, the east Pacific—0.23, the northwest Atlantic—0.19, the southwest Atlantic—0.18, the Labrador Sea—0.13, and the Gulf of Mexico

TABLE 31 | *Silver Content of Sea and Ocean Water*

| Sea or Ocean | Locality | Reference | Ag (ppm) |
|---|---|---|---|
| Sea and ocean water | – | Goldschmidt (1954) from data of F. Haber | 0.0003 |
| Sea and ocean water | – | Goldschmidt (1954) from data of I. and W. Noddack | 0.00015 |
| Sea and ocean water | – | Rankama and Sahama (1950) | 0.00015–0.0003 |
| Sea and ocean water | – | Durum and Haffty (1963) | 0.0003 |
| Atlantic | Between Azores and English Channel | Davankov, *et al.* (1962) | 0.0012–0.0015 |
| English Channel | Twenty miles off Plymouth | Black and Mitchell (1952) | 0.0021–0.0029 |
| Atlantic | Off west coast of Scotland | Black and Mitchell (1952) | <0.0004 |
| Pacific | Kominato Bay, Kagoshima Bay | Yasuda (1927) | 0.02–0.07 |
| Atlantic and Pacific | – | Schutz and Turekian (1963) by neutron activation methods | 0.00026 |
| Marine hydrosphere | – | Goldberg (1957) | 0.0003 |
| Pacific | Forty miles west of San Francisco | Lai and Weiss (1962) | 0.000145 |
| Atlantic, Pacific, Indian, and Antarctic | Various | Schutz and Turekian (1965) | 0.00029 (average) |

—0.16, all values being in $\mu$g Ag/l. Considerable variations were observed within each oceanic body, and a general tendency for silver to increase with depth in areas of high organic productivity was noticed. In this respect the element behaves like barium (Turekian, 1964). Schutz and Turekian (1965) concluded that continental run-off is probably of minor importance in the economy of silver in the oceans, and further that a volcanic source for the element is not indicated in the central Pacific where it is considered that nickel and cobalt may have had such an origin. Removal of silver from the oceans in a near-shore environment may take place on organic material or by precipitation as the sulphide. No mechanism was apparent for the removal of significant quantities of the element from the deep sea.

Silver is probably present in sea water as a complex silver chloride, although some investigators have expressed the opinion that the element is adsorbed on suspended particulate and colloidal matter or is adsorbed on the surfaces or contained in free-swimming marine organisms such as plankton. In the Bering Sea, for instance, Lizunov and Lisitsyn (1955) detected silver in the suspended matter. Future analyses of sea water should employ ultra-filtration methods followed by analysis of the residue (suspended and colloidal matter) and the filtrate.

Transport and

In natural waters silver may occur in one or all of the following forms:

1. As the ion $Ag^+$, dissolved in the form of the sulphate, the hydrogen carbonate, or the nitrate.

2. As the complex ions $[AgCl_2]^-$, $[AgCl_3]^{2-}$, or $[AgCl_4]^{3-}$ where the waters or vapours are highly charged with NaCl, KCl, HCl, etc. The sodium and potassium complexes are probably the most common in natural waters

$$NaCl + Cl^- + Ag^+ \rightarrow Na[AgCl_2].$$

These complexes are easily dissociated, especially in the presence of sulphide ion. Silver could also conceivably occur as the complex bromide ions $[AgBr_2]^-$ or $[AgBr_3]^{2-}$ or the corresponding iodide ions where the solutions were enriched in bromide or iodide.

3. As the complex ion $[Ag(NH_3)_2]^+$ in areas of maximum biological activity, as in or about reef complexes in the oceans.

4. As the complex ion $[Ag(S_2O_3)_2]^{3-}$. This complex is soluble in alkaline and neutral solutions but decomposes into S, $Ag_2S$, and some $Ag_2SO_4$ in acid solutions. It is probably only stable at low temperatures for short periods of time in near-surface environments, as in the oxidizing zones of sulphide deposits. Tyurin (1963) thinks thiosulphates may exist in hydrothermal solutions, but Shcherbina (1964) disagrees with this view. Silver could presumably also migrate as a thionate or polythionate since the last two ions have been found in low temperature spring waters.

5. As the complex sulphide and polysulphide ions $AgS^-$, $[Ag(S_4)_2]^{-3}$, $[AgS_5S_4]^{-3}$, and $[Ag(HS)S_4]^{-2}$, or as the complex hydrosulphides AgHS, $H_3AgS_2$, $(Ag_2S \cdot nH_2S)$, etc. These complexes probably occur in waters and vapours highly charged with $H_2S$, $S^{2-}$, NaCl, and KCl. Anderson (1962), Smith (1963), and Cloke (1963b) have discussed the solubility of $Ag_2S$ in terms of these various complexes in some detail. It also seems probable that silver is dissolved as double complexes of sulphur, arsenic, or antimony and also as complexes of tellurium and selenium in certain hot spring waters and deep seated vapours.

6. As colloids of various compounds of the element. Of these the most common are probably AgCl, AgBr, $Ag_2S$, $Ag_2Te$, $Ag_2Se$, $Ag_3SbS_3$, $Ag_3AsS_3$, etc. There are no data on the occurrence of these colloids in nature.

The silver halide colloids may carry either a positive or negative charge. Their chemistry is, therefore, very complex and their stability and mobility is largely controlled by the electronic nature of other coexisting colloids and electrolytes in solution.

In normal surface waters silver colloids can be expected, but in the waters of oxidizing sulphide deposits the presence of an abundance of electrolytes would tend to inhibit them. On the other hand a variety of protective colloids may be formed in oxidizing zones, and these would permit greater transport of silver compounds in the colloidal form. The presence of silver colloids in waters at high temperatures has not been proven, although they have been suggested as a mode of transport by a number of writers.

Deposition

7. As aerosols in low temperature water gas (steam). The constitution of the aerosols would be varied. In some cases they would be AgCl, $Ag_2O \cdot nH_2O$, $Ag_2S$, etc.; in others the silver would probably be adsorbed to hydrated silica, $SiO_2 \cdot nH_2O$, hydrated alumina $Al_2O_3 \cdot nH_2O$, etc. Aerosols are probably present in volcanic emanations or in steam impregnated rocks near the surface.

8. As dissolved organic compounds. Silver can form a large number of soluble organic compounds, some of the simpler ones being the acetate and tartrate. The occurrence of these in natural organic environments seems probable, although there are no data on their distribution.

9. As an integral part of or adsorbed to the various humic complexes (colloids) that commonly occur in surface waters and in some underground waters.[1]

10. As an integral part of or adsorbed to suspended particulate matter. In some cases this is a major mode of transport of silver in surface waters. The writer (unpublished) found up to 1 ppm Ag in the fine stream sediment of the Walton-Cheverie area, Nova Scotia.

11. As an integral part of or adsorbed to various free swimming or floating micro-animal organisms and plants. Krauskopf (1956) showed experimentally that plankton adsorbs silver strongly.

Some of the possible mechanisms of precipitation of silver from natural waters and vapours are as follows:

1. Precipitation as the chloride, bromide, or iodide due to mixing of silver-bearing waters with those containing $Cl^-$, $Br^-$, or $I^-$ ions. This mechanism is probably operative in the oxidized zones of silver deposits in arid regions, in coastal areas, or where waters leaching salt beds come into contact with meteoric waters leaching silver deposits.

2. Precipitation as insoluble silver phosphate, chromate, or arsenate where silver-bearing waters come into contact with those carrying $PO_4^{3-}$, $CrO_4^{2-}$, $AsO_4^{3-}$. No examples of this type of precipitation have been recorded in nature although they seem to be possible.

3. Precipitation as the sulphide where silver-bearing solutions come into contact with $H_2S$ or $S^{2-}$ either of organic or inorganic derivation. This mechanism appears to be partly responsible for the relatively high contents of silver in the various sulphides in black schists, sulphide schists, and other rocks formed in a reducing environment. The experiments of Krauskopf (1956) suggest that this mechanism is possible in sea water.

In vein systems undergoing oxidation this mechanism probably operates giving a number of secondary silver sulphides. (*See* further the section in this report on the enrichment of silver deposits.) The mechanism is also a satisfactory one to explain the occurrence of silver sulphides in certain sandstones and shales. Thus waters containing silver moving downward or laterally on coming into contact with

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[1] See footnote on page 72.

test Pine Point hydrocarbon

$H_2S$ or $S^{2-}$ bearing waters rising or moving laterally from petroliferous or carbonaceous beds or fetid limestones, etc. would precipitate silver sulphides along their zones of contact. Silver-bearing sulphides in the cap rocks of salt domes and in certain reef complexes probably owe their origin to such a mechanism.

4. Precipitation of silver (or its compounds) owing to the decomposition of inorganic complexes of the type $[AgCl_2]^-$ and $[AgCl_3]^{2-}$ as a result of a decrease in the chloride ion concentration. A decrease in the $CO_2$ concentration similarly causes a breakdown of the soluble hydrogen carbonate complex of silver with consequent precipitation of the silver. These two mechanisms could conceivably operate where silver-bearing waters or vapours come into contact with reactive rocks, or in the case of $CO_2$ where a decrease in pressure takes place as the waters or vapours move toward the surface or into dilatant geological structures such as fractures, faults, etc.

5. Precipitation of silver (or its compounds) owing to a decrease in the hydrogen-ion concentration where the element is transported as $Ag^+$ in solution. In acidic solutions silver ion is more soluble and mobile. As the acidity of the solutions is reduced by reactions with wall-rock or gangue minerals or by dilution, silver tends to precipitate, the compounds or minerals formed being dependent on the composition of the solutions. The pH of hydrolysis of silver from aqueous solution as the oxide or as basic salts is 7.5 to 8.0. Silver is relatively insoluble in alkaline solutions unless ammonia or some other complexing agent is present. Reduction in acidity is partly responsible for the precipitation of silver during secondary enrichment processes, and may also be effective in the primary precipitation of the element in certain cases.

6. Precipitation as $Ag_2S$ due to the decomposition of the complex ion $[Ag(S_2O_3)_2]^{3-}$ as a result of an increase in the acidity of the solutions. Reducing agents, such as carbonaceous matter, also precipitate $Ag_2S$ from solutions containing silver as the thiosulphate complex. These reactions are probably important in the oxidation of silver deposits.

7. Precipitation of silver sulphide and other silver sulphide-arsenide or antimonide, telluride, and selenide minerals owing to an increase in the hydrogen-ion concentration where the element is carried as a sulphide complex, e.g. $[AgS]^-$, arsenide complex, telluride complex, etc. These reactions are probably responsible mainly for primary precipitation of silver, although they may be important in secondary enrichment processes as well.

8. Changes in oxidation-reduction potential. These may work in two ways. Decrease in the oxidation-reduction potential permits a greater concentration of $Fe^{2+}$ in solutions and this ion precipitates the native metal from silver solutions

$$Fe^{2+} + Ag^+ \rightleftarrows Ag + Fe^{3+}.$$

Because the reaction is reversible and the concentration of $Fe^{3+}$ increases with increasing oxidation potential this renders silver more soluble and mobile.

Silver is also precipitated from alkaline solutions by manganese according to the oxidation-reduction reaction:

$$2\ Ag^+ + Mn^{2+} + 4\ OH^- = 2\ Ag + MnO_2 + 2\ H_2O.$$

Increase in the oxidation potential in solutions containing iron and manganese has further effects. Manganese undergoes hydrolysis and is precipitated as the hydroxide or hydrated oxide as the pH increases. These hydrosols carry a negative charge and strongly adsorb the positively charged silver ions. The ferric hydrosols on the other hand carry positive charges and repel the silver ions except where constituents such as $PO_4^{3-}$, $AsO_4^{3-}$, etc. are present to give the ferric hydrosol a combined negative character. These then adsorb the positive silver cations. The adsorption of silver by manganese colloids may give considerable concentrations of the metal from infinitesimally small amounts in natural waters. Thus, Riley and Sinhaseni (1958) found a concentration factor of $1.3 \times 10^5$ for silver in the acid soluble parts of manganese nodules as compared to the content of the element in Pacific Ocean water. In ground and stream waters the present writer has found concentration factors in manganese precipitates ranging from $5 \times 10^2$ to $1 \times 10^6$ compared with the silver present in the waters.

Oxidation-reduction reactions are effective in precipitating silver from natural solutions in a variety of environments—in the sea, in fresh water, in manganese and iron bogs, and in the zones of oxidation of silver deposits.

9. Precipitation of silver can also take place by a number of adsorption processes, some of which probably involve hydrolytic and oxidation-reduction reactions. Here we may mention the strong adsorption and precipitation of silver by various organic colloids and complexes (humic compounds), coalified wood in certain types of sandstones, coal, and carbonaceous sediments. With respect to the latter the experiment by Rickard (1896) in which he was able to precipitate silver from $Ag_2SO_4$ solutions on black bituminous Rico shale seem to be particularly significant. Gold was, likewise, precipitated on the shale with ease. These simple experiments seem to explain the common occurrence of silver and silver sulphides in veins where they cross the black beds, leaders, or indicators. The present writer has also observed secondary native silver in fractures in black shale where this mechanism has obviously been effective. In addition to these reducing and adsorbing agents there are indications that various inorganic colloids, hydroxides, gels, etc. adsorb and coprecipitate silver. These include clay minerals (especially the Na-K-bearing varieties), collophane, aluminum hydroxide, and all varieties of silt. Their action in precipitating silver is effective under practically all geological conditions.

10. Precipitation of silver in jarosites. This is an absorption or coprecipitation reaction that takes place in an acid environment during the hydrolysis of iron sulphate solutions containing potassium, sodium, lead, and silver. In other cases it is evident that the jarositic minerals are evolved by the reaction of acid iron sulphate solutions with K-Na-bearing clay minerals, as in some of the soils overlying the gossans on the massive sulphide bodies in the Bathurst-Newcastle district, New Brunswick. Silver-bearing jarosite is a secondary mineral formed mainly in or near silver deposits, generally in their oxidized parts. The mineral has also been observed

by the writer at the orifices of springs within silver-bearing regions. In a number of deposits only jarosite with minor amounts of Pb and Ag is formed; in other deposits plumbojarosite with traces or minor amounts of Ag occurs; and in exceptional cases argentojarosite is the stable mineral.

11. Precipitation of silver compounds due to evaporation of solutions. This may be an effective means of precipitation in many types of geologic environments.

12. Sublimation. This process is probably effective mainly in volcanic and fumarolic processes. The sublimates incorporate the available silver either in their structures or in an adsorbed form.

13. Precipitation due to a decrease in temperature and pressure on gases and solutions. It seems probable that highly heated water gas under high pressure and charged with NaCl, $CO_2$, $H_2S$, etc. dissolves Ag readily, probably in the form of various complexes. When such a gas enters dilatant fractures or other structures it undergoes a decrease in pressure with consequent precipitation of various minerals as well as other compounds. Similar effects are produced as these gases (or solutions) rise toward the surface where the rocks are cooler, where they mingle with circulating groundwaters, or where they react with the wall-rocks. These mechanisms of precipitation of silver minerals are probably operative during the formation of many primary silver deposits.

14. Decrease in $H_2S$, $S^{2-}$, or $CO_2$ concentration of vapours, gases, or solutions. Where silver is carried as the hydrogen carbonate, hydrosulphide, or other sulphide complexes, reaction of the vapours, gases, or solutions with the wall-rocks or gangue minerals may reduce the concentration of $H_2S$, $S^{2-}$, or $CO_2$ as a result of the formation of pyrite, carbonates, etc. This breaks up the hydrosulphide, sulphide, and carbonate complexes causing the precipitation of silver in one form or another. Similar effects probably result when silver is transported as complex S-Se-Te and S-Sb-As compounds and the $S^{2-}$ ion concentration is reduced by reactions with iron (formation of pyrite) in the wall-rocks.

Reactions such as those noted above appear to be partly responsible for the primary precipitation of silver (and gold) in a number of deposits in basic rocks and in certain types of sedimentary rocks. These reactions may also operate in a modified way in the zones of reduction of oxidized silver deposits.

15. Coagulation of colloids. Colloidal silver compounds and silver adsorbed to various organic and inorganic colloids can be precipitated by a great variety of chemical changes such as a decrease or increase in pH, coprecipitation by other colloids, precipitation by electrolytes, etc. The effect of these in primary vein formation is unknown. In natural fresh and sea water it is probable that much silver is precipitated by colloidal processes.

16. Decomposition of organic (humic) complexes due to oxidation. Humic complexes, carrying silver in an adsorbed state or as an integral part of their structure, on oxidation yield $CO_2$, $H_2O$, etc. and liberate the silver. This silver may then be precipitated by a variety of mechanisms.

17. Sedimentation of particulate matter carrying silver. This process acts in all sedimentary basins in lakes, seas, and in the oceans. The silver is incorporated in the sediments in a variety of forms.

18. Death and sedimentation of silver-bearing plants and organisms. Numerous organisms and plants in natural fresh and saline waters absorb silver into their vital parts, or like plankton adsorb the element on their surfaces. On their death their carcasses are sedimented on the bottoms of lakes, seas, and the oceans. There, further reactions attendant on the decay of the organisms and plants fix the silver in the sediments. One of the most common of these reactions in a reducing environment is the bacterial degradation of the protein complexes of the organisms with the consequent production of $H_2S$, which precipitates silver, as well as numerous other chalcophile elements, as sulphide.

19. Precipitating action of organisms. Certain types of algae are thought to precipitate silver from thermal waters. It also seems probable that the action of bacteria and various fungi may play an important part in precipitating silver from natural waters. Certainly iron and manganese bacteria play an indirect part since they oxidize $Mn^{+2}$ to $Mn^{+4}$ and $Fe^{2+}$ to $Fe^{3+}$, which then undergo hydrolysis and are precipitated as hydrous manganese and iron oxides. During these reactions silver may be coprecipitated or adsorbed by the hydrated oxides. By analogy with copper, it also seems probable that micro-organisms, especially bacteria, can precipitate native silver and perhaps silver sulphides from solution in natural environments. Experimentally, Baas Becking and Moore (1961) prepared argentite[1] in artificial sea water from silver chloride and carbonate on acetate and lactate media by the action of sulphate reducing bacteria.

## Biogeochemistry of Silver

Silver is a microconstituent of practically all plants and animals, including man. The literature on the biochemistry of the element is extensive, but is scattered through a great variety of medical and biological journals, many not readily accessible to the geologist and geochemist. Only a few of the most important papers have been consulted during the preparation of the following compilation. The reader will also find a valuable discussion on the biogeochemistry of silver in the recent compilation by Manskaya and Drozdova (1964) on the geochemistry of organic matter.

### Silver in Plants

The silver content of plants varies over a wide range, and hence average values are practically meaningless. Most investigators report less than 1 ppm Ag in the ash of higher plants, but in some contents as high as 5 ppm have been recorded.

Silver is a microconstituent of many types of marine and fresh-water algae, plankton, and aquatic plants. Few extensive quantitative data are, however, avail-

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[1] According to R.A. MacDiarmid (*Econ. Geol.*, vol. 61, pp. 405–406) the mineral species is acanthite.

able (Vinogradov, 1953). Up to 1.5 ppm Ag have been reported in the ashes of marine algae by several investigators, and plankton are also known to contain about the same amount of silver. Experiments by Krauskopf (1956) show that marine plankton adsorbs silver strongly from solution. Various types of seaweeds also contain silver as a microconstituent. Haber (1927) found from 0.7 to 1.5 ppm Ag in some samples of seaweed, and Black and Mitchell (1952) reported 0.0 to 0.7 ppm Ag in a variety of oven-dried seaweeds from the west coast of Scotland. According to some investigators kelp may contain up to 1 ppm Ag in the ash. Compared with the sea water in which seaweeds grow the enrichment factor in the plants is about 2,500.

There seems to be no data on the silver contents of bacteria of marine, fresh water, or terrestrial origin. The action of bacteria, if any, on the chemistry of silver in the soil and natural waters is unknown.

Ramage (1930) found up to 100 ppm Ag in the various parts of dried mushrooms and 500 ppm or more in the gills. Guelbenzu (1951) also mentions the enrichment of silver in fungi and mushrooms.

In Perthshire, Scotland, Hunter (1953) found less than 0.05 to 0.8 ppm Ag in the dry matter of bracken fronds and rhizomes growing in various acid soils (pH 3.6-6.2) containing less than 0.04 ppm Ag. The amount of silver in the bracken varied erratically during the growing season. Rusoff, *et al.* (1937) detected silver in the wire grasses in Florida.

Lounamaa (1956) detected only small amounts of silver in the various species of lichens he investigated in Finland. Over silicic and ultrabasic rocks the silver content in the ash was generally less than 1 ppm. Higher contents were found (up to 10 ppm) in the vicinity of the mining district of Orijärvi and elsewhere. Of the various species of mosses investigated only those collected from silicic and ultrabasic rocks contained silver. The contents recorded ranged from 1 to 6 ppm Ag in the ash. Over serpentine outcrops certain samples of the mosses contained 10 ppm Ag, the highest amounts found for any of the mosses. The frequency of the occurrence of silver in ferns was low, only 25 per cent of the samples analyzed showed the presence of the element. The fronds appeared to be richest in silver compared with the subterranean parts. The highest content recorded was 60 ppm Ag in the ash for a sample taken over granite.

Shacklette (1965) found silver in 7.9 per cent of the samples of bryophytes (mosses and liverworts) he investigated. The average content of silver in the samples in which the element was found was 9 ppm in the ash. The ratio of the silver content in the bryophytes to that in the soil substrate in which they grew was greater than 15. In vascular plants (ferns and seed plants) growing in the same areas as the bryophytes silver was found in only 1.5 per cent of the samples, and in these the average silver content was 5 ppm in the ash. These results indicate a tendency for silver to accumulate in bryophytes compared with vascular plants growing on the same substrate.

There are numerous references to the presence of silver in practically all types of terrestrial plants, shrubs, and trees. In general the contents are relatively low in the ash, usually of the order of 0.2 ppm. Higher values often occur in regions of silver mineralization, although in some cases there seems to be no particular correlation between the amount of silver in a plant and the content of the element in its soil substrate.

Ono, *et al.* (1959) detected silver in many samples of *Filicales* (ferns), *Musci* (mosses), *Hepaticae*, and lichens, and Guelbenzu, *et al.* (1947) noted the presence of the element in the lentil (*Lens esculenta*). The latter investigators found that the underground organs store silver. López de Azcona, *et al.* (1949) found silver in the seeds of the *Graminaceae*, including wheat, barley, oats, rye, corn, etc. Borovik and Borovik-Romanova (1944) also found silver in the seeds and fruits of various plants and trees such as the sunflower, pumpkin, horse chestnut, walnut, peanut, etc. They noted that silver tended to concentrate in the inner layer of the endosperm of the seeds and fruits. In fact, seeds, nuts, and fruits in general seem to have higher than normal amounts of silver according to a number of investigators. The writer for instance found that the seeds of the pine in the Walton-Cheverie area, Nova Scotia, have much higher silver contents (up to 1 ppm Ag in the ash) compared to the cones, needles, twigs, etc. ($<0.05$ ppm Ag). The seed of the poppy (opium) contains silver according to Bartlet and Farmilo (1955), and whole wheat contains an average of 0.4 ppm Ag (Kent, 1942). The latter investigator found an average of 0.8 ppm Ag in the germ of wheat. Other investigators have detected silver in berries, coffee, tea leaves, and various other natural foods and beverages.

A number of investigations have been carried out to determine the concentration of silver in various shrubs and trees. Some of these have been done for biochemical purposes and others to test methods of biogeochemical prospecting. Practically all of the shrubs and trees investigated contain silver as a microconstituent in their wood, bark, buds, and leaves. The contents of silver are generally low, of the order of 0.1 ppm or less in the ash, but some investigators have found up to 3.0 ppm.

Webb and Millman (1950-51) determined up to 2.7 ppm Ag in oven-dried twigs and leaves of various types of savannah trees in the Nigerian lead-zinc belt. The normal concentration of silver in dried twigs and leaves of several species of trees growing in unmineralized areas was essentially constant at about 0.05 ppm Ag. In the vicinity of mineralization the silver content showed an erratic increase up to values of 0.25 ppm or more. In parts of some profiles the silver content exhibited a sympathetic variation with lead in the plants; in other parts there was no particular relationship.

Warren and Delavault (1950) found that the dried fresh young growth of horsetails, first-year twigs and needles of conifers, and first-year twigs of deciduous trees in the Watson Bar Creek area of British Columbia generally carried between 0.1 and 0.5 ppm Ag. Their data are given in greater detail in Table 32.

Harbaugh (1950) observed no correlation between the silver content of blackjack oak, *Quercus marilandica*, and mineralized (lead-zinc) zones in the Wentworth area, Lawrence county, Missouri (Tri-State Mining district). The average concentration of silver in the ash of twigs of the blackjack oak from the Wentworth and other areas ranged from 1.8 to 2.5 ppm.

Lounamaa (1956) carried out an extensive investigation of the silver content

TABLE 32 *Silver Content of Trees and Plants, Watson Bar Area, British Columbia (Warren and Delavault, 1950)*

| Species | Per cent ash | Ag ppm ash | Ag ppm in dry plant material |
|---|---|---|---|
| *Pseudotsuga taxifolia* | 2.30 | 17 | 0.39 |
| *Juniperus communis* | 3.25 | 8 | 0.26 |
| *Pinus contorta* | 1.90 | nil | nil |
| *Populus tremuloides* | 2.40 | nil | nil |
| *Salix* sp. | 2.20 | 1.3 | 0.28 |
| *Equisetum* sp. | 22.75 | 1 | 0.23 |
| *Pseudotsuga taxifolia*–composite 5 samples | 4.75 | 13 | 0.60 |
| *Pseudotsuga taxifolia*–composite 5 samples | 3.00 | 27 | 0.80 |
| *Juniperus communis* –composite 4 samples | 4.68 | 4 | 0.20 |
| *Pinus contorta*–composite 2 samples | 2.42 | 25 | 0.60 |
| *Populus tremuloides* –composite 2 samples | 6.90 | 1 | 0.10 |
| *Salix* sp. Okanagan | 6.00 | 3 | 0.20 |
| *Pinus ponderosa*–composite 5 samples | 4.68 | 30 | 1.40 |
| *Pinus ponderosa*–composite 5 samples | 5.37 | 4 | 0.20 |

of various species of conifers, deciduous trees and shrubs, dwarf shrubs, grasses, and herbs. The element was detected in the ash of most species, the highest contents recorded being 10 ppm Ag for the needles and twigs of conifers, 10 ppm for leaves and twigs of deciduous trees, 30 ppm for stems and leaves of dwarf shrubs, 100 ppm for herbs, and 30 ppm for grasses. The reader should consult the original paper for the variation of silver with species, seasons, rock and soil types, etc.

Millman (1957) observed that up to 0.2 ppm silver may occur in a variety of trees growing on soils with less than 1 ppm Ag in areas of copper-tin mineralization in eastern Cornwall, England. He further found that silver tends to be preferentially concentrated threefold in the leaves of birch (*Betula* sp.) and oak (*Quercus* sp.) compared with the twigs.

A few experiments have been carried out to determine the rate of uptake by and the nature of silver in plants. Porutskii, *et al.* (1961) observed that the Ag/Mn ratio varies with plant growth and development. Suzuki (1958) found that only very small amounts of $Ag^{110}$ tracer were taken up by mint plants. The $Ag^{110}$ in the plant was in a form not readily soluble in petroleum ether, ethyl ether, or methanol. The $Ag^{110}$ in the ash was almost completely dissolved out by excess HCl.

Bohn and Drzewina (1932) found experimentally that silver stimulates the root growth of watercress and various other plants, but inhibits the root growth of the tobacco plant. Except for these observations there appears to be no other data on the nutritive or toxic effects of the element on plants.

## Silver in Animals

Silver appears to be a relatively frequent microconstituent of practically all types of animals. The contents of the element in the various dried animal components are, however, generally very low, of the order of 0.5–1.0 ppm Ag. Higher values than this have been reported by a number of investigators. Most of the investigations carried out on the content of silver in animals are incidental to work on other trace elements, although a few investigations dealt specifically with silver. The published works on silver in animals is largely of a biological nature or deals with natural and processed foods. General reviews and compilations of the silver content of animal components and products can be found in the works by Sheldon (1934) and Kehoe, *et al.* (1940).

TABLE 33 | *Silver in Some Marine and Fresh-water Animals*

| Phylum | General Remarks | Ag ppm range in dry matter |
|---|---|---|
| Protozoa | Foraminifera, radiolaria, etc. | No data |
| Porifera | Marine sponges | Up to 1.0 |
| Coelenterata | Jellyfishes, anemones, corals, etc. | 2.0–6.0 |
| Platyhelminthes–Annelida | Worms | Present in some species |
| Echinodermata | Starfishes, sea-urchins, sea lilies, etc. | 1.0–4.0 |
| Mollusca | Oysters, clams, snails, mussels, etc.<br>(soft parts)<br>(Concentrations often in liver, kidney, and blood) | 1.0–10.0 |
| Arthropoda | Class Crustacea: lobsters, crabs, etc.<br>(Ag found both in tissues and blood)<br>(Gills of river crustaceans take up Ag) | Up to 2.0 |
| Chordata | Vertebrata: class Pisces—fishes<br>(Ag found in flesh, blood, entrails, etc.) | Up to 12 |

The general range of silver in marine and fresh-water animals and fishes is given in Table 33. The data were taken from Noddack and Noddack (1939), Vinogradov (1953), various other scattered publications, and some analyses done in the laboratories of the Geological Survey. According to Forchhammer (1865) F. J. Malaguti was the first to show that silver occurs in the organisms of the sea.

Folsom and Young (1965) report that Ag 110$^{m}$, with a half-life of 253 days, is often concentrated in the digestive tissues of molluscs and crustaceans. In the livers of squids from the Pacific and Atlantic oceans they found from 150 to 4,200 picocuries Ag 110$^{m}$ per Kg of wet tissue. In the livers and soft tissues of mussels, barnacles, albacore, and a shark they found much less Ag 110$^m$ (0–120 picocuries/wet Kg).

Note

The enrichment factor for silver in marine animals over sea water as given by the Noddacks (1939) is + 22,000. There are no data on the enrichment factor in fresh-water animals, but presumably it is of the same order of magnitude. This phenomenal enrichment factor is of great importance in the geochemical cycle of silver, since the dead bodies of the animals may contribute their silver to sediments in reducing environments. This partly explains the great enrichment of silver in black shales and in certain calcareous rocks where galena and sphalerite appear in the mineralogical assemblage.

Silver is a general microconstituent in many land animals. Borovik and Borovik-Romanova (1949) found traces of silver in all of the insects they investigated, and there are numerous references to the occurrence of the element in the ash of the vital parts, tissues, and blood of rats, dogs, and cattle. The amounts of silver recorded in the ash generally range from 1 to 10 ppm, but in some cases amounts up to 50 ppm Ag have been detected in liver and other vital parts. Bell (1938) found 4 and 1 ppm Ag respectively in the ash of the yolks and white of eggs, and there are various references to the occurrences of silver in the ashes of cow's milk and animal feces.

The silver content of the organs, tissues, and blood of the human being has been extensively investigated. The element occurs as a microconstituent (0.25–10.0 ppm Ag) in the ash of the blood, liver, thyroid, heart, spleen, kidney, brain, hair, skin, and teeth. Silver is said by Sheldon (1934) to be concentrated in the thyroid gland and in the tonsil. Urinary calculi contain from 3 to 150 ppm Ag in the ash.

The role of silver, if any, in animal metabolism is relatively unknown. Its presence, however, in most animals suggests that it may serve some purpose in complex biochemical reactions. Comenge and Guelbenzu (1951) found, for instance, that mulberry leaves containing no silver failed to serve as food for the silkworm. Except for these observations there appear to be no other data on the essential nutrient value of the element for animals.

Silver ions in water have a marked oligodynamic or germicidal effect even at very low concentrations. They effectively kill many lower organisms, but are generally harmless to higher animals. This feature is the basis of the Katadyn process of sterilizing water. It seems unlikely, however, that the normal concentrations of silver in natural waters (~0.0002 ppm) would have any particular toxic effects on bacteria and other lower organisms.

## Silver in Humus, Peat, Bogs, Muskegs, and Marshes

Silver, in common with many of the metals, tends to become enriched in humus and humic deposits. The reasons are the strong adsorptive and absorptive capacity of humus for metals and the presence in humic deposits of various reducing substances and $H_2S$.

Goldschmidt (1935) found up to 5 ppm Ag in the ash from oak and beech humus, a considerable enrichment over that present in the ash from the leaves. Salmi (1956) found silver in the ash of a number of mixed *Carex* and *Sphagnum* peat samples from the Vihanti pyritic zinc-lead ore field in Western Finland. The contents ranged from $<1$ to 30 ppm Ag. The pH of these peats ranges between 3.0 and 5.3. Ashed samples of the leaves and twigs of *Ledum palustre* growing in the peat gave values of $<1$ to 3 ppm Ag for the leaves and $<1$ to 600 ppm for the twigs. The value of 600 ppm Ag for one of the samples deviated by a large factor from the rest, which range from $<1$ to 10. The high value was confirmed, however, indicating that certain bog plants can accumulate a relatively large amount of silver. Presant (1963) observed marked enrichments of silver in the $A_0$ (humic) horizons of the soils in the Bathurst area, New Brunswick. In the normal soil profiles he found an average of 1.6 ppm Ag in the humic horizons; over some lead-zinc-copper deposits the average was 45 ppm Ag. (*See also* Table 27.)

The organic matter in bogs, muskegs, and marshes is enriched in silver in certain areas. The copper bog near Sackville, New Brunswick, which contains up to 4 per cent copper, is also enriched in silver in amounts up to 15 ppm in the ash. Organic matter in some of the bogs and marshes in the Walton area of Nova Scotia is also slightly enriched in silver. In places these contain up to 0.89 ppm in the dried matter.

Other types of humic deposits also seem to be high in silver in places. Blanchard (1933) mentioned organic (probably humic) substances near seepages in New Guinea that carry up to 457 oz/ton Ag (1.5 per cent).

The manner of occurrence of silver in humic deposits is relatively unknown. In some deposits a small part of the silver appears to be in an adsorbed form, since it can be removed by weak acetate and acidic solutions. The remainder, generally the greater part, is tightly bonded in the brown humic complexes and may be fixed as silver-organic acid compounds, silver humates, chelated complexes, and in certain cases as organic sulphide complexes.

## Silver in Coal

Silver is a frequent microconstituent of many coal seams, but is generally present in amounts less than 10 ppm in the ash (Table 34). Certain coal seams, however, appear to be greatly enriched in silver. Those mentioned by Stone (1912) in parts of Wyoming and South Dakota contain up to 34 ppm (1 oz/ton) in the coal. Others in South Wales, described by Briggs (1934), also contain appreciable contents of silver, especially in the pyritic roof rocks. Gold accompanies the silver in both cases.

How muc
gold ?

The coalified plant fragments in the Carboniferous rocks of Nova Scotia and New Brunswick are highly enriched in silver locally. In the Dorchester mine area, near Sackville, New Brunswick, the coalified fragments contain up to 190 ppm Ag in the ash. In nearby areas, however, as at Dorchester Cape and Upper New Horton the plant fragments contain practically no silver. Similar pyritized plant fragments contain up to 300 ppm Ag in the Walton area of Nova Scotia (Table 35). There, the silver-bearing coalified fragments occur mainly near sets of fractures and faults, some of which carry silver minerals.

Headlee and Hunter (1955) carried out an extensive investigation of the silver content of the coalfields of West Virginia. In the ash of the coal they found a minimum of less than 5 ppm, a maximum of 90 ppm, and a median value of less than

TABLE 34 | *Silver Content of Coal*

| Locality | Remarks | Reference | Ag ppm (range) |
|---|---|---|---|
| Germany and England | In ash | Goldschmidt and Peters (1933) | 5–10 |
| Wales | Pyrite from roof of coal seam | Briggs (1934) | Appreciable amounts |
| North Wales | Ash from vitrains | Reynolds (1948) | Traces |
| Eastern and Central Germany | In ash | Leutwein and Rösler (1956) | <1.0–12.0 (0.1–2.5 in coal) |
| Portugal | In ash of anthracites | di Brito (1955b) | <1–10 |
| Various | In ash | Katchenkov (1952) | Up to 50 |
| India | In ash | Mukherjee and Dutta (1950) | Strong traces |
| Wyoming–South Dakota | In coke; gold also present in average amounts of 3 ppm (0.1 oz/ton) | Stone (1912) | 0–34 (0–1 oz/ton) |
| West Virginia | In ash of bituminous coal | Headlee and Hunter (1953) | <4–27 |
| Texas, Colorado, North Dakota, and South Dakota | In ash, erratic distribution | Deul and Annell (1956) | 1–10 |
| Oklahoma, Kansas, Missouri, U.S.A. (Pennsylvania coals) | In ash of coal from beds | Hyden and Danilchik (1962) | 1.5–15 |
| Nova Scotia | In ash of bituminous coal from Lloyd Cove seam | Hawley (1955) | <1–3 |
| New Brunswick (Carboniferous sandstones) | In ash of coal material, Dorchester mine area | Smith, A.Y. (unpubl.) | 19–190 |
| Nova Scotia (Carboniferous sandstones) | In pyritized coal material, Walton area | Boyle (unpubl.) | 10–300 |
| Nova Scotia Cape Breton Is.; Gaspereaux R. area, near Silver Mine | In ash of bituminous coal | Boyle (unpubl.) | 0.5–1.0 |

7 ppm. The high values in silver occurred in the low ash coals, and the element was higher in the northern fields than in the southern. From their distribution curves they concluded that there was no appreciable secondary mineralization of silver. The same authors found from <5 ppm Ag up to 225 ppm Ag in the various types of ash from flue and gas synthesis dusts.

There seem to be no detailed investigations on the silver content of the different ranks of coal or of the different components, viz. fusain, vitrain, clarain, and durain. Analyses for silver of specialized types of coal such as torbanite, cannel, boghead, jet, and natural coke are lacking as are also those for the various resinous substances such as amber associated with coal or derived from it. These substances would seem to provide an interesting field of investigation.

The occurrence of silver in coal seams is generally erratic and is commonly related to a number of features, which can be summarized as follows:

1. Higher contents of silver are generally recorded from coal seams low in ash and rich in other trace elements, such as copper, lead, and zinc.

2. Higher contents of silver often accompany parts of the coal seams or overlying or underlying rocks that are enriched in sulphides, particularly pyrite. Splits containing abundant pyrite are sometimes greatly enriched in silver as well as in various other chalcophile elements.

3. Leutwein and Rösler (1956) noticed a parallel relationship between the content of lead and that of silver in the coals they investigated in Germany. The writer has noticed a similar relationship in some coal seams in Nova Scotia and has also observed a parallel enrichment between silver and copper, zinc, lead, cobalt, nickel, tin, molybdenum, arsenic, antimony, and barium in coalified fragments in the Walton area in Nova Scotia (Table 35).

4. Higher silver contents tend to occur in the coal near the top and the bottom of individual seams. There are also a number of references in the literature to higher contents of silver and other trace elements in the rocks immediately overlying the seams.

5. In some coal seams, and in sandstones containing coal fragments, higher silver contents tend to occur in the coal or in coalified fragments near faults, fractures, or crushed zones.

The mode of occurrence of silver in coal and coalified fragments has not been extensively investigated. Some general observations from the literature and the writer's research follow:

1. Some silver is probably associated with the coaly substance of coal and may be bound as a metal-organic complex.

2. A very small amount of the silver in coal may be adsorbed to the coaly substances.

3. Much silver is present in or associated with pyrite (Table 17), and some silver is generally present in the small amounts of galena, chalcopyrite, arsenopyrite, bornite, sphalerite, and marcasite, found in some coal seams. Very small amounts of silver may also occur in minerals such as calcite, siderite, barite, and hematite in some coals. In rare instances silver may be present in silver minerals such as argentite and freibergite.

4. The silver in coalified fragments in sandstones is either in or associated with pyrite, chalcocite, bornite, and galena. In some samples it may occur as specks of separate silver minerals such as argentite and freibergite either alone or in the pyrite nodules and crystals. Native silver and chlorargyrite have also been observed in coal fragments in sandstone, particularly in those at Silver Reef, Washington county, Utah (Jenny, 1903).

5. In the weathered parts of coal seams silver may occur in jarosites and iron oxides.

How many samples are data available for ?

### TABLE 35 Analyses of Pyritized Coal Fragments, Walton–Cheverie Area, Nova Scotia

(All values in ppm except where noted)
NF = not found
ND = not determined

| Enclosing Rock and Locality | Ag | Cu | Pb | Zn | Ni | Co | V | Cr | Ba | As | Sb | Cd | Sc | Mo | Sn | Sr | Mn | Bi |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sandstones; Cheverie Formation; Magnet Cove Mine, 690-foot level; not in ore zone | 300 | 1,500 | 1% | 150 | 5,000 | 1,000 | <50 | <50 | ~3% | ~3,000 | 100 | NF | 50 | 140 | ND | 700 | 700 | NF |
| Shales and sandstones; Cheverie Formation; Southwest of Cheverie. Fractures present | 40 | 1,000 | 250 | 230 | 700 | 1,900 | <50 | <50 | 2.6% | 2,500 | 16 | NF | ND | 38 | 44 | 820 | 3,600 | NF |
| Sandstones and shales; Cheverie Formation; Southwest of Kempt Shore; fractures present | 120 | ~6,000 | Up to 1,000 | 25 | 250 | 220 | Up to 150 | 110 | Up to 2% | 5,000 | 5 | NF | Up to 50 | 5 | ND | 600 | 935 | NF |

Silver may be concentrated in coal by one or all of the following processes:

1. Goldschmidt originally suggested that silver and other trace elements were first concentrated by the coal plants, and these in turn contributed the elements to the humic substances that are the mother of coal. We have seen in the section on the biogeochemistry of the element that silver is a microconstituent of practically all plants, and hence it seems logical to conclude that some of the silver in coals came directly from the accumulated plant material.
2. Precipitation of silver from surface waters flowing into or through the ancient coal swamps. Humus in bogs and swamps tends to adsorb and absorb the available silver from surface waters and thus becomes relatively enriched. Some silver is also precipitated by $H_2S$ derived from the bacterial decay processes operating on protein and other organic complexes. During humification and coalification processes this silver is incorporated in the coal.
3. Precipitation of silver from circulating groundwaters that course through the coal seams during and after coalification processes. In this case the source of the silver may be the coal itself, and the element is simply redistributed within the seam. More generally, however, much of the silver probably comes from the enclosing sedimentary rocks. Some investigators maintain, however, that the silver is of hydrothermal origin, especially where the element is precipitated in zones containing coal fragments in sandstones.

In coal seams and zones of coalified fragments silver is precipitated by adsorption processes, by $H_2S$ that is always present in small amounts in most coal seams, and by reduction of the silver ions in solution to the metal. Where $H_2S$ is abundant the silver may be precipitated as the sulphide, but more generally it is coprecipitated with iron, lead, and other sulphides and partakes of the structure of these sulphides or forms disseminated specks of silver minerals in the matrix of the sulphides.

The enrichment of silver in most coal seams and in coalified fragments in sandstones seems to be best explained by the circulating water hypothesis.

### Silver in Oil Shales, Petroleum, and Other Natural Hydrocarbons

Oil shales tend to be enriched in silver compared with normal shales. Like the black slates and schists the distribution of silver is, however, commonly erratic. Goldschmidt (1954) recorded a content of 5-10 ppm Ag for some bituminous marls he investigated. The writer found much lower amounts in the petroliferous Albert Shales of New Brunswick. These contain less than 0.1 ppm Ag in most places.

Some types of petroleum contain silver as a microconstituent, but the amounts are generally low in the bulk of the hydrocarbon substance. Katchenkov (1952) gives 100 ppm Ag as the maximum content in the ashes of oils from Russian and other fields. Hyden (1961) found up to 100 ppm Ag in the ash of the oils of the western half of the United States. He found silver in all samples of the light and medium paraffinic oils, but none in the heavy naphthenic or aromatic oils. The silver in the oil of the Alluwe pool of the Nowata field, Oklahoma, was largely concentrated in the ash of the residue of the oil left after thermal fractionation.

The mode of occurrence of silver in petroleum is unknown. It seems probable, however, that the element is combined as some type of silver-organic acid complex or as a chelated complex. Sulphide complexes of silver may also be present in certain oils.

The silver in petroleum may be derived from the following sources:

1. From the original plants and animals whose remains gave rise to the petroleum. In the present section on biogeochemistry we have reported that many marine plants and animals concentrate silver, and it seems logical to suppose that some silver in petroleum came from this source.

2. By adsorption and absorption processes from sedimentary rocks. Petroleum migrating through sedimentary rocks on its way to reservoirs probably adsorbs and absorbs some silver from these rocks.

3. By contact with connate and other waters. These waters carry small amounts of silver, which may be absorbed by petroleum when the two solutions come into contact.

There are no published data on the silver content of the natural bitumens and asphalts and the various solid hydrocarbons such as gilsonite, ozokerite, grahamite, anthraxolite, thucolite, etc. There are a few scattered references in the old literature, however, to the occurrence of native silver with solid hydrocarbons in veins. One of these is well described (Koenig and Stockder, 1880-81). Recently the writer found 15 and 5 ppm Ag, respectively, in the ash of anthraxolite from Pennsylvania, U.S.A., and the Sudbury area, Canada.

Ag in Athabasca tar sands?

## *Chapter III*

# SILVER DEPOSITS

Ag pentlandite

The silver content of pegmatites is low compared with that of veins and other types of deposits. Some pegmatites may contain traces of silver, generally in the few scattered sulphides in these bodies. Tourmaline and other typical pegmatite minerals may also contain traces of the element. There are few, if any, economic silver-bearing pegmatites.

Silver is rarely enriched in deposits of the copper-nickel type associated with basic rocks. Some silver is won from these deposits, but only as a minor by-product of smelting operations. The element is likewise not greatly enriched in the skarn-type deposits, but small amounts of silver are won from some of these deposits, generally as a by-product of copper or lead smelting.

Not so for some

?? Phoenix

In hypogene veins, lodes, stockworks, mantos, and other types of similar deposits, silver is strongly enriched, and these deposits are the main sources of silver production in the world.

Silver may be enriched locally in certain types of copper shales and in the copper- and lead-bearing sandstones. The amounts of silver in such deposits are, however, generally low, and the element is won mainly from the copper and lead concentrates. A few sandstone-type deposits have been mined essentially for their silver.

Silver is present mainly in the native metal, alloyed with gold, or as a constituent of a great variety of sulphides, tellurides, selenides, and sulphosalts in hypogene deposits. In the oxidized zones of veins and other deposits silver occurs most frequently in the native form, as the halides (generally chlorargyrite), as the ruby silver minerals, or as the basic sulphate, argentojarosite.

The elements with which silver is generally associated in hypogene deposits are mainly chalcophile and include S, Se, Te, As, Sb, Cu, Fe, Ni, Mn, Ca, Co, Bi, Sn, Zn, Cd, Ba, Si, Pb, and Au. With the last two elements there is a marked coherency, and with certain particular reservations most gold and lead deposits are enriched in silver. In certain silver veins and in some silver deposits in sandstones, uranium is an associated element. Tin and silver are frequently associated, as in a

Sb any association with "precious metal" factor in M.S. deposits?

number of silver mines in Bolivia particularly in the Oruro and Potosí districts (Chace, 1948); in U.S.S.R.; at the Snowflake Mine in British Columbia (Gunning, 1931); and elsewhere. Silver and thallium often show a certain degree of geochemical coherence in lead-zinc deposits, a feature that probably has something to do with the fact that the silver and thallous sulphides are somewhat analagous in their precipitation characteristics and that the silver and thallous halides and halide complexes resemble one another in their solubility relationships and in their reactions in solutions. In deposits, both silver and thallium tend to be concentrated in galena, less commonly in the sulphosalts, and in the rare minerals crookesite and hutchinsonite. Indium and silver also exhibit a geochemical affinity in some zinc-silver-lead deposits, the two elements being concentrated principally in galena, chalcopyrite, tetrahedrite, and sphalerite (Badalov, 1961). Tungsten is likewise frequently found with silver and gold; one need only recall the numerous occurrences of scheelite in the gold-quartz veins of the Canadian Shield, and the common presence of small amounts of both scheelite and wolframite in the polymetallic silver deposits of the Western Cordillera, South America, U.S.S.R., etc. The association, tungsten (scheelite), gold, silver, antimony, is a common one in a number of mineral belts; e.g., Stibnite, Idaho (Cooper, 1951), and Yellowknife, N.W.T. (Boyle, 1961). Boron frequently accompanies silver, mainly in deep seated gold deposits, but also in certain galena-sphalerite-pyrite-arsenopyrite veins such as those in or near monzonite in the Helena mining district, western Montana (Knopf, 1913); also in certain massive galena-sphalerite deposits such as the Sullivan mine, British Columbia. Bismuth and silver show a moderate geochemical coherency in a number of deposits, principally in the native silver-cobalt-nickel arsenide type, but also in numerous instances in lead-zinc-silver veins, mantos, etc. The relationship also seems to extend to various types of deposits containing copper sulphides and molybdenite. The latter mineral may be enriched in both bismuth and silver in places (Pidzhyan, 1960). Certain types of Ag-Sn-Pb-Zn veins in Bolivia, Chile, Peru, New South Wales, and elsewhere are enriched in bismuth, as are also a number of gold-silver veins in Queensland (Burnett District), New South Wales, Norway (Svartdal), Japan (Nishizawa and Nakanosawa mines), the United States, Canada (Hazelton and other areas in British Columbia), and elsewhere. One of the best known examples of the gold-silver-bismuth type of deposit is at Goldfield, Nevada, where bismuthinite is found with pyrite, marcasite, sphalerite, enargite, tellurium tetrahedrite (goldfieldite), arsenical famatinite, tennantite, various gold-silver tellurides, and native gold, all in irregular silicified and alunitized zones referred to as 'ledges' by Ransome (1909). Silver is frequently associated with cobalt and nickel, particularly in the Ag-Ni-Co-As vein deposits. The same association, especially for cobalt, extends as well to the Cu-Ag shale type of deposits and to the silver-bearing 'red bed' deposits. In these same two types of deposits, silver, molybdenum, vanadium, and sometimes chromium may show a parallel enrichment. Mercury and silver are often associated, the former element occurring principally in native silver or in gold-silver alloys and amalgams. Chlorine, bromine, and iodine may accompany silver in the oxidized zones of silver deposits in arid regions.

Bi-Ag

The principal gangue minerals in silver deposits are quartz, calcite, siderite, barite, pyrite, arsenopyrite, and various Ni-Co arsenides. Tourmaline may be present in the gangue or developed in the wall-rocks of certain deposits.

On a statistical basis, silver tends to occur in veins where the gangue is carbonate and/or barite. Especially characteristic is the frequent occurrence of manganiferous siderite, rhodochrosite, and manganiferous calcite among the carbonates found in silver deposits. This indicates a certain geochemical coherence between silver and manganese. Silver also shows a marked tendency to be either in or associated with galena, sphalerite, tetrahedrite, various copper and lead sulphosalts, and the Ni-Co arsenides. Gold, on the other hand, favours a quartz gangue and is either in or associated with arsenopyrite, pyrite, and chalcopyrite. These associations have been known for centuries, particularly the carbonate (carbon dioxide)—silver parallel enrichment in vein deposits, and the silica (quartz)—gold parallel enrichment. The precise reasons why these associations are so frequent have, however, escaped us to the present.

?

Au

$SiO_2$-A

Reason

The distribution of silver within individual orebodies, veins, beds, etc., apparently depends on a variety of factors such as mineralogy, paragenesis, fracturing, secondary enrichment, and others. Practically every deposit has its individual peculiarities and has to be studied as an entity. Some examples will serve to illustrate this point.

In the copper-silver shale (Kupferschiefer) type of deposit silver is enriched in the same layers that exhibit marked concentrations of copper (*see* Fig. 1), and it is certain that silver follows copper closely and was probably precipitated under the same chemical conditions. Some of the 'red bed' copper-silver deposits such as those in the Dzhezkazgan area of Kazakhstan, U.S.S.R., exhibit a similar relationship; the silver and copper exhibit a parallel enrichment in the orebodies. In other 'red bed' types of deposits, however, silver follows lead.

Ag-Cu

Ag-Pb

At Keno Hill, Yukon, the writer (Boyle, 1965) found that the near surface parts of the lead-zinc-silver veins were greatly enriched in silver due to oxidation processes (Table 49). Similar relationships have been observed by Anderson (1940) at the St. Louis mine in Butte county, Idaho. In this mine hypogene aikinite, $PbCuBiS_3$, was replaced by supergene native silver and argentite. Below the zone of supergene replacement the ore was uneconomic as regards silver. Numerous other examples of the downward decline in silver content of deposits are given in the section on oxidation of deposits.

At Keno Hill some of the primary ore shoots maintained a relatively constant silver to lead ratio on their rake despite the fact that argentiferous galena decreased with depth. This circumstance was due to the fact that freibergite, while decreasing in quantity at depth, did not do so as rapidly as galena. In other words this argentiferous mineral had a greater vertical range than galena. Similar relationships have been noted by the writer in other silver-lead-zinc deposits in Canada.

ote

In some massive sulphide deposits silver often follows lead closely and is enriched in the galena-rich parts of the bodies. Such a relationship is evident in some of the Bathurst-Newcastle sulphide masses (Boyle and Davies, 1964). In other massive sulphide deposits in many parts of the world silver appears to follow copper. Stanton and Richards (1961) investigated the distribution of silver and other ele-

Ag-Pb

Ag-Cu

Note

ments in the great lodes at Broken Hill in some detail. They found variations in the silver content of the individual lodes and thought there was a suggestion that the element decreased in stratigraphical height. That is, the higher lodes were lower in silver. For the higher lodes the histogram distributions are regular and sharply skewed, but as the mean values increase (in the lower orebodies), the skew flattens to greatly extended, flat, distributions. In a limited way they also found a general correlation between silver and lead, and that the Ag/Pb ratios were related to ore type and stratigraphical position. The silver-lead ratios in the deposits were also found to be closely related to those of the earth's crust, with perhaps a slight impoverishment of silver relative to lead in the deposits.

Numerous other relationships can be cited about the distribution of silver in certain ore shoots. In some mining camps, enrichment of silver minerals is marked at vein junctions or where late fracturing of veins has taken place. At the points of intersection of veins with black pyritiferous beds (the so-called 'leaders') enrichments of silver (and gold) are frequently encountered, and there are numerous references in the literature to deposition of rich silver lenses, pods, etc., below impervious layers such as shales, gouge, etc.

With the exception of certain native silver veins relatively few deposits are mined solely for the element. More commonly silver is won as a by-product from gold, copper, lead-zinc, and nickel-copper mines. In some remote regions, however, the presence of silver in quantity is a major economic consideration. Certain deposits are highly enriched in silver in their oxidized parts, and the element may be the principal product of such deposits. At depth, however, these deposits generally grade into lead, zinc, or copper deposits, and mining is carried on mainly to extract these metals with silver as a by-product. Deposits of this nature were widespread in Mexico, South America, and other countries, and have produced enormous amounts of silver in past centuries.

## Ag/Au Ratios of Deposits

The Ag/Au ratios of various types of deposits, especially with respect to geological provinces and epochs, is a fascinating problem, but one on which little research has been done. Shcherbina (1956) has given a number of Ag/Au ratios of various deposits throughout the world and drawn a few conclusions which merit repeating here. He found:

Related to metamorphism?

1. That gold enrichment (a low Ag/Au ratio) is present mostly in higher temperature and deeper seated ore deposits, whereas silver enrichment (a high Ag/Au ratio) is characteristic of low temperature ore deposits formed at intermediate depths or near the surface. This is correlative with the vapour pressures of the elements, viz. Ag has a higher vapour pressure than gold at temperatures above 700°C. Silver is, therefore, more volatile than gold and hence migrates farther from the source of heat (magma) and tends to be enriched near the surface.

2. That deposits in older geological formations are frequently richer in gold

neg. correlation Ag/Au with age

(a low Ag/Au ratio), whereas in younger formations silver is more abundant (a high Ag/Au ratio).

3. That ore deposits formed by more alkaline hydrothermal solutions, as witnessed by the alteration of the wall-rocks, are richer in gold, whereas those formed by weaker alkaline solutions are richer in silver. This circumstance is explained as due to the different modes of transport of gold and silver in alkali sulphide solutions.

4. That gold is predominant in telluride ores, whereas silver is generally dominant in selenide ores. An analogous, but not as strict, relationship is observable with respect to As and Sb. Thus gold prefers the arsenopyrite or smaltite mineral association, whereas silver favours antimony assemblages.

Au-T
Ag-Se
Au-A
Ag-S

5. That the Ag/Au ratio depends on regional metallogenic peculiarities, being high for the Circum-Pacific belt of America and low for the countries bordering the Pacific Ocean on the southwest.

?

Bruce (1943) investigated the Ag/Au ratios in certain Ontario gold mines (Porcupine, Kirkland Lake, Malartic) and concluded that:

1. The Ag/Au ratio for some deposits seems to increase with depth.

2. The ratio is different for different kinds of wall-rocks even on the same mine level.

3. Silver shows less variation than gold.

Thomson, *et al.* (1950) and Charlewood (1964) gave average Au/Ag ratios for most of the gold mines along the main ore zone at Kirkland Lake. Recast as Ag/Au ratios, these range from 0.11 to 0.25, despite the fact that the ores are relatively uniform as regards their mineralogy. The ratio Ag/Au, calculated from the yearly production figures, shows an erratic behaviour. In some mines the ratio decreases with time and in others an increase or erratic behaviour is evident. Whether these ratios can be keyed to depth is a question since there is seldom an orderly production depthwise with passing years in gold mines.

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In the publication by Thomson, *et al.* noted above, Hopkins discussed the Ag/Au ratios in the Wright-Hargreaves mine. He noted that the Ag/Au ratio increases with depth and remarked that this is due to an increase in the silver content rather than a decrease in the gold content. Hence, the trend in the Ag/Au ratio does not help to predict the depth at which the precious metal content will be below ore grade.

In the precious metal deposits of the western United States, Nolan (1933) observed that the Ag/Au ratios varied within wide limits. In some of the mines in the Silver City–De Lamar region the ratio is greater than 100:1, but in a number of other camps it is almost 1:1. Nolan thought that the ratios were perhaps related to the temperature of deposition since he found an Ag/Au ratio of 105:1 in the (hot) central focus of mineralization whereas the ores more distant from the central focus, in the cooler zones, have a ratio of about 95:1. Addie (1964) in a more recent paper likewise thought that the Ag/Au ratios are a sensitive geothermometer. He interpreted the Ag/Au ratio to be an expression of exsolution of a silver-gold solid solution as the temperature changes. Thus, he maintained that low Ag/Au ratios represented higher temperatures and high Ag/Au ratios lower temperatures. A deposit that shows a decrease in the Ag/Au ratio with depth would, therefore, indicate that the thermal source was being approached. Such a simplification seems too general in view of the data presented by Bruce, although it agrees with the chemical fact that silver is more mobile than gold.

When one attempts to compile the Ag/Au ratios of deposits on a world-wide basis he is beset with many inconsistencies and difficulties, too numerous to mention here. Some of these are related to the inadequacy or lack of suitable assays, others derive from the process of compiling from production data where the grade and percentage of recovery of the two metals are unknown. Despite these problems Table 36 has been compiled from the world-wide literature according to the type of deposit in which silver and gold occur. The following features are apparent:

1. Only three types of hypogene deposits have Ag/Au ratios less than 1. These are the conglomerate type gold deposits, certain skarn type deposits, and gold-

TABLE 36 | *Ag/Au Ratios of a Variety of Mineral Deposits*

| Type of Deposit | Ag/Au Ratio (Range) | Remarks |
|---|---|---|
| Shale deposits (Kupferschiefer type) | 40–150 | |
| Disseminations, veins, etc. in sandstones (red-bed type) | 100–300 | Variable |
| Conglomerates (Rand type) | 0.05–0.20 | Witwatersrand bullion ranges between 0.064–0.173 (Hargraves, 1963). On channel samples of the Ventersdorp Contact Reef and Main Reef the Ag/Au ratios range from 0.073–1.0 (Von Rahden, 1965) |
| Disseminated lead-zinc deposits in carbonate rocks (Mississippi Valley–Pine Point type) | 10–1,000 | Few data |
| Skarn-type deposits | 0.1–200 | Variable |
| Massive sulphides (Ni-Cu Sudbury type) | 15–31 | Shcherbina (1956) gives 15 for Norilsk, and Hawley (1962) gives 31 for Sudbury ores |
| Porphyry copper type | 10–800 | Few data |
| Polymetallic massive sulphides (Flin Flon–Noranda–Bathurst type) | 1–170 | Average about 40 |
| Polymetallic veins, mantos, etc. (Keno Hill–Sullivan–Coeur d'Alene type) | 50–>10,000 | |
| Gold-quartz veins, lodes, etc. (Precambrian, Palaeozoic, and Mesozoic age) | 0.08–0.73 | Average about 0.28 |
| Gold-quartz veins, lodes, etc. (Tertiary age) | 3–200 | |
| Native silver-Co-Ni-As-Bi veins | 100–>10,000 | |
| Hot spring siliceous sinters | >1 | |
| Gold placers (all types and ages) | <1 | |

quartz veins in Precambrian, Palaeozoic, and Mesozoic rocks. All the other hypogene deposits have Ag/Au ratios greater than 1. Gold placers always have an Ag/Au ratio less than 1.

2. The Ag/Au ratios in shale deposits and sandstone deposits are generally high, indicating a relatively high degree of mobility and concentration of silver during the formation of these particular deposits. Since these deposits probably are the result of low temperature aqueous processes, the ratios are what one would expect because silver is much more soluble and hence more mobile and more easily concentrated under such conditions.

3. In the gold conglomerate type of deposit the range of the Ag/Au ratios is generally narrow, but there are some significant differences in some deposits such as the Witwatersrand, which have been intensively studied by Hargraves (1963) and Von Rahden (1965).

Hargraves found that low grade samples have high silver contents and vice versa, and that the silver content of bullion from individual reefs varies as a function of the relative elevation of the reef, i.e. the bullion of the shallow reefs has a higher silver content than deeper reefs of comparable grade. Hargraves interpreted these compositional gradients as the result of chemical rather than physical (detrital) processes and stated that in terms of the modified placer hypothesis for the origin of the gold, the gradients imply considerable redistribution of silver relative to gold during the 'solution' stage. This is, therefore, again a case of the greater mobility of silver compared to gold during relatively low temperature processes.

Von Rahden thought that his data, which show wide variations in the apparent fineness (and hence in the Ag/Au ratios) of channel samples from the same elevations and stopes in the Ventersdorp Contact Reef and Main Reef, could be ascribed to the presence of silver minerals (mainly native silver) in the ore. The silver minerals, he felt, were due to the redistribution of silver relative to gold during the solution stage of the modified placer theory suggested to explain the Rand deposits. Von Rahden further concluded that his results did not tend to confirm Hargraves' hypothesis that the silver content of the reefs varied with elevation. He recommended electron microprobe studies of the ore to resolve the problem.

Addie (1964), commenting on Hargraves' paper, considered that the decrease in the Ag/Au ratio in the Witwatersrand deposits with depth is due to exsolution of a silver-gold solid solution as the temperature changes. By this he apparently meant that since the silver is more mobile it migrates out of the system. He thought that the decreasing Ag/Au ratio signalled an approach to a thermal centre and postulated a thermal source for the mineralization.

4. There are few data on the gold content of the 'Mississippi Valley type' lead-zinc deposits, and hence a precise knowledge of the Ag/Au ratios is not obtainable. Certainly silver is generally greatly enriched compared to gold, and the ratios are, therefore always high. This indicates a higher mobility for silver compared to gold, a feature that one would anticipate since these deposits are probably concentrated by low-temperature connate or circulating groundwaters.

5. The Ag/Au ratios in skarn deposits are exceedingly variable and apparently related to the mineralogy and hence the chemistry of formation of these deposits. Taking some Canadian deposits as examples one notes that a deposit such as the Nickel Plate at Hedley, B.C., where arsenic is abundant, is characterized by a low Ag/Au ratio (<0.1), and in this respect is similar to certain gold-quartz veins high in arsenic. Probably the mode of transport of the two noble metals during the formation of the two types of deposits has been the same, although the geological setting differs. It would seem that the migration of gold was greatly enhanced by the presence of arsenic in the diffusion or solution system. On the other hand the New Calumet and Tetreault lead-zinc deposits in the Grenville Province both have high Ag/Au ratios (>100) and simulate the normal type of silver-rich Pb-Zn deposits. These deposits are not particularly enriched in arsenic, but contain significant amounts of antimony present in tetrahedrite, polybasite, stibnite, etc. Hence, it seems probable that antimony has had a marked influence on the mobility of silver.

Not skarns

6. Massive nickel-copper sulphides of the Sudbury type, generally associated with basic igneous rocks, seem to have a narrow range of Ag/Au ratios from about 15 to 31, indicating a considerable enrichment of silver over gold at the relatively high temperatures at which these ores are supposed to have formed. Both the silver and gold appear to follow copper, although it would be interesting to know the relationships with arsenic and antimony. According to Hawley (1962) chalcopyrite is the principal argentiferous mineral at Sudbury.

u-Ag-Au

7. The porphyry copper deposits tend to have a relatively high Ag/Au ratio judging from the few good data available. Certainly many of the high-grade copper and lead-zinc deposits associated with the porphyry copper bodies are greatly enriched in silver compared to gold.

8. The massive polymetallic sulphide deposits (Flin Flon–Noranda–Bathurst type) nearly all have relatively high Ag/Au ratios, which average about 40. In some of these deposits silver follows lead and in others an association with copper is evident. Gold seems to follow arsenic and is concentrated in pyrite and arsenopyrite in some deposits, in others gold appears to be associated mainly with chalcopyrite, galena, and sphalerite. The occurrence of gold and silver in most deposits of this type is not well defined, and more research on this feature of the geochemistry of the deposits is desirable. A number of deposits contain argentiferous tetrahedrite and other silver-bearing sulphosalts, and hence there may be a relationship between silver and antimony. Other silver and gold minerals such as argentiferous tennantite, argentite, electrum, gold, sylvanite, and altaite have been recorded from a number of deposits, and these may be responsible for part of the gold and silver content of the ores.

Ag-Pb
Ag-Cu
Au-As
Au-Cu-Pb-Zn

Ag-Sb
Te-Au-Ag

9. The polymetallic veins and the native silver-cobalt-nickel arsenide veins have the highest ratios of all of the various types of hypogene deposits, indicating an extreme mobility for silver and practically no mobility for gold during their formation. The reasons for the great enrichment of silver in these deposits are indeed obscure but must be related either to the source of the mineralizing media or to

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particularly good agents of transport for silver. In many of the polymetallic veins and mantos silver follows lead closely, and there appears to be a close association with antimony and sometimes with arsenic. In other deposits of this type silver and copper exhibit a close affinity. High contents of manganese in siderite are characteristic of a number of silver-rich polymetallic veins. In the Ni-Co arsenide type there is often an association of silver with antimony, as witnessed by the presence of antimonian silver and dyscrasite in these deposits. The association of the native silver with the arsenides is, however, often so close as to suggest that the silver migrated as some highly mobile Ag-As complex. Why gold in quantity did not go along with the silver is an enigma since the element tends to follow arsenic in other types of deposits. An answer to this may lie in the complex composition of the solutions or diffusion currents, which precipitated the silver and arsenides. These solutions were evidently greatly enriched in carbonate as witnessed by the general abundance of calcite and other carbonates in the veins. Silver carbonate is relatively soluble, especially where $CO_2$ is in excess, and this feature could account for the relatively great mobility of silver during the formation of the Ag-Ni-Co-As veins. On the other hand gold does not seem to be capable of forming a carbonate, and in fact there are indications from the natural associations of the element that solutions or diffusion currents enriched in $CO_2$ actually depress the solubility and mobility of gold.

Ag-As

10. Gold-quartz veins in Precambrian, Palaeozoic, and Mesozoic rocks generally have Ag/Au ratios less than 1, and these average about 0.28. There are, however, some local exceptions to this generalization that seem to correlate with the mineralogy and hence chemistry of formation of the deposits. At Yellowknife, N.W.T., veins with arsenopyrite and pyrite tend to have normal ratios for this class whereas others with a high stibnite and sulphosalt (antimony) content tend to have ratios equal to or greater than 1. This suggests that the mobility of silver was considerably increased when antimony was present in quantity in the chemical system. Another example in the Canadian Precambrian Shield is the Ross mine, near Ramore, Ontario. The orebodies in this mine have an Ag/Au ratio of about 1.5, much higher than those in the nearby Porcupine and Kirkland Lake camps. Two periods of mineralization are evident in this mine; the first consists of blue quartz veins with pyrite, chalcopyrite, sphalerite, galena, and gold, and the second is marked by the development of quartz-dolomite veins containing pyrite, sphalerite, galena, tennantite, chalcopyrite, gold, and native silver. In the first period of mineralization gold predominated over silver, and in the second the reverse is true. Here again we note a preponderance of silver where carbonate was present in some abundance in the chemical system.

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11. Gold-quartz veins, lodes, etc. in Tertiary andesites, dacites, rhyolites, etc. generally have ratios greater than 1 in contrast to their counterparts in older rocks. The young deposits are, however, mineralogically different from the older deposits in that many of them contain much larger amounts of galena, chalcopyrite, sphalerite, tetrahedrite-tennantite, argentite, and silver sulphosalts. In this respect they are analogous to the polymetallic veins and have similar ratios. By contrast veins with a simple mineralogy, containing essentially gold tellurides, gold, pyrite, and minor

amounts of the base metal minerals, such as those at Cripple Creek, Colorado, have Ag/Au ratios less than 1.

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exhalite

12. Siliceous sinters precipitated from present-day hot springs generally have Ag/Au ratios greater than 1. In this respect they are similar to many of the Tertiary deposits.

13. Gold placers always have Ag/Au ratios less than 1 regardless of the age of the source deposits. This is due to the natural refining action that takes place during weathering processes. It seems highly probable that at one time or another most of the gold in secondary zones and in placers was in solution and that during this process much of the accompanying silver was removed. This seems to follow naturally from the chemistry of the two elements. Silver is much more soluble than gold in ground and surface waters and is not as readily reduced to the metal. A natural separation is, therefore, inevitable.

Some investigators would perhaps disagree with this interpretation. For instance, Mertie (1940) is of the opinion that the differences in the fineness between lode and placer gold are related to depth of erosion of the mother lodes. Thus the placer gold, which is usually of great fineness, probably comes from the apical near-surface areas of lodes whose hypogene gold was of greater fineness than the deep-seated parts of the lodes that are now exposed to view. This opinion is certainly contrary to that held by Mackay (1944), who showed almost conclusively that the gold in the oxidized zones of a number of mines in Tanganyika and Nigeria has been greatly increased in fineness as the result of oxidation and secondary enrichment processes.

14. Deposits in older geological formations are frequently richer in gold than those in younger formations. There are, however, numerous exceptions to this generalization in a number of mineral belts.

15. The evidence of the Ag/Au ratio as an index of temperature of formation or recrystallization of deposits is conflicting. In some deposits the ratio increases with depth, in other deposits an increase or erratic behaviour is evident. However, few precise studies of the variation of the Ag/Au ratios of single ore shoots or veins with increasing depth have been made, and judgment on the effectiveness of the ratio as a temperature index should be reserved. Furthermore the assumption that the deep parts of the deposits were formed at temperatures higher than the near-surface parts may be in error. On a statistical basis, however, there is some evidence to support the contention that deep-seated (high temperature?) deposits have a lower Ag/Au ratio than those formed at intermediate depths or near the surface, presumably under conditions of lower temperature.

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16. Shcherbina's view that gold is predominant in telluride ores whereas silver is dominant in selenide ores appears to be true. The analogous situation that gold tends to follow arsenic, and that silver is associated with antimony, is likewise marked on a statistical basis. There are, however, some striking examples where gold is enriched in antimony-bearing ores and silver in arsenical ores.

17. Gold and silica (quartz) show a marked association whereas silver tends to be concentrated in an environment where carbonates are abundant. The association of silver with siderite, manganiferous calcite or dolomite, and rhodochrosite is striking in some districts.

18. The Ag/Au ratios seem to depend on regional metallogenic peculiarities in a crude way, if only certain types of deposits are considered. When all deposits are brought into the picture no particular relationships emerge. There are perhaps as many gold-quartz deposits with ratios less than 1 in the Circum-Pacific belt of America as there are other deposits with ratios greater than 1. The same is true for the Appalachian belt and the Canadian Shield. The ratios seem to depend more on the type of deposit (i.e. its mineral constitution and hence chemical history) than on its position in the earth's crust.

## Classification

In the following summary of silver deposits a departure has been taken from the commonly accepted classifications in most textbooks on economic geology. This departure may or may not be justified, but it is the writer's opinion that a classification based on the geological and geochemical setting of silver deposits is much more valuable than any based on their origin be it magmatic, hydrothermal, sedimentary, or otherwise. It seems best to state objectively in what types of rocks and structural settings the deposits occur. With this clearly set down and a knowledge of the geochemistry of the deposits, it may be possible to discern their origin and, more important, to predict the environment where one may prospect for similar deposits. In the last twenty-five years many investigators have advocated a magmatic hydrothermal origin for all silver deposits—an extreme view that is fundamentally erroneous because it fails to consider many of the geochemical features of silver, especially the behaviour of the element in the cycle of weathering and the part played by biochemical processes in concentrating the element.

The classification followed by the writer considers silver deposits under seven main categories, as follows:

1. Shale deposits: Kupferschiefer type—silver is won mainly as a by-product of copper mining.
2. Disseminations, veins, stockworks, etc. in sandstones, arkose, red shales, etc.—'red-bed type'—silver is won as a by-product of either copper or lead mining. Certain deposits contain silver as the principal economic element.
3. Silver-bearing skarn-type deposits.
4. Lodes, veins, stockworks and mantos dominantly in sedimentary rocks, principally shales, phyllites, schists, quartzites, and limestones. Silver is generally won as a by-product of gold, lead-zinc, or copper mining, but some native silver, silver sulphide, and silver sulphosalt deposits occur in this setting.
5. Silver-gold and gold-silver veins and lodes in or associated with volcanic flows, tuffs, etc.

6. Silver deposits in a complex geological environment, comprising sedimentary rocks, volcanic rocks, and igneous or granitized rocks.
7. Miscellaneous sources of silver: The element is won as a by-product from a great variety of deposits mined essentially for copper, nickel, lead, zinc, and gold. The content of silver in these deposits is generally low and rarely influences the worth of the deposits.

The various silver deposits in Canada are shown on the metallogenic map accompanying this report, where a simplified version of the above classification is employed.

A few words should be said at this juncture about the unique native silver-nickel-cobalt arsenide type of deposits, which occur in various parts of the world. These deposits occur in a variety of geological settings and are not easily categorized. Some fall into type 4 above, and some into type 6. Their origin is, likewise, enigmatic in that a completely satisfactory solution as regards the source of their constituent elements and the mode of their concentration has not yet been given.

The deposits occur in a variety of rock types and in a number of diverse geological situations. In age they range from Precambrian to Tertiary. Nearly all are short narrow veins containing phenomenally rich concentrations of native silver, together with variable amounts of argentite, freibergite, other silver sulphides and sulphosalts, various cobalt-nickel arsenides, native bismuth, bismuthinite, and native arsenic. A few contain pitchblende. The gangue is invariably calcite with some barite and quartz. The mineralogical textures are characteristic and are familiar to every student of geology and mineralogy. The characteristic elements and compounds concentrated in the veins are Ag, Ni, Co, As, Sb, Bi, U, Hg, S, Ca, Mn, Ba, and $CO_3$.

Examples are numerous in a number of countries. The best known and most productive are those at Cobalt and Silver Islet, Ontario; Great Bear Lake area, N.W.T.; Kongsberg, Norway; Jáchymov (Joachimsthal) Czechoslovakia; and others in the Erzgebirge of Saxony and Bohemia. These are described in some detail in the sections that follow.

Less well known members of this group of deposits are those at Batopilas, Mexico and Bullards Peak, New Mexico (Krieger, 1935a); Black Hawk District, New Mexico (Gillerman and Whitebread, 1956); Sabinal, Mexico (Krieger, 1935b); Wickenburg, Arizona (Bastin, 1922); Rocher Déboulé deposit, British Columbia (Kindle, 1954); Sarrabus, Sardinia (Piepoli, 1933); Chalanches, France (Rickard, 1894; Ypma, 1963); St. Andreasberg in the Harz, Wittichen and others in the Black Forest (Schneiderhöhn, 1955; Wimmenauer, 1962); Bou-Azzer, Southern Morocco (Jouravsky, 1948); Junten mine, Ze ranando, Korea (Watanabe, 1943); Akol, Minusinsk region, U.S.S.R. (Barsanov and Pogonia, 1947); and Altai-Sayan area, U.S.S.R. (Unksov, 1958).

Space does not permit describing each of these occurrences, but during the compilation of the data on these deposits the writer was struck by the frequent reference to the occurrence of basic magnesium-rich rocks in the vicinity of the deposits. In some cases the rocks are diabase or gabbro, in others serpentinites, in still others amphibolites or talc-tremolite schists. These rocks could be the source of the nickel and cobalt in the deposits as has been suggested by a number of investigators. However, this association is not invariable. Some of the deposits seem to be related to granitic intrusions especially monzonites or diorites. Other deposits show no such relationships. A few deposits are enriched where they intersect sulphide-bearing schists (fahlbands), but in others these rocks are not present. A number of deposits occur either in or near black shales or other sediments that could have provided the silver, uranium, arsenic, sulphur, and their other constituent elements, but again this relationship is not invariable. The presence of mercury, a low temperature volatile element, with nickel and cobalt, elements generally found in high temperature deposits, is puzzling, as is also the presence of uranium in some deposits and the virtual absence of this element in others. All these features serve only to point out the enigmatic nature and origin of these deposits, further discussion of which is reserved for the sections where the deposits at Cobalt and elsewhere are described in some detail.

## Shale Deposits: Kupferschiefer Type

In this category belong the famous copper shales (Kupferschiefer) of the Mansfeld and adjacent areas in Germany, the White Pine copper shale deposits of Michigan, the Zambian (Northern Rhodesian) copper shales and quartzites, the Boléo copper deposits of Baja California in Mexico, and others. All differ somewhat in their geological and mineralogical details, but they are similar in that they are bedded deposits and are mined principally for copper with silver and cobalt as by-products in some cases. Table 37 gives the generalized details of six deposits in this category.

Nearly all of the deposits occur in sequences of shale, siltstone, argillite, tuffs, and impure calcareous and dolomitic rocks, that are closely associated with or sometimes interbedded with sandstones, quartzites, and conglomerates. The depositional environment of these rocks often suggests near-shore conditions, sometimes in bays, in estuaries, in a deltaic environment, in shallow basins, in coastal lagoons, or occasionally in parts of the sea cut off from the main body of water. Some may have been deposited in stagnant lakes or inland seas. Basins which received much volcanic debris seem favourable in some areas. The land masses that provided the sediment appear to have nearly reached maturity and then undergone uplifts, yielding a series of sand and pebble beds followed by a cyclic series of fine silts and sapropelic material. Arid conditions appear to have prevailed before and sometimes after the deposition of the favourable sediments in some areas. According to a number of African geologists the sediments containing the deposits in Africa were deposited in zones of considerable subsidence, generally bordering on folded zones (Assoc. African Geol. Surveys, 1962).

The environment of deposition was invariably a near-shore reducing one, as witnessed by the large amounts of carbonaceous matter present in many deposits. Fragments of coalified wood and land plant leaves occur in a few of the deposits, and fossil fishes and the skeletons of reptiles have been noted in some of the younger deposits. Bottom-type marine fossils are generally local or lacking, probably because of the foul reducing conditions on the bottoms, a feature that prevented their existence. Oxidizing conditions with the formation of iron and manganese oxides

TABLE 37 | *Characteristics of the Copper-Silver Shale Deposits*

| Name | Age | Rock types | Degree of folding | Nature of faulting in ore beds | Grade of metamorphism |
|---|---|---|---|---|---|
| Kupferschiefer, Germany | Permian | Shales, siltstones, sandstones | Gentle | Minor | Diagenetic effects only |
| White Pine, Michigan, U.S.A. | Precambrian | Shales, siltstones, sandstones | Gentle | Minor | Low grade (greenschist) |
| Zambian (Northern Rhodesian) Copperbelt | Late Precambrian | Shales, siltstones, argillite, impure dolomite, micaceous quartzite, greywacke | Complex series of anticlines and synclines. Some orebodies exhibit complex folding | Minor | Low grade (greenschist) to medium grade (epidote amphibolite) |
| Boléo, Mexico | Pliocene | Clay tuffs, tuffaceous sandstones | Relatively flat-lying | Minor | Low grade, mainly diagenetic changes |
| Creta area, Oklahoma, U.S.A. | Permian | Shales and siltstones | Flat-lying | Minor | Low grade, mainly diagenetic effects |
| Redstone River area, N.W.T., Canada | Late Precambrian or Early Cambrian | Argillaceous limestone, silty limestone, siltstone | Folded | Faulted | Low grade, mainly diagenetic effects |

prevailed for periods of time in a few of the basins. The available evidence from the salt and boron contents of some of the shales suggests increasing salinity during the formation of the sediments.

Some of the deposits are nearly flat lying or have only an initial dip, others are gently folded. Only the Zambian (Northern Rhodesian) ones are intricately folded. Most of the areas are faulted, but the ore beds are rarely if ever severely faulted. There are generally no definite systems of channels in any of the deposits along which mineralizing solutions could have entered to mineralize the sedimentary beds.

The grade of metamorphism of the rocks comprising the deposits is low. Most fall into the greenschist facies or lower, but some of the Zambian deposits are in the hornfels and epidote-amphibolite facies. There is no clear indication of wall-rock alteration in any of the deposits as far as this writer can ascertain. In thin sections the rocks exhibit a mineral assemblage similar to that found in sedimentary rocks in the respective facies in which the deposits occur.

TABLE 37

| Type of ore shoots (Minerals) | Late veins | Principal elements | Grade Cu % | Grade Ag (ppm) | Remarks |
|---|---|---|---|---|---|
| Beds, layers, elongate lenses, disseminations (Bornite, chalcocite, chalcopyrite, pyrite, galena, sphalerite) | "Rucken" (Barite, calcite, niccolite, pyrite, chalcopyrite, etc.)<br>(Secretion veins?) | Cu, Zn, Pb, Ag, Mo, Co, Cd, As, Sb, S | 2.5 | 150 | Carbonaceous matter is abundant in some beds. Silver is recovered |
| Beds, layers, and disseminations (Chalcocite, native copper, pyrite) | Veinlets and veins with associated halos (Calcite, quartz, chalcocite, native copper, etc.)<br>(Secretion veins) | Cu, Ag, S | 1–3 | Up to 150 | Carbonaceous matter is abundant in some beds. Silver is recovered |
| Beds, layers, elongate lenses, disseminations (Chalcopyrite, bornite, chalcocite, pyrite, linnaeite, carrollite) | Metamorphic veins. (Quartz carbonate, feldspar, pyrite, chalcopyrite, bornite, chalcocite)<br>(Secretion veins) | Cu, Co, S | 3.0 | ∼1–10 | Carbonaceous matter is abundant in some beds. Silver is not recovered |
| Beds, ribs, elongate lenses (Chalcocite, chalcopyrite, bornite, covellite, native copper, pyrite, galena) | None | Cu, Mn, Zn, Pb, Cl, Co, S | 5.0 | 9 | Carbonaceous matter is abundant in some beds. High Mn and Cl contents in ore.<br>Silver is recovered |
| Beds | None | Cu, S | Up to 4 | 1 | |
| Seven mineralized beds | Veins of quartz, calcite, bornite, etc. in general area | Cu, Ag, Co, S | 2.5 | ∼10 | At exploration stage |

The ore shoots are mainly beds, layers, ribs, and elongate lenses. Many are continuous over great distances, others are separated by barren stretches. Some deposits consist only of a single bed or layer, others have as many as five layers or beds. Nearly all the deposits are stratigraphically controlled over distances as much as 100 miles. Some of the strata-bound deposits have associated disseminated deposits, generally in stratigraphically lower sandstones or quartzites.

Later veins and veinlets are common in the older deposits, but seem to be lacking in the relatively young deposits. These veins, called 'Rücken' in the Kupferschiefer, metamorphic veins in the Zambian Copperbelt, and veins and halos in the White Pine deposit, have been shown to be due to a process of lateral secretion.

The principal copper minerals in the stratified deposits are chalcocite, bornite, and chalcopyrite. There are also pyrite, galena, sphalerite, molybdenite, and a few other sulphides in some deposits. Native copper and native silver occur in the White Pine deposit. In the late veins, copper sulphides, barite, calcite, and other minerals may be present. The late veins appear to reflect the degree of metamorphism that the copper-bearing beds have undergone. Thus, in the low-grade metamorphic deposits only calcite, barite, and minor quartz occur. In the higher grade metamorphic deposits feldspar and abundant quartz make their appearance.

In most of the deposits the copper and other sulphides exhibit a paragenetic sequence similar to that found in epigenetic deposits. This is interpreted by the investigators who are most familiar with the deposits as due to either diagenetic or metamorphic reactions.

The principal elements concentrated in the deposits are chalcophile and include Cu, Pb, Zn, Ag, Cd, Mo, Co, Ni, Fe, Mn, As, Sb, and S. Manganese and chlorine are strongly enriched in the Boléo deposits. Uranium may occur in some deposits but generally only in small amounts.

The copper content of the deposits ranges from 1.5 to 5 per cent with 3 per cent as an average. The silver content of the ores is highly variable. In some it is negligible, in others it approaches 150 ppm (4.5 oz/ton). The tonnage of the deposits is generally large. Some of the orebodies on the Copperbelt of Zambia have reserves of 170 million tons or more. Other deposits have much less tonnage, measured in several tens of millions of tons. The amount of low-grade copper ore in some of the deposits is very great.

There has been much controversy about the origin of the copper shales. Some investigators maintain that the deposits are essentially syngenetic, others that they are epigenetic. The arguments for a syngenetic sedimentary origin are strong.

### Kupferschiefer

The Kupferschiefer of Mansfeld, Germany, is the classic type in this category. This deposit has been repeatedly described since mining began about A.D. 1150. The more recent detailed descriptions are by Stelzner and Bergeat (1904–1906), Trask (1925), Gregory (1930), Gillitzer(1935, 1936), Deans (1950), Eisenhuth and Kautzsch (1954), Schneiderhöhn (1955), Knitzschke (1961, 1965), Wedepohl (1964), and Rentzsch (1964). Some recent opinions on the origin of the Kupferschiefer and similar deposits may be found in the papers by Bain (1960), Davidson (1962a, 1965), Love (1962), Lovering (1963), Dunham (1964), Wedepohl (1964), and Knitzschke (1965).

In the vicinity of Mansfeld the sedimentary rocks are of Permian and Triassic age. They include a lower division, the Permian Rotliegende, composed of sandstones, shales, and conglomerates and various lava flows, tuffs, and breccias, all regarded predominantly of continental origin; and an upper division, the Permian Zechstein, consisting of three groups, the lowest composed of a lower conglomerate overlain in turn by the Kupferschiefer beds and a marine limestone (the Zechstein limestone). The latter is overlain by the upper two groups of the Zechstein, which are composed essentially of evaporite deposits, including salt, potash salts, and gypsum. The Zechstein is overlain by Triassic sandstones.

The sedimentary rocks are gently folded into a number of anticlines and synclines. The main cupriferous deposits of the Mansfeld district occur in the Mansfeld and Sangerhausen synclines (troughs), which are complicated by the presence of a number of small faults and sharp folds (the so called Rücken), which strike approximately parallel to the axes of the synclines.

The copper-shale (Kupferschiefer) averages about 10 inches in thickness, but ranges between 5 and 20. It is copper-bearing throughout this width, averaging about 2.5 per cent. In addition the shale is characterized by the enrichment of practically all of the common chalcophile elements (Table 39). There is a vertical zonation of the metals—high copper values occur at the bottom and these grade upward into low copper values and high lead-zinc values (Table 38 and Fig. 1). Silver tends to follow the copper and is enriched toward the bottom of the shales. The copper content near some of the Rücken is increased relative to other parts of the bed, in other areas there is no apparent relationship. In some of the Rücken nickel-cobalt arsenides, molybdenum minerals, and uraninite have been found, but only in small amounts.

TABLE 38 *Stratigraphy of the Kupferschiefer and Associated Rocks, Mansfeld District, Germany*

| Local Name | | Description | Copper Content | Silver Content | Lead Content | Zinc Content |
|---|---|---|---|---|---|---|
| Zechstein | | Bituminous marine limestone (12–15 feet) | Traces | – | Traces | Traces |
| Fäule | | Fissile, earthy limestone (3–8 inches) | Traces | – | Traces | ~0.5% |
| Dachklotz | | Dense grey pyritic limestone (6–8 inches) | Traces | – | Traces | ~0.5% |
| Dachberge | | Compact limestone (2–3 inches) | Traces | – | Traces | ~0.5% |
| Schwarze Berge | | Dark limestone (3–5 inches) | ~0.5% | Traces | ~1.0% | ~1.0% |
| Schieferkopf | (Kupferschiefer) | Top of cupriferous shale (4–5 inches) | ~0.75% | ~0.5 oz/ton | ~1.0% | ~2.0% |
| Kammschale | | Shale with horizontal lenses of ore (1–2 inches) | ~1.0% | ~1 oz/ton | ~1.5% | ~2.0% |
| Grobe Lette | | Black bituminous calcareous shale with disseminated grains of ore minerals (1–3 inches) | ~3.5% | ~3 oz/ton | <0.25% | <1.0% |
| Feine Lette | | As above; usually the richest ore (1–2 inches) | ~3.5% | ~3 oz/ton | <0.25% | <1.0% |
| Sanderz | | Sandstone (dune sand) | 1–3% | 1–3 oz/ton | <0.25% | <0.1% |

The predominant minerals in the copper shale are bornite, chalcocite, chalcopyrite, galena, and sphalerite. Less common are native silver, argentite, tetrahedrite, and molybdenite. In some of the Rücken there are small amounts of calcite,

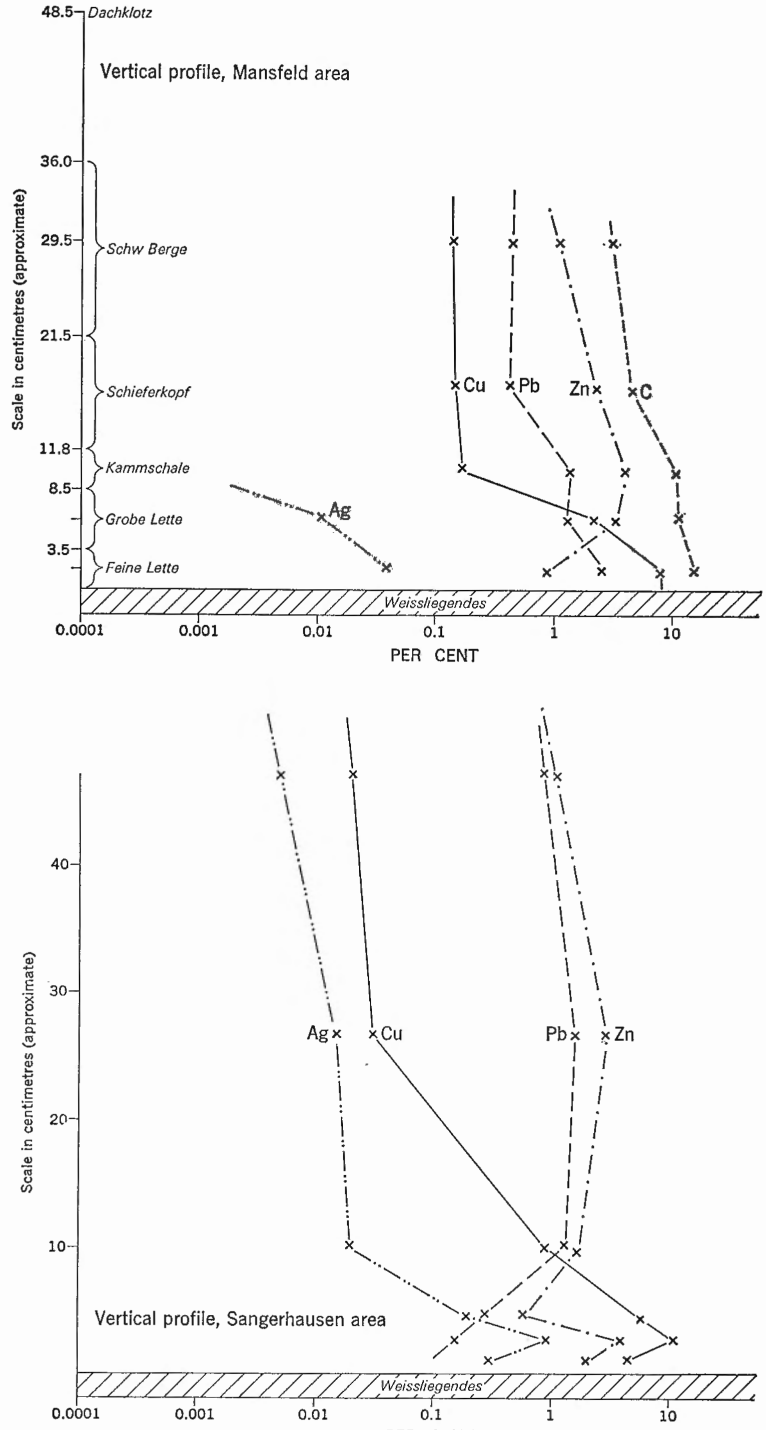

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**FIGURE 1.** Vertical distribution, of Cu, Pb, Zn, Ag, and C in the Kupferschiefer, Germany (after Eisenhuth and Kautzsch, 1954; Wedepohl, 1964).

TABLE 39 | *Analysis of the Kupferschiefer*

| Constituent | Per cent (range or average) | Remarks |
|---|---|---|
| $SiO_2$ | 32.0 — 33.5 | |
| $Al_2O_3$ | 13.0 — 17.5 | |
| CaO | 10.0 — 11.0 | |
| MgO | 1.0 — 4.0 | |
| $Fe_2O_3$ | 1.0 — 10.0 | |
| $Na_2O$ | 0.5 — 1.5 | |
| $K_2O$ | 2.5 — 3.5 | |
| $H_2O$ | 0.7 — 1.7 | |
| $CO_2$ | $<$0.1 — 38.7 | |
| S | 0.1 — 3.5 | |
| C | 0.1 — 15.1 | In bitumen or carbonaceous matter. |
| Cl | 0.13 | Water soluble |
| Cu | 0.005 – 3.5 | |
| Pb | 0.005 – 2.6 | |
| Zn | 0.001 – 5.0 | |
| Cd | up to 0.05 | |
| Ag | $<$ .001 – 0.88 | Mansfeld trough, average 72 ppm Ag.<br>Sangerhausen trough, average 295 ppm Ag |
| Ni | 0.003 – 0.12 | |
| Co | $<$0.001 – 0.036 | |
| Mn | 0.011 – 0.60 | |
| Mo | 0.001 – 0.15 | |
| Ti | 0.028 – 0.86 | |
| V | 0.001 – 0.50 | |
| Cr | 0.001 – 0.033 | |
| Re | 0.002 – 0.15 | Mainly in molybdenite |
| Au | 0.00001 – 0.0001 | |
| Pt | $\sim$0.0001 | |
| Ir | $\sim$0.0001 | |
| Pd | $\sim$0.0001 | |
| Sn | 0.001 | |
| As | 0.01 – 0.50 | |
| Sb | up to 0.03 | |
| Bi | up to 0.01 | |
| P | 0.09 | |
| Te | $\sim$0.0002 | |
| Se | 0.001 – 0.04 | |
| W | up to 0.01 | |
| U | Traces | |
| Ge | 0.0005 – 0.0016 | |
| Ba | 0.003 – 0.54 | |
| Sr | 0.005 – 0.068 | |
| Rb | 0.003 – 0.019 | |
| B | 0.003 – 0.028 | |

Sources: Stelzner and Bergeat (1904–1906), Hoffmann (1924), Trask (1925), Cissarz and Moritz (1933), Deans (1950), Knitzschke (1961), Wedepohl (1964), and others.

barite, anhydrite, pyrite, niccolite, chloanthite, molybdenite, uraninite, and, according to some investigators, small amounts of copper minerals locally. The silver in the bedded deposits occurs mainly in the native state and as a minor constituent of bornite, chalcocite, chalcopyrite, galena, and tetrahedrite.

The ore occurs in three forms: the bulk consists of minute particles of copper minerals and other sulphides irregularly disseminated through the shale or concentrated in lines as streaks. This ore is the so-called 'Speise' of the Kupferschiefer. The second type consists of small nodules or concretions of sulphides, and the third type is as thin horizontal lenses and discontinuous veins that tend to lie along the bedding planes, though some cut across the bedding laminations. The second type is characteristic of the Dachklotz and Sanderz and the third of the Kammschale layers.

The shale matrix consists essentially of clay matter, sericite flakes, fine quartz, and carbonate minerals. Some layers, especially the Grobe and Feine Lette, are highly bituminous, and there are scattered plant fragments and the occasional remains of terrestrial reptiles and marine fishes throughout the Kupferschiefer. There are no indications of what one might term 'normal wall-rock alteration' in any of the shale layers. In the 'Sanderz', however, the sandstone is bleached where copper mineralization has been notable.

The paragenesis of the sulphides as seen in polished sections is complex, and not all investigators are in agreement. The bornite and chalcocite do not appear to replace the shale, but chalcocite replaces the bornite and carbonates in places. Sphalerite and galena appear to be the same age as the bornite. All workers agree that the chalcopyrite is later than the bornite and the chalcocite for it replaces both of these minerals in all occurrences.

These relationships suggest rearrangement of the metallic components within the shale to some investigators, and introduction from outside sources to others. The consensus of opinion and the facts, however, weigh heavily on the side of the rearrangement hypothesis. There is no doubt that some of the metallic components have migrated laterally, because near some of the Rücken there are marked enrichments of copper and other metals. In addition there appears to have been some downward migration of metals and sulphur into the underlying crossbedded (dune?) sandstones to form the so called 'Sanderz'.

A volume could be written on the various hypotheses suggested to explain the origin of the Kupferschiefer. Two general hypotheses have been extensively discussed—the syngenetic and epigenetic. These turn on a number of salient facts which will be briefly discussed in turn. For details and variations on the two themes the interested reader should consult the selected bibliography.

### *Arguments for the syngenetic hypothesis*

1. The sedimentary (bedded) nature of the deposit and its great lateral extent. The ores are thin sedimentary beds of considerable lateral extent. While the Kupferschiefer is only ore-bearing within certain districts, its equivalents and lateral facies are metal-bearing from the northeast of England through central Germany to Silesia and beyond (Deans, 1950; Hirst and Dunham, 1963). Certainly no magma or

groundwater circulation could have produced such a widespread mineralization restricted to such definite stratigraphic horizons.

2. The Kupferschiefer bears the stamp of a typical black shale deposit formed in a reducing environment. The metals enriched are those found in any normal black bituminous shale anywhere in the world. The only difference is the marked degree of enrichment of copper, silver, lead, zinc, molybdenum, etc. This means that there was evidently an abundance of these elements contributed to the Permian Sea or that the conditions were particularly favourable for precipitation and retention of the metal sulphides in the sediments. Perhaps bacteria played a large part in the precipitation processes (Love, 1962). The varied assortment of chalcophile and other elements is not characteristic of single magmas nor for that matter of multiple magmas. In any event, there are no igneous rocks that are particularly associated with the mineralized rocks either in England, Germany, Silesia, or elsewhere.

*Arguments for the epigenetic theory*

1. The evidence of enrichment near the Rücken. Zones near some of the Rücken are greatly enriched in copper and other metals. This is taken by some investigators to indicate that solutions bearing the metals rose up the Rücken and spread laterally into the adjacent rocks, precipitating in the largest amounts near the Rücken.

This view has been disputed by several investigators, who point to the facts that not all Rücken have adjacent enriched zones, and that the age of the Rücken is at least late Cretaceous or Tertiary whereas the igneous rocks from which the solutions could have logically been derived are of early Permian age. In other words the Rücken were formed long after the igneous rocks were fully cooled and had ceased to give forth magmatic water, metals, etc.

Other investigators mention the fact that the layers of the Kupferschiefer are relatively impermeable to solutions, and rightly enquire why the ore has concentrated in these layers whereas lower and higher beds are quite porous and more susceptible to precipitation and replacement.

Most investigators now agree that the evidence of enrichment near the Rücken is inconclusive. They say it is more probable that the enrichment is due simply to a rearrangement of metal components and sulphur within the beds.

2. The paragenetic relationships of the sulphides. Some of the sulphides replace other sulphides and carbonates, and the chalcopyrite is late and appears to have been introduced. Such relationships exist in normal epigenetic deposits.

Most investigators now agree that the paragenetic relationships may be due simply to a rearrangement of the mineral components as a result of diagenesis or low-grade metamorphism.

It is perhaps worth while commenting here that the present writer has noted paragenetic relationships in the sulphide nodules of black shales that closely resemble those in veins and other deposits. Certainly in many black shales the chalcopyrite is late since it seams pyrite and pyrrhotite and bornite where it is present. Since the sulphides in the shales investigated have no magmatic affiliations whatsoever, it seems nearly certain that diagenesis and metamorphism give paragenetic relationships in sedimentary sulphides that closely resemble those in epigenetic deposits.

3. The evident epigenetic nature of a number of ore and gangue elements in the Rücken and of ore minerals in the underlying crossbedded sandstones (the 'Sanderz'). These points are agreed upon by practically all investigators, but the source of the mineral components is disputed. Most investigators lean to the view that this type of mineralization is due to a lateral and downward secretion process from the copper shales.

When all of the facts, both geological and chemical, are taken into consideration, it seems nearly certain that the Kupferschiefer and its equivalents are unique sedimentary deposits in which the mineral components have undergone some rearrangement during diagenesis and structural disturbance. While many of the palaeogeochemical processes that led to the concentration of the various chalcophile elements are in some doubt, it seems evident that the copper, silver, lead, and zinc were concentrated in a basin or series of basins where reducing conditions and probably bacterial action prevailed. Following diagenesis, during which there was evidently some rearrangement of the mineral components, the beds were faulted and otherwise mildly disturbed with the formation of the Rücken. These small faults and disturbed zones constituted dilatant zones into which local mineral matter migrated. If this concept is accepted it provides the key for explaining the origin and features of the other deposits of the Kupferschiefer type.

### White Pine, Michigan

The White Pine copper deposit is in the southwestern part of the Keweenaw Peninsula, Michigan, some 45 to 70 miles southwest of the native copper deposits in the same peninsula. Like the Kupferschiefer, it has also been the subject of much controversy as regards its origin.

The geology of the deposit has been described in some detail by White and Wright (1954) and the geochemical features have been discussed by Wiese (1960) and Carpenter (1963). The deposit produces essentially copper with some silver as a by-product. It bears gross similarities to the Kupferschiefer and Zambian copper deposits and in some respects is similar to certain 'red bed' copper deposits.

Briefly, the deposit occurs in shales, siltstones, and sandstones at the base of the Precambrian Nonesuch shale. These rocks lie in a syncline and near the White Pine mine dip gently northward and are transected by a righthand tear fault (White Pine fault) with a horizontal displacement of over a mile. A number of curving minor faults and fractures, thought to be related to the White Pine fault, cut the copper-bearing beds in many places.

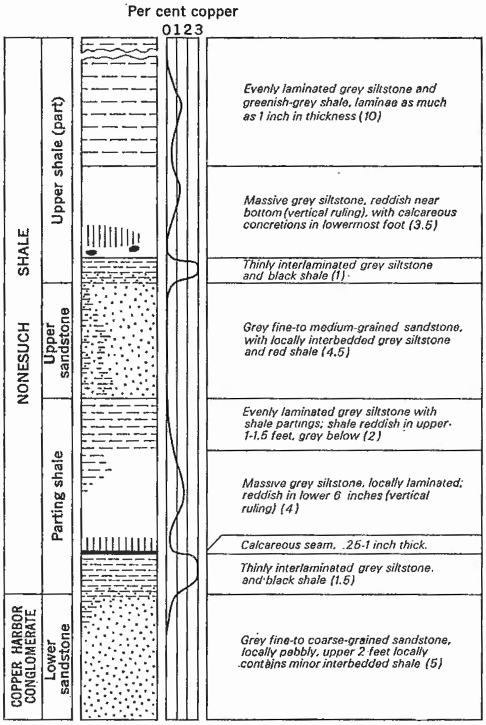
The copper orebodies occur in a 25- to 30-foot sequence of rocks whose generalized stratigraphy is shown in Figure 2. The main cupriferous zones occur in the lower parts of the Parting Shale and Upper Shale. The upper parts of the Lower

Sandstone and Upper Sandstone are also mineralized. Normally these sandstones are reddish, but in the mineralized zones they are grey-green. The reader will note many geological similarities to the Kupferschiefer (Table 38).

In the Parting Shale and Upper Shale about 85 per cent of the copper occurs as chalcocite and the remainder as the native metal. There are also minor amounts of covellite, bornite, and chalcopyrite, the last two minerals occurring mainly in small seams and fissures. The principal copper minerals in the Lower Sandstone and Upper Sandstone are native copper and chalcocite; in some areas native copper predominates over chalcocite, in others the reverse is true. Carbonaceous matter (solid hydrocarbons in part) and other types of organic substances accompany the copper minerals in places (Nishio, 1919; Barghoorn, *et al.*, 1965).

The chalcocite and native copper in the shale members occur mainly as fine disseminations. Chalcocite, in addition, forms small nodular masses occurring individually or in groups strung out like beads in bedding planes. Pyrite, where present, occurs as disseminated cubes or clusters of cubes. In the sandstones the native copper and chalcocite clearly fill interstitial voids or replace minerals or detritus in the matrix.

The copper content of the orebodies in the White Pine deposit ranges between 1 and 3 per cent (Fig. 2).



*Note: numbers in parentheses refer to thickness in feet* GSC

**FIGURE 2.** Typical stratigraphic section of cupriferous zone, White Pine area, Michigan, U.S.A. (*after* White and Wright, 1954).

Silver is a trace constituent of all the copper-bearing rocks. According to White and Wright (1954) it is present mainly as the native metal. The same authors also state that native silver was mined from the top of the Lower Sandstone a little north of the White Pine area from 1872 to 1875. The silver content in the White Pine area is highest in the Parting Shale, intermediate in the Upper Shale, and lowest in the Upper Sandstone. The higher grade beds of the Parting Shale contain up to 5 oz/ton Ag. White and Wright (1954) stated that high and low silver contents are interspersed irregularly over the White Pine area, and there seems to be no particular systematic areal variation in silver content or in the ratio of silver to copper.

Two types of fracture-controlled mineralization occur in association with the copper minerals in the sedimentary layers (Carpenter, 1963). These are:

1. Fracture-filled veins mineralized with calcite, quartz, and chalcocite. Native copper, native silver, blue chalcocite, covellite, bornite, chalcopyrite, and pyrite also occur in certain veins, and according to Carpenter formed after the calcite-quartz-chalcocite assemblage.

2. Halos. These are chalcocite-bearing zones in wall-rock adjacent to the veins and symmetrical with respect to the veins. The halos are distinct from the adjacent wall-rock in that native copper is absent, and the average copper content is low. The amount of chalcocite varies systematically across the halos, decreasing outward from the veins and becoming sparse in the outer parts of the halos.

White and Wright (1954) thought that the copper (and presumably the silver and other ore elements) was derived essentially from the waters in which the beds themselves were laid down. They conjectured that precipitation of the copper on or within the mud of a foul bottom provides the simplest explanation for the apparent stratigraphic control of its occurrence. They envisaged the progressive inundation of a sand plain, with deltas of sand extending out beyond the main shoreline at the mouths of streams. The silts and shales of the Parting and Upper Shales are thought to have been deposited in the lagoons, ponds, or swamps between separate distributaries.

There is much evidence to support the sedimentary origin of the copper and other elements at White Pine. There is the intimate stratigraphic control and the fact that copper is found in practically every place where the base of the Nonesuch shale is exposed for more than 100 miles in length and 10 miles in width.

There is, likewise, considerable evidence to suggest that some of the copper and silver is epigenetic in the sense that it has been redistributed, probably from the cupriferous sedimentary layers. Carpenter (1963) has shown convincingly by means of chemical profiles that the minerals in the fractures and joints in the cupriferous horizons (the Rücken of the White Pine area) are probably of local derivation. Thus he found that, in general, a deficiency of copper and silver in the halos is compensated by their occurrence in the veins. Carpenter's statement that there is no evidence for the introduction of copper into the fractures from outside the cupriferous sequence seems amply justified when one considers his chemical and mineralogical data in detail.

The occurrences of copper (and silver) in the upper parts of the Lower and

Upper Sandstones are probably also the result of a redistribution of these elements and sulphur during diagenesis or metamorphism (Rand, 1964). Groundwaters may also have played a part. White and Wright (1954), however, think that the copper in the sandstones was introduced by hydrothermal solutions from the White Pine fault.

The arguments for an epigenetic hydrothermal (magmatic) origin for the White Pine deposit turn on the presence of the White Pine fault as the channel from which the cupriferous solutions gained access to the mineralized horizons, the epigenetic nature of some of the mineralization, and other features such as the presence of a large quartz-porphyry body within a few miles of the White Pine area. All these arguments and others have been discussed by Sales (1959). They do not sound convincing in the light of the facts presented by White and Wright (1954), White (1960), and Carpenter (1963).

### Zambian (Northern Rhodesian) Copperbelt

These famous deposits have been repeatedly described in nearly all of their aspects and are the subject of an extensive symposium edited by Mendelsohn (1961). All of the deposits produce copper and some produce cobalt and uranium as by-products. The silver content of the ores is very low as far as can be ascertained from the literature. The only silver analysis quoted in the above symposium shows that the ores of the Bwana Mkubwa area contain from a trace to 9 ppm Ag.

The cupriferous beds occur in the Katanga system whose generalized stratigraphy is given in Table 40. The rocks of the system are folded into a number of complex anticlines and synclines, and there are a few regional faults that cut the strata. Within the mines, however, there is little evidence of faulting of any major significance. Most of the rocks of the Katanga system have been affected by regional metamorphism. In the northern part of the Copperbelt the rocks fall into the greenschist facies; in the southern part, rocks belonging to the epidote-amphibolite facies are developed.

The copper deposits occur in three settings: in the Ore shale of the Ore Formation; in foot-wall (quartzite) deposits; and in quartzites and greywackes of the Mufulira syncline. The first type provides about two-thirds of the ore on the Copperbelt. Mendelsohn (1961) divided the deposits into two categories—those west of the Kafue anticline and those east of this structure. In the first category belong the Bancroft, Nchanga, Chambishi, Chibuluma, Nkana, Baluba-Muliashi, and Roan Antelope deposits. In the second are the Mufulira and Mokambo deposits.

The ore shale ranges from a true shale to an argillite with a hornfelsic texture. The main constituents are mica, quartz, feldspar, carbonate, tourmaline, chlorite, and carbonaceous material locally. The copper minerals, including chalcopyrite, bornite, and chalcocite, and the other sulphides, mainly pyrite, carrollite ($Co_2CuS_4$), and linnaeite ($Co_3S_4$), are disseminated through the rock and concentrated along bedding planes as irregular grains of similar size to the constituents of the shale. Other minerals present in small amounts are covellite, molybdenite, and scheelite. Locally uraninite and pitchblende occur, but generally only in trace amounts. The

TABLE 40 *Generalized Stratigraphy of the Katanga System (after Mendelsohn, 1961)*

GABBRO—Intrusive, commonly into the Upper Roan dolomites

| Series | Group | Formation | Rock Types (minor or rare rock types in parentheses) |
|---|---|---|---|
| KUNDELUNGU | UPPER | – | Shale, quartzite |
| | MIDDLE | – | Shale<br>Tillite |
| | LOWER | | Shale |
| | | KAKONTWE (limestone) | Dolomite and shale |
| | | TILLITE | Tillite |
| MINE | MWASHIA | – | Carbonaceous shale, argillite (dolomite and quartzite) |
| | UPPER ROAN | – | Dolomite and argillite (quartzite, breccia) |
| | | – | Argillite and quartzite |
| | LOWER ROAN | HANGING-WALL | Quartzite<br>Argillite and feldspathic quartzite (dolomite) |
| | | ORE | Argillite, impure dolomite, micaceous quartzite (greywacke, arkose) |
| | | FOOT-WALL | (Foot-wall conglomerate)<br>Argillaceous quartzite<br>Feldspathic quartzite<br>Aeolian quartzite<br>Conglomerates |

UNCONFORMITY

BASEMENT COMPLEX

paragenesis of the principal minerals is pyrite, followed by chalcopyrite, bornite, and chalcocite. There is some overlapping in the depositional sequence.

Copper is mined from the ore shale at Roan-Muliashi, Bancroft-Nchanga, Chambishi-Nkana, and elsewhere along the west side of the Kafue anticline for a distance of more than 80 miles. In the mines the shale ranges widely in its copper content, from 1.5 to 5.5 per cent, with an average of about 3 per cent. The ore shoots are great folded layers, beds, and elongated lenses that vary in width from 5 to 125 feet.

The foot-wall quartzite deposits occur west of the Kafue anticline and about

80 feet stratigraphically below the base of the Ore Formation. Those found to date occur in the central part of the Copperbelt, in or near the Chambishi-Nkana basin. The mineralization is variable. The core of the Nkana Footwall orebody contains mainly bornite with an envelope of chalcopyrite, the latter extending up the thinner east limb of the fold in which the orebody occurs. Pyrite may be present above and below the chalcopyrite. The Chibuluma orebody contains abundant chalcopyrite with bornite on the fringes and pyrite in the centre. The Chambishi orebody is mineralized mainly with bornite and chalcopyrite. At Mimbula, chalcocite (supergene?) and bornite predominate, and there is a little chalcopyrite. Cobalt is abundant at Chibuluma in the form of linnaeite and cobaltiferous pyrite. The copper grade of the orebodies is similar to those in the ore shale. The cobalt content is about 0.20 per cent. The descriptions of the foot-wall quartzite orebodies in the Copperbelt remind one of the foot-wall sandstone deposits in the Kupferschiefer and White Pine deposits.

The quartzite orebodies occur in the Mufulira syncline on the east side of the Kafue anticline. The host rock is a sericitic quartzite with carbonaceous or greywacke facies in places. These rocks are at the same stratigraphic position as the ore shale on the west side of the Kafue anticline. They may represent a near-shore more clastic facies of the ore shale. The principal copper minerals in the quartzite orebodies are chalcopyrite, bornite, and chalcocite, which are said to occur as interstitial disseminations, blebs, and irregular masses of replacive habit. The orebodies are great layers and elongated lenses that range in thickness from 20 to 75 feet. The grade is about the same as that given for the ore shale.

Much has been written about the origin of the deposits of the Copperbelt and it is apparent that the last word has not been said about the details. Garlick (1961), Brummer (1955), and others maintained that the deposits are of sedimentary origin and were later modified by metamorphism. On reading the symposium edited by Mendelsohn (1961) one is left with the general impression that most of the mine geologists on the Copperbelt support this origin. There are dissenters to the theory, however, as one can see by reading the recent criticism of the syngenetic theory by Sales (1962) and Gillson (1963).

Having reviewed the geochemical and geological aspects of the Copperbelt as well as those of other similar deposits such as the Kupferschiefer, the present writer sees no particular objections to an initial syngenetic theory later modified by migration of copper in ancient groundwaters, followed by later metamorphism. The deposits of the Copperbelt bear all of the marks of syngenetic deposits, as witnessed by the presence of organic carbon in places, and a suite of chalcophile elements that one normally finds in black shales and other reduzates. The presence of copper and other sulphides in horizons other than the ore shale and in veins simply means that the elements have undergone some migration from their initial site of deposition. This is, however, normal and on no account indicates introduction by hydrothermal solutions. In nature the simplest answer is usually the correct one, and the simplest answer in the case of the Copperbelt is that the copper was originally deposited in the sedimentary rocks under reducing conditions. Later it and other elements apparently underwent some migration in places, resulting in their concentration in horizons and sites other than those in which it was originally deposited.

It should be mentioned in passing that deposits similar to those in the Copperbelt occur in the northwestward extension of this belt in Katanga (de Kun, 1965). There the deposits occur in two dolomitic formations, which appear to be stratigraphically younger and higher than the Ore Formation in Zambia. There are few recent descriptions of these deposits, although Oosterbosch and Schuiling (1951) thought that the deposits were epigenetic. De Kun, however, ascribed a syngenetic origin to them.

### El Boléo

The famous Boléo deposits, the second largest producers of copper in Mexico, are in Baja California, near the town of Santa Rosaléa. Small amounts of silver are recovered from the blister copper. The deposits have been described in numerous papers. Among these the most comprehensive and recent are those by Touwaide (1930), Locke (1935), Wilson and Rocha (1955), and Nishihara (1957).

The Boléo copper deposits occur in the gently dipping lower Pliocene Boléo Formation, which consists of five relatively impervious, moist, soft, dark coloured clay tuff beds, each underlain by conglomerate or tuffaceous sandstone. These beds overlie the Comondú volcanic rocks of Miocene age and are overlain unconformably by sediments of Pliocene and Pleistocene age. The Boléo Formation is generally considered to have originated by deltaic deposition along a marine shoreline.

The Comondú volcanic rocks were faulted and tilted before the deposition of the Boléo Formation. The latter was cut by many faults in échelon systems near the close of the Pliocene.

Each of the copper-bearing beds averages about 2 feet in thickness and is composed principally of montmorillonite, manganese and iron oxides, and small amounts of gypsum, calcite, chalcedony, and jasper. The principal primary copper mineral is chalcocite, with subordinate amounts of chalcopyrite, bornite, covellite, and native copper. Small amounts of pyrite occur locally, and galena has been observed in some of the beds. Primary zinc minerals have not been identified despite the presence of considerable amounts of zinc in the ore. In the oxidized zones there is a veritable host of supergene minerals, including various oxides, carbonates, silicates, and oxychlorides of copper, lead, iron, manganese, and to a lesser extent of silver, zinc, and cobalt. Among these the most common are probably chrysocolla, azurite, malachite, atacamite, wad, limonite, cuprite, anglesite, cerussite, phosgenite, and pyromorphite. Rare minerals include the silver-bearing copper oxychloride, boleite, and pseudoboleite, cumengite, and cobaltiferous smithsonite.

The chalcocite occurs as small crystals and disseminated grains scattered through the clay tuff matrix giving it a sooty-black to dusky-blue appearance. According to Wilson and Rocha (1955), the chalcocite replaces the tuff, and in places veinlets of the mineral cut across the laminations of the tuff. Touwaide (1930) found that chalcopyrite, bornite, and covellite replaced chalcocite and that chalcopyrite also replaced bornite in places. Some later chalcocite replaces chalcopyrite and bornite.

The copper ore is concentrated in narrow elongated lenses or ribs that are more or less parallel and separated from one another by other ribs of lower grade ore. The high-grade ribs contain up to 10 per cent copper, the intervening lower grade ribs average 2 per cent copper or less.

An average analysis of the Boléo copper ore is given in Table 41. Of particular interest are the relatively large amounts of manganese, iron, chlorine, carbon, zinc, and other chalcophile elements.

TABLE 41 | *Average Analysis of Boléo Copper Ore*

| Element | Average amount % |
|---|---|
| Si | 13.67 |
| Mn | 6.54 |
| Fe | 6.43 |
| Cu | 4.86 |
| Al | 4.06 |
| H | 2.60 |
| Ca | 2.55 |
| S | 2.13 |
| Mg | 1.77 |
| Cl | 1.35 |
| Na | 0.93 |
| K | 0.88 |
| Zn | 0.81 |
| C | 0.72 |
| Ti | 0.28 |
| Co | 0.12 |
| Pb | 0.06 |
| Ni | 0.04 |
| P | 0.03 |
| As | 0.03 |
| Sb | 0.02 |
| Sr | 0.0X |
| Ba | 0.0X |
| V | 0.0X |
| Mo | $< 0.01$ |
| Zr | 0.00X |
| Y | 0.00X |
| Ag | 0.0009 |
| Cr | 0.000X |
| Be | 0.000X |
| Au | $< 2 \times 10^{-5}$ |

Analysis from Wilson and Rocha (1955)

Manganese occurs throughout the ore in various oxides, mainly cryptomelane and pyrolusite. In fact, some of the beds represent low-grade manganese ores. Iron oxides, mainly hematite and limonite, are also common in the ore beds. Chlorine is present in sodium chloride, which occurs in amounts up to 6.40 per cent and averages 2.20 per cent. Free carbon, combined in carbonaceous matter, is variable, ranging in amount from 0.12 to 3 per cent with an average of about 0.25 per cent. Zinc is widespread throughout the ore beds, and as in the Kupferschiefer tends to be concentrated in the upper parts of the beds. Cobalt is also markedly concentrated in some of the beds as in the Zambian deposits. The silver content is low in all of the ore beds. It ranges from 7 to 12 ppm and averages 9 ppm (0.28 oz/ton).

The mode of origin of the Boléo deposits has been a much debated question. Early investigators pronounced the deposits to be of sedimentary origin. Later Touwaide (1930) maintained that the copper was leached from the overlying rocks and was carried downward in descending groundwaters and precipitated in the receptive tuff beds. Wilson and Rocha (1955) proposed a hydrothermal origin for the deposits, stating that the copper solutions rose from depth along faults and fractures in the Comondú volcanic rocks, spread laterally through the porous beds of the Boléo Formation, and precipitated their copper and other elemental constituents in five favourable tuff beds. Pélissonnier (1965) advanced the hypothesis that the copper was of hydrothermal origin, and was delivered during tectonic subsidence through the faults of the district to the basin of deposition now occupied by the cupriferous beds.

The Boléo deposits, in the writer's opinion, bear the stamp of typical sedimentary deposits. The presence of abundant manganese and iron oxides, sodium chloride, organic matter, etc. cannot be ignored. Practically all the features of the deposits can be explained by a sedimentary hypothesis. The most probable origin of the copper and other elements seems to have been thermal springs associated with volcanism, a source suggested by several other investigators who have commented on the deposits. Normal weathering processes acting on volcanic debris may also have been a contributing factor. Whatever was the source of the elements, the concentration took place partly under oxidizing conditions (manganese oxides) and partly under reducing conditions (chalcocite). Bacteria working in the foul muds of a volcanic basin probably provide the answer to the precipitation of copper as the sulphide. The same process of concentration has been repeated five or more times, a feature which is apparently normal in volcanic sedimentary environments.

### Creta Area, Oklahoma

The cupriferous shales recently described by Ham and Johnson (1964) in the Creta area, Jackson county, Oklahoma, appear to belong in the category of the 'copper shales'.

Two cupriferous shale beds are recognized, one "the lower copper bed" is 6 inches thick and has a copper content ranging from 2.65 to 4.45 per cent and averaging about 3.8 per cent, the other "the upper copper bed" has little economic potential because its copper content ranges only from 0.38 to 1.27 per cent, averaging about 0.8 per cent. The silver content of the lower bed is about 1 ppm. Cobalt is enriched over nickel, the amounts being 200 and 50 ppm respectively. There is twice as much boron in the lower copper bed as in the other shale beds of the district.

The flat-lying, undisturbed, cupriferous shale beds occur in the upper part of the Flowerpot Shale of Medial Permian age. The principal primary copper mineral is $\alpha$ (low temperature) chalcocite, which is set in a greenish grey shale matrix. At the surface the chalcocite is altered to malachite and brochantite.

Ham and Johnson (1964) postulated a sedimentary origin for the copper in the shale beds, supporting their view by the facts that illite with a high boron content is common in the cupriferous beds, and that this mineral is diagnostic of marine deposition where the salinities are relatively high. They further pointed out that the rocks are undisturbed by faults and that the known igneous rocks in the area are much older than the cupriferous beds.

### Redstone River Area, N.W.T.[1]

These deposits have been recently discovered and are now at the exploration stage. They are bedded deposits confined to certain stratigraphic horizons. Seven mineralized silty limestone and siltstone beds ranging from 6 inches to 15 feet in thickness occur in a sequence of sediments thought to be of Late Precambrian or Early Cambrian age. These beds, occurring one above the other, are referred to as the "Copper Formation" and have been traced along strike for more than 3 miles. Drilling along part of the formation for 1,100 feet revealed an average grade of about 2.5 per cent copper over an average width of 5 feet. The silver content is low, averaging about 10 ppm (0.3 oz/ton). In one part of the formation 0.12 per cent cobalt was found in massive sulphides.

The principal ore minerals in the mineralized calcareous beds are chalcopyrite, bornite, and chalcocite. Fine-grained disseminated pyrite is present in some beds, and galena has been recognized in the bottom bed. The chalcopyrite is the most abundant copper sulphide. It occurs as disseminated grains often elongated perpendicular to the bedding. Locally, stringers of massive chalcopyrite occur parallel to and crosscutting the bedding. Pyrite and copper minerals appear to be mutually exclusive, there being no pyrite where copper minerals are most abundant and only a few copper minerals where pyrite is dominant. Much of the silver appears to be associated with the bornite. Minerals near the surface include limonite, malachite, and azurite.

The company geologists maintain that the deposit is essentially syngenetic. Later remobilization of the copper and other elements in the "Copper Formation" effected local enrichments in places.

## Sandstone Deposits—'Red Bed' Type

In general this category includes a number of important bedded and vein type copper, lead, silver, vanadium, and uranium deposits in many parts of the world. We shall, however, confine our description to generalities, and essentially to those deposits containing silver. In the general category, however, belong the numerous uranium-vanadium-copper deposits of Texas, Oklahoma, New Mexico, Arizona, Colorado, Wyoming, Utah, and Idaho; the Silver Reef deposits in Utah; the num-

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[1] Compiled from data and reports kindly provided by J.A. Harquail, President, Redstone Mines Ltd., Toronto.

TABLE 42 | *Characteristics of the 'Red Bed' Sandstone Deposits*

| Country and location | Rock types and age | Form of deposits | Primary ore minerals and gangue |
|---|---|---|---|
| *Canada*: New Brunswick Dorchester, New Horton Goshen | Relatively flat lying Carboniferous arkose, grit, conglomerate, and sandstone | Disseminated lenses and layers, nodules, replaced plant fragments. Irregular veins | Chalcocite, bornite, pyrite. No gangue |
| *Canada*: Nova Scotia | Relatively flat lying Carboniferous grit, sandstone, and conglomerate | Disseminated lenses and layers, nodules, replaced plant fragments. Irregular veins | Chalcocite, bornite, pyrite. No gangue |
| *Canada*: Walton, Nova Scotia | Carboniferous sandstones, shales, limestone, and evaporites | Raking pipe-like deposit in brecciated zone. Small disseminated zones with replaced plant fragments | Barite, pyrite, chalcopyrite, galena, sphalerite, tennantite, proustite, siderite, hematite |
| *Canada*: Nova Scotia, Salmon River, Cape Breton Island | Gently dipping Carboniferous sandstones | Lenses and layers of disseminated galena | Galena, pyrite, minor barite |
| *Southwestern U.S.A.*: Texas, Oklahoma, New Mexico, Arizona, Colorado, Wyoming, Utah, and Idaho | Arkosic sandstone, conglomerate and shale of Permo-Carboniferous, Triassic, Jurassic or Tertiary age | Lenses and layers of disseminated ore minerals, nodules, replaced plant fragments. Irregular veins | Chalcocite, bornite, chalcopyrite, covellite, pyrite, uraninite; silver sulphides at Silver Reef, Utah |
| *U.S.A.*: New Jersey (Newark Series) | Triassic sandstones and shales. Extrusive basalt and intrusive diabase sills | Lenses and irregular bodies of disseminated ore minerals near faults and fractures | Native copper, chalcocite, bornite, chalcopyrite, pyrite |
| *U.S.A.*: Michigan | Precambrian Copper Harbour conglomerate and sandstone and Nonesuch shale and sandstone | Irregular tabular lenses mainly in sandstone. Disseminations in sandstone | Native silver, native copper, solid hydrocarbons, chalcocite, etc. |
| *U.S.A.*: Colorado. Cashin mine, Montrose county | Jurassic flat-lying sandstones and shales | Pods and lenses in fissure cutting La Plata sandstone | Argentiferous chalcocite, covellite, bornite, native copper, argentite, native silver, kaolin, calcite, and barite |
| *U.S.A.*: Wyoming Silver Cliff mine, Lusk | Gently dipping Cambrian (?) calcareous sandstone | Pods and irregular replacement deposits along a fault zone | Native silver, chalcocite, and pitchblende. Calcite is the principal gangue. There is also some clinozoisite |
| *U.S.A.*: Emery county, Utah | Near base of Shinarump conglomerate<br>Upper Triassic conglomerate and sandstones | Lenses and tabular bodies of mineralized sandstone, conglomerate, and shale. Numerous fossil trees and plant fragments | Uraniferous asphalt and woody fragments |

erous copper deposits in the Carboniferous sandstones of New Brunswick and Nova Scotia; the barite-lead-zinc-copper-silver deposit near Walton, Nova Scotia; the lead deposit in the Salmon River area, Cape Breton Island, Nova Scotia; the lead deposits of Laisvall and other areas in Sweden; the copper deposits of Corocoro, Bolivia; the Cu-Ag deposits at Negra Huanusha, central Peru (Kobe, 1960); the copper-lead deposits of Alderly Edge, near Manchester, England; the lead deposits of the Kaller Stollen–Maubach area in Germany; and the extensive copper sandstone deposits of Dzhezkazgan, Kazakhstan, U.S.S.R. (Narkelyun, 1962). The general details of these and other deposits are given in Table 42.

TABLE 42

| Secondary ore minerals | Grade and tonnage | Reference | Remarks |
|---|---|---|---|
| Malachite, azurite | Cu — 0.5 – 5%<br>Ag — 0.5 – 2.0 ppm | Papenfus (1931);<br>Brummer (1958);<br>Smith (1960, 1963) | Not economic. Dorchester deposit was mined in the past |
| Malachite, azurite | Cu — 0.5 – 1.0%<br>Ag — 0.5 – 2.0 ppm | Papenfus (1931);<br>Brummer (1958) | Not economic |
| Manganese oxides, malachite, azurite, limonite, cobalt sulphates | Pb — 5 – 25%<br>Zn — 1 – 20%<br>Cu — 0.5 – 5%<br>Ag — 20 oz/ton | Boyle (1963a) | Economic for barite, lead, zinc, copper, and silver |
| None | Pb — 1 – 4.5%<br>Ag — 1.5 ppm<br>Large tonnage | Carter (1965) | Exploration stage |
| Malachite, azurite, carnotite, autunite; cerargyrite at Silver Reef, Utah | Variable Ag content generally low in most deposits. Ag content at Silver Reef, Utah averaged 20 oz/ton | Proctor (1953);<br>Wyman (1960);<br>Fischer and Stewart (1961) | Economic uranium and vanadium deposits. Generally uneconomic for copper. The Silver Reef deposits were economic for silver and uranium |
| Malachite, azurite, brochantite, chrysocolla, cuprite, tenorite, and secondary native copper and chalcocite | Low grade. Ag content very low | Woodward (1944) | Not economic. Some of the deposits contain small amounts of uraninite and other uranium minerals |
| | Ag content highly variable, assays from 1 oz Ag/ton to 70 oz Ag/ton or greater recorded | Rominger (1876);<br>Nishio (1919);<br>White and Wright (1954) | Mined for silver prior to 1900 (*see also* description of White Pine mine) |
| Azurite, malachite, cuprite, iron sulphate, argentite, native silver | Very high grade copper and silver, but small ore shoots. Some assays show up to 512 oz Ag/ton | Emmons, W.H. (1905) | Exhausted. Worked for copper and silver |
| Malachite, azurite, cuprite, native copper, chrysocolla, limonite, gummite, uranophane, metatorbernite | High grade silver and low grade uranium deposit | Wilmarth and Johnson (1954) | Silver ore shoots exhausted |
| Autunite (?), gummite (?), carnotite, malachite, azurite, chrysocolla, cobalt bloom, native sulphur | Ag uniformly distributed throughout uraniferous zones.<br>Ag 0.44 – 1.64 oz/ton<br>Ag (average) 0.70 oz/ton | Reyner (1950) | |

Deposits of the so called ‘red bed’ type fall essentially into three categories—the copper-silver sandstones, the uranium-copper-vanadium sandstones, and the lead-zinc sandstones. In some areas gradations between the three varieties are known. Vein type deposits are associated with the bedded deposits in some areas. All deposits occur in sediments generally far from igneous rocks which could logically have supplied their constituent elements via hydrothermal solutions.

The ores are generally low grade (*see* Table 42), but the available tonnages are usually large. The mineralogy of the deposits is varied and depends on the type of deposit. In the bedded copper-silver deposits the principal economic minerals are

TABLE 42 | *Characteristics of the 'Red Bed' Sandstone Deposits (cont'd)*

| Country and location | Rock types and age | Form of deposits | Primary ore minerals and gangue |
|---|---|---|---|
| *England*: Alderly Edge | Relatively flat lying Triassic sandstones and conglomerates | Lenses and irregular bodies of disseminated ore minerals. Irregular veins | Chalcocite, chalcopyrite, bornite, pyrite, galena, barite, manganese oxides, cobalt minerals |
| *Germany*: Maubach-Kaller Stollen area | Mesozoic flat-lying Bunter sandstone and conglomerate | Layers, lenses, and irregular bodies of disseminated ore minerals. Irregular veinlets | Galena, sphalerite, nickeliferous pyrite, pyrite, chalcopyrite, boulangerite, tetrahedrite, linnaeite. "Knotten" of galena are characteristic. Veinlets of barite and chalcopyrite |
| *Sweden*: Laisvall, Maiva, Dorotea, and Vassbo | Horizontal Cambrian quartzites and quartzitic sandstones | Layers, lenses, and elongate bodies of disseminated ore minerals | Galena, sphalerite, pyrite, calcite, barite, fluorite |
| *Norway*: Dalane area | Folded and metamorphosed Precambrian quartzites and conglomerates with associated greenstones and quartz porphyries | Impregnation zones in quartzite near contact of younger greenstone | Native copper, native silver, cuprite, calcite |
| *Europe*: Various countries, particularly U.S.S.R. | Permian and Triassic sandstones, shales, and conglomerates | Layers, lenses, irregular bodies of disseminated minerals | Chalcocite, bornite, chalcopyrite, barite |
| *U.S.S.R.*: Kazakhstan, Dzhezkazgan area | Permo-Carboniferous sandstones, siltstones, argillites, minor thin limestone and flintstone. Abundant plant remains. Eight ore-bearing horizons are present | Beds, layers, sheets, seams, blankets, lenses, ribbons, and irregular bodies of disseminated ore minerals; also veins. Veins are not economic | Chalcocite, bornite, chalcopyrite, pyrite, domeykite, tetrahedrite, galena, sphalerite, molybdenite, betechtinite, arsenopyrite, native copper, native silver; minor barite, calcite, etc. |
| *Bolivia*: Corocoro | Steeply dipping, faulted Tertiary sandstones and conglomerates | Lenses, elongated lenses, and beds of disseminated ore minerals | Chalcocite, native copper, galena, native silver, domeykite, pyrite, chalcopyrite |
| *China*: Yunnan | Folded Mesozoic sandstones and shales | Lenses, layers, beds, and irregular bodies of disseminated ore minerals; also veins | Chalcocite, bornite, chalcopyrite, pyrite; minor calcite, quartz, and barite. Chalcopyrite, Co-bearing tennantite, barite, and siderite in veins |

chalcocite, bornite, chalcopyrite, domekyite, native copper, native silver, chlorargyrite, azurite, and malachite. Similar copper and silver minerals occur in some of the copper-uranium-vanadium deposits, and there are in addition, uraninite, carnotite, vanadinite, and a host of other uranium, vanadium, and copper minerals, many of supergene derivation. The bedded lead-zinc sandstones contain essentially galena and sphalerite with cerussite, pyromorphite, and anglesite in the zones of oxidation. Gangue minerals are sparse in most of the bedded deposits, but some barite, calcite, fluorite, and gypsum may occur. Pyrite and marcasite are found in nearly all of the deposits, in variable amounts. Outcrops of the copper and uranium types are generally marked by blooms of azurite, malachite, and the various secondary uranium

TABLE 42

| Secondary ore minerals | Grade and tonnage | Reference | Remarks |
|---|---|---|---|
| Malachite, azurite, pyromorphite, anglesite, vanadinite, mottramite, cerussite, asbolite | Low grade.<br>Cu — 1.5 – 2.0%<br>Ag very low.<br>Ni and Co present | Warrington (1965) | Exhausted. Lead ore contained from 0.09 to 7.5 oz Ag/ton |
| Malachite, cerussite, pyromorphite, anglesite, etc. | Pb — 1 – 3%<br>Zn — 1.5%<br>Ag — 3.5 ppm<br>Relatively large tonnages | Behrend (1950);<br>Fritzsche (1951);<br>Schachner (1958) | Economic |
| | Pb — 4%<br>Ag — 10 ppm<br>50,000,000 tons | Grip (1960) | Economic |
| | 2.6 to 6.7 parts Ag per 100 parts copper | Neumann (1944a) | Mined for copper and silver prior to 1917 |
| Malachite, vanadinite, azurite, volborthite, etc. | Cu — 0.5 – 1.0% | | Generally not economic |
| Malachite, azurite, native silver, native copper | Cu — 1.0 – 3.5% (?)<br>Large tonnages.<br>Ag follows copper and is present mainly in chalcocite | Narkelyun (1962);<br>Davidson (1962, 1965) | One of main sources of copper in U.S.S.R.; deposits also produce lead, silver, and some zinc. Narkelyun considers the bedded deposits to be of sedimentary origin later modified by diagenesis, others think an epigenetic origin more likely. Narkelyun concludes that the veins are of secretion origin |
| Malachite, azurite | Cu — 3 – 5% or higher<br>Ag — 7 – 16 ppm<br>Large tonnages | Ljunggren and Meyer (1964); Berton (1937) | Economic. Continued development work. Local concentrations of native silver (Singewald, 1933) |
| Malachite | No data. Chalcocite and other copper minerals contain traces to small amounts of silver and gold | Li *et al.* (1964) | At exploration stage. Li *et al.* consider that the deposits are essentially sedimentary, later modified by post-depositional processes. The veins are thought to owe their origin to secretion processes |

and vanadium minerals. The lead-zinc sandstones and quartzites are extremely difficult to recognize in outcrop since they rarely exhibit any marked blooms, iron stain, or other distinguishing features.

The vein type deposits and irregular lenses in faults and fractures may contain all the minerals present in the bedded deposits, in addition to argentite, tennantite-tetrahedrite, stromeyerite, native silver, betechtinite, hematite, gypsum, celestite, and abundant galena and sphalerite. Barite is a major mineral in some areas. The main gangue is calcite and siderite; quartz is usually rare.

The elements enriched in the various types of deposits include the following: Cu, Ag, Pb, Zn, Cd, Fe, Mn, Co, Ni, U, V, Cr, P, Mo, Re, Bi, As, Sb, Se, S, Ba, Cl, and F. A number of these elements may be only slightly enriched or lacking in individual deposits. In the bedded deposits silver generally occurs in the native state or as a constituent of chalcocite, chalcopyrite, galena, and native copper, and, in certain rare cases, of tetrahedrite. The galena is generally silver-poor and rarely contains more than 150 ppm Ag. In the vein-type deposits silver occurs in the native form, in argentiferous galena, argentite, stromeyerite, betechtinite, tetrahedrite-tennantite, proustite, pyrargyrite, and a variety of other rare sulphosalts. In the oxidized zones of the various deposits chlorargyrite and native silver may be present in economic quantities as at Silver Reef, Utah.

In some of the bedded deposits silver follows copper closely, and there is a parallel enrichment of the two elements. In other bedded deposits silver seems to follow lead and zinc, although the relationships are not always obvious. The relationships in the vein-type deposits differ; in some silver follows lead and antimony or arsenic, in others the element follows copper.

In most of the Dzhezkazgan deposits (Narkelyun, 1962) there is a vertical zonation of the metals. At the bottom of the orebodies copper is the most abundant element and this in turn grades upward into ores high in lead followed by those high in zinc. Silver is strongly enriched in the copper ores, less so in the lead ores, and only weakly in the sphalerite ores. It will be noted that this distribution is the same as that found in the Kupferschiefer ores (Fig. 1). In the Dzhezkazgan ores, silver is concentrated in the highest amounts in chalcocite with diminishing amounts in bornite and chalcopyrite, respectively. According to Narkelyun most of the silver is present in the native state. Compared to the primary ores silver is present in smaller amounts in the oxidized zones and in much larger amounts in the zone of secondary sulphide enrichment.

The deposits invariably occur in sandstones, arkosic sandstones, grits, microconglomerates, conglomerates, or in associated shales. These rocks are generally part of a thick series of continental terrigenous or shallow-water sediments (molassic-type facies). According to Fischer and Stewart (1961), most of the copper deposits of the 'red bed' type in the United States are in first-generation sandstones, vanadium deposits are mainly in second-generation sandstones, and uranium deposits occur in sandstones of both first and second generation origin. Judging from the literature and the writer's experience some of the lead-zinc deposits are in first-generation sandstones, and others seem to be in second-generation sandstones and conglomerates.

While most of the deposits occur in relatively unmetamorphosed sediments there are examples in highly folded metamorphic terrains, e.g. Laisvall, Sweden; Dalane, Norway; and those in the Udokanian Series, U.S.S.R.

In age the sediments containing the deposits range from Precambrian to Tertiary. Most deposits occur, however, in rocks of Permo-Carboniferous and Triassic age.

The nature of the sediments (viz., channelling, crossbedding, etc.) in most cases suggests an environment of rapid clastic sedimentation on extensive flood plains coursed by numerous meandering streams that migrated from channel to channel. The location of the flood plains has long been a matter of much debate.

From the distribution of the sediments some appear to have covered vast stretches of country and must have bordered on shallow inland seas or large lakes. Others, such as those on which some of the Mississippian and Pennsylvanian sandstones in Nova Scotia were laid down, appear to have occupied wide intermontane valleys and received sediment from a variety of granitic and metamorphic rocks. Still other sandstones in this category are obviously deltaic deposits formed at the mouths of great river systems in inland seas or lakes. All appear to be near-shore shallow-water facies, as witnessed by the nearly universal occurrence in them of carbonized logs, leaves, and other plant remains. Finch (1964) concluded that the continental sediments containing the 'red bed' deposits in the United States nearly all accumulated in shallow, poorly drained foreland or post-orogenic basins.

The great bulk of the sandstones, shales, microconglomerates, etc. are frequently of reddish colour, contain a large amount of ferric oxide and apparently formed in an environment where the oxidation potential was high. Black schists and shales of terrestrial origin may occur in some of the sedimentary sequences.

Most of the deposits consist of lenses, layers, irregular bodies, amoeba-shaped bodies, and streaks of ore minerals either disseminated or in the form of knots, nodules, aggregates, concretions, or plates. Most of the deposits occur in channels, near or in structural rolls, in porous crossbedded zones, in porous sandstone lenses, in porous conglomeratic zones, in structural and sedimentary pinch-outs in porous beds below shale beds, in crushed zones, or in faulted and fractured zones. Some deposits are found in strata rich in plant remains, and the chalcocite and other minerals may replace the plant remains in the greatest detail. In other deposits the minerals replace the cement of the sandstone or simply fill the porous parts of sandstone lenses and sandy beds. A few deposits are veins and irregular lenses that occupy faults, fractures, diatremes, breccia pipes, or zones of structural disturbance. A number of the deposits exhibit a relationship to faults of small displacement and to fracture zones in that the ore minerals spread out laterally through favourable beds from these structures.

Nearly all the deposits exhibit evidence of epigenetic deposition. While the deposits may be confined to certain members or formations they are seldom restricted to individual beds and rarely show the characteristics of having been deposited during sedimentation processes.

Many of the deposits occur in bleached, green, or greyish sandstones, microconglomerates, or conglomerates despite the fact that they are commonly referred to as the 'red bed' type. In most deposits the bleaching and the greyish or greenish colour is due to a reduction and sometimes leaching of the ferric oxide, apparently by the solutions that deposited the ore minerals. The light colour often crosses bedding planes and spreads out from fractures and jointed areas. In some deposits the bleached zones are mildly silicified, and there is sometimes a development of sericite, kaolinite, or other type of white mica in the sandstone.

A great many of the bedded deposits are too low grade at present to be economically exploited. The economic copper deposits average about 3 per cent Cu and the lead-zinc varieties about 3.5 to 4 per cent Pb. The uranium-vanadium deposits generally have a variable and often erratic grade but rarely exceed 1 per cent $U_3O_8$. The silver content of nearly all of the bedded copper and lead-zinc deposits is low and usually makes little difference to the value of the ore. A few bedded deposits, however, such as those at Silver Reef, Utah, and Brush Creek, Colorado (Hess, 1933), are greatly enriched in silver.

The vein-type deposits and irregular lenses in faults are relatively high grade, but their tonnage is generally small. Some of the deposits such as the one at Walton, Nova Scotia, yield much barite, lead, zinc, copper, and silver.

The Silver Reef and Walton deposits are characteristic examples, respectively, of the bedded and irregular lens-type deposits in which silver is concentrated in economic amounts. They are described briefly below.

The silver deposits of Silver Reef, Utah, now exhausted, have been described by Hess (1933), Proctor (1953), and Wyman (1960). The orebodies were restricted to the Silver Reef sandstone of the Upper Triassic Chinle Formation and occurred on the limbs and nose of a major anticline and a subsidiary anticline and syncline. Recent basalts cover the sandstones in places. Proctor stated that there was no constant relationship between the orebodies and folds or faults, but Wyman disagreed, claiming that many of the orebodies occurred on an anticline and were localized underneath clay beds, and in highly fractured zones, especially near faults of small displacement.

The ore shoots were noted for their irregularity both in shape and grade of ore. Some shoots were dish-shaped or elongate lenses in plan; others are amoeba-like and highly irregular in plan. The shoots ranged from a few feet in diameter to bodies several hundred feet in length and a hundred or more feet wide. In thickness they varied from thin plates to zones as much as 20 feet thick. Some ore shoots ended abruptly, others graded imperceptibly into the sandstone. The grade of the ore was extremely variable—some zones contained hundreds of ounces of silver to the ton, others only a few ounces. The average grade of the ore was about 20 ounces to the ton.

Most of the silver occurred as chlorargyrite in the near surface shoots. At greater depth silver sulphide was reported. Malachite and azurite in some places were associated with the chlorargyrite but mainly were found separate. The silver sulphide at and below the water-table was commonly associated with fossil trees, which also contained chalcocite and pyrite. In recent years uranium was mined from the Silver Reef sandstone. While details are lacking in the descriptions, it is apparent that near the surface the minerals were mainly the secondary uranium-vanadium types and at depth unoxidized black uranium minerals (uraninite?). The uranium and vanadium minerals in some places were closely associated in stratigraphic position with the silver and copper minerals. In other places the relationship was less intimate. Wyman mentioned a zoning in the Big Hill mine that was related to an area of strong fractures of small displacement as follows: a central zone of high-grade uranium and much limonite surrounded by a zone of silver-bearing uranium ore. Farther out and surrounding this, there was a broad area of silver ore with little or no uranium, and this gradually decreased in grade to an economic limit. There was some increase in the copper content in the peripheral area.

Proctor distinguished four important varieties of silver ore and a minor fifth one as follows:

1. Small fossil plant and large tree replacements by chlorargyrite in buff to white fine-grained sandstones. At depth silver sulphide occurred in the fossil tree remains. Iron oxide nodules, pseudomorphic after pyrite, and chalcocite nodules also occurred with the plant remains.

2. Disseminated specks and thin plates of chlorargyrite parallel to the bedding planes. Rare native silver accompanied the chlorargyrite in places.

3. Chlorargyrite associated with clay gall and clay ball conglomerates.

4. Streaks and small grains of chlorargyrite in sheared lavender to brownish red sandstone.

5. Chlorargyrite films and occasionally some native silver on slickensides within the shales.

The origin of the Silver Reef deposits has long been an enigma. Some early investigators thought that the deposits were strictly syngenetic and formed contemporaneous with the strata. Later it was recognized by many, and it is now generally accepted, that the deposits in their present form are epigenetic. The source of the silver (and the other elements) is now the principal point of contention.

Proctor (1953) hypothesized that the silver came from underlying Triassic volcanic tuffs (bentonites) and was transported as a sulphate into plant-bearing zones, in the Silver Reef sandstones. There the silver sulphate was reduced to silver sulphide by the generation of hydrogen sulphide through bacterial action on the vegetation or by the direct or indirect action of sulphate reducing bacteria associated with the plant remains. In some places adsorption on clay galls or on finely divided carbonaceous particles may also have been effective in localizing the minerals. Pyrite appears to have been one of the first minerals to form, and hence it may have acted as a precipitant of chalcocite and other sulphide minerals. With uplift and erosion of the area the pyrite and other sulphides underwent oxidation, their constituents were taken into solution, carried downward and reprecipitated in favourable porous zones and around plant remains. The principal silver mineral formed during this secondary enrichment process was chlorargyrite, the silver chloride.

Wyman (1960) doubted this hypothesis as regards the source of the silver and other elements. He felt that the silver and other elements had a hypogene origin and related the ore-bearing solutions to igneous activity that manifests itself in the form of an igneous mass some 6 miles distant from the deposits. Stugard (1952) also related the deposits to hydrothermal solutions arising from trachyte porphyry that occurs as a laccolithic body nearby.

The barite-lead-zinc-copper-silver deposit in the Walton area of Nova Scotia has been described by the writer (Boyle, 1963a). The deposit is a large raking pipe-like mass of barite with associated sulphides, localized in a complex breccia zone between intersecting faults that cut through sedimentary rocks of Early Carboniferous age. The barite and sulphides formed by fracture-filling and replacement of fissile limestone, limestone-conglomerate, and their underlying sandstones and shales. In the general area there are small plant-bearing zones in the sandstones enriched in copper and silver near faults and fractures with small displacements. None of these, however, is of economic interest.

The geological setting of the Walton deposit suggests that it belongs to the 'red bed' type of deposit, although it is unique in that it contains a large tonnage of barite and has a somewhat different sulphide mineralogy. Nevertheless the elements concentrated in the deposit are those generally found in 'red bed' deposits and it appears to combine the features of the lead-zinc and copper-silver types.

The rock formations in the Walton area are given in Table 43. The Cheverie Formation is a typical 'red bed' series overlain by marine limestones and evaporites. The Horton Bluff Formation is also of terrestrial and estuarine origin and is interesting in that it contains an upper member composed in part of black pyritiferous shales and argillites that have higher than normal concentrations of copper, lead, zinc, arsenic, antimony, silver, cobalt, and nickel. Barium and strontium, likewise, are relatively enriched in these rocks as well as in the various sandstones, shales, etc. of the other formations.

The Horton Bluff rocks are intricately folded, but the sandstones and shales of the Cheverie Formation are only gently flexed. The Triassic sandstones and conglomerates that overlie the Carboniferous rocks in places are nearly flat lying. All rocks in the area are cut by innumerable faults, some of which show sizable displacements. The only evidence of igneous activity in the area is the presence of two highly faulted diabasic sills some 6 miles west of the deposit.

The surface plan of the barite part of the deposit (Fig. 3) is a pear-shaped lens that becomes elongated and rather irregular at depth. In longitudinal section, it is a pipe-like mass that rakes about 35 degrees to the east. Vertical sections of the mass exhibit a lens-like shape with protuberances on the upper and lower extensions that interfinger with the enclosing sediments. The sulphide body did not outcrop, its highest point being about 250 feet from the surface. In detail, it is an irregular lens that lies in the foot-wall of the barite orebody and is particularly well developed where the barite in plan curves southward into the foot-wall sediments.

The structure in the vicinity of the deposit is exceedingly complex. The dominating feature is a predominant east-west fault zone with an approximate dip of 70 degrees to the north. This fault lies in the foot-wall of the barite mass, and is joined by another that strikes northwest and marks the approximate position of the hanging-wall of the barite. Both faults, particularly the foot-wall one, are marked by extensive brecciation over several tens of feet. The age of the foot-wall and hanging-wall fault zones is pre-ore, but there was also much post-ore movement, resulting in brecciation of the barite and sulphides. In addition to these two faults there are numerous others, which represent a stage of severe block-faulting. The age of these faults, like the other two mentioned above, is both pre- and post-ore.

The evidence from surface and underground mapping indicates that the barite pipe was localized by the hanging-wall and foot-wall faults, whose intersection rakes 35 degrees to the east. Between these faults, the evaporites, the Macumber, the Pembroke, and the upper part of the Cheverie Formation were probably highly

**TABLE 43** *Table of Formations*[1], *Walton Area, Nova Scotia*

| Era | Period or Epoch | Group | Formation | Lithology |
|---|---|---|---|---|
| Cenozoic | Recent and Pleistocene (0–75 feet) | | | Soil, till, gravel, sand, tidal alluvium |
| | | | Unconformity | |
| Mesozoic | Triassic | Fundy | | Gabbro, diabase |
| | | | Wolfville | Red conglomerate, sandstone, minor red shale |
| | | | Unconformity | |
| Palaeozoic | Mississippian | Windsor | Undivided (1,500+ feet) | Limestone, dolomite, shale, sandstone |
| | | | Tennycape (± 600 feet) | Red and greenish sandy shale and siltstone, minor gypsum and anhydrite |
| | | | Evaporite (± 125 feet) | Anhydrite, gypsum, calcareous and petroliferous shales |
| | | | Pembroke (0–100 feet) | Limestone-conglomerate, limestone, minor shale |
| | | | Macumber (0–25 feet) | Fissile limestone, minor shale |
| | | | Conformity or disconformity (?) | |
| | | Horton | Cheverie (± 1,000 feet) | Red and grey arkosic and feldspathic conglomerate, red and grey sandstone, arkose, shale, siltstone |
| | | | Unconformity | |
| | | | Horton Bluff (± 3,500 feet) | Quartzitic sandstone, siltstone, shale, ferruginous limestone, feldspathic conglomerate |

[1] Adapted from Bell, W.A. (1960): Mississippian Horton Group of type Windsor-Horton district, Nova Scotia; Geol. Surv. Can., Mem. 314

contorted and dragged, and this composite dilatant zone was replaced and partly infilled by barite. The sulphide orebody lies mainly within the brecciated zone created by the foot-wall fault. It represents replacement and fracture filling of a dilatant zone in Pembroke and Macumber limestone and underlying Cheverie sandstone, quartzite, and shale.

The principal primary mineral in the Walton deposit is barite, which is accompanied by small amounts of siderite, dolomite, and hematite. In the sulphide deposit the main primary minerals are siderite, galena, sphalerite, nickelian and cobaltian pyrite, bravoite, marcasite, tennantite, proustite, chalcopyrite, bornite, acanthite, gersdorffite, and barite. Supergene minerals include pyrolusite, psilomelane, manganite, secondary hematite, secondary barite, limonite, chalcocite, malachite, azurite, calcite, and two new cobalt sulphates, moorhouseite and aplowite.

Field observations suggest that most of the barite mineralization preceded the sulphides. This is substantiated by the fact that along the foot-wall the barite has been fractured and healed by galena, sphalerite, and tennantite. On the other hand, parts of the foot-wall sulphide zone contain an intimate mixture of barite and sulphides, suggesting contemporaneous deposition of both. Following deposition of both barite and sulphides, brecciation along the foot-wall permitted further deposition of sulphides and barite, generally with good crystal habit. Some, or perhaps all, of the latter sulphides and barite probably represent a redistribution of material within the confines of the orebody.

Wall-rock alteration is not particularly marked in the rocks adjacent to the deposit. Some of the sandstones are, however, densely impregnated with siderite and pyrite.

The barite orebody has produced more than 3 million tons of barite, and the deposit probably has about the same tonnage in reserve. The sulphide deposit is relatively small, about 350,000 tons, and the grade is highly variable. The representative range of assays from the sulphide zone is given below.

| | |
|---|---|
| Lead | 5–25% |
| Zinc | 1–20% |
| Copper | 0.5–8% |
| Silver | 2 oz/ton–400 oz/ton |
| $BaSO_4$ | 10–25% |

The deposit is epigenetic and represents a major concentration of Ba, Sr, Pb, Zn, Cd, Cu, Ag, Fe, Mg, Ca, As, $CO_2$, and S; and a minor concentration of Sb, Co, and Ni. Vanadium and uranium are not present in other than traces in the deposit, but this is in accord with most of the other 'red bed' deposits of the Maritime Provinces of Canada. Minor amounts of selenides (clausthalite and penroseite) have, however, been identified in some of the faults of the area, but in general the content of selenium in the main deposit is low.

The source of the silver and the other elements concentrated in the deposit is somewhat speculative. There is no logical igneous source for the elements, and one is forced to the conclusion that the country rocks probably provided the elements. The deposit lies above a series of rocks (Horton Bluff and Cheverie Formations) that are collectively relatively rich in sulphur, arsenic, zinc, lead, copper, silver, and barium. It seems probable that these rocks supplied the elements that migrated along the extensive fault systems and were deposited in favourable brecciated (dilatant) zones, particularly those developed in limestones, limestone-conglomerates, evaporites, and porous sandstones.

### Observations on the Origin of 'Red Bed' Deposits

Probably no simple mechanism can explain the origin of all of the 'red bed' types of deposits because they are so varied in their habit and the elements concentrated are numerous and have marked geochemical differences. There are, however, a number of features of nearly all of the deposits which suggest that certain uniform mechanisms are operative in their formation. These are:

1. Most of the deposits occur in continental sediments formed under oxidizing conditions. In some places there is evidence of volcanic activity, and in a number of places there are associated basaltic or other types of basic flows that presently overlie the favourable beds or have been removed by erosion. Such conditions occur at Walton, Silver Reef, and at Dalane, Norway. Since it is well known that basic volcanic rocks are often enriched in copper as well as nickel, cobalt, and silver in some cases, it follows that they could be the source of some of the elements in the deposits. It is evident in some places that the 'red bed' mineral deposits were formed long after the consolidation of the volcanic rocks, and hence one must call on a later secretion mechanism if the metals in the deposits came from the rocks. In a number of places, a groundwater concentration seems evident.

2. In a number of areas, the 'red bed' deposits are underlain or overlain by black shales or petroliferous shales and limestones. It is again well known that such rocks are greatly enriched in copper, silver, cobalt, nickel, uranium, sulphur, and other elements. These rocks could, therefore, be the source of the elements in the deposits. In fact, such a source seems probable for most of the 'red bed' deposits in the Maritime Provinces of Canada.

3. In a few areas, e.g., Kupferschiefer of Germany and White Pine area of Michigan, the native silver in sandstones is closely associated with the cupriferous shales. In these areas it seems probable that the silver was originally deposited in the cupriferous shales and was later redistributed and concentrated by ground or connate waters in the more porous parts of upper or lower sandstone sequences.

4. The 'red beds' may themselves contain sufficient amounts of copper, silver, cobalt, barium, uranium, etc. to provide a source for the elements in the deposits. During the intense weathering that took place to form the continental sediments it is logical to suppose that enormous amounts of copper, silver, uranium, etc. would be released and ultimately find their way into the basins of sedimentation. There, under the oxidizing conditions that prevailed, much of the copper, silver, and other elements would be adsorbed by the abundant iron and manganese oxides and by the clay portion of the shales. Later during diagenesis and subsequent processes these elements would be readily available for solution and migration in groundwater.

5. There are generally no igneous granitic bodies near the deposits to which one could ascribe a logical magmatic source for the elements in the deposits.

6. Many of the deposits, as they now occur, are definitely epigenetic, indicating that the constituents of the ore and gangue minerals have been introduced into favourable geologic sites, such as porous zones, fractures, etc.

7. Many of the deposits are associated with plant remains, and there are indications that these have been effective in precipitating the ore minerals. In other cases, there is evidence that the ore minerals have been precipitated in porous sandstones or conglomerates. These are generally bleached, indicating a reduction of the iron oxides during the process of precipitation of the ore minerals. In a few areas the deposits occur along faults or fracture zones, and there are indications of both fracture filling and replacement. A number of deposits contain small amounts of bitumen closely associated with the ore and gangue minerals.

These facts suggest to the writer that the source of the elements lies in the sedimentary pile in which the deposits occur. In some places it seems evident that the elements came from the red beds themselves; in other places they may have been contributed from underlying or overlying black or petroliferous shales. In still other places, a contribution of certain elements from overlying or underlying volcanic flows seems probable. Perhaps the source of the elements for some deposits lies in the collective sequence of sediments and volcanic rocks enclosing the deposits.

The mechanisms whereby the elements have been concentrated appear to be varied and each deposit probably has to be considered as a special problem. Nevertheless some generalizations seem to be justified.

In most cases the medium of transport for the ore and gangue elements appears to have been groundwaters or connate waters. Two mechanisms seem to have operated in the concentration of the elements—mass transport by the waters (flow) and diffusion of ions, hydrated ions, molecules, and gases through the stationary ground or connate water that pervaded all fractures, breccia zones, porous zones, pores and other discontinuities in the rocks. Both mechanisms may have operated depending on the geological setting. Near the surface the mass transport mechanism would probably be the most effective, whereas at depth the diffusion mechanism probably prevailed.

The nature of the dissolved elemental species is a matter of speculation. Judging from the known composition of typical groundwaters the elements probably migrated as the sulphates, hydrogen carbonates, and chlorides. Where $H_2S$ and alkalies were present in solution one can postulate soluble complex sulphides, sulphide-arsenides, or sulphide-antimonides. Our knowledge of the chemistry of silver suggests that this element was probably transported as the sulphate, as the hydrogen carbonate, as the complex ion $[AgCl_2]^-$ in solutions charged with sodium chloride, or as the complex sulphide ion $AgS^-$ or some other soluble silver sulphide-arsenide or sulphide-antimonide ion.

The mode of precipitation of the elements seems likewise to be varied and depends on the geological situation. Some general mechanisms can however be suggested:

1. Reduction of sulphates, chlorides, hydrogen carbonates, etc. by reaction

with organic matter (coal fragments, etc.). The reduction may be direct in some cases. In other cases bacteria associated with the organic matter may have effected the reduction. Some of the sulphur to form the sulphides may have been contributed by the plant matter. In still other cases the plant matter seems to have acted only as a catalyst during the breakdown of the various sulphide complexes to form the sulphides.

2. In some deposits it is evident that the plant matter was responsible for the precipitation of pyrite. Later this sulphide was replaced by the copper, silver, and other sulphides. This phenomenon is normal and is in accord with Schürmann's series which gives the order of the solubility of the various sulphides (viz., $Ag < Cu < Pb < Zn < Ni < Co < Fe^{2+}$, etc.).

3. In deposits where plant matter is sparse or lacking, precipitation of sulphides from sulphates may have taken place by the action of sulphate-reducing bacteria at or just below the level of the groundwater table. As the sulphate is isolated from the system as sulphide, say in the porous zones where the bacteria are operating, the concentration of the sulphate component is decreased, causing an upward or lateral diffusion of more sulphate to these zones. By such a process extensive sulphide deposits can be built up.

4. An inorganic precipitation of sulphides may take place where dissolved metal sulphates, chlorides, hydrogen carbonates, etc. come into contact with $H_2S$ diffusing upwards or laterally from black or petroliferous shales. As the metal ions and $H_2S$ are used up they would be replaced by a diffusion of more metal ions and $H_2S$ from the surrounding stagnant water medium. The size, distribution, and form of the deposits would depend, therefore, essentially on the degree of porosity of the rocks and on the distribution of the porous zones.

5. Precipitation of ore and gangue elements in fractures, faults, and breccia zones may result from a variety of mechanisms such as dilatancy, chemical inequilibrium, reaction of metal-bearing solutions with favourable wall-rocks, and mingling of solutions or diffusion currents bearing chemically reactive components.

## Silver-Bearing Skarn-Type Deposits

The general features of these deposits are well known and need not be described in detail. Most of the deposits occur in highly metamorphosed terrains in which there has been much granitization and injection of granitic rocks. Some deposits occur near the contacts of the granitic rocks and have long been called 'contact metamorphic'; others are developed in favourable reactive beds or zones some distance from granitic contacts.

Most of the deposits occur in skarn zones or are associated with skarn minerals, developed in limestones, dolomites, or calcareous schists. The form of the deposits is irregular and bunchy, but many of them are tabular, following beds that have been selectively replaced.

The deposits usually contain a characteristic suite of relatively high temperature Ca-Mg-Fe-silicate and carbonate minerals such as garnet, epidote, vesuvianite, diopside, tremolite, scapolite, wollastonite, and crystalline calcite and dolomite. The sulphide minerals are generally chalcopyrite, bornite, pyrite, pyrrhotite, galena, sphalerite, and molybdenite. Magnetite and hematite occur in many of the deposits.

Silver is concentrated mainly in the lead-zinc deposits of this type and is associated principally with the galena of the deposits. The well known contact-metamorphic copper types tend to have low contents of silver. In various parts of the world there are also a few skarn-type gold deposits in which silver is present in the free gold or is concentrated with the gold in arsenopyrite, pyrrhotite, or pyrite. An example of the latter in Canada is the Nickel Plate Gold Mine, near Hedley, British Columbia.

Examples of silver-bearing lead-zinc skarn-type deposits are known in various countries. In Sweden the Åmmeberg deposits carried up to 25 oz/ton in the galena concentrate. Numerous lead-zinc deposits of this type are known in the western United States, particularly in the Bingham district, Utah, in the Central mining district, New Mexico, in the Coso district, California, and in Mexico, particularly in the Chihuahua and Zacatecas mining districts.

In Canada the highly metamorphosed Precambrian Grenville series contains a number of lead-zinc deposits carrying some silver. The best known of these are the Tetreault deposit near Quebec City and the New Calumet deposit on Calumet Island in the Ottawa River. The Tetreault deposit produced several million ounces of silver before ceasing production in 1954. The silver is associated principally with galena and probably occurs mainly in tetrahedrite. Electrum and native silver have also been reported and accounted for part of the silver and gold content of the ore. The grade of the deposit was 7 to 10 per cent Zn, 1 to 3 per cent Pb, 0.09 ounce Au, and 5 to 9 ounces Ag per ton. The New Calumet deposit, which is still being mined, is a tabular body of massive and disseminated sulphides in a highly altered impure limestone now essentially composed of pyroxene, tremolite, feldspar, chlorite, garnet, and calcite. The principal sulphides are pyrite, pyrrhotite, sphalerite, and galena. The silver content ranges between 5 and 10 ounces to the ton, and there is about 0.05 ounce gold to the ton. The silver is closely associated with the galena and is present in various silver-bearing minerals, including tetrahedrite, argentite, and polybasite. The gold is mainly in the native form associated with all the sulphides and as minute grains in the silicate gangue. One variety of ore, characterized by fine-grained pyrite and pyrrhotite in coarse calcite with feldspar and tremolite, is relatively rich in native gold. This native gold appears to have been introduced late in the mineralization history of the deposit. It carries minor amounts of silver.

Most of the contact metamorphic and skarn types of deposits are relatively low in silver. A survey of the literature shows that the silver content of most deposits ranges from 5 to 10 ounces to the ton. A few deposits are of higher grade and may contain up to 30 ounces Ag/ton.

## Veins, Stockworks, Mantos, and Tabular Bodies, Essentially in Sedimentary Rocks

Deposits of this type include as their members some of the most productive silver mines in the world. They also include those gold-silver deposits that occur essentially in sedimentary rocks and many great lead-zinc deposits that have a similar setting and which produce large amounts of silver as a by-product.

Many deposits in this category are localized by particular structures such as faults, fractures, shear zones, sheared beds, dragfolds, and breccia zones. Some are controlled by chemically favourable beds, which they replace, often in great detail. Most of the deposits are discordant with the enclosing sediments, but a number have conformable attitudes.

Most of the deposits occur in low-grade metamorphic rocks, but some occur in gneisses, schists, and other high-grade rocks. Porphyries cut the sedimentary rocks in places and sills or flows of basic volcanic rocks may be present. In many areas the sediments may be intruded by granitic rocks or granitized over large areas. Most of the deposits show no obvious relationship to the porphyries or granitic rocks and in nearly all places where the two are in contact, the veins, lodes, etc. cut the granitic rocks and were formed long after their consolidation.

The principal primary silver minerals in deposits of this type are argentiferous tetrahedrite-tennantite, argentite, proustite-pyrargyrite, and argentiferous galena. In a few deposits native silver and dyscrasite occur as primary minerals. Pyrite, sphalerite, and chalcopyrite are the main associated minerals, but in some deposits, nickel-cobalt arsenides, bismuthinite, native bismuth, and pitchblende are abundant. Cassiterite and wolframite are uncommon minerals in these deposits, but are present in some areas. The most common gangue minerals are siderite, calcite, dolomite, quartz, and barite. Fluorite is uncommon in most deposits, but tourmaline may be present in places. Zeolites may occur in a few deposits, but they are generally late minerals and may not be associated with the deposition of silver.

Many of the vein deposits in the low-grade sedimentary rocks are markedly vuggy and crustiform in character. In the higher grade metasediments the structure of the veins tends to be more compact. The tabular deposits generally have compact structures and commonly replace the host rock in the minutest detail.

A characteristic suite of elements exhibits a high frequency of concentration in deposits of this type. These include Pb, Zn, Cd, Cu, Ag, In, Fe, Mn, Mg, Sb, As, S, $CO_2$, and $SiO_2$. Less frequent are Ba, F, Sn, Au, Co, Ni, Bi, Se, and Te. Rare are U and W.

The source of the ore and gangue elements in the deposits has long been attributed to granitic magmas, although in many areas granites and allied rocks are not found at the present level of erosion. In other deposits the source of the metals and gangue has been attributed to exhalations from diabasic magmas despite the fact that in nearly all places the evidence shows that the veins cut the diabases from which the exhalations supposedly came. Furthermore, in some areas diabase or other basic rocks are not present. Granitic rocks or diabase do not, therefore, seem to be the source of the elements in the deposits.

During the writer's long association with these deposits he has been struck by the nearly constant presence of black pyritic shales or pyritic argillites and greywackes in their vicinity. This particular association is so marked in districts such as Keno Hill, Slocan, British Columbia, and Thunder Bay, Ontario, as to suggest that these rocks may be the source of most of the elements in the deposits. In certain areas diabase may also have contributed some of the elements, especially nickel and cobalt, since nickel-cobalt arsenides are often found in the veins where diabase is present. Diabase need not be present, however, since most black pyritic sediments also tend to be somewhat enriched in both nickel and cobalt.

It has been shown in a previous section that carbonaceous sediments are enriched in silver, and these rocks are also great reservoirs of sulphur, arsenic, lead, zinc, and numerous other chalcophile elements. They constitute, therefore, an adequate source for all of the elements present in the deposits.

It is evident that nearly all of the deposits in this category are either structurally or chemically controlled. In a great many cases the veins and lodes occur in fracture systems in competent quartzites, diabase, greenstones, or even in granitic stocks above, below, or to the flanks of sequences of pyritic sediments. In other cases they are mantos or pipes in limestones, calcareous shales, or argillites below or above which lie the source beds of pyritic sediments.

Considering these features it seems probable that the deposits are largely the result of metamorphic secretion processes. As the faults, fractures, disrupted beds, and other structures dilated they drew in the various elements that constitute the ore and gangue mainly from the enclosing sediments, but also perhaps in certain places from diabase and other rocks. The mode of transport of the ore and gangue elements was probably largely by diffusion, although in certain cases solutions may have been the active transfer agents. The way in which the silver migrates is highly speculative. The element may have travelled as the carbonate or sulphate or as the chloride complex $[AgCl_2]^-$. In the presence of alkalies, the polysulphide ions $[Ag(S_4)_2]^{-3}$, $[AgS_4S_5]^{-3}$, $[Ag(HS)S_4]^{-2}$, and others offer possibilities as do also the complex ions of silver combined with sulphur, arsenic, or antimony.

The number of deposits in this category are legion and only a few examples can be cited and briefly described. In Canada the deposits of the Keno Hill-Galena Hill area, Yukon, the Slocan and Ainsworth areas, British Columbia, the Bluebell mine at Riondel, British Columbia, the great Sullivan mine at Kimberley, British Columbia, and the silver deposits in the Thunder Bay district of Ontario are typical examples. In the United States the Coeur d'Alene deposits and those in the East Tintic district, Utah, and Leadville and Aspen districts of Colorado provide further examples. Many of the Mexican deposits belong in this category, especially those in the Santa Eulalia (El Potosí mine) and in the Zacatecas silver districts. In Europe classic examples are found in the Kongsberg district of Norway, in the Clausthal and Freiberg silver districts of Germany, at Jáchymov in Czechoslovakia, and in the Laurion district, Greece. It seems probable that the great lead-zinc-silver lodes of Broken Hill and Mount Isa, Australia, belong in this category as do also many of the polymetallic silver-bearing deposits of the U.S.S.R. (Nerchinsk district and elsewhere). The enigmatic Kurokô (black ore) deposits of Japan seem to be best classified in this category.

## Keno Hill–Galena Hill Area, Yukon

The geology of the Keno Hill–Galena Hill area has been described by Kindle (1962) and McTaggart (1960), and the geology and geochemistry of the lead-zinc-cadmium-silver deposits by Boyle (1956, 1957, 1965).

The consolidated rocks (Fig. 4) underlying the area are mainly sedimentary in origin and include black and green pyritic schists, pyritic phyllites, slates, and quartzites of Precambrian or early Palaeozoic age. Conformable greenstone lenses and sills, probably of Palaeozoic age, occur in profusion in places in the sedimentary strata, and a few narrow lamprophyre and quartz-feldspar porphyry dykes and sills (Jurassic?) are present locally. The rocks dip gently south and are cut by numerous early and late brecciated fault zones. The early fault zones strike northeast, generally dip southeast, and contain the lead-zinc-silver lodes. Most of the late fault zones strike northwest, dip southwest, offset the early fault zones and lodes, and are essentially barren.

The principal lodes occur in the competent greenstones and thick-bedded quartzites at three structural sites: at the junction of two or more faults; at the junction of a fault and subsidiary fracture; and in greenstones or thick-bedded quartzites at or near the sites where the faults pass upward from these rocks into incompetent schists or thin-bedded quartzites.

Two types of lodes are present in the early faults: an early one contains essentially quartz with pyrite, arsenopyrite, boulangerite, meneghinite, bournonite, and small amounts of galena and sphalerite; the later one is mineralized with manganiferous siderite, argentiferous galena, sphalerite, pyrite, freibergite, chalcopyrite, meneghinite, boulangerite, pyrargyrite, dolomite, quartz, and minor amounts of barite. Although both types may occur separately, it is more usual to find hybrid lodes consisting of the quartz type, which have been fractured and later cemented with minerals characteristic of the siderite type. Lodes of the quartz type are not economic, but do carry a little gold. The siderite lodes are the source of the silver-lead-zinc-cadmium ores.

Three zones can be recognized in most lodes: an upper oxidized zone, an intermediate zone of reduction, and a lower primary zone. The oxidized and primary zones are present in all lodes and are generally well developed and demarcated. The zones of reduction are generally diffuse and telescope both the oxidized and primary zones. The depth of the oxidized zones is variable. In some mines the oxidization terminated at a depth of 20 feet, in others the oxidized zones extend to depths ranging from 250 to 500 feet.

The oxidized parts of the lodes contain a veritable host of minerals. Limonite (goethite, lepidocrocite, hematite), wad, anglesite, cerussite, and silver-bearing beudantite, plumbojarosite, and jarosite are the most characteristic. In addition to these the following are present: gypsum, native sulphur, malachite, azurite, smithsonite, pharmacosiderite, pyromorphite, mimetite, bindheimite, scorodite, melanterite, gunningite, calcite, aragonite, montmorillonite, serpentine, quartz, covellite,

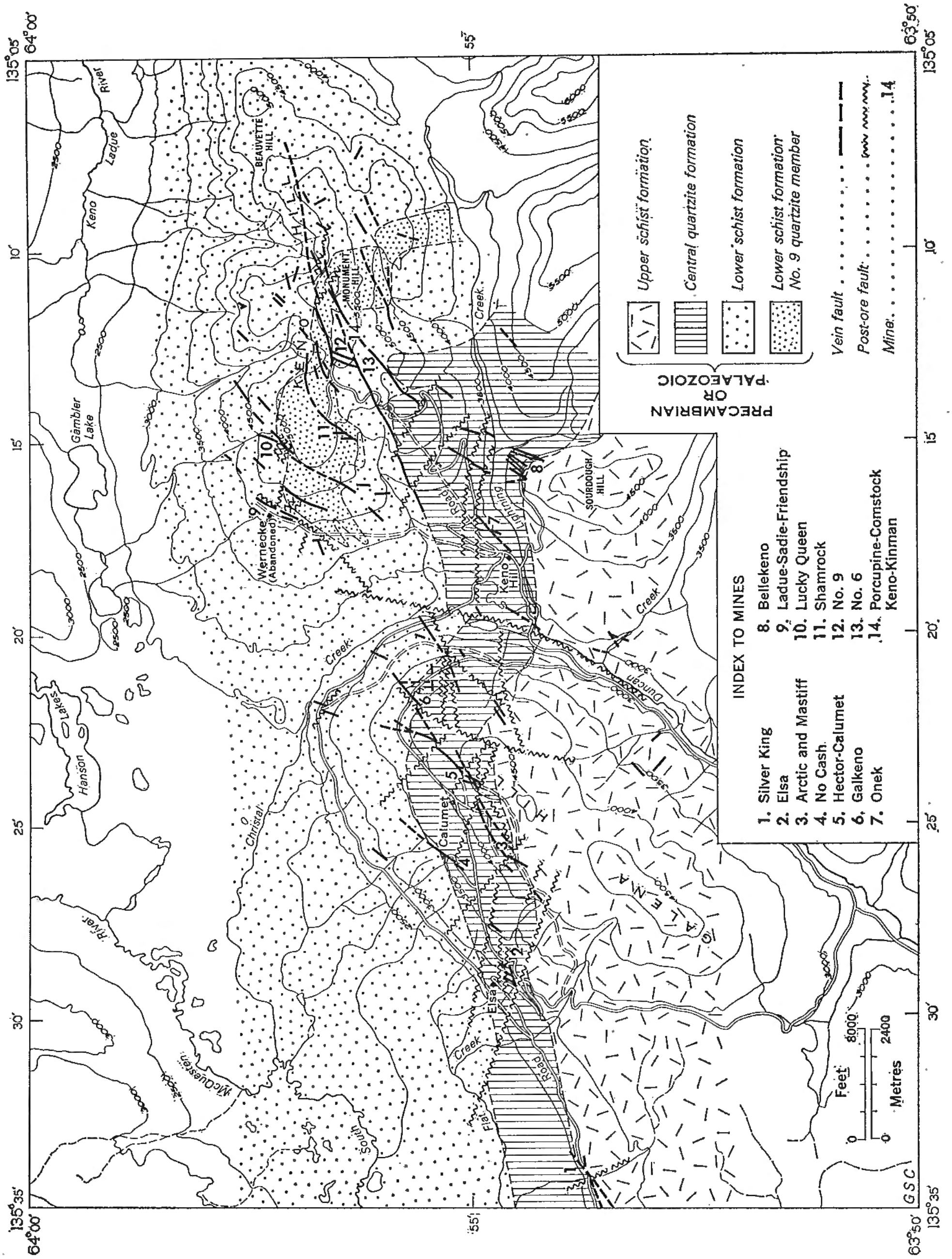

FIGURE 4. Main geological features and principal mines, Keno Hill — Galena Hill area, Yukon Territory.

pyrargyrite, acanthite, native silver, and an occasional speck of native gold and native zinc.

The minerals in the zones of reduction include those commonly present in both the primary and oxidized zones augmented by characteristic developments of pyrargyrite, native silver, acanthite, and small amounts of supergene calcite, siderite, sphalerite, galena, pyrite, and hawleyite.

As a whole, the lodes exhibit a marked enrichment of silver and lead and a depletion of zinc and cadmium in the oxidized zones compared with the primary zones (Table 49). Many of the zones of reduction are greatly enriched in silver.

### Slocan Area, British Columbia

The geology and deposits of the Slocan area have been described by Cairnes (1934, 1935, 1948), Hedley (1948, 1952), and Ambrose (1957). The deposits produce silver, lead, zinc, and some cadmium.

Three main series of rocks occur in the area between New Denver and Kaslo. These include the Late Precambrian Lardeau Series, and the Triassic Kaslo and Slocan Series. Most of the deposits occur in or are associated with the Slocan Series.

The Slocan Series is about 6,800 feet thick and is composed essentially of strongly folded, faulted, and sheared, thick- and thin-bedded quartzites, phyllites, black schists, argillites, various tuffaceous rocks, and limestones. A conspicuous feature of many of the argillites, black schists, and quartzites is the presence of abundant pyrite and carbonaceous matter.

The Slocan Series has been invaded by a host of small granitic and porphyritic stocks, sills, and dykes. These are older than the veins and in places are folded with the sediments. South of the main mineral belt and in the area north of New Denver, the Slocan Series is intruded by and granitized to a porphyritic granite, which forms part of the Nelson batholith.

Deposits occur both in the Slocan Series and in the porphyritic granite. In the Slocan Series, the deposits are single fissure veins, composite veins, lodes, and replacements of limestone in or near fractures, faults, and shears that have a general northeasterly strike and a southeasterly dip. The economic shoots tend to occur in the more massive strata of the series and in zones where the strata are buttressed by swarms of granitic dykes. Another localizing feature is the presence of thick limestone beds into which the mineralization spreads from the fractures and faults.

In the porphyritic granite and its highly metamorphosed enclaves of schists, quartzites, etc. (probably derived from the Slocan Series), the deposits are veins generally with northeast and northwest strikes.

The mineralogy of the deposits in the Slocan Series differs somewhat from that in the granite. In the former the principal hypogene ore minerals are argentiferous galena, freibergite, pyrite, chalcopyrite, and sphalerite. The pyrite carries a little gold in some veins. Manganiferous siderite is an abundant gangue mineral, and there is generally some quartz and locally some calcite. In the granite, freibergite, native silver, pyrargyrite, argentite, stephanite, argentiferous galena, and sphalerite are the chief ore minerals. Quartz is generally the most abundant gangue. Manganiferous siderite, calcite, barite, and fluorite are less common, but in some veins they are abundant.

Some of the deposits are oxidized, in places down to depths ranging from 50 to 200 feet. The principal oxidation minerals are limonite, wad, anglesite, cerussite, smithsonite, malachite, azurite, native silver, pyrargyrite, minor chlorargyrite, and various other sulphates, carbonates, etc.

### Ainsworth Area, British Columbia

The geology and lead-zinc-silver deposits of the Ainsworth Camp have been described by Rice (1944, 1948). The camp is on the west side of Kootenay Lake, 14 miles south of the town of Kaslo.

The bedrocks consist of a succession of complexly folded quartzite, quartz-mica schist, hornblende schist, and limestone bordered on the west by granodiorite. The deposits are fissure veins and replacement deposits in limestone along transverse fissures. The gangue is mainly quartz and calcite. The principal ore minerals are argentiferous galena, sphalerite, freibergite, and native silver. Most of the deposits are lead-zinc deposits with low amounts of silver. Some, however, are high-grade silver deposits.

### Bluebell Mine, Riondel, British Columbia

The Bluebell mine of The Consolidated Mining and Smelting Company Limited is at Riondel on Kootenay Lake, British Columbia. It is essentially a lead-zinc producer, but is an excellent Canadian example of a low-grade silver deposit in crystalline limestones. The geology of the mine area is described by Walker (1929) and Irvine (1957).

The lead-zinc-copper-cadmium-silver lodes occur in a crystalline limestone (Bluebell limestone) member of the Lardeau Series of Palaeozoic age. The limestone is flanked by slates, phyllites, schists, and quartzites, and these and the limestone are warped into a broad syncline with a series of gentle anticlinal arches (cross-folds) in the vicinity of the mine. The tension fractures containing the lodes are developed in the limestone near the crests of the anticlinal arches. The detailed stratigraphy of the rocks in the mine area as given by Irvine (1957) is as follows:

| *Thickness* (feet) | *Description of Member* |
|---|---|
| 400 ± | *Hanging-wall quartzite*: Strong competent white quartzite bands interlayered with platy quartz-mica schist and a 15-foot layer of banded limestone. |
| 100–150 | *Bluebell limestone*: Banded limestone in alternating dense and coarsely crystalline layers. |
| 700 | *Quartz-mica schist*: Quartz-mica schist, including interlayered graphite, garnet, and limy schist. |
| 500 | *Hornblende schist*: Hornblende schist with some interlayered quartz-mica schist and limy schist. |
| 300 | *Pegmatite sill member*: Coarse pegmatite sill with some interlayered inclusions of quartz-mica schist and hornblende schist. |

The Bluebell limestone is cross-faulted into a number of segments, which dip westerly at 55 degrees. Granitic intrusions and the Nelson batholith of post-Triassic age occur some 5 miles or more from the mine.

The ore shoots occur in three groups spaced at intervals of 1,000 feet or so along the strike of the Bluebell limestone. The Northern Comfort zone consists of at least five orebodies, all more or less tabular, which occupy steeply dipping transverse fracture zones or spread out along beds under the hanging-wall quartzite. The Bluebell or central ore zone has three ore shoots in the form of stubby keels in steeply dipping tension fractures. In places these spread out along limestone beds below the hanging-wall quartzite. The Kootenay Chief or southern ore zone has five principal shoots that occupy cross-fractures and spread out into irregular bodies along beds near the hanging-wall of the limestone. All the ore shoots were apparently formed by both fracture filling and replacement.

The orebodies are chiefly massive bodies of sulphides, the main hypogene minerals being pyrrhotite, marmatitic sphalerite, and galena, in that order of abundance. There is also some pyrite, chalcopyrite, and arsenopyrite. Quartz is a common gangue mineral and knebelite, a manganiferous orthosilicate, is found in limited amounts in or near most of the orebodies.

The ore shoots were highly oxidized down to a depth of 300 feet or more. The principal minerals in the oxidized zones were limonite, black and grey mud, anglesite, cerussite, oxidized galena masses and nodules, some smithsonite, gypsum, melanterite, pyromorphite, malachite, native copper, and a number of unidentified secondary minerals. In places the pyrrhotite is converted to marcasite. The average assay of this oxidized material was about 7 per cent Pb, 8 per cent Zn, and 5 ounces Ag per ton. The average assay of the primary ore is about 5.5 per cent Pb, 5.5 per cent Zn, 0.07 per cent Cu, 0.03 per cent Cd, and 1.3 ounces Ag per ton.

In the deep parts of the mine there are heavy flows of hot water charged with carbon dioxide.

Structurally and mineralogically the Bluebell deposits are remarkably similar to those in the Laurion district of Greece.

### Sullivan Mine, British Columbia

This great mine is well known to economic geologists and students of ore genesis and requires only a brief description. The deposit is one of the largest lead-zinc-cadmium-silver producers in the world, and indium, tin, iron, and sulphur compounds are also won from the deposit.

The geology, nature, and age of the Sullivan deposit have been described by Swanson and Gunning (1948), the staff of The Consolidated Mining and Smelting Company Limited (1954), and Leech and Wanless (1962). The orebody is a large gently dipping tabular sulphide replacement of certain beds in the late Precambrian Aldridge Formation. This formation is composed essentially of argillite, siltstone, and quartzite with an average dip of about 30 degrees to the east. Two large diorite masses intrude these rocks near the mine. A number of late faults cut the orebody in several places.

The principal sulphide minerals are argentiferous galena, sphalerite, pyrrhotite, and pyrite. Chalcopyrite and arsenopyrite are minor constituents, and there is some boulangerite in parts of the orebody. Magnetite is fairly common, and cassiterite is present in recoverable amounts.

There is a marked alteration associated with the orebody. Above the sulphide mass evidence of albitization and chloritization is common and below it there is a great zone of tourmalinized rock in what appears to be a marked brecciated zone.

The ore is typically banded, the layers of one or the other sulphides ranging from a fraction of an inch to several feet in thickness. To Swanson and Gunning the banding is clearly the result of selective replacement of the original laminae and strata. With this conclusion this writer would agree, since one can see relict layers and laminae composed of quartz, sericite, chlorite, tremolite, garnet, etc. in various parts of the orebody. The replacement by sulphides is, however, extremely intimate and the original beds, folds, and crenulations are replaced in the minutest detail in places. This feature, on first examination, gives the impression that the bands are sedimentary, but on closer scrutiny it is apparent that the sulphides are later than the beds and were apparently deposited essentially contemporaneously with the movement that gave rise to the dragging, crenulation, and minor folding. Furthermore, there are fractures in both the hanging-wall and foot-wall that carry galena, sphalerite, quartz, calcite, and in the foot-wall relatively high amounts of tin, mainly in the form of cassiterite.

The origin of the Sullivan orebody has given rise to some controversy in recent years. There are some who ascribe to it a sedimentary origin, but the alteration, presence of mineralized fractures, details of the banded ore, and zoning of the sulphides argue against such an hypothesis. To this writer the body is epigenetic. Actually it is a great, nearly massive sulphide manto, not unlike some of the lead-zinc mantos in Mexico. The source of the metals and gangue is of course somewhat enigmatic, but the writer noted an abundance of rocks of the black and grey argillite type, many containing abundant sulphur and presumably also lead, zinc, silver, etc., in the general area in which the deposit is set. These rocks could well be the source of the elements found in the deposit. The ore elements were apparently drawn into and partly replaced a great dilatant zone marked by intra-bed dislocations, dragged and crenulated beds, folded beds, and breccia zones.

## Thunder Bay Silver Area

The silver deposits in the Thunder Bay district of western Ontario have been described by Ingall (1888), Bowen (1911), and Tanton (1931), and more recently by Oja (1964). Bowen grouped the deposits into two belts, which he designated as the "grey argillite" belt and the "black slate" belt. Oja has named these, respectively, the "Island belt" and the "Mainland belt".

The "Island belt" includes a string of diabasic islands in Lake Superior extending from Victoria and Spar Islands, near the International Boundary at Pigeon River, northeastward for 50 miles beyond the famous Silver Islet mine. The "Mainland belt" is roughly 4 miles wide and lies on the mainland 20 miles northwest of the "Island belt" and extends from the area northeast of the city of Port Arthur some 80 miles southwestward to the vicinity of Whitefish and Arrow Lakes.

All of the consolidated rocks in the two belts are Precambrian in age (*see* Table 44). The Keewatin-type rocks are mainly steeply dipping metamorphosed volcanic rocks, gneisses, and schists. These are intruded or granitized to granite, granite

TABLE 44 *Table of Precambrian Formations, Thunder Bay Silver Area*

| Era | Period—system | Epoch—series | Lithology |
|---|---|---|---|
| Proterozoic | Keweenawan | | Diabase sills and dykes |
| | | Intrusive contact | |
| | | Sibley | Various sediments including conglomerate, sandstone, limestone, and tuff |
| | | Unconformity | |
| | | Animikie | Rove Formation—black shale, argillite, greywacke<br>Gunflint Formation—argillite, conglomerate, calcareous rocks, taconite |
| Unconformity | | | |
| Archaean | Algoman | | Granite, granite gneiss, migmatite, granodiorite, pegmatite, and related rocks |
| | Intrusive or granitized contact | | |
| | Keewatin | | Metavolcanic and metasedimentary rocks |

gneiss, and migmatite of Algoman age. Unconformably overlying these rocks are the Gunflint and Rove Formations of the Animikie Series, which are overlain in turn, apparently unconformably, by the Sibley Series. All these formations are intruded by Keweenawan diabase sills and dykes.

The two silver belts are severely faulted, chiefly in northeast and northwest directions.

The principal deposit in the "Island belt" was the famous Silver Islet mine, which was mined during the period 1868-1884. The best descriptions of this deposit are those by Ingall (1888), Chadbourn (1923), and Tanton (1931).

The Silver Islet vein system produced more than $3 million in silver during its lifetime and was the first essentially silver mine to be worked in Canada. The problems with which the miners had to deal on such a small islet of rock some 80 feet in diameter, exposed to the fury of Lake Superior, are legendary.

The steeply dipping vein system was mainly in a 250-foot wide diabase dyke that cuts through relatively flat lying Animikie argillites, greywacke, and slates. The main vein averaged 8 feet in width and was productive to a depth of some 1,300 feet, below which the vein became too low grade to be worked economically at that time. The gangue was mainly calcite and manganiferous dolomite with a little quartz. Rhodochrosite and barite occurred in places. The metallic minerals included abundant native silver, argentite, galena, sphalerite, chalcopyrite, pyrite, marcasite, tetrahedrite, domeykite, niccolite, cobaltite, smaltite, breithauptite(?), millerite(?) and other poorly differentiated arsenic, antimony, cobalt, nickel, and silver minerals. Graphite (or carbonaceous matter) occurred in quantity in parts of the vein. Methane and hydrogen sulphide were encountered in relatively large quantities in some parts of the vein, and flows of salt water were common. The principal secondary minerals were quartz, calcite, barite, marcasite, nickel bloom (annabergite), cobalt bloom (erythrite), pyrolusite, native silver, and chlorargyrite. The shoots occurred as fabulously rich bonanzas along the vein system and were separated by relatively lean stretches.

A close examination of the old plans and sections of the Silver Islet mine indicates that the diabase, which the vein cuts nearly at right angles, acted only as a structural site for the mineralization. It probably played little part in the mineralization of the vein, although it may have supplied some of the gangue elements and perhaps some cobalt and nickel. The sediments seem to be the most likely source of the metals, arsenic, sulphur, etc. The unique presence of abundant graphite (carbonaceous matter) seems to add weight to this conclusion, since this material is abundant in the sediments.

The Sibley Peninsula and islands near Silver Islet have numerous diabase dykes and sills and would seem to offer good prospecting possibilities, since structural conditions similar to those on Silver Islet probably prevail. Geochemical prospecting using soils should be an effective method in searching for veins of the Silver Islet type on the Peninsula and adjacent islands.

On Spar Island, east of Jarvis Bay, there are a number of steeply dipping veins. One of these is 10 to 15 feet wide and cuts through grey argillites and slates and two diabase dykes. The gangue is chiefly calcite and barite, and there is a little tetrahedrite, bornite, pyrite, and sphalerite. The silver content of the vein is said to be low.

Numerous other occurrences of silver-bearing calcite veins are known on the string of islands that constitute the "Island belt" of Lake Superior. These would seem to merit attention using geochemical prospecting methods.

The prospects and mines in the 'Mainland belt' include the Beaver, Silver Mountain, Badger and Porcupine, Rabbit Mountain, Shuniah, Jarvis, Thunder Bay, 3A and Beck, and several others. The first three have produced about half a million dollars of silver each. The geology and mineralogy of these veins are similar in most respects.

The country rocks are mainly black pyritic slates and argillites, greywacke, and phyllite intruded by Keweenawan diabase sills that have been repeatedly faulted up and down giving rise to numerous buttes, mesas, and cuestas. The sediments belong to the Rove Formation and are relatively flat lying.

The deposits are veins, lodes, and irregular stockworks in steeply dipping faults and subsidiary fractures, some of which strike northeast and others north to northwest. Most of the known veins occur in the Rove sediments, but some extend into the diabase sill and at least one (the Shuniah vein) cuts into the Keewatin basement complex. A few occurrences are also known in the Gunflint Formation.

The gangue minerals are mainly calcite, white, smoky, and amethystine quartz, fluorite, barite, and some witherite. Metallic minerals include native silver, argentite, sphalerite, galena, pyrite, pyrrhotite, and chalcopyrite.

Oja noted that most geophysical methods failed to locate the veins in the 'Island belt'. Geochemical methods using zinc and silver as indicators in the humus and soil were found to be useful in tracing the veins.

### Coeur d'Alene, Idaho

This district ranks as one of the leading silver producers in the United States and in the world. The principal mines are the Bunker Hill and Sullivan, Morning-Star, Hecla, and Sunshine. On the average, the ores carry 3 to 12 per cent Pb, 3 to 6 per cent Zn, and 2 to 10 ounces Ag. The famous Sunshine mine and the adjacent Polaris mine in the so-called 'Silver belt' of the district have much higher silver contents with grades up to 30 oz/ton or more.

The geology of the Coeur d'Alene area and the nature and age of its deposits have been discussed by Ransome and Calkins (1908), Shenon (1950), Long, *et al.* (1960), Searls (1960), and Fryklund and Weis (1964).

The country rocks are folded and faulted Precambrian quartzites, phyllites, argillites, slates, calcareous argillites and quartzites, and black schists of the Belt Series. These have been intruded by Cretaceous monzonite stocks and related monzonite dykes.

The ore shoots occur in veins and replacement type deposits in shear zones, faults, and fractures in quartzite and other more competent rocks. There is a marked bleaching of the rocks adjacent to the ore shoots as a result of the destruction and degradation of pigmented minerals such as hematite, carbonaceous material, and chlorite and the concomitant development of sericite clay minerals and carbonates. The mineralization took place in six stages with the deposition of massive siderite and some quartz and barite with argentiferous galena, freibergite, sphalerite, chalcopyrite, pyrite, boulangerite, pyrrhotite, marcasite, magnetite, and arsenopyrite. Less common are bornite, chalcocite, stibnite, boulangerite, jamesonite, bournonite, polybasite, proustite, hematite, uraninite, and scheelite. Fryklund and Hutchinson (1954) have drawn attention to the presence of cobalt and nickel in the Silver Summit mine. These elements are present mainly in primary gersdorffite $(Ni,Co,Fe)AsS$ and in the secondary cobalt minerals erythrite and bieberite. There is also a little mercury in the freibergite in some mines. The oxidized zones of the veins are shallow and rather irregular.

Arnold, *et al.* (1962) determined the range of crystallization of the pyrrhotite and sphalerite from the Highland-Surprise mine to be between 370° and 492°C using the pyrrhotite-pyrite and sphalerite-pyrrhotite geothermometers. No systematic temperature gradients were observed in the deposit.

### Santa Eulalia District, Chihuahua, Mexico

The El Potosí mine of the Santa Eulalia district is one of the richest silver-lead mines in Mexico and provides an excellent example of the mantos, chimneys, irregular replacements, and fissure veins that are so common in the silver districts of Mexico.

The best overall description of the Santa Eulalia district is that by Horcasitas and Snow (1956). The country rocks enclosing the deposits are mainly Middle to Lower Cretaceous thick-bedded limestones, shales, and argillites. These rest on a dioritic mass of unknown extent and are capped by a limestone-conglomerate, tuffs, flows, and marls of Tertiary age. The Cretaceous rocks are gently folded and faulted, fractured, and cracked in all directions. Sills, sheets, and dykes of diabase, feldspar porphyry, and felsite intrude the Cretaceous sediments in many places. These produce contact effects in the limestones, but are themselves cut by the economic sulphide bodies.

The deposits of the El Potosi mine are massive and disseminated replacements of limestone along fracture zones in a number of favourable beds. Some of the orebodies are mantos conformable with the beds, others are large chimneys that cut across several beds and connect with the mantos. Still others are replacements along systems of fractures and fissures. Some of the great mantos extend along the dip of the beds for 5,000 feet or more and are 2,000 feet and more in width. Their thickness ranges from 10 to 75 feet or more. The large "P" chimney was more than 1,000 feet high and 3,000 square feet in cross-section.

The ore is of three types: oxidized ore now exhausted, nearly massive sulphides, and low-grade sulphide-silicate ore.

The massive sulphide ore is composed of galena, sphalerite, pyrite, pyrrhotite, and some chalcopyrite, tetrahedrite, calcite, and dolomite. The silicate ores consist of a mixture of masses, stringers, and disseminated grains of pyrite, pyrrhotite, argentiferous galena, sphalerite, and minor silver minerals in a matrix of quartz, silicified limestone, ilvaite, actinolite, hedenbergite, olivine, hematite, and magnetite. The massive sulphides are said to average about 10 per cent each of lead and zinc and about 10 ounces of silver to the ton. The oxidized ores derived from the more or less massive sulphides ran 12 to 15 per cent Pb, 2.5 per cent Zn, and 15 to 25 ounces Ag/ton. The fresh silicate ores average about 20 ounces Ag whereas their oxidized equivalents ran about 30 to 40 ounces. The zinc and lead contents of the silicate ores are about 10 per cent combined.

The lead-zinc-silver silicate bodies more properly belong in the category of the skarn-type deposits. They are remarkably similar to the ores of the New Calumet mine in Quebec.

## Other Silver Districts in Mexico

In Mexico there are a host of other silver deposits that occur in sedimentary rocks, principally quartzites, argillites, black schists, limestones, and associated tuffs and interbedded volcanic rocks. Many of these closely resemble the deposits in the Cordillera of Canada and the western United States.

The famous Fresnillo mine in the Zacatecas district obains its ore from a great stockwork and system of veins in slate, greywacke, argillite, and altered volcanic rocks. The principal primary minerals are pyrite, sphalerite, argentiferous tetrahedrite, argentiferous galena, argentite, chalcopyrite, polybasite, pyrargyrite, and native gold. Quartz is the main gangue mineral. The characteristic secondary minerals are native silver, argentite, bornite, covellite, chlorargyrite, cerussite, anglesite, kaolinite, and limonite.

The Taxco silver-lead-zinc deposits are veins and replacement deposits cutting a variety of folded and faulted black schists, sericite schists, limestone, shale, and tuffaceous rocks. The principal gangue is quartz, hematite, and carbonate in which there are variable amounts of argentiferous galena, sphalerite, chalcopyrite, pyrite, argentite, ruby silver, and other silver sulphides.

The mines of Taxco are probably the oldest in North America. The veins are reported to have been discovered in 1522 and various metals have been won from them since that date. The Spaniards mined the oxidized parts of the veins mainly for silver and gold. The primary ores in more recent times have yielded lead, zinc, silver, and gold.

### Kongsberg District, Norway

The silver lodes of Kongsberg are located some 50 miles west of Oslo in a belt about 20 miles long and 4 miles wide. They have been repeatedly described in the older literature especially by Vogt (1899)and Bugge (1931), and more recently by Neumann (1944b), Vokes (1960), and Gammon (1966).

The country rocks are a Precambrian complex of gneisses and schists containing dark bands and layers a hundred feet or more wide of schistose rock heavily impregnated with pyrite, pyrrhotite, and minor amounts of chalcopyrite, arsenopyrite, cobaltite, and galena (the so-called "fahlbands"). These bands appear to be of sedimentary origin, although the sulphides have probably been redistributed and recrystallized during regional metamorphism. They also seem to be similar in many respects to the numerous bands of sulphide schists in the rocks of the Precambrian Shield of Canada. Some of these, as in Norway, can be traced for several miles and may be hundreds of feet wide.

Two ages of veins are found in the Kongsberg area: an older set consisting essentially of quartz with some pyrite, pyrrhotite, sphalerite, and galena; and a younger set containing calcite, cobalt-nickel arsenides, and native silver. Only the latter were economic, and their silver shoots were localized principally where the fractures intersected the fahlbands.

The principal ore mineral was native silver, mostly in crystallized and wire forms. In addition there is some argentite (acanthite), a little dyscrasite and ruby silver, and variable amounts of stephanite, pyrite, pyrrhotite, niccolite, rammelsbergite, safflorite, chloanthite-smaltite, chalcopyrite, and galena, the last poor in silver. The main gangue mineral is calcite with some barite, fluorite, quartz, chlorite, axinite, and zeolites. Hard bitumen (coal blend, anthraxolite) occurs in a number of veins. Native bismuth is not found in the deposits, but there is a little native arsenic. The native silver contains mercury. The mineralogy is remarkably similar to the Cobalt, Ontario, deposits except that bismuth appears to be missing in the assemblage.

The silver veins are said by some investigators to be of Late Palaeozoic age genetically connected with the Oslo series of igneous rocks. One wonders, however, whether the fahlbands are not the source of the minerals in the veins. Certainly these sulphide-rich rocks would seem to contain sufficient quantities of the metals, and these could have been mobilized and drawn into any fractures which cross them.

The fahlbands are of interest in that they contain relatively high amounts of cobalt and some molybdenum in places. Near Skutterud and Snarum in Norway these bands are relatively rich in cobaltite, in addition to pyrite, arsenopyrite, chalcopyrite, pyrrhotite, galena, and some molybdenite. These were worked from 1776 to 1899 and were among the world's chief sources of cobalt at that time. At Cobalt, Ontario, there are also what one might call fahlbands of steeply dipping black and grey schists (sediments) impregnated with pyrite, pyrrhotite, galena, some sphalerite, and chalcopyrite, interbedded with the Keewatin greenstones. Curiously enough in places there are very rich cobalt-nickel-arsenic-silver veins developed in fractures in the Cobalt sediments on the upward projection of these fahlbands. (*See* further the discussion on the origin of the Cobalt deposits.)

### Clausthal and Freiberg, Germany

These deposits are classical and well known to students of ore genesis. They are now largely exhausted.

The deposits of Clausthal are in the Harz Mountains in a folded complex of Devonian and Carboniferous slates, greywackes, black schists, and argillites. There are no igneous rocks nearby.

The deposits are veins and lodes in faults and fractures. The main sulphide minerals are argentiferous galena, sphalerite, tetrahedrite, chalcopyrite, pyrite, bournonite, and marcasite. Quartz and calcite are the main gangue minerals in some veins; in others barite and siderite predominate. The slates and other sediments are mildly sericitized adjacent to some of the veins.

The Freiberg district is in Saxony and has long been famous for its silver-lead-zinc veins and its renowned mining academy.

Five systems of intersecting veins traverse gneiss, schist, and other metamorphosed sediments. The mineralogy is complex and has been worked out in the greatest detail and described in a large number of papers. Briefly there are older veins mineralized with quartz, ankerite, rhodochrosite, pyrite, arsenopyrite, sphalerite, chalcopyrite, argentiferous galena, tetrahedrite, ruby silver, polybasite, argentite, native silver, and arsenopyrite, and younger veins containing barite, fluorite, quartz, calcite, silver-poor galena, chalcopyrite, tetrahedrite, and sphalerite. Some of the baritic veins carry nickel and cobalt. The oxidized ores were rich in native silver and argentite.

The ore shoots are irregular, and the richest parts are frequently concentrated at or near vein intersections.

### Jáchymov, Czechoslovakia

The deposits of Jáchymov (Joachimsthal) are classical and have been described by many investigators. Historically it will be recalled that the deposits supplied the pitchblende from which Madame Curie first separated radium. In the past the veins have produced considerable quantities of Ag, Ni, Co, Bi, and U. The veins are now largely exhausted after being worked nearly continuously since the end of the 15th century.

The country rocks of the Jáchymov distrist are pre-Hercynian coarse- to medium-grained schists, gneisses, and minor crystalline limestone of sedimentary origin and orthogneisses and quartz porphyries representing early granitic and porphyritic intrusions. The schists and gneisses pass into phyllites, quartzites, and graphitic schists in the less metamorphosed terrains. The sedimentary rocks are folded in an east-west direction and are invaded by Late Variscan granites and related granite porphyries and lamprophyres. Basalt dykes and tuffs of Tertiary age occur in parts of the district.

The veins cut across the early quartz porphyries and in turn are themselves traversed by the Tertiary basalts. Three distinct types occur in the district. The oldest are quartz and quartz-feldspar veins containing small amounts of molybdenite, arsenopyrite, wolframite, cassiterite, and tourmaline. These occur near the granite, and are intersected in places and offset by two later systems of veins. One of these systems strikes northeast and is mineralized with an early generation of quartz, galena, sphalerite, bornite, and chalcopyrite; the other strikes northwest to north and has a varied mineral association, which consists of quartz, calcite, ankerite, pitchblende, rarely fluorite, various arsenides (skutterudite, rammelsbergite, niccolite, safflorite, loellingite), dendritic native silver, native bismuth, native arsenic, proustite, stephanite, realgar, argentite, bismuthinite, pyrite, sphalerite, galena, chalcopyrite, bornite, and arsenopyrite. From samples seen at Jáchymov and from those in the mineralogical museum of the National Museum in Prague the writer observed that the mineralization has occurred in a number of stages that were punctuated by extensive reopening of the fissures. This is also borne out by the recent descriptions of the deposits (Mrňa, 1963 a, b, c) and by older descriptions in the literature.

The sequence of elemental deposition in the three types of veins at Jáchymov is of interest. Examination of samples and a study of the literature suggest the following sequence. A more detailed account may be found in the papers by Mrňa (1963) and Mrňa and Pavlů (1964).

Stage 1. $SiO_2$, K, Na, Al, Mo, As, W, Sn, B, and S present in quartz, feldspar, molybdenite, arsenopyrite, wolframite, cassiterite, and tourmaline (veins near granite contact).

Stage 2. $SiO_2$, Pb, Zn, Cu, Fe, S present in quartz, galena, sphalerite, bornite and chalcopyrite (NE-SW veins, rare in NW-SE to N-S veins).

Stage 3. $SiO_2$, Ca, Fe, $CO_2$ present in barren quartz, calcite, and ankerite (NW-SE to N-S veins).

Stage 4. U, Ca, Mg, $CO_2$, F (rare), present in pitchblende, dolomite, and rare fluorite (NW-SE to N-S veins).

Stage 5. Ni, Co, Fe, As, Ag, Bi, and $SiO_2$ present in various arsenides, native silver, native bismuth, and ore-bearing quartz (NW-SE to N-S veins).

Stage 6. As, Sb, S, Ag, Bi, Ca, Mg, $CO_2$ present in various sulpharsenides and sulphantimonides, native arsenic, realgar, argentite, sternbergite, bismuthinite, dolomite, etc. (NW-SE to N-S veins).

Stage 7. Fe, Zn, Pb, Cu, S, As, Ca, $CO_2$, $SiO_2$ (minor) present in pyrite, sphalerite, galena, arsenopyrite, chalcopyrite, calcite, and locally quartz (NW-SE to N-S veins).

The Jáchymov deposits are similar to those at Great Bear Lake, N.W.T., Canada, as regards the depositional sequence of elements, although in some cases there are marked differences. The native silver and cobalt-nickel arsenide minerals are similar to those at Cobalt, Ontario, both in texture and type. Mercury is present in small amounts at Cobalt, especially in the native silver and dyscrasite, but according to F. Mrňa (pers. com.) this element is essentially absent in the deposits at Jáchymov.

Veins, similar to those at Jáchymov, occur at Annaberg, Marienberg, Schneeberg, and Johanngeorgenstadt on the Saxon side of the Erzgebirge, at Wittichen in the Kinzig valley, and at Wolfach in the Black Forest.

### Laurion, Greece

These deposits have been known and mined for more than 3,000 years for lead and silver and more recently for zinc as well.

The deposits are irregular, bedded, and keel-like replacements in crystalline limestone, dolomite, and calcareous schists. The important hypogene ore minerals are fine-grained argentiferous galena, sphalerite, and minor arsenopyrite and chalcopyrite. The gangue minerals are mainly carbonates and fluorite. The fluorite is often associated with Ag-rich galena and is an indicator mineral of rich ore shoots according to some writers. The deposits are deeply oxidized—the principal supergene minerals include cerussite, anglesite, smithsonite, hemimorphite, greenockite, and limonite. In addition there is some native silver and a host of supergene lead, zinc, copper, iron, manganese, and nickel minerals. The oxidized lead-zinc ores were very rich in silver, averaging 10 per cent Pb, 250 ounces Ag per ton, and a little gold. The hypogene lead ore averages 12 per cent Pb and 5 ounces Ag per ton.

A more detailed description of the Laurion deposits is given by Putzer (1948).

### Broken Hill and Mount Isa, Australia

These great deposits are large silver producers, but are generally thought of as lead-zinc deposits. Cadmium, copper, and some gold are also produced.

The Broken Hill deposits are described in detail by Andrews (1950), King and Thomson (1953), King and O'Driscoll (1953), O'Driscoll (1953), and Carruthers and Pratten (1961).

Briefly they are immense lenses and saddles of sulphide ore in Precambrian sillimanite-garnet-mica-feldspar gneisses, quartz schists, mica schists, and amphibolites in a highly granitized terrain injected by numerous pegmatites. The lenses and saddles of ore are mainly conformable with the metasediments.

The principal sulphide minerals are coarse galena, sphalerite, and pyrite associated with either a silicate gangue or a carbonate gangue. The silicate gangue consists mainly of quartz, manganese garnet, rhodonite, and minor amounts of fluorite; the carbonate gangue consists mainly of calcite and quartz. The average grade of the ore is 14 per cent Pb, 13 per cent Zn, and 8 ounces Ag per ton.

Andrews and others considered that the great lodes were of replacement origin, developed in drag-folds and contorted zones of the sediments. In recent years a number of papers have appeared suggesting that the deposits are of sedimentary origin later modified by metamorphism. The first hypothesis seems the more probable when all of the facts are taken into consideration.

The Mount Isa deposits have been described by Carter (1950, 1953). They are conformable lenses and tabular bodies in siliceous, dolomitic, and carbonaceous shale of Precambrian age. The ore consists of massive and disseminated sulphides, the former exhibiting an intricate fine banding probably inherited from the shale. The principal minerals are pyrite, some as spherical aggregates, sphalerite, chalcopyrite, arsenopyrite, pyrrhotite, marcasite, galena, tetrahedrite, polybasite, pyrargyrite, and proustite. The bulk of the silver is contained in tetrahedrite and galena. The average grade of the deposits is about 10 per cent Zn, 8 per cent Pb, and 7 ounces Ag per ton.

The origin of the Mount Isa deposits has recently been the source of much debate. According to the earlier writers the deposits were formed by replacement along a zone of shearing, crenulation, and folding parallel to the bedding. Recent writers have regarded the deposits as sediments with some remobilization of the sulphides. This view is based in part on the evidence of sulphur and lead isotopes and on the presence of spherical pyrite thought to have been precipitated by micro-organisms (Love and Zimmerman, 1961).

To this writer the evidence from the spread in the sulphur isotopic values is inconclusive, as are also the data on the lead isotopes. We simply do not know enough about the geochemistry of the isotopes of these two elements to tell whether the ratios indicate sedimentary, remobilization, or secretion processes.

The evidence of precipitation of pyrite by micro-organisms seems more convincing, although there has been much controversy about the precise origin of the pyrite spheres. Schouten (1946), for instance, considered that the spheres were essentially inorganic. The writer and his colleagues have also found pyrite spheres identical to those figured by Love and Zimmerman (1961) in undoubted epigenetic deposits, suggesting that the presence of these spheres is not a criterion for syngenesis. We shall have to wait for further research on all these matters. It could be that the pyrite, as well as the other sulphides, are largely of syngenetic (biogenic) origin in deposits of the Mount Isa type, and that they were later extensively remobilized as suggested by Fisher (1960).

## Kurokô (Black Ore) Deposits of Japan

These unusual deposits are characteristically developed along the inner zone of Tertiary sediments and effusive rocks in northeast and southwest Japan. The geology near the numerous mines is complex and differs from district to district. Briefly, the rocks are a volcanic sequence of tuffs, breccias, conglomerates, black shales, eruptive liparites, rhyolites, dacites, and andesites, and intrusive dolerites, andesites, diorites, and quartz porphyries. The best general descriptions of the deposits are those by Kinoshita (1931), Horikoshi (1951-52), and Ishikawa, *et al.* (1962).

Most of the deposits occur in the tuffs and shales, and consist of veins, stockworks, irregular masses and nodules, and conformable beds. They consist of an intimate mixture of very fine grained sphalerite, galena, and barite, usually accompanied by some chalcopyrite and often large masses of pyrite. In some areas large masses of gypsum occur in the vicinity of the sulphide bodies. The name 'kurokô' derives from the black colour of the ores, but the colour as well as the texture and mineral composition varies considerably and a number of varieties are distinguished. These include massive 'kurokô', brecciated 'kurokô', banded 'kurokô', ôkô, or yellow ore, which is a crystalline mass of pyrite and chalcopyrite accompanied by some quartz, and 'keikô', or siliceous ore, which is composed of silicified liparite or tuff heavily impregnated with pyrite, sphalerite, galena, and other ore minerals. All of these varieties may occur individually or they may be intimately related in a single deposit.

The country rocks of the kurokô deposits are affected by marked alterations in places. These include propylitization, albitization, kaolinization, and silicification. In some mines these alteration effects appear to be related spacially to the deposits; in other mines the relationships are not clear since the alteration effects spread throughout the country rocks.

The grade of the deposits is variable. Some deposits yield essentially lead, zinc, and copper; others yield mainly copper or zinc. All types yield some silver and gold. The lead-rich deposits tend to have the highest contents of silver (up to 40 ounces Ag per ton or more) and very little gold. On the other hand the pyrite and chalcopyrite deposits are richer in gold with smaller amounts of silver. Most of the published analyses of these ores show that silver is always in excess of gold and that the Ag/Au ratio ranges from 5 to 220.

A number of the deposits are deeply oxidized and present a vertical profile consisting of a surface gossan zone, a leached zone, an oxide enriched zone, and a secondary sulphide enriched zone. The gossan is composed mainly of iron oxides and hydrated oxides and barite. The components of the sulphides are nearly completely leached out. The leached zone is depleted in copper and zinc and enriched in silver and gold. The oxide enriched zone may contain iron oxides, marcasite, pyromorphite, native copper, linarite, malachite, cerussite, anglesite, and native silver. Copper and silver are greatly enriched in some of the deposits. The secondary sulphide enriched zone contains chalcocite, bornite, covellite, argentite, etc. It is enriched in copper, silver, and a variety of other elements. The secondary sulphide zone is generally less than 5 metres thick.

There has been considerable discussion on the origin of the kurokô ores. Most of the Japanese geologists consider them to be epigenetic replacement deposits derived by hydrothermal processes related to Tertiary magmatism. Some investigators, noting the conformable banded nature of the ores consider them to be of sedimentary origin. From the detailed descriptions of most of the deposits the weight of the evidence appears to favour an epigenetic origin.

The kurokô ores are interesting in that they are probably young equivalents of the massive sulphide deposits found in older rocks. Had they gone through a period of metamorphism and recrystallization they would probably present the features we now see in the older massive sulphide bodies found in Precambrian, Palaeozoic, and Mesozoic volcanic terrains. In this respect we may note that the Buchans lead-zinc-copper-silver-gold deposits in Newfoundland are remarkably similar to the kurokô bodies. The Buchans deposits, described in some detail by Relly (1960) and Swanson and Brown (1962) occur in the western part of the central volcanic belt of Newfoundland, which consists of a complex series of Ordovician andesites, dacites, rhyolites, volcanic breccias, tuffs, and arkose. The orebodies consist of great lenses and irregular bodies of massive and disseminated sulphides in volcanic breccias and tuffs. The principal minerals are sphalerite, galena, chalcopyrite, tetrahedrite, and pyrite. The main gangue minerals are barite and quartz. The wall-rock alteration effects are those of sericitization, silicification, pyritization, and chloritization. The grade of the ore is about 15.5 per cent Zn, 7.8 per cent Pb, 1.4 per cent Cu, 3.5 ounces Ag, and 0.05 ounce Au per ton. The silver occurs in the native form, in argentite, in galena, and probably also in the chalcopyrite and tetrahedrite. There are no obvious correlations of the two precious metals with Cu, Pb, or any other element in the orebodies.

### Gold-Silver Veins, Lodes, etc. in Sediments

These deposits are widespread throughout the world and have supplied a large amount of silver as a by-product of gold mining. The types of deposits are well known. They include veins and lodes in faults and fractures in greywacke, slate, argillite, and phyllite; irregular masses in drag-folds in these rocks; and saddle-reefs and legs on the noses and flanks of tight anticlines (Bendigo type). The principal gangue is quartz, generally with a little calcite or ankerite. The valuable ore minerals are native gold, auriferous pyrite, and auriferous arsenopyrite. There is also more or less of scheelite, galena, sphalerite, chalcopyrite, tetrahedrite, and pyrrhotite; more rarely argentite, stibnite, boulangerite, and other sulphosalts.

Deposits of this type are widespread in Canada, particularly in Nova Scotia (Meguma Group), in various parts of the Canadian Shield, and in British Columbia and the Yukon Territory.

## Silver-Gold and Gold-Silver Veins and Lodes in or Associated With Volcanic Flow Rocks

Representatives of this type of deposit are widespread throughout the folded volcanic terrains of the earth. The deposits occur in rocks of all ages, but the largest number occur in Precambrian and Tertiary rocks.

The favourable host rocks are commonly andesites, latites, trachytes, and rhyolites. In Precambrian rocks such assemblages are usually referred to as 'greenstones'. Deposits in basalts are rare. Many deposits occur in tuffs, agglomerates, and sediments interbedded with the volcanic flows. In the older terrains, the rocks are generally regionally metamorphosed and exhibit the characteristic regional metamorphic facies outward from igneous or granitized centres. The younger rocks generally show the effects of chloritization (propylitization) over broad areas, but locally some of the andesites and rhyolites may be relatively fresh.

In the older rocks the deposits are veins, lodes, stockworks, pipes, and irregular masses generally in extensive fracture and shear zone systems. Some occur in dragfolds. The deposits in the younger rocks are usually confined to fissures, fractures, and faults that often have a limited horizontal and vertical extent. Others, however, are associated with fracture and fault systems that extend for many miles.

The structure of the veins and lodes in the older rocks is generally compact and the minerals are commonly intimately intergrown with one another. Recrystallization and a coarse-grained character are common. The structure of the younger, generally Tertiary, deposits is characteristic. Open cavities are abundant, and filling, crustification, and comb and cockade structures are conspicuous. The vein walls are often irregular, and the vein matter is generally frozen to the walls. Banding and repeated surges of mineralization witnessed by numerous overgrowths are characteristic.

Quartz is the most important gangue in these deposits. In the older rocks the quartz is colourless, white, milky, grey, or black, and forms coarse granular aggregates, intimately intergrown with the other vein minerals. Most of the quartz gives the appearance of being considerably recrystallized. Some varieties have a definite schistose and gneissic appearance. Vugs and crusts of quartz crystals occur in some deposits, but they are rare. The quartz in the younger rocks is characteristically white or light grey, and in some deposits an amethyst colour is often noticeable. It is usually fine grained and often chalcedonic. Some varieties exhibit a delicate colloform banding suggesting colloidal deposition. Several generations are often present, and these cement older brecciated quartz aggregates, ore minerals, and wall-rock fragments.

Other gangue minerals in the older deposits include calcite, dolomite, and ankerite. In the younger deposits, barite and fluorite are also common, and rhodochrosite and rhodonite may be present in places. Adularia is characteristically developed in some Tertiary deposits, and kaolinite, sometimes in abundant amounts, is present in the veins. It may be a product of descending surface waters. Zeolites occur in a few of the younger deposits.

The metallic minerals are varied and seem, in part, to be dependent on the age of the deposits. Native gold is the most common. In the older deposits it tends to be relatively pure with only a little silver, the ratio of Ag/Au ranging between 1:5 and 1:50. The gold of the younger deposits is usually much richer in silver, the ratio Ag/Au approaching 1:1 in some districts. Gold and silver tellurides commonly occur in all ages of deposits, but are particularly abundant in the younger deposits. Both the native gold and gold-silver tellurides tend to be late minerals in the paragenetic sequence of the veins. Gold-silver selenides occur in some of the younger deposits, but these minerals are generally rare.

The principal silver mineral in the deposits is acanthite (argentite). In addition there may be proustite, pyrargyrite, miargyrite, stephanite, polybasite, and tetrahedrite. Native silver is common, but is often an oxidation product. These silver minerals are rare in the older (Precambrian) deposits, but a little silver-bearing tetrahedrite may occur in some veins. Most of the deposits that are rich in silver minerals are in Palaeozoic, Mesozoic, or Tertiary rocks.

Among the other metallic minerals, pyrite, arsenopyrite, argentiferous galena, sphalerite, and chalcopyrite are nearly ubiquitous in all ages of deposits, although the last three minerals are generally present in only small amounts in the Precambrian deposits. Pyrrhotite occurs in some of the older deposits, but is rare in the younger. Stibnite and a variety of sulphosalts are most common in the younger deposits, but also occur in some abundance in certain Precambrian ones. Alabandite is usually restricted to the younger deposits. Molybdenite and scheelite are present in certain Precambrian deposits, but are relatively rare in younger veins, although there are some exceptions to this generalization.

Characteristic types of wall-rock alteration are generally developed adjacent to and in the vicinity of nearly all deposits in this class. In the old Precambrian rocks the most common types of alteration are chloritization, sericitization, carbonatization, pyritization, and silicification. In the younger rocks propylitization (chloritization and pyritization) is especially characteristic, and there may also be a development of adularia, silicification, kaolinization, sericitization, and more rarely alunitization.

Veins in Precambrian greenstones and in certain younger andesites and trachytes are generally flanked by zones of carbonate-sericite schist, which grade imperceptibly into zones of chlorite-carbonate and chlorite schist. In general these alteration zones represent a loss of silica and some of the cafemic elements, and major increases in water, carbon dioxide, sulphur, and potassium. Sodium is generally leached. The reactions to produce the alteration zones are complex and have been discussed in detail by the writer (Boyle, 1961). The most significant feature is the transfer of silica to the vein sites where it probably crystallizes as quartz. By means of detailed chemical profiles it has been shown that most of the vein quartz owes its origin to this process.

Where rhyolites or dacites are present the alteration effects are less marked. Sericitization, pyritization, and silicification are, however, characteristic. Sediments, interbedded with the volcanic rocks, are not markedly affected in most places, although there may be a development of pyrite, sericite, and some carbonate minerals near the veins.

Propylitization is characteristic of many Tertiary deposits. The mineralogical changes include the abundant development of chlorite and pyrite, sometimes also epidote, from the ferromagnesian minerals of andesite and similar rocks. There is also a development of carbonates and some sericite in certain areas. The chemical changes consist of a moderate leaching of potassium and sodium, a decrease of silica and cafemic elements, and additions of water, sulphur, and carbon dioxide in some areas. The propylitization is pervasive, being developed usually adjacent to the veins as well as in great volumes of rock in the general vicinity of the mineralized zones.

The alteration in the younger rhyolites and dacites is usually sericitization and silicification. Alunitization, the development of adularia, and carbonatization may affect all younger rock types. Silicification, without the development of lime silicates, may take place in limestones and limy shales. Sandstones, shales, and argillites are generally little altered.

The elements commonly concentrated in this class of deposits include Ag, Au, Te, Sb, As, Cu, Pb, Zn, Ca, Mg, Fe, Mn, K, $SiO_2$, $CO_2$, and S; less common are Mo, W, Se, Ba, and F. The source of these elements is probably in the volcanic pile in which the deposits are developed. Interbedded sediments, tuffs, and agglomerates may also have made a contribution. The manner of concentration is probably similar to that suggested above for deposits in sedimentary rocks.

Numerous deposits belong in this category. At least three types can be recognized. Briefly these are with examples:

1. Gold deposits. Native gold, alloyed with variable, though generally small, amounts of silver, is the principal economic mineral. There may be subordinate amounts of acanthite (argentite), tetrahedrite, sulphosalts, ruby silver, etc. Quartz is the principal gangue.

Numerous examples occur in the greenstone belts of the Canadian Precambrian Shield, including Yellowknife, Red Lake, Porcupine, Kirkland Lake, and western Quebec. Other examples occur in the Canadian Cordillera, as in the Bridge River district where the veins occur in augite diorite. There are many examples in Australia (Kalgoorlie), in U.S.A. (Mother Lode system where the veins cut greenstones), and elsewhere. In all these deposits native gold is the economic mineral. There may be minor amounts of gold-silver tellurides in some deposits. Silver is won as a by-product.

Deposits in Tertiary andesites, rhyolites, and allied rocks are found in various parts of the world. In these, native gold, often greatly enriched in silver (up to 40 per cent or more), is the principal economic mineral. Gold-silver tellurides are generally subsidiary. Examples occur in Roumania (Transylvania), New Zealand (Hauraki), Mexico (El Oro), U.S.A. (Black Mountains, Arizona; De Lamar, Idaho; Rawhide, Nevada), Japan, and elsewhere.

None in Canada ?

2. Silver-gold-quartz deposits. Most of these deposits occur in rocks younger than Precambrian. Many occur in Tertiary andesites and rhyolites and in underlying Palaeozoic or Mesozoic sediments and volcanic rocks. The principal economic minerals are silver-rich native gold (electrum), argentite, tetrahedrite, ruby silvers, silver selenides, and polybasite. Typical examples are found in the Tonopah district in Nevada where the veins cut Tertiary volcanic rocks and are mineralized with electrum, argentite, polybasite, pyrite, chalcopyrite, galena, sphalerite, silver selenides, and small amounts of scheelite and wolframite in a gangue of quartz, sericite, rhodochrosite, and adularia. Another example is the Comstock Lode in Nevada. This famous deposit was localized in a fault separating intensely propylitized and sericitized Tertiary and older volcanic rocks from Mesozoic rocks. The great bonanzas consisted of crushed quartz and some calcite in which were electrum, gold, pyrite, argentite, polybasite, a variety of other silver sulphosalts, and minor amounts of sphalerite and galena. In the deeper levels, flows of hot (170°F) calcium sulphate waters and rock temperatures of 115°F made mining of the lode difficult.

Further examples of this type of deposit are common in Mexico, especially in the Pachuca, Hidalgo district and at Guanajuato. In the Pachuca district the fissure veins carry quartz, rhodonite, galena, sphalerite and an abundance of argentite, polybasite, stephanite, and traces of gold. They cut Lower Cretaceous sediments and a variety of Tertiary intrusive and extrusive rocks which exhibit widespread propylitization, chloritization, and silicification. The great lodes of the Guanajuato district, of which the Veta Madre is the most famous, occur in extensive fault zones that cut through pre-Cretaceous shales, sandstones, and conglomerates cut by rhyolite, andesite, porphyry, and monzonite and overlain by Tertiary volcanic rocks. The vein matter is quartz, in part amethystine, carbonate, adularia, pyrite, argentite, native silver, native gold, various silver sulphosalts and minor amounts of galena, sphalerite, and chalcopyrite. The Ag/Au ratio in the ores is about 100/1.

3. Gold-telluride and gold-selenide deposits. These deposits are veins, pipes, and stockworks generally in Tertiary volcanic rocks, although some are known in older rocks. The deposits are mined essentially for gold with silver as a by-product.

Cripple Creek, Colorado, is the best known example of the gold-telluride deposits (Lindgren and Ransome, 1906). The country rocks are Precambrian granites and gneisses broken through by a great mass of Tertiary volcanic rocks probably representing a large volcano. The core of this volcano is composed of tuffs and breccias of latite-phonolite, which are cut by dykes and masses of phonolite, syenite, monchiquite, and vogesite. The deposits are veins, mineralized sheeted zones, replacements in breccia and along fissures, and irregular pipes in mineralized breccia. These cut both the Precambrian and Tertiary rocks, but are best developed in the latter. The principal ore mineral is calaverite, $AuTe_2$, with a silver content generally less than 4 per cent. There is practically no hypogene native gold. Associated with the calaverite are small amounts of sylvanite, petzite, pyrite, sphalerite, galena, tetrahedrite, stibnite, cinnabar, molybdenite, and minor amounts of wolframite (huebnerite). The gangue is quartz, fluorite, carbonate, and roscoelite (the vanadium mica). The vein structure is drusy. The alteration is pyritization, carbonatization, and propylitization. Adularia is developed in some veins. The deposits are now largely exhausted.

None in Canada!

The gold-selenide deposits are rather rare. There are, however, examples at Republic in Washington, in the Radjang-Lebong gold field in Sumatra, Indonesia, and at the Kushikino mine, Kagoshima Prefecture, Japan. Most of the deposits are veins, stockworks, and pipes in Tertiary or younger andesites. The principal gangue is quartz and calcite, sometimes adularia, usually in banded and colloform arrangements or in fine-grained intergrown aggregates. The principal ore minerals are native gold often high in silver, electrum, various silver, lead, and copper selenides, such as aguilarite, naumannite, and berzelianite, pyrite, tetrahedrite, chalcopyrite, galena, and sphalerite. The alteration attending the veins is generally silicification, pyritization, or propylitization. The Ag:Au ratio, in the Radjang-Lebong field varies from 1:1 to 90:1 (Van Bemmelen, 1949).

None in Canada

## Silver Deposits in a Complex Geological Environment Comprising Sediments, Volcanic, and Igneous or Granitized Rocks

Deposits in this category combine nearly all the epigenetic features described for the previous categories. The origin of their metallic and other components may lie in the combined group or groups of rocks in which they lie. The deposits are best illustrated by specific examples. Those chosen include Cobalt, South Lorrain, Elk Lake, and Gowganda, Ontario, the Great Bear Lake silver deposits, the Beaverdell and Torbrit silver deposits in British Columbia, and the deposits of El Potosí in Bolivia.

### Cobalt, South Lorrain, Elk Lake, and Gowganda, Ontario

The best descriptions of the geology, mineralogy, and ore deposits of these silver camps can be found in the publications by Miller (1908, 1913), Burrows (1909), Knight (1924), Moore (1934), Bastin (1917, 1922, 1925, 1939, 1949, 1950), Reid (1943), Thomson (1957, 1964, 1965), Lowes (1963), and Cunningham (1964) for Cobalt and South Lorrain; Burrows (1926), Todd (1926), Reid (1943), Montgomery (1948), Bastin (1949), Moore (1956, 1957), and Scott (1964) for Gowganda; and Knight (*in* Miller, 1913), and Reid (1943) for Elk Lake.

The silver deposits of Cobalt were discovered in 1903 during the building of the Timiskaming and Northern Ontario Railway, and since that time have yielded a large part of the Canadian silver production and some cobalt, copper, nickel, arsenic, and bismuth. The bonanza years were from 1904 until about 1930, after which there was a gradual decline. Today the camp is experiencing a rejuvenation. The production of silver to 1964 is about 400 million ounces. In addition, 25 million pounds of cobalt, 3 million pounds of nickel, and about 1.5 million pounds of copper have been won from the deposits.

The types of country rocks in the Cobalt district are shown in Table 45 (*see also* Fig. 5).

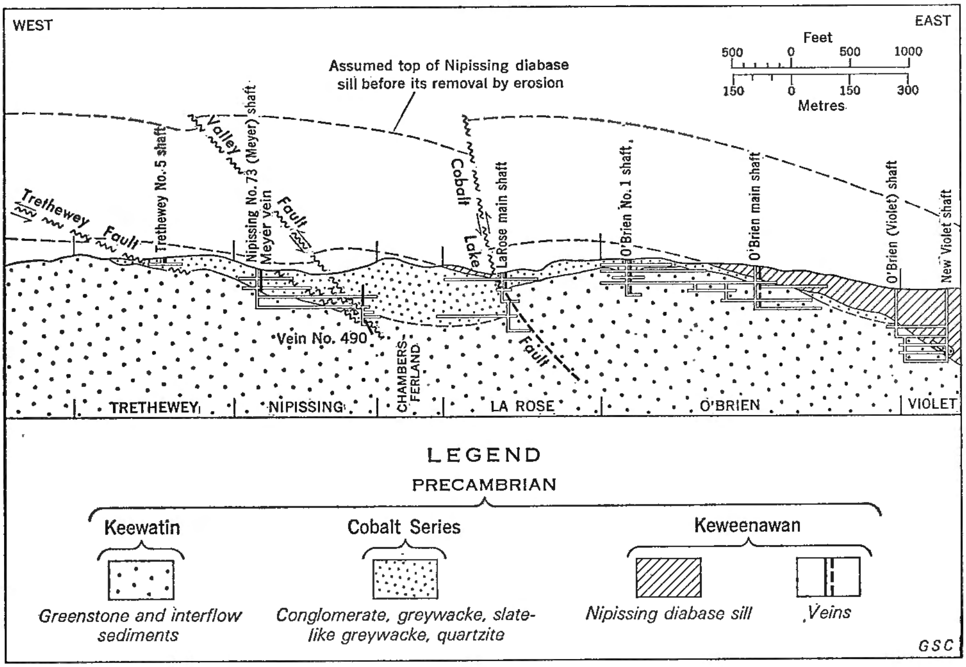

**FIGURE 5.** Generalized geological features of Cobalt area, Ontario (*after* Knight, Miller, Thomson, *and others*).

TABLE 45 | *Table of Formations, Cobalt District, Ontario*[1]

Cenozoic

*Recent* and *Pleistocene* — clay, sand, gravel, till

– – – – – – – – – – Great unconformity – – – – – – – – – –

Palaeozoic

*Silurian* and *Ordovician* — dolomite, limestone, shale

– – – – – – – – – – Great unconformity – – – – – – – – – –

Precambrian

*Keweenawan* — olivine diabase dykes, quartz diabase dykes

Intrusive contact

Nipissing diabase — sills

Intrusive contact

*Huronian* (Cobalt Series)

Lorrain Formation — quartzite, arkose

Firstbrook Formation — greywacke

Coleman Formation — conglomerate, greywacke, quartzite

– – – – – – – – – – Great unconformity – – – – – – – – – –

*Matachewan* — dark intrusive rocks

Intrusive contact

*Algoman* — granite, granite gneiss

Intrusive contact

*Haileyburian* — lamprophyre, minor dark intrusive rocks

Intrusive contact

*Timiskaming* — conglomerate, greywacke, quartzite

– – – – – – – – – – Great unconformity(?) – – – – – – – – – –

*Keewatin* — bedded sedimentary rocks

— acid lava flows

— basic and intermediate lava flows with interflow sedimentary rocks

[1] Adapted from Thomson (1957)

The rocks of particular interest are the steeply dipping Keewatin basic and intermediate lavas (greenstones) and interflow sediments, which are overlain unconformably by the flat-lying to gently dipping Cobalt Series (Coleman Formation) consisting of conglomerate, greywacke, and quartzite and the Nipissing diabase sill, which cuts across these rocks at a low angle.

The deposits occur in the Cobalt Series, in the Nipissing diabase, and in the Keewatin rocks. Most of the high grade deposits are in the first two rock types. The deposits are predominantly short veins, although some have been traced for a thousand feet or more on their strike and dip. An orebody usually consists of one, two, or more veins that ramify and intersect at all angles. The width of the veins varies from a few tenths of an inch up to a foot or more. Most are very narrow and appear inconsequential on a first examination. Some of the deposits occur in extensive faults or in fractures parallel or closely related to the faults. Examples of this feature were the orebodies in the Cobalt Lake fault and those in subsidiary and parallel fractures associated with this structure. Thomson (1957) remarked, however, that regional faults in general are not the controlling features in localizing orebodies. He found that the fissures and fractures are largely controlled by old structures in the Keewatin, particularly interflow sedimentary bands; basins and arches in the Nipissing diabase; and three contacts, the upper and the lower of the Nipissing diabase intrusion and the contact between the Cobalt Series and the underlying Keewatin rocks. The occurrence of steeply dipping veins in Cobalt sediments, which fill small basins in the Keewatin greenstones, is particularly marked in a number of the more recently discovered deposits.

The veins have a very complex mineral assemblage. The principal gangue is white to pink calcite, and there is a little dolomite and quartz and small amounts of hematite in places. The metallic minerals include native silver, dyscrasite, argentite, smaltite-chloanthite, loellingite, safflorite, rammelsbergite, skutterudite, arsenopyrite, gersdorffite, cobaltite, glaucodot, niccolite, breithauptite, chalcopyrite, galena, pyrite, pyrrhotite, sphalerite, tetrahedrite, native bismuth, and minor amounts of pentlandite, polybasite, stephanite, ruby silver, and stromeyerite. Native silver and the Co-Ni arsenides are the most abundant and characteristic minerals. Secondary minerals include erythrite, annabergite, scorodite, manganese oxides (wad), and limonite.

The native silver occurs as specks, spangles, and masses, some of which are huge slabs weighing up to 1,600 pounds. Both the native silver and dyscrasite contain mercury. The silver may be intimately intergrown with the Ni-Co arsenides, calcite, and other minerals or it may occur alone, often without any gangue minerals, in tiny fractures in the wall-rocks. The Ni-Co arsenides, calcite, and other minerals are intimately intergrown, and there has been much controversy on their paragenesis and also on their relationship to the native silver. Many of the arsenides exhibit a 'concretionary' or 'tubercular' texture, which to Lindgren and others suggested crystallization from a gel.

Silver and cobalt-nickel arsenides are intimately associated throughout the camp, and while there is probably no silver vein without cobalt and nickel arsenides there are veins with an abundance of cobalt minerals that have little or no silver.

Many of the veins in diabase are marked by narrow alteration zones rarely over one inch in width (Bourne, 1951). These zones show a good bilateral symmetry with respect to the vein or fracture, and to the eye appear as a narrow dark band immediately adjacent to the vein followed outward by a greyish bleached band. In thin sections the light greyish bleached band consists of severely sericitized feldspar, epidote, clinozoisite, magnesium-rich carbonate, leucoxene, biotite, pyrite, apatite, and quartz, all arising from the alteration of the diabase, which when fresh, contains essentially sodic labradorite, augite, some secondary hornblende and biotite, titaniferous magnetite, pyrite, biotite, apatite, and interstitial quartz. The greyish band is gradational into the dark band which consists essentially of pennine chlorite, minor epidote, oligoclase, carbonate, leucoxene, quartz, pyrite, and apatite. The ophitic texture of the diabase is retained in the grey band but destroyed in the black band.

Some of the veins in the Cobalt sediments are also marked by a faint zone of wall-rock alteration which does not seem to have been investigated. The writer observed that this zone of alteration is rarely more than an inch or so wide and is essentially a greyish bleached zone which grades imperceptibly into the greenish sedimentary rock. In places there is evidence of a darker chloritic zone adjacent to the veins in this bleached zone. In thin sections the bleached zone is seen to consist essentially of a matted aggregate of clastic grains of quartz, highly altered zoisitized feldspar, abundant carbonate, and much chlorite (pennine). The darker zone in the bleached zone is due to increased amounts of chlorite. All of these minerals represent an alteration of the sediment which when fresh contains clastic grains of quartz and feldspar in a matrix of chloritic material and minor carbonate. The texture in the bleached zones is not much different from that in the relatively fresh sediment.

Another interesting type of alteration occurs in the Cobalt area, particularly in the Cobalt sediments. This is a green spotted alteration that occurs scattered throughout the sedimentary rock and does not seem to be related to any particular feature such as the veins. In thin sections the spots are seen to consist essentially of matted aggregates of a greenish chlorite with marked anomalous extinction (pennine). These bind clastic grains of quartz and highly altered feldspar grains. It is not known whether this type of alteration is characteristic of the areas in which veins occur or not. It deserves further investigation.

The deposits of South Lorrain are essentially mineralogically similar to those at Cobalt. Some of the veins occur in the Nipissing diabase near the upper contact of the sill; others occur in the Keewatin rocks above the sill. One of the veins in the Keeley mine (Wood's vein) was deeply oxidized to a depth of 600 feet or more (Bell, 1923). Much of the silver in this oxidized vein was apparently of secondary origin.

The deposits of the Gowganda area are very similar to those at Cobalt and South Lorrain and their geological setting is much the same. The same suite of Ni-Co arsenides is present as well as the other common metallic minerals listed for the Cobalt deposits. The principal economic mineral is native silver. There is some bismuthinite at Gowganda, and hematite is present in a few of the veins. The principal gangue is calcite, but some veins contain more quartz than calcite. Epidote and axinite occur in some of the veins and are generally earlier than the metallic minerals.

Some of the veins in the Gowganda area are unusual in that they contain red granophyre or micropegmatite material. In some of these the granophyre abuts against the diabase walls and is followed inward by quartz, then calcite with Co-Ni arsenides, and silver in the centre. The nature and origin of the granophyre and its relationship to the silver veins at Gowganda and Cobalt has been a subject of much debate. Bastin (1935) called the red rock 'aplite' and considered it to be the product of hydrothermal alteration along fractures. Bourne (1951) likewise held this view after examining one of the 'aplites' near Cobalt in detail. Moore (1934, 1956) on the other hand, termed the rock a granophyre and considered it to be an acid differentiate of the diabase sill. Sampson and Hriskevich (1957) called the bodies at Cobalt aplites and thought that they were late-stage differentiates from the tholeiitic magma that gave rise to the diabase. Collins (1913) long ago likewise considered the granophyre or micropegmatite to be a differentiate of the sill and thought that the granophyre continued to differentiate until the silver veins formed as the end product of the process.

At present there appears to be no resolution of the aplite problem. There may actually be several origins for these unusual rocks. The aplites, or some of the rocks called aplites, may be the result of magmatic differentiation processes within the diabase, and the 'red rock', granophyre, or what is called 'aplite' by some investigators may be due to assimilation of sediments by the diabase or may be produced by alteration processes related to the formation of the silver veins. The writer is of the opinion that the silver- and Ni-Co arsenide-bearing aplites originated by diffusion processes just after the solidification of the diabase but while it was still at a high temperature. The mineral constituents probably came in part from the diabase and in part from the neighbouring sediments and volcanic rocks. The presence of albite in the veins simply reflects a higher temperature of formation. Under conditions of lower temperature, when the majority of the silver veins seem to have formed, the sodium in the diffusion currents gave rise to an albitization of the wall-rocks in places (Bastin, 1935). The whole problem of the mineralized aplites and their relationship to the silver veins should be studied further by means of detailed chemical and spectrographic analyses.

Most of the veins in the Gowganda area are fissure-fillings, and are localized mainly in a Nipissing diabase sill usually within 300 to 400 feet from its upper contact. A few of the productive veins occur in the Keewatin greenstones and Cobalt Series conglomerates, but these are rather rare.

The silver veins in the Elk Lake area are essentially the same as those at Cobalt. The gangue is principally calcite with a little barite in places. Native silver is the economic mineral and the Ni-Co arsenides and other metallic minerals noted for Cobalt are present. Unusual aplite veins, or dykes carrying some silver and similar to those in the Gowganda area, cut the Nipissing diabase in places.

Most of the veins in the Elk Lake area are in the Nipissing diabase. To date none has produced more than a few tons of ore.

The origin of the Cobalt deposits and those in nearby areas has been debated for many years and still remains an enigma. An excellent summary of the various early theories may be found in Knight (1924) and Moore (1934).

Most early investigators considered the diabase to be the source of the silver and many consider this theory to be valid today. Van Hise thought that the diabase was the source of the ore minerals and that the Keewatin and Cobalt conglomerates were the main sources of the calcite in the veins. Collins (1913) also considered the diabase as the logical source for the elements in the veins and thought that the veins originated during differentiation of the sills. At Gowganda he felt that the granophyre (or aplite) was a product of the differentiation of the diabase, and that it continued to differentiate until the mineral veins formed as an end product of the process. Spurr (1923) expressed the opinion that the veins at Cobalt were intrusive vein dykes of magmatic origin. Others debated the problem of the origin of the silver, whether or not it was primary or secondary, with the consensus weighing heavily on the side of a primary origin. Miller, who studied the Cobalt deposits for many years and knew them better than any other geologist, was somewhat cautious in expressing an opinion on their origin. At times he favoured the theory that the metals were leached out of the Keewatin greenstones and other associated rocks; at other times, especially in his final report (Miller, 1913), he felt that the diabase and the ores came from one and the same magma. Moore (1934, 1956) considered that there are only two possible sources for the mineral content of the veins—the Nipissing diabase sills or a source beneath the sills, presumably the parent magma of the sills. He favoured the latter and concluded that the ores came from a somewhat more acid phase of the magma than that which gave rise to the sills. Hriskevich (1952) thought that the cobalt-silver mineralization was derived in part by differentiation within the diabase sheet, and in part from another magmatic source—the parent quartz diabase magma. Later Sampson and Hriskevich (1957) ascribed the major mineralization of the Cobalt region to the differentiation of a tholeiitic (diabasic) magma at depth.

Whitman (1920) took a different view of the origin of the veins at Cobalt than that of most investigators. He concluded that:

1. The cobalt-nickel-silver ores of the Cobalt district were derived by diffusion and metasomatic fixation from the sill of Nipissing diabase with which they are associated.

2. They were deposited essentially in their present form below the groundwater level, not by circulating solutions, but by migrant ions traversing virtually stagnant or slowly circulating aqueous solutions, that coursed all parts of the diabase. Deposition took place in such favourable seats of deposition as were accessible in the neighbourhood of the margins of the diabase.

3. Mineral-laden water filled all the pores, joints, and fractures of the diabase and its neighbouring rocks, and through it moved the ions of vein material, at a temperature considerably below the melting point of the diabase, and at a pressure of several thousand feet of hydrostatic head.

Later Whitman (1928) substantiated his theory at least in part by laboratory experiments.

It is strange how Whitman's two papers have been lost in the literature of economic geology despite the fact that they are based on good geological reasoning and laboratory work. With some modification they appear to be valid not only for the deposits at Cobalt but for many other types of deposits in a variety of geological settings.

In considering the origin of the Cobalt-type deposits, the present writer has been struck by a number of features that appear to bear directly on the problem. These can be enumerated as follows:

1. The deposits, in addition to silver, are greatly enriched in cobalt, nickel, bismuth, arsenic, and sulphur, and a source for all of these elements must be found before any adequate theory can be formulated.

2. The deposits are structurally controlled in fractures or faults that cut all the rocks in the area, with perhaps the exception of the late Keweenawan diabase dykes. Certainly the Nipissing diabase sills were completely crystallized before the veins were formed. It follows, therefore, that the sills could not have yielded the constituents in the veins by the classical differentiation mechanism.

3. While diabase is present at Cobalt, Gowganda, and Silver Islet and in other areas such as Chalanches, France, this rock or its equivalent is lacking in many other areas where native silver deposits identical in mineralization to those at Cobalt are present, e.g., Jáchymov and Kongsberg. The diabase may not, therefore, be the key to the source of all of the elements in the veins.

4. Many of the veins at Cobalt cut deeply into the Keewatin rocks, occurring both in greenstones and in interbedded sediments. With respect to the latter it is interesting to note that some veins occur in the Cobalt conglomerate and Nipissing diabase on the upward projection of some of these interbedded Keewatin sedimentary layers.

5. Many of the Keewatin greenstones, and particularly the graphitic interbedded sedimentary layers, contain an abundance of sulphides, mainly pyrite and pyrrhotite. The interbedded sediments also contain small amounts of galena, sphalerite, and chalcopyrite in places. These could be interpreted as introduced sulphides, but their persistence in similar sediments in many parts of the Canadian Shield suggests that they were originally sedimentary. They have been recrystallized and probably partly mobilized during regional metamorphism.

In order to determine a source for the elements in the veins at Cobalt, composite samples of the Keewatin greenstones, their interbedded sediments, the Cobalt conglomerate and greywacke, and the Nipissing diabase sill, were collected and analyzed for Cu, Pb, Zn, Ni, Co, Bi, Ag, As, Sb, and S. The results are shown in Table 46. It will be noted that the black pyritiferous sediments interbedded with the Keewatin greenstones exhibit the greatest enrichment in all of the elements noted above. This feature is not unique for the Cobalt district as a glance at the data from the Yellowknife samples will show. The sediments could, therefore, have been a major source of the elements in the deposits. The greenstones, likewise, are relatively rich in most of the elements found in the veins at Cobalt. The Nipissing diabase[1] is

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[1] Thirty-six samples representing 825 feet of diamond drill core through a complete section of the Nipissing diabase sill in Henwood twp., Cobalt district, were analyzed. These were supplied by Dr. R. Thomson, Resident Geologist, Ontario Dept. Mines, Cobalt, Ontario. The samples were deemed by Dr. Thomson to be representative of the diabase in the Cobalt district and as far as is known are well removed from the effects of mineralization. The silver contents ranged from $< 0.05$ to 0.24 ppm. It will be noted that these values are somewhat less than those quoted by Moore, and Fairbairn *et al.* (*see* Table 14).

TABLE 46 *Analyses of Rocks From Cobalt and South Lorrain, Ontario*

All values in parts per million except where noted
NF — not found
ND — not determined

| Description of Samples | Cu | Pb | Zn | Ni | Co | Bi | Ag | As | Sb | S | Au |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Composite sample of Keewatin greenstone, South Lorrain area | 330 | <5 | 95 | 130 | 67 | NF | 0.30 | 15 | 2.5 | 1,700 | ND |
| Composite sample of Keewatin greenstone, Cobalt area | 120 | <5 | 215 | 105 | 69 | NF | 0.19 | 2 | 0.5 | 775 | ND |
| Composite sample of Cobalt conglomerate and greywacke, Cobalt area | 20 | <5 | 20 | 60 | 25 | NF | <0.05 | <2 | <1 | 180 | ND |
| Nipissing diabase: average values computed from 36 samples from drill-hole through diabase, Henwood twp., Cobalt area | 83 | <2 | 70 | 128 | 40 | <0.05 | 0.11 | <2 | <1 | 590 | ND |
| Composite sample of Keewatin black pyritiferous slate, schist and greywacke, Cobalt area | 420 | 75 | 2,400 | 160 | 74 | 0.83 | 0.83 | 140 | 12.5 | ~6% | ND |
| Sulphides (mainly pyrite with some pyrrhotite, chalcopyrite, etc.) separated from above sample | 750 | 200 | 4,400 | 570 | 217 | NF | 5.7 | 1,150 | 46 | ND | 0.128 |
| Sulphides (mainly pyrite and pyrrhotite) separated from Keewatin greenstone, South Lorrain area | ND | ND | ND | 1,500 | 3,000 | NF | 7 | ND | ND | ND | ND |
| Composite sample of black pyritiferous slate, schist, greywacke, tuff, etc. Yellowknife area (range in ppm) | <5—400 | <5—20 | 10—1,600 | 10—110 | <5—110 | ND | 0.33—1.6 | <5—15 | <1—1.0 | ~5% | 0.01—0.07 |

Gold analyses by Mines Branch, Ottawa; other analyses by Geochemical laboratories, Geological Survey of Canada remarkably low in the vein elements with the exception of nickel and cobalt. The Cobalt conglomerates and greywackes are likewise low in most of the vein elements. From the data it would appear that the only readily available source of arsenic, one of the principal elements in the veins, is the Keewatin sediments and greenstones. The same can be said for antimony and bismuth, two other unique elements in the veins.

Because the Cobalt and similar veins are so restricted in their lateral and vertical extent it seems probable that their constituents were derived from sources nearby. As the fractures dilated it seems likely that they drew in the more mobile constituents of the Keewatin greenstones and sediments, namely, Ni, Co, As, Ag, Bi, S, and $CaCO_3$. The Nipissing diabase may have contributed some Ni and Co, and the heat associated with the intrusion of the sill may have had a stimulating effect in mobilizing the elements. The mode of migration of the vein constituents was probably by diffusion through a static water medium as suggested by Whitman many years ago. In other words, the veins of Cobalt are essentially secretion veins, and their constituents are late 'distillates' from the country rocks.

### Great Bear Lake, Northwest Territories

A number of silver deposits and occurrences are known in a belt that stretches along the eastern shore of Great Bear Lake southward to Hottah Lake. This belt includes the now exhausted Port Radium uranium mine of Eldorado Mining and Refining Limited. Descriptions of the deposits and occurrences of silver are given in detail by Ellsworth (1932), Lord (1951), and Lang, *et al.* (1962), and the Port Radium mine has been described by Campbell (1957).

The rock formations in the Port Radium area, as given by Campbell (1957), are outlined in Table 47.

The deposits are veins and stockworks in faults, shear zones, and fractures that cut all the consolidated rocks of the area. Most of the productive deposits, however, occur in the Echo Bay Group, generally in the lower part, but some occur in the granodiorite and other granitic rocks.

The principal gangue is quartz and hematite, and there is some carbonate, usually calcite. In some veins the principal economic mineral is pitchblende, in others native silver. Other metallic minerals include a great variety of Co-Ni arsenides and sulphides, chalcopyrite, argentite, galena, molybdenite, pyrite, and native bismuth. Secondary minerals include yellow and orange uranium ochres, azurite, malachite, erythrite, annabergite, and various manganese oxides.

Campbell (1957) recognized five stages of mineralization in the Port Radium mine as follows:

1. Hematite, quartz
2. Pitchblende, quartz, hematite
3. Quartz, Co-Ni arsenides and sulphides
4. Copper sulphides, chlorite, dolomite
5. Carbonate, silver, bismuth, chalcopyrite.

This sequence is somewhat similar to that at Jáchymov, Czechoslovakia, although there are differences. The sequence of quartz and hematite followed by pitchblende and the Ni-Co arsenides, in turn with silver and bismuth as a late phase, seems to be common in a number of the deposits of this type.

According to Campbell the principal alterations in the Port Radium veins are argillic, chloritization, hematitization, and carbonatization in order of importance. There is also some silicification, sulphidization, and the development of apatite in some veins.

TABLE 47 | *Table of Formations, Port Radium Area, N.W.T.*

| Era | Series | Lithology |
|---|---|---|
| Proterozoic | | Diabase dykes and sills |
| | Intrusive contact | |
| | Hornby Bay | Sandstone, quartzite, conglomerate |
| | Erosional unconformity | |
| | | Biotite granite |
| | Intrusive contact | |
| | | Granodiorite complex |
| | Intrusive contact | |
| Archaean(?) | | Hypabyssal intrusive rocks — feldspar porphyry |
| | Intrusive contact | |
| | Cameron Bay Group | Cobble conglomerate |
| | Echo Bay Group | Upper: Andesite flows, tuffs, conglomerate, tuff- and breccia-filled vents<br>Lower: Tuffs, fragmental rocks, and conglomerates. Cherts, quartzites, some limy beds |

The Echo Bay group of veins (Lord, 1951) occur in fractured and shear zones in tuff, dacite, feldspar porphyry, and fine-grained, banded sediments of the Echo Bay group. The principal gangue is quartz and manganiferous carbonate. The metallic minerals include the Ni-Co arsenides and sulphides, pyrite, galena, chalcopyrite, stromeyerite, and native silver. There is a little pitchblende in one of the veins.

The Camsell River silver deposits (Lord, 1951) are veins and stockworks in fracture and shear zones in a variety of rocks, mostly andesitic tuffs and agglomerates, diabase, and quartz-feldspar porphyry. The economic mineral is native silver in a gangue of quartz and carbonate. The familiar Ni-Co arsenides and sulphides, native bismuth, and bismuthinite are present in a number of the veins, and there is some pyrite, chalcopyrite, sphalerite, and galena. Hematite and minor amounts of pitchblende are reported from some of the veins.

The veins of the International Uranium Mining Company on the north shore of Contact Lake about 9 miles southeast of Port Radium are in fractured and sheared zones in granodiorite, probably of Proterozoic age (Furnival, 1939; Lord, 1951). The gangue is quartz and carbonate, and the minerals of interest are native silver and pitchblende. Other metallic minerals include the Ni-Co arsenides and sulphides, arsenopyrite, the common base metal sulphides, native bismuth, bismuthinite, pearceite, stromeyerite, argentite, and hessite.

### Beaverdell, British Columbia

The deposits at Beaverdell, some 25 miles east of Penticton, occur on Wallace Mountain. The geology of the area and the deposits have been described by Reinecke (1915) and Kidd and Perry (1957).

The silver-rich deposits are veins and stockworks in fractures, shear zones, and small faults that cut quartz diorite or monzonite. This rock is intrusive into the Wallace Formation of metamorphosed tuffs, hornfels, tuffs, basic intrusions, andesitic lavas, limestone, and schist. The contact of the quartz diorite dips gently east, and many of the veins lie in the intrusive rock underneath the various tuffs, sediments, and lavas. The veins are severely faulted in a most complex manner.

The principal gangue mineral is quartz, and there is a little calcite and minor amounts of fluorite. The main metallic minerals are pyrite, sphalerite, galena, freibergite, acanthite, pyrargyrite, polybasite, native silver, and minor amounts of chalcopyrite and arsenopyrite. Sericitization is widespread in the quartz monzonite, and chloritization is present in places in the granitic rocks and in the Wallace Formation.

The source of the vein constituents is not readily apparent. They may have come from a very deep source, i.e., from the crystallizing parent magma of the quartz monzonite. Alternatively, they may have been derived from the Wallace Formation and migrated downward into dilatant zones formed in the more competent quartz monzonite. Neither hypothesis can be advanced with any degree of certainty without detailed chemical work.

### Torbrit Silver Mine, British Columbia

The Torbrit Silver mine is located along the upper part of Kitsault River in the Portland Canal area of British Columbia. Its geology and geochemistry have been described in some detail by Campbell (1959).

The table of formations as given by Campbell is shown in Table 48. The sedimentary and volcanic formations include argillites, greywackes, tuffs, andesites, and volcanic breccias and pyroclastic rocks folded into a syncline and intruded by late Cretaceous (?) feldspar porphyry and Tertiary (?) andesite dykes.

The Torbrit silver orebody is pod-shaped and is localized in a horsetail-type shear zone that cuts the Lower Volcanic Formation. The principal ore minerals are galena, tetrahedrite, pyrargyrite, argentite, and native silver, with variable amounts

TABLE 48 *Table of Formations, Torbrit Silver Mine Area, British Columbia (after Campbell, 1959)*

| Period | Group | Formations | Members |
|---|---|---|---|
| Tertiary (?) | | Andesite dykes | |
| | | Intrusive contact | |
| Jurassic (?) | Hazelton Group | Upper Sedimentary Formation | Argillite, greywacke and conglomerate |
| | | Local unconformity | |
| | | Lower Volcanic Formation | Albite breccia and tuffs |
| | | | Grey breccia |
| | | | Albite andesite |
| | | | Purple and green pryoclastic rocks<br>Undifferentiated<br>Bedded tuffs<br>Marker tuffs |
| | | Lower Sedimentary Formation | |

of chalcopyrite, pyrite, sphalerite, magnetite, and hematite. The native silver, argentite, and pyrargyrite are of hypogene origin. The gangue minerals are quartz and barite with jasper, calcite, and siderite. The vein material exhibits a marked crustified and colloform banding, but there is also much replacement of the wall-rock in places. The wall-rock alteration associated with the orebody is mainly chloritization, pyritization, silicification, and sericitization. The average grade of the ore is 17.2 ounces Ag and 0.42 per cent Pb per ton. There is practically no gold, the Ag/Au ratio being greater than 100. This is in agreement with the situation at the adjacent Dolly Varden silver deposit, but in marked contrast to the other deposits of the area, a number of which contain appreciable gold contents.

By means of the sphalerite geothermometer and argentite-silver assemblage as a sulphur barometer, Campbell (1959) determined the temperature of formation of the deposit to be approximately 270°C under a hydrostatic pressure of 300 atmospheres. According to the same investigator the orebody was formed in late Cretaceous to early Tertiary time, from solutions genetically related to the last phase of the Coast Range intrusion in the area.

### Potosí, Bolivia

Since their discovery in 1544 the famous deposits of Potosí are said to have produced more than 2 billion ounces of silver, and the mountain on which the deposits occur, the Cerro Rico de Potosí, is said to be the richest silver hill on earth. The best comprehensive descriptions of the Potosí deposits are by Lindgren and Creveling (1928), Evans (1940), and Turneaure (1960).

The basement rocks of the Cerro Potosí are highly folded and contorted Ordovician shales, slates, argillites, and quartzites (Fig. 6). These are overlain unconformably by a horizontal to gently dipping Middle (?) Tertiary conglomerate series and a sandstone-ash (tuff) series. Intensely altered quartz porphyry occupies the core and forms the conical peak of the mountain. Evans thought that part of the porphyry was extrusive and part intrusive. Turneaure referred only to the intrusive nature of the porphyry, stating that it cuts the Ordovician sediments and Tertiary volcanics.

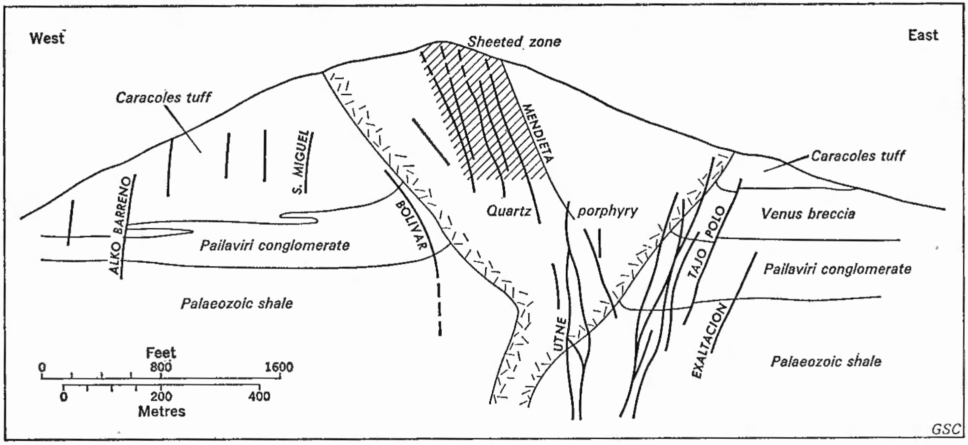

FIGURE 6. Ideal section of Cerro Rico de Potosi, showing distribution of rock types and main vein systems (after Turneaure, 1960).

The quartz porphyry, Tertiary sediments, and Ordovician shales, argillites, and slates are cut by a host of fissures, faults, and sheeted zones that contain the productive veins. Many of these branch upward and form horsetails. Evans (1940) recognized three distinct periods of hypogene mineralization as follows:

1. An initial period of pyrite, arsenopyrite, and quartz of contemporaneous deposition, and coincident with wolframite and bismuthinite at greater depth.
2. A second period of quartz with cassiterite and pyrite.
3. A final period of quartz carrying chalcopyrite and stannite at depth, but with chalcopyrite, stannite, and a variety of complex silver-bearing sulphides and sulphosalts, including tetrahedrite, andorite, ruby silver, and matildite, at higher levels.

The main economic minerals are those containing silver and tin. The primary silver-tin ore averages about 10 to 15 ounces per ton silver and 1 to 5 per cent tin. Silicification and sericitization of the quartz porphyry are the most characteristic types of alteration.

The veins were oxidized to a depth of a thousand feet or more. The oxidized zones contained limonite, malachite, cassiterite, native silver, chlorargyrite, some argentite, and ruby silver. These ores averaged about 100 ounces Ag per ton and 4 per cent tin.

The origin of the rich hypogene ores of Potosí has been attributed to Tertiary magmatic activity related to the quartz porphyry intrusions. But again the veins are much later than the porphyries, and one wonders whether these famous veins are not the result of a secretion phenomenon attendant on extensive dilation of myriad fractures. The underlying Ordovician slates, etc., are probably an adequate source for the silver, tin, sulphur, and other components of the veins. The presence of tin is interesting, not only in this deposit, but in a number of other silver deposits in Bolivia and other South American countries. This element often seems to be associated with the Tertiary rhyolites and porphyries and may well have had its source in these rocks. It would be interesting to have a number of fresh specimens of these Tertiary rocks analyzed for tin as well as for silver and other elements.

## Miscellaneous Sources of Silver

Silver is won from a great variety of deposits not specifically mentioned in the above descriptions. These include the following:

1. Nickel-copper ores associated with basic intrusions—Sudbury type. The content of silver in these ores is very low and is present mainly in the chalcopyrite (Hawley, 1962). Some silver is, however, won from the deposits during smelting and metallurgical treatment. The deposits at Sudbury, for instance, produce about 1.5 million ounces of silver annually.

2. Massive sulphide deposits containing essentially iron, copper, lead, and zinc sulphides. These include Noranda, Flin Flon, Geco, Willroy, Bathurst, N.B., Rammelsberg, Germany, Cerro de Pasco, Peru, and a host of others. The silver content of the hypogene ores rarely exceeds 5 ounces per ton, and is generally associated with the higher grade lead parts of some deposits and with the high-grade copper zones in others. Most of the primary silver is in either galena or tetrahedrite; some may be associated with sphalerite or chalcopyrite. In some deposits, much silver is contained in argentite, native silver, electrum, gold, sylvanite, altaite, stromeyerite, and other silver-bearing sulphides, sulphosalts, tellurides, and selenides. Supergene silver in these deposits occurs as the native metal, in chalcocite, covellite, and acanthite, and in chlorargyrite, argentojarosite, etc. Considerable quantities of silver are won as a by-product of the smelting and metallurgical treatment of the ores from these deposits

One of the largest silver producers of this type in the world is the great Cerro de Pasco deposit in Central Peru. This deposit is an enormous crescent-shaped pyritic lens localized at the eastern contact of a Tertiary volcanic explosion vent or diatreme, composed of volcanic agglomerates, tuffs, volcanic breccia, monzonite dykes, etc., with sediments, mainly Mesozoic limestones and Devonian slates, phyllites, and quartzites. The pyrite lens, formed partly along a fault and partly by replacement of limestone, is nearly 6,000 feet long, about 1,000 feet wide at its widest point, and extends to a depth of at least 2,800 feet. It is a complex body marked by several periods of mineralization, containing pipes and irregular shoots of pyrrhotite and minor cassiterite, galena-sphalerite, enargite, and silver sulphosalts and argentite. East-west veins cut the western part of the pyrite body and continue for some distance into the explosion vent. These contain pyrite, enargite, minor galena, sphalerite, argentiferous tetrahedrite-tennantite, and chalcopyrite. Some carry gold.

The principal hypogene minerals are pyrite, pyrrhotite, enargite, sphalerite, galena, marcasite, tennantite-tetrahedrite, aramayoite, polybasite, acanthite, arsenopyrite, bournonite, gratonite, emplectite, bismuthinite, and realgar. There is little gangue, but some cherty quartz, barite, sericite, alunite, and clay minerals occur in parts of the deposit.

Silver is irregularly distributed in the hypogene ore. In the lead-zinc ores, it averages about 4 ounces per ton and is largely present in argentiferous tennantite. Certain late anastomosing pipe-like bodies within the lead-zinc zones contain much argentiferous tennantite, acanthite, polybasite, and aramayoite, giving assays of more than 100 ounces Ag per ton.

The pyritic mass and other ores have been deeply oxidized to a depth of 300 feet or more. The oxidized zone, termed *pacos*, consists mainly of a rusty, porous, weak aggregate high in silica, limonite, jarosite, plumbojarosite, cerussite, and some smithsonite. Much of the iron, lead, and copper and most of the zinc in the original sulphide mass has been leached. A large proportion of the lead and silver in the *pacos* is in plumbojarosite.

Immediately underlying the oxidized capping, and mainly above or adjacent to the lead-zinc zones, are discontinuous blankets up to 100 feet thick of supergene copper sulphides, principally chalcocite with some covellite. These minerals have replaced mainly galena and sphalerite and to a lesser degree pyrite. The chalcocite is silver rich, approaching stromeyerite in composition in places.

The Cerro de Pasco deposit has been mined for centuries, first within the *pacos* for silver, then in the secondary copper zones for silver and copper, and now mainly in the hypogene sulphide ores. The shoots in the *pacos*, exploited during early times, were probably very high in silver because great tonnages of *pacos* still remain carrying up to 12 ounces Ag and a little gold per ton. These are now being slowly exhausted for use as siliceous flux. The annual production from the deposit today is about 12 million pounds of copper, 7 million pounds of lead, 20 million pounds of zinc, 1.5 million ounces of silver, and 1,200 ounces of gold.

Detailed geological and mineralogical descriptions of this remarkable deposit are given by the Geological Staff of the Cerro de Pasco Copper Corporation (1950) and Ward (1961).

Another massive sulphide body with a huge potential for silver production is the recently discovered Texas Gulf Sulphur Kidd Creek deposit near Timmins, Ontario. This deposit is said to contain some 60 million tons averaging 4.85 ounces Ag per ton, 1.33 per cent Cu, and 7.08 per cent Zn. The total content of silver is, therefore, of the order of 300 million ounces, an amount approaching that of the whole of the Cobalt Camp. The sulphide minerals are mainly pyrite, chalcopyrite, and sphalerite. In addition there are small amounts of bornite, covellite, digenite, pyrrhotite, marcasite, galena, and arsenopyrite. The silver occurs as the native metal in small inclusions in the pyrite and in stromeyerite as specks and small streaks in digenite.

3. Polymetallic vein deposits containing essentially iron, copper, lead, and zinc sulphides. These are widespread throughout the mineral belts of the world. Most of the primary silver occurs in galena or in tetrahedrite. Some of the deposits contain the silver sulphides, sulphosalts, and native silver. The primary ore of the veins grades all the way from a few tenths of an ounce of silver per ton to 40 or more ounces. Some of those which are usually considered as major silver producers have been described in the sections above. Silver is won from the deposits during metallurgical treatment of the ores.

4. Lead-zinc deposits in carbonate rocks (Pine Point–Mississippi Valley type). The silver content of these ores is generally low, the concentrates ranging from 10 ounces per ton to 0.1 ounce per ton or less. The crude ores rarely contain more than 0.05 ounce Ag per ton. The silver is generally associated with the galena, but in some deposits such as those in southeast Missouri, silver seems to follow zinc and is concentrated in the sphalerite.

5. Native copper deposits in amygdaloidal basalts, conglomerates, sandstones, etc. Small amounts of by-product silver have been won from the Michigan Copper deposits and similar deposits in other parts of the world. The grade of such deposits as regards silver is generally low and irregular, often decreasing with depth in the deposits. The average is probably about 0.01 ounce Ag per ton. Most of the silver is present in the native form with small amounts in the native copper.

6. Porphyry copper deposits. These deposits yield large amounts of silver as a by-product of copper refining in various parts of the world. The hypogene silver is mainly in chalcopyrite, bornite, covellite, enargite, or in minute specks of tennantite-tetrahedrite, stromeyerite, and other silver minerals in some deposits. Much silver occurs in the secondary chalcocite formed in the zones of reduction. The deposits of Butte, Montana, which can be considered as porphyry copper deposits with somewhat enlarged veins, contain from 1 to 3 ounces Ag per ton. In the large disseminated types such as Bingham, Utah; Ely, Nevada; Ajo, San Manuel, and Ray, Arizona, the silver content ranges from 0.01 to 0.1 ounce Ag per ton of ore.

7. Gold deposits. All gold deposits, no matter what type, yield some silver. The older (Precambrian) deposits tend to have much lower contents than the younger (Tertiary) deposits.

8. Certain eluvial and alluvial fans and similar deposits associated with mineralized stocks or belts may contain argentiferous galena, anglesite, bindheimite, oxidized products of silver minerals etc., in addition to cassiterite, cinnabar, and other valuable minerals. The silver content rarely exceeds 0.5 ounce per ton, but the combined Pb, Ag, Au, Sn, Hg, etc., contents may be sufficient in the future to warrant exploiting such deposits. The tonnage in some places is very great. Deposits of this type are common in a number of unglaciated countries. Those in Mexico, near a mineralized porphyritic granite stock at Guadalcázar, have received detailed attention (Foshag and Fries, 1942; Fries and Schmitter, 1948).

Other types of residual (eluvial) concentrations of argentiferous galena, tetrahedrite, native silver, etc., are known but are comparatively rare. Most of these are derived from the weathering of sparsely mineralized dolomites, limestones, calcareous shales, sandstones, shales, etc. Scattered galena veins and stockworks in various types of rocks also give similar deposits on weathering. The argentiferous galena nodules generally collect in low topographic areas, occasionally in draws and streams, and in some places in sink-holes and other depressions. Searls (1952) has described examples of the latter type of deposit in China. Somewhat similar deposits associated with a sink-hole terrain developed on limestones have been described by Rundall (1927–28) in the Shan States of Burma. Few of these residual types of deposits are economic, although the tonnage of argentiferous material in some may be very large.

9. Gold placers. Some silver is won from the native gold of placer deposits.

10. The sea. Sea water contains an average of 0.0002 ppm Ag, and the element is present in marine manganese nodules and other marine sediments and debris. Processing of these materials in the future could give sizable quantities of silver as a by-product. The economics of winning metals from the sea are discussed in detail by Mero (1965).

## Origin of Silver Deposits

In the foregoing description of the various types of silver deposits, probable origins for the principal types of deposits have been outlined. It now remains to summarize these and to amplify some of the concepts.

The main syngenetic and epigenetic deposits originated by one or other of the following mechanisms: precipitation from surface waters; precipitation from ground, connate or metamorphic waters[1] or mixtures of these; and concentration by diffusion.

Before continuing with a discussion of each of these mechanisms, the following abridged view of the writer's ideas on the genesis of veins and other types of epigenetic deposits should be quoted (Boyle, 1963b).

"The writer holds the opinion that the elements in veins and similar epigenetic deposits came from their enclosing country rocks and that they are concentrated mainly by diffusion processes either in groundwater systems or as the result of the interaction of metamorphic reactions and the dilatant effects imposed by structures.

"Following the structural geologists, one recognizes two extreme zones in the crust of the earth where veins, lenses, and similar deposits may form—the near-surface zone of fracture and the deep zone of flowage and metamorphism. An intermediate zone combines the features of both these zones to a degree dependent upon the prevailing tectonic and geochemical conditions.

"In the zone of fracture, especially under near-surface conditions, open structures such as fractures, faults, breccia zones, and porous zones are formed and preserved, and these will fill with connate water, groundwater, metamorphic water,

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[1] Metamorphic water is here defined as that water expelled from deep zones as a result of the dehydration of shales and other hydrous rocks undergoing regional or thermal metamorphism.

or mixtures of these. Under certain conditions, this water will form a static medium through which ore and gangue constituents derived from the country rocks will migrate in the form of ions, hydrated ions, molecules, and gases to sites of deposition determined by differences in the free energy of the system. Under other conditions, the water may be in motion, and mass transport and subsequent deposition of dissolved constituents gathered from the country rocks will take place (the lateral secretion theories of Agricola, Sandberger, and Van Hise). Even under these conditions diffusion processes are at work, but they are of a short range nature, whereas in the first situation they are of a relatively long range order.

"In the zone of flowage and intense metamorphism, water cannot exist in the liquid state because of the relatively high temperature conditions[1]. Instead, gaseous water may pervade all grain boundaries and other discontinuities in the rocks, thus forming a more or less stationary medium through which diffusion of ore and gangue constituents may take place. In other circumstances, as in intensely metamorphosed zones, water may be largely expelled from the rocks, thus necessitating a dry diffusion of constituents along grain boundaries, etc.

"Under both these conditions, the dilatant effect of structures largely controls the formation of veins, lenses, and similar deposits. As fractures, sheared zones, and other structures dilate, they set up zones of low pressure and low chemical potential, thus disturbing the chemical equilibrium in the enclosing rocks. To establish equilibrium the more mobile constituents in the country rocks will migrate into these zones where they will precipitate until the chemical conditions in the structures and throughout the enclosing rocks are in balance. The magnitude of the structure or the degree of dilatancy, therefore, not only decides the size of the deposit but may also influence the kind of constituents that are concentrated. Thus, if the metamorphic and dilatant conditions are of low intensity, only relatively easily mobilized constituents such as silica may be concentrated, and barren quartz veins will result. With increasing intensity of these two interacting forces, carbon dioxide, sulphur, arsenic, antimony, silver, and other chalcophile elements may be set in motion and metalliferous veins will result. The key, therefore, to the formation of epigenetic mineral deposits in the deep zones of the earth's crust is to be found in the proper timing and intensity of two geological events—mobilization of the elements in the country rocks (a metamorphic event), and the dilatancy of structures (a tectonic event).

"Regional zonation and many other features of mineral deposits can be readily explained by the above theory. Thus, near granites or granitization centres, only those elements such as tin and tungsten with high mobilization energies can be concentrated from the enclosing rocks. Elements with lower mobilization energies will be set in motion in these situations but they cannot be precipitated, and hence they will migrate into cooler zones where they are subsequently precipitated."

## Precipitation from Surface Waters

The copper-silver shale deposits are thought to owe their origin to this process.

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[1] There is much confusion in the geological literature on the subject of critical phenomena. There are three commonly accepted states of matter—solid, liquid, and gas. In the supercritical region with which we are dealing in this instance the state of the water is best referred to as a dense gas whose properties approach that of a liquid.

The source of the silver, copper, and other elements is the main problem. In some cases the metals, sulphur, etc., may have been contributed by volcanic action; in other cases normal weathering processes may have contributed the ore elements to the basin of deposition.

The precipitation mechanisms are probably manifold, but appear to depend largely on the action of micro-organisms, adsorption, coprecipitation, and other normal chemical phenomena. These are discussed on pages 81 to 85.

### Precipitation from Ground, Connate, or Metamorphic Waters

The 'red bed' type silver deposits probably owe their origin to this mechanism and certain near-surface polymetallic and silver-gold veins may have been deposited in this way.

In the case of the bedded 'red bed' deposits the source of the ore and gangue elements was probably the enclosing terrestrial sediments or underlying or overlying black shales, copper-silver-rich shales, volcanic flows, tuffs, etc. For the veins a variety of sedimentary or volcanic rocks may have provided the elements. Each deposit has to be studied in its own geological setting as regards the source of its constituent elements.

In the case of the ground and connate waters the silver compounds were simply dissolved from the country rocks, migrated with these waters by mass transport, and were finally deposited in any favourable porous zone, fracture system, etc. The controlling factors in most places have been an adequate source for the elements, a favourable hydrologic gradient, and suitable receptacles for precipitation. For the metamorphic waters and gases a somewhat similar mechanism has operated. As the metamorphic gaseous water was driven out of high temperature zones under a driving gas pressure, it gathered silver from the rocks and moved it by mass transport into suitable porous zones, dilatant fracture systems, etc., where the silver was precipitated in a variety of minerals as a result of decreases in pressure, cooling, and a great variety of other chemical reactions. Some silver may also have been contributed to circulating groundwaters in the zone where metamorphic waters and groundwaters mix. This silver may have been carried to various sites of deposition by the mixed ground and condensed metamorphic waters, or, in certain situations, the silver in the dense gaseous metamorphic water may have been precipitated in the zone of mixing as a result of cooling by interaction with the groundwaters. The dissolved silver species in ground and metamorphic waters and their possible modes of precipitation are discussed in detail in Chapter II.

### Concentration by Diffusion

All types of epigenetic silver deposits may owe their origin, at least in part, to this process. Four mechanisms are possible:

1. Migration of ions, hydrated ions, and molecules through a stationary liquid water phase that occupies all fractures, breccia zones, pores, and other discontinuities in rocks. This mechanism is identical to that of the diffusion of a dissolved silver

compound in water, and probably applies to the concentration of silver in the sandstone deposits and to certain veins in relatively unmetamorphosed rocks.

The diffusion coefficient, D, for most soluble silver compounds at a concentration of 0.01 molar in pure water is of the order of $1.5 \times 10^{-5}$ cm$^2$/sec at 25°C.[1] By using the mean displacement equation, $x^2 = 2Dt$, where x is the average length of the path of the diffusing particle through time t, we can calculate the distance travelled by a silver ion or molecule in a rock if we can make a reasonable estimate of the time during which a deposit is formed.

We are told that the Carboniferous and Triassic rocks containing the copper-silver bearing sandstones are some 200 million years old. Furthermore we can assume that these rocks have been water saturated with either connate or groundwater for this length of time, and that this water contained copper and silver since we find these elements in the groundwaters of these rocks today. In this great expanse of time the maximum distance a diffusing silver ion or molecule could have travelled is

$$x = \sqrt{2 \times 1.5 \times 10^{-5} \times 24 \times 60^2 \times 365 \times 200 \times 10^6} \quad \text{cms}$$
$$x = \sim 4{,}300 \text{ metres at } 25°\text{C.}$$

Of course this is the ideal case and does not take into account the porosity and permeability of the rock, which are the principal governing factors in this type of diffusion mechanism. While these factors would reduce the diffusion rate, higher temperatures to which the rocks were probably subjected at depth would greatly increase the rate. Probably one would cancel the other, and we can logically conclude that for the formation of deposits of the 'red bed' type, silver would be contributed by rocks some 4,300 metres distant from the sites of deposition.

There seems, therefore, to be no problem of transport of silver by diffusion through a static water medium. The problem lies in an adequate source for the element and in a mechanism to reduce the concentration at the site of deposition, and thus maintain a concentration gradient in the diffusion system. In porous zones this may be maintained by a number of mechanisms too numerous to mention here. Some of these are noted on pages 81 to 85. Near fractures the concentration gradient is maintained in part by dilatancy and also by numerous chemical reactions in the vein systems, which withdraw silver from the diffusion current.

2. Migration of ions, hydrated ions, and molecules through a relatively stationary water gas or other natural gas such as carbon dioxide that pervades the grain boundaries, pores, and other discontinuities in rocks at high temperatures and pressures. This mechanism is probably operative in the formation of silver veins of many types in low- to high-grade metamorphic terrains, and may have played a part in the formation of the skarn type of deposits. The mechanism is the same as that outlined in (1) above, with the exception that the water constituting the diffusion medium has the properties of a dense gas.

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[1] This value is an average of those calculated for a number of silver salts from the Stokes-Einstein and Nernst diffusion equations, and is in reasonable agreement with published experimental values that range from 1.44 to $1.61 \times 10^{-5}$ cm$^2$/sec (Wahl and Bonner, 1951). The value is an approximation and does not take into account perturbation effects due to other dissolved ions, changes in concentration gradients, etc.

There are no experimental data on the diffusion coefficient of silver compounds in such a gas, but a calculation from the Stokes-Einstein diffusion equation using the data of Fano, *et al.* (1956) on the viscosity of water at high temperatures and pressures (500°C, 2,000 atmospheres) shows that $D = \sim 5 \times 10^{-4}$ cm$^2$/sec for a 0.01 molar solution of most silver salts, at least one order of magnitude greater than that found for water at 25°C. The distance an ion or molecule of a silver salt would migrate by diffusion in the dense water gas pervading the grain boundaries in 1 million years would be approximately 1,750 metres at temperatures ranging from 300° –500°C.

Since a million years seems a reasonable minimum time for the formation of a vein deposit, silver would be drawn into dilatant and low chemical potential zones such as fractures, etc., from as far as 1,750 metres provided the concentration gradients were maintained. Again we encounter little difficulty with the diffusion hypothesis since only a few tenths of a part per million of silver drawn from the rocks over such a distance would easily form a sizable deposit.

3. Migration in a gaseous state, or as ions and molecules along grain boundaries and fractures and through pores and other discontinuities in rocks. The migration is accomplished in part by surface diffusion, but where gases are involved there may also be some mass transport. This type of diffusion is essentially a dry one, although there may be some pore water present in the form of a dense gas as in (2) above. It is probably operative in deep seated zones undergoing metamorphism and probably plays a part in the formation of deep seated veins, skarn type deposits, etc.

There are no data whatever on the surface diffusion of silver compounds on silicates, nor is it possible to make a reasonable estimate of the diffusion coefficient for such phenomena. Silver and some of its compounds seem to have a moderately high vapour pressure at high temperatures judging from the data of Clarke (1924, p. 274), Cipriani (1953), Krauskopf (1964), and others. It would seem, therefore, that some silver may be transported in the vapour phase. Its rate of migration either by mass transport or by diffusion would be fast, certainly two or more orders of magnitude greater than that postulated above for liquid and dense gaseous water.

4. Diffusion of ions, atoms, and molecules through the crystal lattices of the constituent minerals of rocks. At low temperatures the rate is extremely slow and is probably not important in the formation of any type of silver deposit. At high temperatures and where the crystal lattices of the constituent rock minerals are under intense shear, the rate is greatly increased and probably approaches that found for the diffusion of silver in glass—of the order of $5 \times 10^{-4}$ cm$^2$ per day at 550°C. (Pask and Parmelee, 1943).

Since diffusion of this type can only be assumed to take place during metamorphism and granitization, the duration of these events must be estimated. Probably they extend over a period of 100 million years or more in most geosynclines. If so silver would migrate a distance of only 60 metres, certainly insufficient to form a deposit. In 1 million years the distance would only be 6 metres. Thus, it seems unlikely that silver is concentrated by any mechanism of diffusion through the crystal lattices of minerals.

The mechanism is important, however, in one aspect of the problem of concentration—namely migration of the element through the crystal lattice of silicates, sulphides, etc., to the grain boundaries along which extensive migration does take place. As can be seen by the above calculation of 6 metres in 1 million years, silver from the minerals of the rocks would be delivered to the grain boundaries in sufficient quantity to form a deposit provided the necessary concentration gradients existed.

The data presented above on the diffusion rates for silver, and the fact that the element is relatively soluble as one or other of its various complexes, suggest that the element is relatively mobile during both surface and deep seated ore-forming processes. This is probably the reason why silver is found in such a large variety of deposits in so many contrasting geological environments. In this respect it is much like copper, lead, zinc, and gold, the elements with which it is so often associated.

*Chapter IV*

# OXIDATION AND SECONDARY ENRICHMENT OF SILVER DEPOSITS

## General Principles

Silver deposits, subjected to oxidation, generally become enriched near the surface both as a result of chemical processes involving the migration of silver and by the removal of soluble gangue and sulphides. Where lead occurs in quantity in the silver deposits as galena or other sulphides, there is also a parallel enrichment of this element as a result of oxidation processes. In contrast to copper, however, silver exhibits less tendency to form secondary sulphide zones in veins and other deposits.

The mobility, migration, and concentration of silver during the oxidation of silver deposits are strongly influenced by the following factors:

1. The type of deposit and its mineral composition. The nature of the gangue, types of sulphides, and primary silver minerals are the main considerations.
2. Types of enclosing rocks
3. Climatic factors
4. Position of the water-table
5. Organic agencies. Sulphate reducing bacteria may contribute materially to the precipitation of silver in the zones of reduction.

All these factors interact to produce a variety of complex chemical systems that are impossible to follow in detail here. We shall have to restrict the discussion to some of the general features of oxidized silver deposits and to a relatively simple view of the chemical processes involved. Data on the oxidation of silver minerals and deposits may be found in the publications by Weed (1901, 1902), Stokes (1906), Cooke (1913), Palmer and Bastin (1913), Grout (1913), Ravicz (1915), Emmons, S. F. (1901), Emmons, W. H. (1917), Whitehead (1919), Smirnov (1951), Morris and Lovering (1952), Shcherbina (1956), Kreiter, *et al.* (1958), Sato (1960), and Boyle (1965).

The principal hypogene silver-bearing minerals are native silver, argentiferous galena, acanthite (argentite), freibergite, proustite, pyrargyrite, polybasite, matildite, and various rare selenides and tellurides.

The distinctly supergene minerals comprise native silver, pyrargyrite, proustite, acanthite, stromeyerite, chlorargyrite, bromargyrite, iodargyrite, and argentojarosite. Pearceite, polybasite, and dyscrasite have been reported as secondary minerals in some deposits. Dyscrasite occurred in some quantity in parts of the oxidized zones of Broken Hill, Australia and Chañarcillo, Chile.

Native silver, the ruby silvers, and acanthite are probably the most frequent of the supergene silver minerals. Native silver may occur in any of its various forms, although wires and spangles are most frequent. The ruby silvers are generally well crystallized, but earthy and microcrystalline varieties have been reported in a number of secondarily enriched zones. Acanthite is most frequently found as sooty or earthy accumulations ('Silver black') along seams, fractures, and in vugs. In some deposits it is inextricably mixed with microcrystalline chalcocite or stromeyerite.

Meteoric waters containing oxygen attack the common hypogene silver sulphides and sulphosalts such as acanthite and freibergite, forming relatively soluble silver sulphate. Waters containing dissolved carbon dioxide yield slightly soluble silver hydrogen carbonate.[1] The simplified equations for acanthite (argentite) may be written as follows:

$$Ag_2S + 2O_2 = Ag_2SO_4$$
$$Ag_2S + 2CO_2 + 2H_2O = 2AgHCO_3 + H_2S\,.$$

Silver, combined in freibergite, argentiferous galena, and various other sulphide and sulphosalt minerals, would probably also be taken into solution as the soluble sulphate and hydrogen carbonate. Where nitrate is present in the oxidizing solutions some of the silver may migrate as the soluble nitrate. Under arid conditions or where highly saline solutions containing the alkali chlorides are available from salt beds, etc., some of the silver may be solubilized as the chloride complex, $[AgCl_2]^-$. In an environment where pyrite is oxidizing and where ferric sulphate is abundant the sulphate may react with native silver or silver combined in sulphides and sulphosalts to give soluble silver sulphate:

$$2Ag + Fe_2(SO_4)_3 \rightleftharpoons Ag_2SO_4 + 2FeSO_4\,.$$

This reaction is reversible depending on the $Fe^{2+}/Fe^{3+}$ ratio in solution.

Sulphuric acid, derived from the oxidation of pyrite and other sulphides, slowly dissolves acanthite, various other silver sulphides and sulphosalts, and native silver. The reactions for acanthite and native silver probably run as follows:

$$Ag_2S + H_2SO_4 = Ag_2SO_4 + H_2S$$
$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2\,.$$

In the former the reaction does not proceed far as long as $H_2S$ is present. This con-

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[1] For solubility of silver salts see Table 3.

stituent may, however, be oxidized on to sulphur and/or sulphate by the oxygen in the waters or by ferric sulphate. For the latter the reaction may be written as:

$$Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S.$$

The dissolving action of natural organic substances on native silver, silver sulphides, and silver sulphosalts is not well known. It seems probable that some of the humic acids are capable of taking considerable amounts of silver into solution.

The role of colloids in the transport of silver is also not well known. The element does form a number of colloids readily, as shown by Bastin (1915) and others, but the presence of these in natural solutions has not been investigated. A silver chloride sol, AgCl, and a sulphate sol, $Ag_2SO_4$, are known and may be present in some of the solutions traversing the upper parts of silver deposits. A sulphide sol can also be made, and it seems possible that some silver may be transported in this manner under certain conditions.

Once silver is liberated from its constituent minerals, its mobility and precipitation depend essentially on the type of associated ore and gangue minerals in the deposit, the chemical nature of the enclosing rocks, the permeability of the deposits, and a variety of chemical factors, particularly the pH, Eh, presence of complexing agents, and the presence of precipitating constituents such as $H_2S$, Cl, Br, I, primary sulphides, carbonaceous materials, etc.

The presence of iron sulphides, principally pyrite, in the deposits greatly influences the mobility of silver. These sulphides oxidize initially to give acid solutions containing ferrous sulphate and sulphuric acid. The latter enhances the solubility of silver as noted above, but the former tends to precipitate it according to the reaction:

$$Fe^{2+} + Ag^{+} \rightleftarrows Ag + Fe^{3+}.$$

Near the surface, however, where free oxygen is abundant and the oxidation potential is high, the ferrous ion is oxidized rapidly to the ferric state. Under these conditions the above reaction is reversed and silver is rendered relatively mobile in the ionic state. As the solutions pass downward, however, and the oxidation potential decreases the ferrous ion in solution increases greatly and precipitation of silver may take place.

Siderite, chalcopyrite, and other iron-bearing sulphides and sulphosalts yield ferrous ions initially and ferric ions ultimately near the surface, and hence influence the mobility of silver in a manner similar to that of pyrite. In addition, manganiferous siderite and certain manganiferous varieties of sphalerite release manganous ion, which may also have a precipitating effect on dissolved silver where the conditions are very feebly acid, neutral, or alkaline:

$$Mn^{2+} + 2Ag^{+} + 4OH^{-} = 2Ag + MnO_2 \cdot H_2O + H_2O.$$

Oxidation of the familiar Ni-Co arsenides does not seem to have much effect on the mobility of silver in solution, although there are practically no data on this aspect of the problem. Some of the sulphosalts contain sufficient iron and sulphur to yield ferrous and ferric sulphate, and hence these minerals would have the same effect as pyrite.

Carbonate gangue minerals in silver deposits or in their wall-rocks rapidly neutralize the acidic oxidizing solutions arising from the oxidation of pyrite. Since silver is more soluble in acid than in neutral or alkaline solutions, the general effect is to reduce the mobility of silver. On the other hand the action of $H_2SO_4$ on carbonates yields an abundance of bicarbonate ion, which enhances the solubility of silver as the hydrogen carbonate. The problem is, therefore, a rather complex one. Quartz and silicates have little effect on the acidic solutions or neutralize them only slowly. Hence the mobility of silver in deposits with a quartz gangue or silicate wall-rocks (schists, quartzites, etc.) is not radically affected except where the oxidizing solutions are in long contact with the silicates in the gangue or wall-rocks.

Lovering (*in* Morris and Lovering, 1952) found that silver migrated only a few feet in the Tintic Standard mine where the wall-rocks are carbonates. The migration capacity of the element was also severely curtailed in the presence of sulphides such as galena and sphalerite. On the other hand the migration was extensive where the wall-rocks are shale and quartzite. The order of the mobility of the various metals in the Tintic Standard mine as determined by Lovering is Ag > Zn > Cu > Au > Pb.

The pH and Eh of the solutions and environment markedly affect the mobility and precipitation of silver in a number of ways. Silver ion is much more soluble in acid than in neutral and alkaline solutions, the pH of precipitation of silver (as the oxide) being about 7.5 when the concentration of its salts fall within the range from 0.1M to 0.025M. While the $Ag^+$ ion is not markedly affected by changes in Eh, the ferrous-ferric and manganous-manganese dioxide couples on the other hand are sensitive, and these in turn affect the mobility of silver, as explained above.

Not much is known about the effect of complexing agents on the mobility of silver in natural solutions. Silver chloride is more soluble in sodium chloride solutions than in pure water because of the formation of complex chloro-ions:

$$AgCl + Cl^- \rightleftarrows [AgCl_2]^-.$$

It seems probable, therefore, that where the solutions are highly charged with NaCl, silver would have an enhanced mobility. Thiosulphate ion also renders silver relatively soluble as a complex ion:

$$Ag^+ + 2(S_2O_3)^{2-} \rightleftarrows [Ag(S_2O_3)_2]^{3-}.$$

According to Tyurin and Kakovskii (1960), the ion $(S_2O_3)^{2-}$ is formed in neutral and alkaline solutions during the oxidation of sulphides as the first intermediate product of the reaction of sulphides with dissolved oxygen:

$$S^{2-} \rightarrow (S_2O_3)^{2-} \rightarrow (SO_3)^{2-} \rightarrow (S_nO_6)^{2-} \rightarrow (SO_4)^{2-}; \ (n = 2 - 6).$$

The thiosulphate ion binds easily with silver (and gold), especially in the presence of cupric ion, which catalyzes the reaction, and the complex ion migrates readily as the sodium, potassium, calcium, etc. species in neutral and alkaline waters. In acid waters the silver complex dissociates with the formation of S and $Ag_2S$. Silver carbonate is only slightly soluble in water, but increases in solubility with increase in $CO_2$, probably as the result of the formation of a silver hydrogen carbonate complex.

Numerous other complexes may be present in natural oxidizing solutions in veins. These include various possible colloidal complexes, organic complexes, and perhaps sulphide complexes under certain conditions.

A number of mechanisms for the precipitation of silver minerals from downward migrating solutions are possible. Some of these are:

1. Reduction of acidity due to reaction with gangue minerals and wall-rocks. The silver may be precipitated initially as the oxide or hydrated oxide, but these compounds are relatively unstable in the presence of reducing substances and break down with the formation of native silver.

2. Precipitation of native silver from solution by ferrous ion. As the silver-bearing solutions pass downward they enter regions where ferrous ion is relatively stable because of a reduction in the oxidation potential. This results in the precipitation of native silver according to the reaction:

$$Fe^{2+} + Ag^{+} \rightleftarrows Ag + Fe^{3+}.$$

3. Precipitation or coprecipitation of silver from solution during the hydrolysis of ferric sulphate under conditions of decreasing acidity. The minerals formed are basic salts and include silver-bearing jarosite and plumbojarosite and argentojarosite.

4. Precipitation of silver from solution by manganous ion in very feebly acid, neutral, or alkaline solutions. As the solutions pass downward they may be neutralized by reaction with carbonates, silicates, or alkaline waters. Silver may then be precipitated by manganous ion according to the reaction:

$$2Ag^{+} + Mn^{2+} + 4OH^{-} = 2Ag + MnO_2 + 2H_2O.$$

This reaction is particularly efficient in removing very small amounts of silver from solution. The writer's observations on natural silver-bearing manganese dioxide (wad) suggest that initially the reaction is essentially an adsorption phenomenon, that is, the product is negatively charged colloidal manganese dioxide with positive silver ions adsorbed to the miscelles of the colloid or gel. No native silver can be observed even under the highest powers available with the optical microscope. With aging of the gel some of the silver may be desorbed and split out from the complex, yielding small spangles and filaments of native silver in the general vicinity of the wad. In other situations the silver is retained by the wad complex probably as a silver manganite or as an adsorbed phase at the grain boundaries of the manganese dioxide microcrystals.[1]

Numerous examples of silver-rich wads have been described from the oxidized zones of silver deposits in U.S.A., Mexico, South America, Sumatra, and elsewhere.

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[1] See the recent papers by Hewett and Radtke (*Econ. Geol.*, vol. 62, pp. 1–21) and Radtke, Taylor, and Hewett (*Econ. Geol.*, vol. 62, pp. 186–206). These investigators have identified three supergene silver-bearing manganese oxides from 'black calcite' (calcite containing manganese oxides) at the Aurora mine (Treasure Hill), Hamilton, Nevada. The manganese minerals are (1) argentian chalcophanite (aurorite), $(Ag_2,Ba,Ca,Pb,K_2Cu,Mn^{+2})\ Mn_3^{+4}O_7 \cdot 3H_2O$; (2) argentian todorokite $(Ag_2K_2,Ca,Ba,Na_2,Cu,Pb)\ Mn_4^{+4}O_9 \cdot 5H_2O$; and (3) hydrous silver-bearing lead manganese oxide $(Pb,Cu,Ba,Sb,Ag_2,Ca,K_2) - Mn_5^{+4}O_{11} \cdot 5H_2O$.

5. Precipitation of silver as the halides, chlorargyrite, bromargyrite, and iodargyrite where chloride-, bromide-, and iodide-rich waters mingle with those carrying silver in solution. In other cases it is evident from pseudomorphs that these halides also form by the direct action of chloride, bromide, and iodide solutions on primary silver-bearing minerals such as native silver, acanthite, and freibergite. The simplified reactions with chloride for silver ion in solution, native silver, and acanthite may be written as follows:

$$Ag^+ + NaCl = AgCl + Na^+$$
$$Ag + NaCl = AgCl + Na^+$$
$$Ag_2S + 2NaCl + 2O_2 = 2AgCl + Na_2SO_4.$$

In certain oxidized deposits some silver may be incorporated in the copper halides such as marshite, $(Cu,Ag)I$, and in the complex lead and copper hydroxyhalides such as boleite, $Pb(Cu,Ag)Cl_2(OH)_2 \cdot H_2O$. These minerals are, however, generally rare.

6. Precipitation of $Ag_2S$ as a result of the decomposition of the thiosulphate complex, $[Ag(S_2O_3)_2]^{3-}$, where an increase in the acidity of the supergene waters takes place. $Ag_2S$ may also be precipitated when waters carrying silver as the thiosulphate complex come into contact with reducing substances such as carbonaceous matter.

7. Precipitation of silver in the native form by sulphides and other geological materials. Various field and laboratory observations (Palmer and Bastin, 1913; Jensen, 1939; and others) show that native silver is precipitated from neutral and slightly acid solutions containing $Ag_2SO_4$ (and presumably also $Ag_2CO_3$ or $AgHCO_3$) by pyrrhotite, chalcocite, enargite, alkali-rich silicates, iron silicates, galena, sphalerite, pyrite, chalcopyrite, quartz, mica, tetrahedrite-tennantite, niccolite, smaltite, cobaltite, covellite, arsenopyrite, native copper, magnetite, ilmenite, kaolinite, gouge, and clay. Carbonaceous matter and graphitic substances in some cases appear to be effective precipitants of silver. According to Ravicz (1915) the carbonates—calcite, siderite, and rhodochrosite—do not precipitate silver from dilute solutions containing $Ag_2SO_4$ and $Ag_2CO_3$, but mixtures of metallic sulphides and carbonates precipitate silver readily.

8. Precipitation of silver as various sulphides and sulphosalts by the reaction of silver-bearing solutions with various primary sulphides. In the scheme of precipitation of the sulphides (Schurmann's series) silver sulphide, $\beta\ Ag_2S$, with $Ksp = 1.1 \times 10^{-49}$ is much less soluble than the sulphides of copper, zinc, and iron (pyrite, $Ksp = 4.9 \times 10^{-18}$) in that order. Hence silver should replace these elements in their sulphide combinations.

Jensen (1939) has shown experimentally that various sulphides and sulphosalts are indeed very effective precipitants of silver from solution. All those investigated gave silver sulphide and some gave native silver as well. Their capacity to precipitate silver is roughly parallel to their solubility or sulphur ion activity. Jensen also found that arsenopyrite and the Ni-Co arsenides have considerable ability as silver precipitants.

Despite these theoretical considerations and experimental facts, there are few good examples of extensive developments of supergene silver sulphides, sulphosalts, and native silver formed by the action of primary sulphides on downward percolating silver-bearing solutions. One particularly good example of extensive enrichment of this type, however, is that described by Anderson (1940) at the St. Louis mine, Butte County, Idaho. In this mine there was extensive supergene replacement of aikinite, $PbCuBiS_3$, by argentite and native silver. Another example is Chañarcillo, Chile, where the primary sulphides, pearceite, proustite, and pyrargyrite were extensively replaced by secondary argentite (acanthite?), dyscrasite, and native silver (Whitehead, 1919).

9. Precipitation of silver as various sulphides and sulphosalts by the reaction of silver-bearing solutions with those carrying $H_2S$, sulphide ion, and antimony or arsenic. The reactions leading to the formation of supergene acanthite, stromeyerite, pearceite, polybasite, proustite, and pyrargyrite are not well known despite the fact that a number of deposits contain an abundance of these supergene minerals. It is apparent that some $H_2S$ and sulphide ion either escape oxidation in the upper parts of the veins and migrate downward or are generated in the deeper parts of some oxidized zones. Antimony and arsenic also find their way in solution to the deeper parts of the deposits. When these various elements come into contact acanthite or pyrargyrite or proustite are deposited. The reaction to produce acanthite is relatively simple:

$$2Ag^+ + S^{2-} = Ag_2S.$$

A somewhat similar reaction could be written for the formation of stromeyerite. That giving pyrargyrite or proustite is probably very complex. For pyrargyrite the following simplified reaction can be written:

$$3Ag_2SO_4 + Sb_2(SO_4)_3 + 6H_2S = 2Ag_3SbS_3 + 6H_2SO_4.$$

Ravicz (1915) suggested that pyrargyrite and proustite probably formed as a result of the intermingling of solutions containing silver sulphate with those carrying alkali sulphantimonite (or sulpharsenite) derived from the attack of alkaline solutions on primary arsenic and antimony sulphides or sulphosalts. He gave the following reaction, which must take place in an alkaline environment:

$$2Na_3SbS_3 + 3Ag_2SO_4 = 2Ag_3SbS_3 + 3Na_2SO_4.$$

A similar reaction could be written for proustite, the arsenic ruby silver.

Somewhat similar reactions are probably responsible for the formation of polybasite, pearceite, stephanite, and dyscrasite.

10. Precipitation of silver as various sulphides by the action of silver-bearing solutions with those bearing $H_2S$ generated by sulphate-reducing bacteria in the lower parts of the zones of oxidation and in the zones of reduction. The existence of this mechanism has not been tested as far as is known to the writer. It does seem to be a probable one, however, in the light of the experiments carried out by Baas Becking and Moore (1961).

11. Adsorption and coprecipitation of $Ag^+$ by negatively charged sols such as

manganese dioxide (*see* (4) above). Positively charged sols such as ferric hydroxide likewise appear to adsorb and coprecipitate $Ag^+$, especially where their charge has been reversed by adsorption of phosphate or other anions. The writer has observed a number of silver-bearing limonites in veins. On examination some of these contain wad with which much of the silver is associated. Other samples of limonite contain minute spangles of native silver, and in still others, argentojarosite and silver-bearing plumbojarosite, beudantite, and bindheimite are inextricably intermixed in a manner suggesting nearly simultaneous coprecipitation of all the mineral constituents.

Humic limonites appear to adsorb silver as do also various colloidal clay complexes, siliceous precipitates, and amorphous antimony and arsenic ochres.

12. Precipitation of silver and silver compound sols by various charged ions and sols. Jensen (1939) found that silver sulphide sols were not significantly precipitated by any of the sulphide ores. Calcite, on the other hand, and presumably the other carbonates as well, caused rapid precipitation (coagulation) of the silver sulphide sols. There are also reasons to believe that argillaceous materials, colloidal alumino-silicates, kaolinite, and carbonaceous matter will precipitate silver sols of various types. This feature coupled with the fact that such materials also precipitate silver ion from solution may help to account for the frequent enrichment of silver in secondary zones where much clay and kaolinite are found, e.g., Mount Morgan and Broken Hill, Australia.

13. Numerous secondary minerals tend to precipitate silver and incorporate small amounts in their lattices. Among these may be mentioned the jarosites, particularly plumbojarosite, beudantite, bindheimite, anglesite, and the various copper carbonates.

Although there is no invariable rule respecting the vertical zonation of secondary silver minerals in oxidized silver deposits, there is often a crude arrangement of the various minerals with depth. In the upper horizons of the oxidized zones the silver halides predominate if the conditions are favourable for their formation. In this halide zone the chloride, chlorargyrite, tends to be concentrated in the gossan and in the near-surface parts. It may be succeeded in depth by the chlorobromides and these in turn by iodargyrite. This ideal succession of halides, which it must be remarked appears to be rare is, however, present at Chañarcillo (Lindgren, 1918; Whitehead, 1919) and at Wonder and Tonopah, Nevada (Burgess, 1911, 1917). It was explained by Emmons (1917) as due to the fact that of the three halides chloride is in vast excess in most solutions and hence chlorargyrite, while more soluble than the bromides and iodide, is precipitated first. Knopf (1918), on the other hand, suggested that no iodide can be precipitated before the ferric ion has been reduced to the ferrous state, a situation that obtains only in the deeper parts of the oxidized zones. In the intermediate horizons of the oxidized zones native silver tends to become widespread and continues to the water-table and often below it. The appearance of native silver in the intermediate horizons seems to be conditioned by a decrease in the acidity of the downward migrating solutions and an increase in the content of ferrous or manganous ions. At or near the water-table where reducing conditions prevail, supergene acanthite makes its appearance and is followed in depth by the bulk of the sulphosalts, especially pyrargyrite and proustite. In this vertical scheme argentojarosite occurs in the upper and intermediate horizons of the oxidized zones with a marked development in the latter. It is rare in the lower horizons of the oxidized zones and generally absent in the zone of reduction.

While the above vertical zonation scheme conforms to well-established chemical principles with respect to the migration of silver, one often observes numerous divergences from this ideal zoning arrangement in veins and other deposits. Thus, in some deposits the halides and native silver are often intimately associated and show no marked vertical separation. Likewise, acanthite and pyrargyrite are often inextricably mixed, and may even occur in some parts of the oxidized zones of certain deposits. These examples only serve to emphasize the vagaries of the chemical processes operating during the oxidation of silver deposits.

## Examples of Silver Enrichment in Deposits

The supergene enrichment of silver in deposits is often highly irregular and not all deposits exhibit the same features. Practically every deposit is a study in itself. There are, however, certain general regularities that deserve mention, and these are best outlined by dealing individually with the types of deposits in which silver occurs.

There are no adequate descriptions of the oxidation of the copper shale deposits containing silver mainly as a trace or minor constituent. In these deposits most of the hypogene silver probably occurs in or associated with the bornite, chalcopyrite, chalcocite, tetrahedrite, and galena. In some deposits the element has been noted in the native form. Presumably the deep oxidation of such deposits yields the familiar secondary iron, copper, and lead minerals near the surface and abundant chalcocite at or near the groundwater table. Native silver would be expected in the oxidized zones if the proper conditions prevailed, and argentojarosite or argentian plumbojarosite would form in the intermediate parts of the oxidized zones of those deposits containing abundant pyrite and some lead. The main features of the oxidation and secondary enrichment would be the accumulation of silver as the native metal in the oxidized zones and as the native metal, acanthite, stromeyerite, and incorporated in the lattice of chalcocite in the chalcocite zones. This phenomenon is similar to that described below in greater detail for enriched copper deposits.

In the 'red bed' type of deposit the principal primary silver-bearing minerals are usually native silver, tetrahedrite, tennantite, acanthite, argentiferous chalcocite, and argentiferous galena. At Silver Reef, Utah, chlorargyrite and native silver were developed above the water-table, probably from acanthite, although some investigators think derivation from primary argentiferous chalcocite is the probable genesis. At Walton, Nova Scotia, where the lead-zinc-copper-silver deposit occurs in a lens in a complex fault zone there was some oxidation in the upper part of the sulphide body leading to the development of limonite, hematite, wad, copper carbonates, and secondary cobalt minerals. No definite supergene silver minerals have yet been identified in this oxidized zone although it is known that the limonitic and manganese materials contain some silver. In the sulphide zone there is an abundance of silver-bearing tennantite, acanthite, and proustite, but these appear to be hypogene minerals.

Oxidation of silver-bearing gold-quartz and gold-quartz-carbonate veins generally results in only a limited migration of silver and gold, although both elements may be enriched in the near surface parts of the veins mainly as a consequence of the removal of some of the gangue. In addition there is probably also some chemical accumulation of both gold and silver from the parts of the veins eroded away. In most cases the silver is present in the flakes and small nuggets of gold left behind after oxidation or it is incorporated in the small particles of gold precipitated locally from the oxidizing solutions. There is some evidence of a depletion of silver in gold-quartz deposits during oxidation processes since the fineness of the secondary gold in a number of deposits is greatly increased compared to the primary gold. The observations of a number of early investigators and more recently of Mackay (1944) are of considerable interest in this respect.

There are only a few data on the oxidation processes in gold-silver telluride deposits. At Cripple Creek, Colorado, the deposits are oxidized from 300 to 900 feet below the surface to a brownish clayey material containing mainly kaolin, hydrous silica, wad, basic ferric sulphates, and limonite. Fluorite and carbonates are removed, and the tellurides are altered to dark brown spongy, porous, and powdery gold, tellurite ($TeO_2$), and various ferric tellurites such as emmonsite, blakeite, etc. Some tellurium is leached out. There is little or no enrichment of gold in the oxidized zone, but a definite leaching of most of the silver originally incorporated in the tellurides, tetrahedrite, and other minerals appears to have taken place. Only a small amount of the silver remained behind in the free gold in many of the veins. According to Lindgren and Ransome (1906) no secondary silver sulphides were detected, nor is there evidence of secondary deposition of tellurides.

Little is known about the oxidation of gold-silver selenide deposits. Presumably they oxidize in a manner similar to the telluride deposits. The oxidation products to be expected would be native gold, selenolite ($SeO_2$), and various selenites, together with the common secondary iron, manganese, and silica minerals such as limonite, wad, kaolin, and hydrous silica. Silver may be leached in certain deposits, although there are references to the formation of native silver and stephanite from aguilarite, $Ag_4(Se,S)$, at Guanajuato in Mexico and at the Comstock Lode in Nevada.

Among the gold-silver deposits the greatest enrichment of silver (and gold) as a result of oxidation occurs in those deposits that abound in the various base metal sulphides, pyrite, pyrrhotite, and arsenopyrite. In these deposits ferrous sulphate and manganese sulphate play a leading part in the reactions that precipitate silver and gold. Secondary silver sulphides and sulphosalts may be developed in the zones of reduction, and argentojarosite may be formed in the intermediate parts of the oxidized zones. Silver halides are common in the upper parts of the oxidized zones of certain deposits. The trend of oxidation and secondary precipitation of silver follows somewhat the same course as that described below for the silver-bearing polymetallic deposits, and need not be elaborated upon at this point.

Practically all types of copper deposits, including the vein and porphyry varieties, contain small amounts of silver either in or associated with the primary copper minerals chalcopyrite, bornite, enargite, and tetrahedrite. Most of these deposits also contain pyrite, pyrrhotite, or arsenopyrite, and these influence greatly the migration of silver.

As the copper deposits oxidize, the iron-bearing minerals yield ferrous sulphate and some sulphuric acid, and the copper-bearing minerals give soluble copper sulphates as well as small amounts of silver sulphate. Ferric sulphate develops under the high-oxidation potential in the surface parts of the deposits and this undergoes hydrolysis with the formation of the familiar limonite that is characteristic of the gossans developed on many types of copper deposits. In addition opaline silica, kaolin, and a great variety of other secondary minerals, among which those of copper are characteristic, may be developed along with the limonite. In some deposits the conditions have been so acid that abundant limonite was prevented from forming or was later leached out, and all that remains is a great siliceous sinter or rubble lightly stained with limonite and occasionally with copper carbonates. Infinite variety between dense limonitic gossans and leached siliceous sinters characterizes many of the oxidized copper deposits of the world.

The most diverse developments of secondary copper minerals occur in oxidized copper deposits. In some deposits such as those at Ajo, Arizona, Chuquicamata, Chile, and elsewhere, the great lodes, under conditions of extreme aridity, have been highly oxidized and great masses of malachite, azurite, chrysocolla, brochantite, and atacamite together with other copper sulphates, carbonates, and silicates have developed. In the Ajo deposits the carbonates appear to have formed by solution and precipitation of copper derived from veins and disseminated bodies of primary chalcopyrite and bornite in a mass of monzonite. At Chuquicamata, however, the sulphates and carbonates of copper apparently developed from a supergene chalcocite-covellite zone, the lower part of which still remains. In other deposits such as those at Ely, Nevada, Bingham, Utah, and elsewhere, great chalcocite blankets, in places with covellite, were developed below the oxidized zones, which consisted of limonite-stained rock, containing local concentrations of copper carbonates.

There is very little information in the literature on the distribution of silver in the great porphyry copper deposits and practically none on the carbonate ores. This restricts somewhat our knowledge of the migration of silver during the oxidation and secondary enrichment of these important deposits. In the old literature there are some references to the fact that the near-surface parts of the oxidized zones of a number of porphyry copper deposits are enriched in gold (and presumably also in silver since the two elements usually go together in such an environment). At Butte both silver and gold were found in notable amounts in the oxidized parts of the veins and these graded downward into the secondary copper ores.

Two features seem important in the migration and enrichment of silver in copper deposits—the presence of abundant ferrous (and manganous) sulphate and the development of secondary chalcocite and/or covellite. As the deposits oxidize, the presence of ferrous sulphate in the oxidizing solutions greatly inhibits the migration of silver (and gold) but has little or no effect on copper in solution as the sulphate. It follows, therefore, that much silver (and gold) would be precipitated in the oxidized zones whereas copper would be largely leached. Such is indeed true of many copper deposits, since there are numerous references in the literature indicating that the oxidized parts of many veins in Australia, U.S.A., South America, and elsewhere were worked for silver and gold and the lower primary parts mainly for copper. Chalcocite and covellite precipitate silver from solutions rapidly as shown by Palmer and Bastin (1913) and Jensen (1939). The reaction with chalcocite is probably as follows:

$$Cu_2S + 2Ag_2SO_4 = 2CuSO_4 + Ag_2S + 2Ag.$$

That this reaction and a similar one for covellite are highly effective is shown by the general enrichment of silver in most secondarily enriched chalcocite and covellite zones in numerous copper deposits. Emmons (1917) has pointed out that there is little chance of any quantity of secondary silver minerals developing below chalcocite zones because of the marked precipitating effect of chalcocite on silver, a feature that appears to be borne out in all descriptions of copper deposits.

The nature of the silver in chalcocite zones has not been intensively investigated as far as the writer is aware. Probably most of the silver is present in chalcocite, since this mineral generally contains small amounts of the element probably replacing copper in its lattice and giving the compound $(Cu,Ag)_2S$. Some silver is probably also bound as acanthite (argentite), as stromeyerite, and as the native metal since these minerals have been reported from chalcocite zones. The presence of other silver sulphides and sulphosalts in chalcocite zones seems to be rare.

The fate of silver during the formation of copper sulphate, carbonate, chloride, and silicate ores appears to be largely unknown. The sulphates and carbonates may contain traces of silver, and it seems probable that the chlorides and silicates may also take some silver into their structure although there are no data on this point. The writer has repeatedly found silver in the copper carbonates, and it seems probable that any migrating silver is quickly precipitated in the neutral and slightly alkaline environments where the carbonates are generally formed. In addition many of the copper sulphate, carbonate, chloride, and silicate ores contain various arsenates, limonite, wad, and secondary minerals of lead and other metals, all of which may contain traces of silver in their lattices or adsorbed to their surfaces.

Massive sulphide deposits of the base metals tend to form characteristic gossans composed essentially of limonite, wad, and hydrous silicates. In many places these gossans and their underlying oxidized zones become enriched in silver (and gold) largely through the precipitating action of ferrous sulphate. Lead may also be enriched in many places but zinc, copper, nickel and other metals are largely leached out.

Numerous examples of silver (and gold) enrichment in the oxidized parts and zones of reduction of massive sulphide deposits have been described. The great Rio Tinto pyritic copper deposits were capped by extensive hematitic and limonitic gossans up to 100 feet thick. These contained practically no copper and only traces of silver and gold. Immediately below the gossan a clearly demarcated earthy zone was present and this was greatly enriched in both silver and gold. Below this zone the massive pyrite was leached for 3 feet or more, and this was followed by an enriched chalcocite zone, also somewhat enriched in silver. Below lie the immense pyritic lenses containing a little chalcopyrite, galena, and sphalerite.

The enormous galena-sphalerite lodes at Broken Hill were highly oxidized down to a depth of 350 feet or more. The zones developed were exceedingly complex and differed in the various lodes (Andrews, 1922; Stillwell 1927). In a general way they may be described as follows.

To a depth of 300 feet a gossan and oxidized zone, some 20 to 100 feet wide, was developed and consisted mainly of limonite, wad, hematite, kaolin, granular garnet, calcite, and quartz, and variable amounts of malachite, azurite, calamine, cerussite, and pyromorphite. This oxidized zone carried 10 to 40 ounces silver and up to 18 per cent lead. Below this there was a thin kaolinitic zone containing in places great masses of cerussite, pyromorphite, anglesite, cuprite, marshite, miersite, and malachite with abundant chlorargyrite, iodian bromargyrite (iodembolite), iodargyrite, and native silver. Gradually at varying depths this zone was succeeded by a zone up to 3 feet thick of silver-rich friable sulphides containing secondary sooty and microcrystalline chalcocite, stromeyerite, acanthite, and jalpaite with primary galena, sphalerite, and chalcopyrite. These so-called "friable sulphides" graded downward into the massive galena-sphalerite ore containing some pyrite, arsenopyrite, chalcopyrite, tetrahedrite, pyrargyrite, other silver sulphosalts, and cubanite with the gangue minerals garnet, rhodonite, pyroxene, and quartz.

The Broken Hill oxidized zones provide an extreme example of the diversity of the processes of silver enrichment as well as a great variety of secondary silver minerals. Native silver and the various halides were developed extensively as well as the various silver sulphides, especially stromeyerite and acanthite. In addition there were spectacular occurrences of apparently secondary dyscrasite, $Ag_3Sb$, later altered to a silver-bearing chloro-antimonate of unspecified mineral composition.

The oxidation zones of the great pyritic lodes of Cerro de Pasco, Peru, are described on page 180. In the *pacos* or gossan the silver is apparently bound mainly in argentian plumbojarosite. In the secondary copper zones the bulk of the silver is in chalcocite.

Some of the massive pyritic deposits containing galena, sphalerite, chalcopyrite, and tetrahedrite in the Bathurst-Newcastle area of New Brunswick are marked by extensive gossans composed essentially of limonite, clay minerals, and fine-grained quartz with variable amounts of anglesite, beudantite, barite, scorodite, jarosite, woodhouseite, and numerous other secondary minerals. None of these gossans exceed 10 feet in thickness, but parts of them are enriched in silver. Much of this silver appears to be held in jarosite although some may be present in the limonitic complex as very finely divided metal. Below the gossans in some deposits there is a thin chalcocite and/or covellite zone that in places extends to a depth of 50 feet or more along fault and crushed zones. Higher than average silver assays occur in these chalcocite zones, the element being apparently largely present in the chalcocite with small amounts in the native form.

There are few good descriptions of deep oxidation of native silver deposits containing the familiar Ni-Co arsenides and sulphides, since most of the oxidized zones in the classical areas were worked out before the turn of the 16th century. The deposits at Sarrabus in Sardinia and Chalanches in France appear to have been relatively deeply oxidized according to the reports by Rickard (1894), Piepoli (1933), and others. Iron oxides were abundant, and there was a general development of erythrite, annabergite, pyromorphite, and other secondary nickel, cobalt, and lead minerals. Chlorargyrite was also a prominent secondary silver mineral at both places. In some parts of the veins there was also much black earthy residuum and mud containing native silver, probably of secondary origin. Some of the iron-stained earthy material in the oxidized parts of the veins at Chalanches contained gold, as high as 7 ounces per ton in places.

The native silver veins discovered in the present century, such as those at Cobalt and Great Bear Lake, generally exhibit an exceedingly shallow zone of oxidation or none at all as a consequence of glaciation. In some veins at Cobalt, however, the writer has observed that the nickel-cobalt arsenides and other minerals are highly altered near the surface to an assemblage of limonitic clay material in which nuggets, plates, and wires of native silver remain. Erythrite and annabergite characterize some of these shallow zones, but with increasing oxidation these minerals appear to be unstable and are apparently leached out. Manganese oxides (wad) occur in a number of the surface exposures of the veins.

One excellent example of deep oxidation did, however, occur in the Cobalt-South Lorrain district at the Keeley mine where Wood's vein was oxidized to a depth of 600 feet or more (Bell, 1923).

Near the surface, parts of Wood's vein were thoroughly oxidized and consisted of a soft heavily iron-stained puggy clay, presumably the oxidized remains of the original calcite, native silver, Ni-Co arsenides, pyrite, etc., mineral assemblage. This oxidized material was practically devoid of silver. At depth (400 feet) the vein material was greatly enriched in silver, the element occurring in the wire form, in spongy accumulations of tiny scaly crystals, as thin plates, and in argentite. Gold was also enriched at depth, an unusual situation, since most of the veins at Cobalt contain only traces of the element.

Bell attributed the silver enrichment to solution of the element in the upper parts of the vein, with consequent downward migration and precipitation at depth. Near the surface he reasoned that ferric sulphate and sulphuric acid generated by oxidizing pyrite dissolved the silver as the sulphate. With downward migration, the acidity of the solutions decreased, ferrous sulphate accumulated, and silver was precipitated.

Another mechanism for the precipitation of secondary native silver in the Ni-Co-As type of deposit seems probable. This is one mentioned by Bastin (1939) and involves the reaction between niccolite and silver sulphate solutions:

$$2NiAs + 5Ag_2SO_4 + 3H_2O = 10Ag + 2NiSO_4 + As_2O_3 + 3H_2SO_4.$$

Similar reactions of silver sulphate with smaltite, loellingite, maucherite, and safflorite, according to Bastin, also lead to the precipitation of native silver.

The surface oxidation of the Great Bear Lake veins was distinctive and attracted the attention of both the geologist who first described the deposits and the prospectors who later rediscovered the veins. It consisted of a shallow zone, usually only a few feet deep, containing a variety of yellow, yellowish green, and orange secondary uranium minerals, azurite, malachite, erythrite, annabergite, secondary carbonates, limonitic material, and clinkery masses of wad.

The familiar polymetallic vein deposits containing galena, sphalerite, pyrite, tetrahedrite, chalcopyrite, argentite, and other silver sulphides in a carbonate, barite, or quartz gangue probably represent the greatest variety of secondary silver minerals and silver enrichment among silver deposits. These veins show an infinite variety of secondary silver minerals. In some veins spectacular developments of the silver halides are present, in others native silver, argentite, argentojarosite, and ruby silvers occur abundantly in the oxidized zones and zones of reduction. In still others, refractory silver-bearing wad is common. Examples are widespread in Canada, the western United States, Mexico, South America, U.S.S.R. and elsewhere. Recently the writer completed an extensive investigation of the geochemistry of silver in the polymetallic deposits of the Keno Hill-Galena Hill area Yukon (Boyle, 1965). The salient features of the oxidation and secondary enrichment of silver in these deposits are as follows.

The deposits of the Keno Hill-Galena Hill area (Fig. 4) are lodes localized in faults that cut through quartzites, phyllites, and greenstones. Two ages of lodes are present—an early type containing essentially quartz with pyrite, arsenopyrite, small amounts of gold, and some galena, sphalerite, boulangerite, meneghinite, and bournonite; and a later type mineralized with manganiferous siderite, argentiferous galena, sphalerite (variety marmatite), chalcopyrite, pyrite, freibergite, and small quantities of other sulphosalts. Although both types of lodes may occur separately, it is more usual to find hybrid bodies consisting of the quartz type, which have been fractured and later cemented with minerals characteristic of the siderite type. The late siderite lodes are economic and produce lead, zinc, cadmium, and silver.

Three zones can be recognized in most lodes—an upper oxidized zone, a zone of reduction, and a primary zone. The oxidized and primary zones are present in all lodes and are generally well developed and demarcated. The zones of reduction are diffuse, and telescope both the oxidized and primary zones. The depths of the oxidized zones are variable. In some mines oxidation terminates at a depth of 20 feet, in others the oxidized zones extend to depths ranging from 250 to 500 feet.

The oxidized parts of the lodes contain a veritable host of minerals. Limonite (goethite, lepidocrocite, hematite), wad (pyrolusite, manganite, psilomelane), anglesite, cerussite, and silver-bearing beudantite and plumbojarosite are the most characteristic. In addition to these the following are present, often in some quantity: gypsum, native sulphur, malachite, azurite, smithsonite, pharmacosiderite, pyromorphite, mimetite, bindheimite, scorodite, melanterite, calcite, aragonite, montmorillonite, serpentine, quartz, covellite, pyrargyrite, acanthite, ice, native silver, and an occasional speck of native gold, and native zinc.

The limonite, jarosite, beudantite, and other secondary iron minerals are derived mainly from siderite, pyrite, and sphalerite. The secondary manganese minerals are formed from manganiferous siderite, the lead oxygen salts from galena, smithsonite from sphalerite, the copper carbonates from freibergite and chalcopyrite, and the secondary antimony and arsenic minerals from arsenopyrite, freibergite, and the other sulphosalts. The derivation of the supergene silver minerals is discussed below.

Nodules and masses of galena, rimmed by anglesite and encrusted with cerussite, anglesite, and other secondary lead minerals, are present in all oxidized zones. Also common are residuals of highly oxidized pyrite, sphalerite, siderite, freibergite, and other sulphosalts.

The oxidized zones are extremely porous and contain numerous cavities, some open and others filled with ice veins and pods since a number of the lodes occur in the permafrost zone. Characteristic boxworks and cellular structures are developed in most zones, and in at least one mine some of the lower parts of the oxidized zones are cemented by finely banded calcite, gypsum, smithsonite, limonite, and secondary quartz.

The zones of reduction telescope the lower parts of the oxidized zones and the upper parts of the primary zones, and were presumably formed in the vicinity of former water-tables. Their development is irregular, probably because of fluctuations in the water-table; in some lodes they are diffuse and minor, in others, marked zones of reduction, some 25 to 50 feet or more in depth, were present. The minerals in the zones of reduction include those commonly present in both the primary and oxidized zones, augmented by characteristic developments of pyrargyrite, native

TABLE 49 *Lead, Zinc, and Silver Contents of Oxidized and Unoxidized Ores, Keno Hill–Galena Hill Area*

| Location | Description | Pb % | Zn % | Ag oz/ton |
|---|---|---|---|---|
| Silver King mine, Galena Hill | Oxidized ore near surface | 61.4 | 1.7 | 374.2 |
| ” | Unoxidized ore 80 feet below surface | 22.3 | 6.8 | 156.8 |
| ” | Unoxidized ore 100 feet below surface | 3.9 | 8.7 | 38.5 |
| Hector-Calumet mine, Galena Hill | Average assay of oxidized ore | 9.87 | 4.29 | 51.18 |
| ” | Average assay of unoxidized ore | 9.2 | 8.4 | 38.4 |
| Lucky Queen mine, Keno Hill | Average assay of upper 50 feet of vein. Sorted ore | 42.0 | 4.5 | 485.3 |
| ” | Average assay of ore below 50-foot level | 6.0 | 8.0 | 77.0 |
| Onek mine, Keno Hill | Average assay of ore—surface to 50-foot level | 42.0 | 0.67 | 88.1 |
| ” | Average assay of ore on 400-foot level | 6.97 | 17.4 | 17.2 |

Assays and analyses of Silver King, Hector-Calumet, and Lucky Queen ores from various private company reports. Assays and analyses of Onek ores by Mines Branch, Ottawa.

silver, acanthite, and small amounts of supergene calcite, siderite, sphalerite, galena, pyrite, and hawleyite.

As a whole, the lodes exhibit a marked enrichment of silver and lead and a depletion of zinc in the oxidized zones, compared with the primary zones (Table 49).

The following explanation of the geochemistry of silver during the oxidation of the Keno Hill lodes is based on a trace-element study of the secondary minerals, and on the oxidizing and reducing conditions existing in the orebodies at the present time. It is assumed that similar conditions prevailed during Tertiary time when most of the oxidation took place.

TABLE 50 | *Dissolved Constituents in Underground Waters; Keno Hill–Galena Hill Area*

| Constituent | Content (in ppm) |
|---|---|
| Calcium ($Ca^{++}$) | 50 – 200 |
| Magnesium ($Mg^{++}$) | 10 – 120 |
| Sodium ($Na^{+}$) | 1 – 3 |
| Potassium ($K^{+}$) | 0.4 – 0.6 |
| Iron (Fe) (total) | 1 – 5 |
| Aluminum ($Al^{+++}$) | 1 – 15 |
| Manganese ($Mn^{++}$) | 5 – 25 |
| Copper ($Cu^{++}$) | 0.001 – 0.65 |
| Zinc ($Zn^{++}$) | 0.001 – 80.00 |
| Lead ($Pb^{++}$) | 0.001 – 1.00 |
| Cadmium ($Cd^{++}$) | 0.001 – 0.5 |
| Arsenic | ~0.002 |
| Antimony | ~0.001 |
| Silver ($Ag^{+}$) | ~0.001 |
| Bicarbonate ($HCO_3^{-}$) | 10 – 100 |
| Sulphate ($SO_4^{2-}$) | 200 – 1200 |
| Chloride ($Cl^{-}$) | 0.1 – 1 |
| Fluoride ($F^{-}$) | 0.3 – 0.5 |
| Nitrate ($NO_3^{-}$) | 0.1 – 0.6 |
| Silica ($SiO_2$) | 5 – 10 |

In the waters now percolating through the lodes the principal anions are sulphate, bicarbonate, and silicate, with traces of nitrate, chloride, and fluoride; the main cations are calcium, magnesium, aluminum, manganese, and iron. Traces of zinc, lead, copper, arsenic, antimony, silver, cadmium, and other elements are also present. Table 50 gives a generalized range of the dissolved constituents in the waters as compiled from hundreds of analyses. The pH of the waters ranges between 4.4 and 7.8; the lower pH's are present in zones where active oxidation of sulphides is taking place, but these increase rapidly as soon as the waters come into contact with siderite. The oxidation-reduction potential (Eh) is relatively high near the surface but decreases rapidly as the waters pass downward and are depleted in atmospheric oxygen. The temperature of the waters ranges between 2° and 5°C.

The oxygenated waters containing $CO_2$, on entering the lodes attack the siderite releasing iron as ferrous hydrogen carbonate, $Fe(HCO_3)_2$, manganese as manganous hydrogen carbonate, $Mn(HCO_3)_2$, and the other constituents as hydrogen carbonates. Pyrite is oxidized to ferrous sulphate and some sulphuric acid, which is quickly neutralized by siderite. Sphalerite (variety marmatite) yields ferrous, zinc, and cadmium sulphates. During these reactions freibergite is attacked, and silver is released as the sulphate and/or carbonate. Argentiferous galena, likewise, on its conversion to anglesite and cerussite yields some silver sulphate and/or carbonate.

Once released from its primary minerals the silver may follow six courses depending on a number of chemical circumstances.

1. Some silver as $Ag^+$ is adsorbed to and coprecipitated by the negatively charged sols of manganese dioxide.A similar phenomenon occurs with ferric hydroxide where this substance has adsorbed arsenate or phosphate. By partial dehydration the hydroxides yield wad and limonite, which retain some silver either as a silver manganite or ferrite, or as an adsorbed phase at the boundaries of the manganese dioxide or ferric oxide microcrystals.

2. Some silver is coprecipitated with and bound in the basic sulphates of iron, lead, and arsenic such as plumbojarosite and beudantite. These basic salts are formed in a mildly acid environment and represent intermediate products in the hydrolysis of ferric sulphate in the presence of soluble potassium, lead, and arsenic. Argentojarosite is apparently not formed, the stable mineral being silver-bearing plumbojarosite. This jarosite, together with beudantite, is commonly found in limonite in such an intimate association as to suggest that all were precipitated together. Some of the highly argentiferous limonite (and wad in places) is due to the presence of admixed argentiferous plumbojarosite and/or beudantite.

3. Traces of silver are bound in bindheimite, anglesite, cerussite, malachite, azurite, and a variety of other secondary minerals. The nature of this silver is largely unknown. In some minerals it may replace lead, in others copper, in still others it may be in an adsorbed or interstitial form.

4. Some silver is precipitated as native silver in the form of leaves, arborescent masses, filaments, tangled wires, small scales, spangles, distorted crystals, and microscopic spongy masses in the near-surface and central parts of the oxidized zones and in the zones of reduction. In some veins in the permafrost zone splendent leaf silver occurs in ice veins (Boyle, 1960).

In most lodes, native silver is present in only minor amounts and its presence does not affect the average grade of the ore. In two of the principal lodes, however, native silver was present in quantities sufficient to enrich parts of the oxidized zones and zones of reduction.

In the zones of oxidation and reduction, the precipitation of silver is controlled in large measure by the oxidation-reduction potential and pH of the environment. In this respect the following couples in alkaline and acid solutions are of interest:

## Alkaline solutions[1]

$Fe(OH)_2 + OH^- = Fe(OH)_3 + e^-$ .............................. $E^\circ = 0.56$
$S^{2-} = S + 2e^-$ .............................. $E^\circ = 0.48$
$Mn(OH)_2 + 2OH^- = MnO_2 + 2H_2O + 2e^-$ .............................. $E^\circ = 0.05$
$Mn(OH)_2 + OH^- = Mn(OH)_3 + e^-$ .............................. $E^\circ = -0.1$
$2Ag + 2OH^- = Ag_2O + H_2O + 2e^-$ .............................. $E^\circ = -0.344$
$4OH^- = O_2 + 2H_2O + 4e^-$ .............................. $E^\circ = -0.401$

## Acid solutions

$H_2S = S + 2H^+ + 2e^-$ .............................. $E^\circ = -0.141$
$Fe^{2+} = Fe^{3+} + e^-$ .............................. $E^\circ = -0.771$
$Ag = Ag^+ + e^-$ .............................. $E^\circ = -0.799$
$2H_2O = O_2 + 4H^+ + 4e^-$ .............................. $E^\circ = -1.229$
$Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$ .............................. $E^\circ = -1.23$

From a study of the above potentials one can see that ferrous iron will be oxidized to the ferric state by atmospheric oxygen in both an acid and alkaline environment; the reaction will, however, proceed with greatest facility in alkaline solutions. As regards manganese, the potential developed by the oxygen couple is not sufficiently powerful to oxidize $Mn^{2+}$ to $MnO_2$ in acid solutions, but is adequate in an alkaline environment. Hydrogen sulphide and any sulphide ion are oxidized rapidly and quantitatively to sulphur by atmospheric oxygen in an alkaline environment and by both atmospheric oxygen and ferric ion in an acid medium. In accordance with the potentials, $Ag^+$ is reduced to the metal by $Fe^{2+}$ in acid solutions and particularly by $Fe(OH)_2$ in basic solutions, because $Fe(OH)_2$ is a much better reducing agent than ferrous ion. $Mn(OH)_2$ has a similar effect in a basic medium. The presence of high concentrations of $Fe^{3+}$ in solution will, however, as noted in a previous section, inhibit the precipitation of silver.

Applying these concepts to the various reactions in the lodes, one can trace the origin of native silver rather precisely. In the oxidized parts of the lodes, hydrogen sulphide, if formed by the action of free sulphuric acid on sulphides such as sphalerite, is largely eliminated from the reactions because it is oxidized rapidly to sulphur by atmospheric oxygen and ferric iron. This inhibits the formation of any silver sulphide and explains the absence of tarnish on the native silver, the general paucity of acanthite and other silver sulphides, and the omnipresence of small quantities of native sulphur in the oxidized zones. With depth, however, as the oxidation potential decreases, some hydrogen sulphide may escape oxidation, pass downward, and be available for binding silver as sulphide in the zone of reduction.

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[1] These couples are taken from Latimer (1952) and are referred to the standard hydrogen gas–hydrogen ion couple, $H_2 = 2H^+ + 2e^-$, with $E^\circ = 0.00$ volt. The potentials given are for unit activity (or concentration assuming complete ionic dissociation), pressure 1 atmosphere, and $T = 25°C$. The potentials of the oxygen couples may be taken for all practical purposes as those of natural solutions containing atmospheric oxygen. The oxidation potentials change with varying concentration, pressure, temperature, and pH. A positive value for E° indicates that the reduced form of the couple is a better reducing agent than $H_2$ and similarly a negative E° indicates that the oxidized form of the couple is a better oxidizing agent than $H^+$. The couples are given in order of decreasing oxidizing power or increasing reducing power, the reduced form of any couple having sufficient potential to reduce the oxidized form of any couple of lower potential. For example, $O_2$ oxidizes $Fe(OH)_2$ and $Mn(OH)_2$ in alkaline solutions and $Fe^{2+}$ and $H_2S$ in acid solutions. Similarly, $Fe^{2+}$ reduces $Ag^+$ in acid solutions.

The near-surface oxidation of the primary lode minerals yields ferrous and manganous ions and the argentous ion to slightly acid solutions. Incipient precipitation of silver may take place by the reduction of $Ag^+$ by $Fe^{2+}$, but this is limited and generally suppressed by two factors—the formation of large amounts of ferric ion in solution because of the high oxidation potential and the oxidizing effect on both the ferrous ions and silver of any manganese dioxide present in the feebly acid to neutral solutions. Silver is, therefore, relatively mobile in the near-surface parts of the lodes, and only small amounts of native silver are formed, a fact substantiated by observation.

As the waters pass downward, atmospheric oxygen is consumed, the oxidation potential decreases, the pH increases due mainly to neutralization of the solutions by siderite, and the concentration of ferric ion in solution decreases. These conditions promote the precipitation of native silver according to the following ionic equations:

$$Ag^+ + Fe^{2+} = Ag + Fe^{3+}$$
$$2Ag^+ + Mn^{2+} = 2Ag + Mn^{4+}.$$

During these reactions, the $Fe^{3+}$ and $Mn^{4+}$ are removed and fixed as insoluble ferric hydroxide and manganese dioxide (limonite and wad).

With further downward migration the silver passes into the zone of reduction. Here $Ag^+$ comes in contact with sulphides such as freibergite, or reacts with solutions containing $H_2S$ and antimony, resulting in the precipitation of pyrargyrite or acanthite. Some of the silver remaining in solution is precipitated by ferrous iron as native silver; the remainder is dispersed through springs into the stream systems.

The occurrence of native leaf and wire silver in the ice lenses is a phenomenon not readily explained. In some places there is evidence suggesting that the ice and silver crystallized nearly contemporaneously. In other places the ice appears to have crystallized around leaf and wire silver after its precipitation in solution channels and vugs. Elsewhere, the silver appears to have precipitated on the ice and within fractures in the ice. Whatever their origin these occurrences of native silver are unique and similar in most respects to occurrences of native gold in ice lenses described by the writer (Boyle, 1951) from Yellowknife, Northwest Territories.

5. Much silver passes downward into the lower parts of the oxidized zones and the zones of reduction. There, some is precipitated as the native metal either by reaction with sulphides or with ferrous or manganous sulphate. Much of the remainder, as noted above, reacts with available $H_2S$ to form acanthite or with solutions or minerals containing sulphide ion and antimony to form pyrargyrite. Acanthite is not common in any of the lodes; pyrargyrite was abundant in a few lodes and formed characteristic secondary enrichments at or near the interface between the fresh sulphides and the oxidized material.

6. The remainder of the silver is ultimately dispersed through springs into the stream system of the area. The amount of mobile silver escaping from the veins after oxidation is very low, of the order of 0.001 ppm or less. Some of this silver is trapped by the stream sediments of the area as shown by the surveys carried out by Gleeson, *et al.* (1966).

## *Chapter V*

# PROSPECTING FOR SILVER DEPOSITS

Silver is largely won as a by-product from gold and various base metal deposits and hence only rarely, as in the case of native silver deposits, is prospecting carried out solely for the element. Because of the by-product nature of silver practically all of the common geological, geochemical, and geophysical methods that can be applied in the search for gold and base metal deposits can be utilized. In the following we shall deal principally with methods applicable to those deposits in which silver is an important constituent.

## Selection of Areas

Those searching for silver-bearing deposits should study carefully the types of deposits and their geological setting as outlined in Chapter III. Particular note should also be taken of the modes of oxidation of the various types of silver deposits as discussed in Chapter IV.

① Despite the controversy surrounding the origin of the silver-bearing copper shales and 'red bed' deposits there is abundant evidence to suggest that palaeogeographic conditions have played a large part in at least the initial concentration of their constituent elements. Our knowledge on these matters is, however, woefully inadequate, but there are some broad features that deserve attention.

The silver-bearing copper shale deposits are either in or closely associated with sediments of all ages deposited under reducing conditions. Most of the sediments are bituminous shales, black shales, tuffs, or calcareous shales, laid down in a near-shore environment probably in restricted bays, inlets, in a deltaic environment, and in cut-off portions of seas. Some appear to have been deposited in fresh-water lakes, others in inland seas. Some of the reduced sediments are associated with others such as red sandstones, gypsum, etc., characteristic of arid conditions. A few of the larger deposits overlie sandstones that represent aeolian conditions or in some cases deltaic conditions. In some situations a hinterland marked by numerous basic to intermediate eruptive rocks and containing earlier epigenetic copper and other deposits is indicated. In other situations volcanic terrains dotted with lakes or in the proximity of seas seem to predominate.

With these palaeogeographic conditions in mind all black and grey shales, calcareous shales, thin limestones, and tuffaceous deposits should be examined carefully for copper and silver, and also it might be remarked for lead, zinc, cobalt, molybdenum, and uranium. Sequences of red sandstones, shales, and evaporite deposits containing black reduced sediments or thin calcareous shales require close scrutiny, as do also tuffaceous beds intercalated with any type of volcanic rock. In Canada such rocks are widespread. They occur in the Mississippian and Pennsylvanian and other Palaeozoic rocks of the Appalachian provinces and in all ages of rocks in British Columbia, Yukon, and the Arctic Islands. The vast expanses of the Canadian Shield likewise contain an abundance of tuffaceous and black sediments intercalated with the Archaean greenstones. These, and the black shales and tuffs in the Timiskaming type sedimentary terrains, as well as those in the Huronian, Animikie, and Keweenawan belts, should not go unnoticed. Of particular interest are the so-called 'copper provinces'. Reduced sediments, tuffs, and calcareous rocks in these provinces should be treated as especially favourable. In Canada these provinces can be roughly defined as the volcanic belts in Newfoundland; Seal Lake area in Labrador; the Mississippian-Pennsylvanian belt of the maritimes; the Bathurst-Newcastle mineral district; the Sudbury basin; the northwestern Quebec volcanic district including Noranda, Waite Amulet, etc.; Timmins volcanic belt, Ontario; the Lake Superior district (in Canada, Port Arthur, Michipicoten and Nipigon areas); the numerous volcanic (greenstone) belts of Manitoba and Saskatchewan that are characterized by the presence of copper-nickel and copper-zinc deposits; the numerous volcanic and associated sedimentary belts in British Columbia; Redstone Mountain and adjacent areas in Yukon; and the Coppermine River area in the Northwest Territories.

It cannot be too strongly emphasized that all black and bituminous shales, tuffs, calcareous shales, and similar associated rocks should be carefully examined for the presence of copper and silver and a variety of other metals. This follows simply from the fact that we do not yet know the precise environment in which silver-bearing copper shales are developed. Another difficulty is that the dark coloured copper and silver sulphides, as well as other sulphides, because of their relatively fine dissemination through black shales and similar rocks may go unnoticed in drill cores and fresh rock samples. Expensive assays are not required in most cases to eliminate barren core. The simple geochemical tests for copper, lead, and zinc, using dithizone concentrations some ten times or more greater than that normally used in geochemical prospecting, are usually adequate for indicating samples that are of possible ore grade. If silver, cobalt, molybdenum, etc. are suspected, rapid qualitative spectrographic analyses will differentiate material that requires detailed assay or analytical treatment.

Silver-bearing sandstone deposits of the so-called 'red bed' type occur almost exclusively in terrigenous or shallow water beds generally far from intrusive igneous bodies such as granites, although in some terrains, tuffs and basaltic flows may be present. Most of the sediments enclosing the deposits are the typical 'red bed' type accumulated under relatively arid conditions. The deposits rarely occur, however, in red sandstones, conglomerates, or shales; their environment is usually in greyish and greenish sandstones, microconglomerates, arkoses, etc. intercalated with the red beds. The typical depositional environment for the sediments was on the wide flood plains of rivers laced by a myriad of shifting channels that are now represented by elongate lenses of porous sand and conglomerate. A few deposits occur in sandstones that appear to have been laid down on wide river flats or on flood plains during quiescent times; others occur in deltaic sands or in a combination of aeolian, river, and deltaic sands.

A number of the sedimentary 'red bed' sequences appear to have been laid down in wide, subsiding intermontane valleys, others flank older continental areas containing copper and other deposits from which the metals in the sediments were probably derived. Some of the sands appear to represent the wash from ancient Precambrian terrains. Deposits in the latter type of sands may not belong strictly in the category of the 'red beds', but their features are similar in many respects.

Many of the sandstones and conglomerates contain abundant coalified plant fragments, and some contain coal seams. Those containing the lead deposits in Cape Breton Island are part of the coal measures.

All sandstones and conglomerates should be carefully examined for the presence of copper and uranium stains, especially those that contain coalified fragments or bituminous matter. It should be emphasized that silver minerals, especially chlorargyrite and finely disseminated argentite are difficult to identify in sandstones and may go unnoticed. The same can be said for finely disseminated galena and copper minerals. The simple geochemical tests or qualitative spectrographic analyses will eliminate barren material.

Particularly favourable areas for the occurrence of silver in red beds in Canada are the districts in the Maritime Provinces underlain by the Mississippian Windsor-Horton and Pennsylvanian sediments. In addition the Palaeozoic sands that overlie the old Precambrian rocks in many parts of the country should not go uninvestigated. Also worthy of consideration are the Proterozoic sandstones in various parts of the Shield and the numerous sandstones and quartzites in the Western Cordillera and Arctic Islands.

2. Silver-bearing skarn and contact metamorphic deposits require little description. They occur mainly in the contact aureoles of granitic and allied rocks and in medium- and high-grade metamorphic terrains. Nearly all deposits are developed in limestones, dolomites, calcareous sandstones, or calcareous shales in these environments. Sedimentary sequences of argillites, black schists, and the various calcareous rocks seem to be particularly favourable as do also sequences containing volcanic rocks and calcareous rocks. The thought should be kept in mind that the black shales and argillites and the volcanic rocks may be the source of the silver and other elements, and that these were mobilized during metamorphism and chemically trapped in the calcareous rocks where the proper structural conditions prevailed.

3. A great many of the metamorphic terrains in Canada are susceptible to mineralization of the skarn and contact metamorphic types. Here one may mention the metamorphic terrains of the Appalachian Belt, the Grenville, the vast metamorphic terrains of the Canadian Shield, and the numerous metamorphic belts and contact zones of the Western Cordillera as broad select areas in which to prospect for silver-bearing deposits of the skarn type. The Grenville rocks of Ontario and Quebec

should receive more attention than they have as favourable sites for the deposition of lead-zinc-silver deposits. In this respect it should be remembered that the New Calumet deposit is considerably enriched in silver with some parts of the deposit containing up to 10 ounces Ag per ton or more. 4.

Among the vein, stockwork, and manto type deposits there are two general types—the gold-silver type in which silver is subsidiary in many cases, and the polymetallic type containing lead, zinc, and copper with silver as a valuable and sometimes indispensable by-product. There appear to be no general rules governing the environment of these deposits, a feature that should be kept in mind by the prospector. There are, however, certain patterns that seem worthy of note.

On a statistical basis the gold-silver veins show two characteristic modes of occurrence with respect to the various types of country rocks. A great many veins occur in folded and metamorphosed volcanic sequences, especially those containing interbedded tuffs and sulphide-bearing black sediments. Andesites, both ancient and relatively recent, and certain types of intrusive quartz-feldspar porphyries appear to be especially favourable. The second greatest concentration of these veins is in metamorphosed sedimentary sequences, especially those containing argillites, pyritiferous black slates, and quartzites. Neither of these modes of occurrence are at all new to the seasoned prospector—the greenstones of many mineral belts and the greywacke-slate assemblages with their characteristic saddle reefs have long been known as favourable areas. The philosophy of prospecting in these belts has, however, been that the metals were derived from local granites or some other suitable igneous rock. Perhaps we should take a more careful look at the country rocks themselves as the source of the metals. There is abundant geochemical evidence to suggest that the black slates and tuffaceous rocks intercalated with the greenstones may be the source of the noble metals, and that the andesites, basalts, trachytes, etc., as well as the intrusive porphyries may also have made their contributions. Likewise, it is also highly probable that sulphide-bearing black slates, phyllites, etc., are the source of the gold and silver in the deposits localized in the greywacke-slate assemblages. As these rocks were structurally deformed and metamorphosed, numerous dilatant zones were formed along the crests of anticlines, along sheared beds, and in local faults and fractured zones. These sucked in the more mobile constituents from the rocks, including quartz, the components of pyrite and arsenopyrite, gold and silver, and other constituents.

The philosophy in prospecting for these two types of gold-silver deposits should be to seek out areas containing the favourable rocks mentioned above, paying particular attention to sulphide-bearing sediments. From this point careful attention should be directed to areas that were structurally deformed during the metamorphic history of the favourable areas. It should perhaps be mentioned in passing that the black schists and phyllites are usually incompetent rocks and do not generally contain the deposits. They probably provided the elements in the deposits; the more competent rocks such as the greywackes and greenstones are the general sites of the structural traps. 5.

The silver-bearing polymetallic veins, mantos, stockworks, etc., exhibit a great preference for low-grade metamorphic sedimentary sequences containing deformed and faulted argillites, black schists, phyllites, calcareous shales, limestones, and quartzites. Some polymetallic belts also contain interbedded volcanic rocks of various types. Geochemical research by the writer in a number of the silver-bearing polymetallic belts in Canada suggests that the sulphide-bearing black shales, argillites, etc., are probably the source of the elements in the deposits. His observations in other polymetallic belts of the world reinforce this view.

Particularly good conditions for the occurrence of silver-bearing polymetallic deposits are in low-grade metamorphic terrains where massive quartzites or other competent rocks are interbedded with sequences of pyritiferous black shales, phyllites, and thin-bedded quartzites. In such situations it is apparent that the competent rocks provide the necessary structures in which the metals secreted from the sulphide-bearing sediments are concentrated. Analogous conditions prevail where rocks such as limestones, calcareous shales, and argillites occur in the sedimentary column. These rocks, in addition to holding fractures, are readily replaced, and hence form chemical traps that precipitate the ore elements as they diffuse through the rocks during low-grade metamorphism.

6. Native silver may occur as a primary mineral in a number of the deposits mentioned above. Here we shall deal only with the Ni-Co arsenide type. These deposits have a rather restricted occurrence and have been mined for many years, but their origin has not always been satisfactorily solved.

On a world-wide basis the Ni-Co-Ag veins generally occur in rocks of Precambrian or Palaeozoic age. In Canada most of the deposits are restricted to the former age of rocks, but those in Rocher Déboulé Mountain near Hazelton, B.C., are in Cretaceous granodiorite. While there appears to be no particular relationship to country rock types a great many of the deposits occur in sediments usually of the greywacke-slate-quartzite type and their metamorphic equivalents. A few characteristic deposits occur in diabase and in sediments of the greywacke type intruded by diabase. Some deposits occur in high-grade metamorphic rocks and in associated granodiorites and granites; others in rocks that exhibit only low-grade metamorphism. Some are said to be genetically related to intrusive granites, others to diabase, and still others show no apparent relationship to any intrusive rock.

In a number of districts the veins are younger than the deposits containing cassiterite, pyrite, galena, sphalerite, etc., in the same area. Certain deposits cut mineralized 'fahlbands' or zones containing carbonaceous material with finely divided sulphides as at Kongsberg and Annaberg. At Cobalt some of the veins are in diabase or greywacke on the upward projections of sulphide-bearing graphitic bands in the underlying Keewatin rocks. These facts have led the writer in Chapter III to suggest that some of the Ni-Co-As-Ag veins are late 'distillates', deriving their constituents by diffusion from the 'fahlbands', sulphide-bearing graphitic bands, and other rocks such as sulphide-bearing greenstones, which may lie either below or lateral to the fractures. The origin of the other veins in diabase and sedimentary rocks is uncertain. A number, such as those in the Port Arthur area, occur in or near pyritiferous black slates. These rocks may well be the source of the silver and other elements in the veins. Where the veins occur in diabase, this rock may have contributed nickel and cobalt and perhaps some silver, and the associated sediments the sulphur, arsenic, the bulk of the silver, and other elements.

It is difficult to frame a philosophy in searching for veins of the Ni-Co-As-Ag type because of their varied environment. The speculations bearing on their origin noted above should be taken into consideration especially in the favourable belts containing these deposits. In Canada some of these are the Cobalt-South Lorrain, Gowganda, Elk Lake, Shiningtree (Langford, 1927), Florence Lake, Rosie Creek, Langmuir township, Otter township, Silver Islet, Port Arthur and Michipicoten Island areas, all in Ontario (Miller, 1913); the Goldfields area, Saskatchewan; the Smithers and Hazelton areas, B.C. (Kindle, 1954); the François River area, Great Slave Lake, N.W.T. (Lord, 1951); Bathurst Inlet area; and the Great Bear Lake area, N.W.T. (*see* accompanying metallogenic map).

## Geochemical Methods

### General

Silver has not been used extensively as an indicator element in geochemical surveys mainly because of difficulties in its estimation in the field. It is, however, a very valuable indicator of various types of deposits as will be shown presently, and for this reason should be employed more frequently. In addition to indicating deposits in which it is a major constituent, silver is also useful in detecting various types of gold deposits, polymetallic lead-zinc-copper deposits, and certain types of copper deposits.

In the silver-bearing copper shale deposits silver is accompanied by the following elements in variable amounts: Cu, Zn, Pb, Mo, Co, V, Se, S and others (*see* Table 39). Among these the best indicators appear to be Cu, Zn, Pb, Mo, and Co.

In the 'red bed' deposits silver is generally associated with Cu, Pb, V, U, Ni, Co, P, Cr, Mo, Re, Se, As, Sb, S, Mn, and Ba. Among these Cu, Pb, and Ba are nearly universal and provide the best indicators. Cobalt, nickel, molybdenum, arsenic, and antimony occur in many of the deposits and are useful indicators in some districts. Uranium, vanadium, phosphorus, chromium, and selenium, while present in trace amounts in most deposits, reach high concentrations only within certain metallogenetic provinces. Where uranium, vanadium, and copper are present the surface outcrops may be marked by the blue blooms of secondary malachite and azurite and the yellow, orange, and greenish blooms of the secondary uranium and vanadium minerals. Where abundant molybdenite is present the deep blue molybdenum hydrous oxide, ilsemannite, may occur as a stain. Uraniferous deposits may be detected by their higher than normal radioactivity.

Many of the 'red bed' deposits are rich in coalified plant remains often replaced by pyrite and copper sulphides. Where found these should be assayed or spectrographically analyzed for silver as well as for copper, lead, etc. Similarly thin coal seams and the bottom and top parts of thick coal seams in sandstones should be checked for silver, lead, and copper. Where substantial amounts of these elements are found it should be taken as a good indication that the processes of mineralization have been active and that the rocks of the area may contain deposits where the proper conditions of porosity, fracturing, etc., prevail.

In the various types of gold-silver deposits the characteristic elements accompanying silver are Au, Fe, Ca, Mg, S, $SiO_2$, and $CO_3$. Arsenic is a common associate of gold and silver in veins and antimony may also be present. Both elements are good indicators. Lead, zinc, and copper may be present in small amounts in certain types of deposits and may also serve as useful indicators. Tellurium and selenium are usually restricted to specific mineral belts, but where found may serve usefully in geochemical surveys. Bismuth is present in some gold-silver deposits, and mercury is characteristic of certain types of shallow veins in Tertiary flow rocks. Both these elements are probably effective indicators where the veins contain reasonable quantities of the two metals. Molybdenum is common in many types of gold-silver veins, but rarely in significant amounts to be useful as an indicator except in certain areas. Tungsten, combined as scheelite, is a frequent associated element of relatively deep-seated gold-silver veins and may also occur in the shallower veins as well. Both chromium and vanadium may be present in certain types of gold-silver deposits in the micas, fuchsite, mariposite, and roscoelite. The significance of Mo, W, Cr, and V as indicators of gold-silver veins is largely unknown.

In polymetallic deposits silver is generally accompanied by the following characteristic elements: Pb, Zn, Cd, Fe, Cu, Au, Mn, Ba, Ca, Mg, Sn, As, Sb, S, $SiO_2$, and $CO_3$. Less frequently Bi, Ni, and Co may be present in significant concentrations. Elements found at the trace level include In, Tl, Ge, Ga, Hg, Se, and Te. Of these various elements, Pb, Zn, Cu, Mn, Ba, Sn, As, and Sb are probably the best indicators of silver-bearing lead-zinc and other similar deposits. Lead and barium are particularly useful in soil analyses and stream-sediment surveys because of their low mobility and tendency to collect near the deposits. Zinc and copper may serve usefully as indicators in hydrogeochemical and biogeochemical surveys. Arsenic and antimony often reflect the presence of silver deposits by their increased amounts in soils and stream sediments. Manganese is useful as an indicator in hydrogeochemical and soil and stream-sediment surveys under certain conditions. Mercury has been used successfully as an indicator element in both soils and rocks in U.S.A., U.S.S.R., and elsewhere (Saukov, 1946; Sergeyev, 1957; Ozerova, 1959; Hawkes and Williston, 1962; Williston, 1964; James, 1962, 1964; and Friedrich and Hawkes, 1965). The mercury anomalies obtained in the soils over most near-surface silver-bearing lead-zinc and other types of deposits, including the copper shales, have a high contrast and some are broader than those given by lead, zinc, and other elements. The latter finding indicates that mercury, because of its high vapour pressure, diffuses farther through rocks and soils than the more common elements in the deposits. Deep deposits may also be indicated because of this phenomenon. Care must be taken, however, in the use of ultraviolet instruments in the determination of mercury vapour in soils and rocks, as certain organic substances interfere and tend to give high spurious anomalies.

The characteristic elemental associates of silver in the nickel-cobalt arsenide type are Ni, Co, Fe, As, S, Sb, Bi, Ca, $CO_3$, and U. The latter element is restricted to deposits in specific mineral belts. For instance it is abundant in the Great Bear native silver province, but entirely lacking at Cobalt. The deposits also contain some Ba, Cu, Zn, Cd, Pb, and frequently a little Hg, the latter mainly in the native silver and dyscrasite. Among these elements the best indicators appear to be Ni, Co, As, and probably Bi and Sb. Where uranium occurs in the deposits it may serve as an indicator element in geochemical surveys, and the veins may also be located by their high radioactivity. The usefulness of Ba, Cu, Zn, Cd, and Pb as indicators of the native silver deposits depends on the content in the veins. Mercury may be useful in soil surveys, although there is as yet no detailed information on its indicative properties.

### Lithogeochemical Methods

Relatively little work has been done using the silver or indicator element content of rocks to outline areas containing silver deposits; hence our knowledge of this aspect of geochemical prospecting is rather limited. Judging from the trace element studies done by the writer at Yellowknife (Boyle, 1961) and Keno Hill (Boyle, 1965) and in the Bathurst-Newcastle district of New Brunswick and the Walton area in Nova Scotia there are no definite elemental patterns in the country rocks that suggest the presence of silver deposits in these areas. Certain of the rocks, especially the black schists in all areas and some porphyries in the Yellowknife greenstone belt, are higher than normal in silver, but this seems to be true also of areas where no silver deposits are known. Only further research comparing the trace elemental content of rocks in mineralized belts with those in barren areas will solve the problem of whether or not there are definite geochemical silver provinces or belts in which it is more probable to find silver deposits.

The primary dispersion halo of silver and its indicator elements in rocks near deposits tends to be a restricted one in most mineral belts. In the shear zones cutting the greenstones at Yellowknife, the silver and gold contents rise significantly in the quartz-sericite schist flanking the veins and lenses, but commonly this halo extends outward from the veins for distances measured in feet, and only rarely in tens of feet. A similar situation prevails in the quartzites and phyllites in the Keno Hill area. There the rise in the silver, lead, zinc, cadmium, and copper contents can be noted only a few feet from the individual lodes or at most a few tens of feet. Analogous results were obtained in the Walton area in Nova Scotia. In the Cobalt area, however, the Cobalt sediments exhibit a general rise in silver, arsenic, cobalt, and other elements as the vein clusters are approached. In some places this rise can be seen as far as 100 feet from the veins. The dispersion of silver and other associated elements outward from the veins in Nipissing diabase, on the other hand, is narrow and seldom more than 5 feet (Boyle, 1966; Boyle, *et al.*, 1968).

Where broad zones of fracturing, alteration, impregnation, or horsetail structures with intervening altered zones prevail the dispersion pattern may be a broad one, but again the limits are likely to be sharply defined. From the writer's research it is evident that increased contents of silver (and other metals) only extend outward into the country rocks as far as the microfractures are developed. Beyond this the silver content drops to the normal value for the particular rock type.

In the literature a few of the more detailed investigations of the silver content of rocks in the vicinity of silver-bearing deposits are those by Jeffs (1955), Starke and Rentzsch (1959), and Ishikawa, *et al.* 1962). Jeffs found that the silver content of the dolomites increased consistently as the lead-zinc orebodies were approached at Pine Point, N.W.T. At Freiberg, Starke and Rentzsch observed a marked increase in the silver content in the gneiss and particularly in the mica of the gneiss as some of the silver veins were approached. Ishikawa, *et al.* also found a consistent increase in the silver content across the altered zones of the 'Kurokô' (black ores) of Japan. They remarked that silver was a useful guide in geochemical prospecting for these types of ores.

When carrying out a lithogeochemical survey using either rock samples or drill cores the following points should be kept in mind. In addition to analyzing the rock and core samples, all shear zones, fractures, contorted zones, and altered zones should, likewise, be sampled and analyzed for silver and its indicator elements. A detailed geological map showing all these features as well as any small veins, no matter what size, should be plotted and the silver values entered at the appropriate sites. Where drilling is done, sections with all of this detail should also be prepared. Only in this way is it possible to observe patterns in the primary silver dispersion in the rocks, and from these patterns to predict the locus of large deposits. It should be constantly borne in mind that most large deposits have a halo of smaller satellites developed in subsidiary or parallel fractures. Trace-element work on small shear zones, fractures, etc. increases our ability to differentiate smaller and smaller satellites. It may well be that the data when plotted will show an increase in the silver content of alteration zones in a certain direction or that the number of silver-bearing fractures, etc. increases toward a certain valley or draw beneath which lies a major shear or fault zone containing deposits. It is also advisable to contour the results since this method often brings out zones that should be trenched or drilled.

### Pedogeochemical Methods

Soil surveys should be conducted on a closely spaced grid (25- to 50-foot centres) because of the relatively narrow width of most silver and silver-bearing deposits. Silver may be the best indicator element in some districts whereas its associated elements may be more effective in others. The selection of the best indicator will depend on the type of deposit and the conditions of oxidation and soil formation. Pilot studies should be carried out if possible before conducting extensive surveys. In the Western Cordillera of Canada the best indicators of silver deposits appear to be Ag, Pb, Zn, Cu, As, and Sb. In the Canadian Shield Ag, Ni, Co, and As are effective for the Ni-Co arsenide type of veins and Pb, Zn, Cu, Sb, and As for the gold-silver and other types of silver-bearing deposits. In eastern Canada the silver-bearing deposits are indicated by Ag, Pb, Zn, Cu and Ba. Other rarer elements such as Hg, Bi, Cd, W, and U may be suitable indicators in some areas, but pilot studies are strongly recommended before surveys using these elements are begun.

Selecting the horizon or horizons from which to obtain the soil samples usually requires some knowledge of the soils and their parent materials in the particular area in which the survey is to be carried out. Here again pilot studies should indicate the best horizons to sample and in addition give information on the normal backgrounds of the various metals in the different horizons. Generally the B horizon is the best, although the A horizon may be effective in some areas. The latter horizon often exhibits an enrichment in silver and the anomalies may have greater contrast than those in other horizons (Boyle, *et al.*, 1968). In some areas only the C horizon close to bedrock gives satisfactory results. In the Keno Hill area, Yukon, the B horizon gives good results where the soils are thin and of a residual nature. The C horizon near bedrock is the most effective, however, but because of permafrost a specially designed pneumatic overburden drill is necessary to obtain samples. (*See* paper by Mine Exploration Staff, United Keno Hill Mines Ltd., 1965.)

Deciding what are anomalous silver values in soils, till, etc. will depend on the area and should be determined by preliminary surveys. The normal silver content of soils ranges from 0.1 to 0.5 ppm. The writer has found that values above 0.7 ppm are generally anomalous and should prompt the prospector to investigate the cause.

A few geochemical prospecting investigations have been described in the literature dealing specifically with the detection of silver deposits.

Koehler, Hostetler, and Holland (1954) describe a geochemical survey at Cobalt, Ontario, using cobalt as an indicator element in glacial materials overlying the silver veins. A cobalt anomaly in the overburden was located, and subsequent drilling proved mineralization in non-commercial quantities in the bedrock. The authors recommend their technique for locating mineralization in geologic settings similar to those at Cobalt.

The recently described method for determining ammonium citrate-soluble cobalt in soils and sediments (Canney and Nowlan, 1964) could probably be used in areas containing Ni-Co-As-Ag deposits, at least on a reconnaissance basis.

Boyle (1965) used Ag and Pb, Zn, Cu, As, Sb, and Mn as indicator elements in locating the lead-zinc silver veins in the Keno Hill area, Yukon. The results of the pedogeochemical survey indicate that zinc is widely dispersed by groundwater, and is, therefore, not suitable as an indicator element using soil analyses. Copper, likewise, due to its erratic dispersion and its general low abundance in the deposits, is not a suitable indicator in the soils. Lead, silver, arsenic, and antimony on the other hand have a relatively limited dispersion and are enriched in soils near the vein deposits, making them excellent indicators. Manganese is less definitive.

The results of analyses of partly residual soil along traverses across known mineralized vein faults indicate that the silver, lead, arsenic, and antimony contents of the soil rise several times above background and give a strongly contrasting anomaly over the veins in some cases and slightly downhill in others. Analyses of near-surface glacial materials, muck, and peat along traverses across known vein faults were generally ineffective for locating vein faults or lodes. Samples of the glacial material taken close to bedrock, however, gave good anomalies with strong contrast over some vein faults and lodes.

Arsenic is a particularly good indicator in soils for detecting quartz-pyrite-arsenopyrite-gold-silver veins in the Keno Hill area. Over these veins marked arsenic anomalies with a high contrast were obtained on Keno Hill and in the adjacent Dublin Gulch area.

In the Keno Hill area the normal background for silver in the residual soils is

~ 0.5 ppm and in the glacial materials ~ 0.3 ppm. Near the lead-zinc-silver veins the values range up to 20 ppm Ag.

Oja (1964) described encouraging results using zinc and silver as indicators in the humus and soil overlying the 'black slate' silver belt in the Thunder Bay district of Ontario. Both the humus and soil samples reflected known mineralization unerringly where the geochemical methods were tried. Compared with the soils, the humus was more sensitive to metal variations, twice as many anomalies being detected in the humus as in the corresponding underlying soils. Oja recommended the sampling of humus for reconnaissance work because of the ease of collecting samples and because of its high heavy metal content. Soil sampling is, however, desirable for more accurate pinpointing of mineralization. The results of analyses taken down through sections of the soil and glacial materials indicate a general enrichment in the near-surface parts of the sections as compared with the lower sections. The zinc values ranged from 400 to 700 ppm at the surface of most sections to 130 to 240 ppm at depths of 25 feet or greater. The silver contents obtained spectrographically ranged from 2.5 to 5 ppm at the surface to 0.5 ppm at depths of 25 feet or more. In general the silver contents of the soil and glacial materials in the centres of the anomalies averaged from 2 to 5 ppm, but scattered values ranging up to 50 ppm Ag were found.

Stream sediment sampling conducted by Oja in the same silver belt around Beaver and Rabbit Mountains indicated that silver mineralization can be located by this method as well.

Little and Croonenberghs (Anon., Engineering and Mining Journal, 1965) used a simple field kit for total heavy metals in soils to define a rich silver vein in the Brooklyn mine area, near Butte, Montana.

Soil methods using lead and zinc as indicators were also effective in the discovery of the Tynagh lead-zinc-copper-silver deposit in Eire (Derry, *et al.*, 1965).

Recent research by the Geological Survey of Canada in the Cobalt area of Ontario using soils, till, and clay to locate the native silver veins is described by Boyle (1966) and Boyle, *et al.* (1968). The results indicate:

1. Analyses of glacial clay and soils developed on them are generally not effective in locating Ag-Ni-Co-As veins or vein clusters. There is good evidence, however, that overburden drilling may be effective if the tills underlying the glacial clay or sand can be sampled.

2. Till analyses are effective in locating veins and vein clusters even where the till is relatively deep (up to 40 feet in one place). The results and contrast in the anomalies are best where the till is relatively shallow, a feature which suggests that the closer the sample is taken to the bedrock the better is the result. The A horizon appears to be the best accumulator of metals and often gives anomalies with high contrast over, or slightly downhill from, known veins or vein clusters. The best indicator elements are Ag, As, Sb, and Mn. Nickel and cobalt are also effective in some places. Mercury tends to be low in most places, but over one vein cluster the content was relatively high (2 ppm). Anomalies in silver in the A horizon may exceed 20 ppm in places, those for arsenic 100 ppm, and those for antimony 7 ppm. In the B horizon the anomalies are lower by an order of magnitude or more. The dispersion

of the metals in tills broadens as the depth of till over the vein clusters increases, and in many places there is a general broad anomaly with numerous high peaks.

3. Radiometric surveys using a sensitive scintillometer are not effective in locating veins using soil, till, glacial clay, glacial sand, or rock. None of the traverses run over veins either at the surface or underground indicated the position of the veins.

There are a number of other references to the use of silver and its indicator elements in soils for detecting deposits. These can be consulted in Geochemical Prospecting Abstracts (Harbaugh, 1953; Erikson, 1957; Markward, 1961).

## Hydrogeochemical Methods

The normal content of silver in natural waters is very low (of the order of 0.001 ppm or less), and hence the element does not lend itself to any simple field method of detection. Even in silver-bearing areas the silver content of spring and stream waters is low, rarely exceeding 0.10 ppm Ag (*see* Table 29). It appears doubtful, therefore, if hydrogeochemical surveys using silver as indicator would be effective using any known field method of estimation of the element in natural waters.

Spectrographic analyses of the evaporated residues of natural spring, stream, and lake waters for silver may be useful in certain areas to delimit the stream systems receiving soluble silver from deposits. In the writer's experience, however, the method is tedious and subject to numerous errors. Extraction of silver from natural waters by resins or organic solvents offers another possibility, although here again there are numerous analytical difficulties, particularly if the waters contain much suspended sediment and humic colloidal material. These methods, the evaporation technique and extraction by resins or organic solvents, require much more research before they can be utilized as practical geochemical field survey methods.

Atomic absorption spectroscopy offers a rapid method for the estimation of silver in natural waters. Using a solvent extraction method the silver contents of the stream, spring, well, and underground waters at Cobalt, Ontario were determined down to 0.0005 ppm (Boyle, *et al.*, 1968).

Zinc and copper appear to be the most effective indicators of silver deposits in drainage systems. Zinc was used effectively by Boyle, *et al.* (1955, 1956) and Gleeson, *et al.* (1965) in the spring and stream waters of the Keno Hill area, Yukon, for detecting the presence of mineralized zones. Most of the known silver deposits were indicated in the spring and stream waters, and numerous anomalies in virgin territory were outlined. The detection limit of zinc by the dithizone method in natural waters is about 0.001 ppm Zn, sufficient for any normal geochemical work.

Water analyses, using zinc as indicator, were also effective in outlining the favourable silver-bearing mineralized zones at the Horton-Windsor contact in the Walton area, Nova Scotia (Boyle, *et al.* 1958).

There is a suggestion from limited work done by the writer in the Keno Hill area, Yukon, and Walton area, Nova Scotia, that the manganese content of spring and stream waters may be useful in outlining drainage systems containing silver-bearing deposits with a siderite gangue. In these two areas the waters are considerably enriched in manganese compared with waters from areas where no siderite deposits are known. The manganese contents of the spring waters in the Keno Hill area range between 5 and 25 ppm; those in the Walton area between 0.03 and 5.6 ppm. In both areas there is much black manganese oxide stain on the rocks in the streams, particularly in the Walton area where small bog manganese deposits are forming in places. Further research on the manganese contents of water and their relationship to silver deposits with a siderite gangue would seem to be desirable.

Analyses of stream sediments using copper, lead, zinc, arsenic, antimony, and silver as indicators are probably generally effective in most mineralized belts for locating silver-bearing mineralized zones. An extensive survey carried out by the writer in the Walton area, and not yet published, indicates that all of these elements as well as barium and manganese yield significant anomalies with a high contrast in structurally favourable areas near the Horton-Windsor contact. The silver content of stream sediments associated with known mineralized zones ranges between 0.5 and 2.0 ppm, while in anomalous virgin areas it ranges between 0.5 and 1.8 ppm. The normal background for silver in the stream sediments is about 0.1 ppm.

A recent geochemical survey carried out by Gleeson, *et al.* (1965) in the Keno Hill silver belt, Yukon, showed that the zinc, lead, and copper content of the stream sediments is particularly useful in outlining mineralized areas. Locally the stream sediments are enriched in silver (up to 10 ppm Ag or more), and anomalous trains up to 2 miles in length occur in some streams (Gleeson, *et al.* 1966).

The literature is replete with examples of stream sediment surveys done to locate lead-zinc and copper deposits (Hawkes, 1957; Ginzburg, 1960; Hawkes and Webb, 1962; Harbaugh, 1953; Erikson, 1957; and Markward, 1961). Frequently these surveys have been effective in localizing mineral belts or mineralized zones. Lead, zinc, and copper have been the metals generally used as indicators. Extension of the analytical work to include silver, as well as arsenic and antimony, would in most cases enhance such surveys and increase the chances of locating silver and gold deposits. For instance, Polikarpochkin, *et al.* (1960) noted the fact that silver is a particularly good indicator element, and that the element only appears in sizable amounts ($\sim 1$ ppm) in the stream sediment dispersion trains associated with polymetallic deposits. Furthermore, they found that the highest contents of silver usually occur in the heads of the dispersion trains, indicating a deposit in the immediate vicinity.

While conducting hydrogeochemical surveys or stream sediment surveys the geochemist should be constantly on the alert for precipitates of all kinds at the orifices of springs, on stream bottoms, or on the stones and rocks in the streams. These precipitates should be carefully studied and samples taken for analysis. Limonite- or wad-cemented conglomerates, composed of stones, sand, rock chips, and vegetable remains cemented by limonite or wad should receive detailed attention. Where found they should be carefully mapped and sampled and their location analyzed with respect to springs and the groundwater systems of the area. In many places these bodies occur near springs issuing from faults that either contain silver-bearing deposits or intersect such deposits along their course.

Frequently manganese and iron oxides, particularly the former, coating stream sediments cause relatively high anomalies due to adsorption and/or coprecipitation of the metals from stream and lake waters. In areas where some streams are manganiferous and others not, this may be a disadvantage since the manganiferous streams tend to concentrate the metals from a normal background, giving false anomalies. On the other hand in areas that are uniformly manganiferous the concentrating action may be advantageous, and one can make good use of manganiferous and ferriferous sediments. In this respect it is desirable, therefore, when carrying out stream sediment surveys to take note of the quantity of manganese and iron oxides present and devise a qualitative index for each stream or part of a stream surveyed. If spectrographic analyses are done on the stream sediments both iron and manganese should be determined semi-quantitatively and plotted. Comparison of the heavy metal maps with those of manganese and iron will reveal the effects of these two elements on concentrating the metals.

In silver-bearing areas manganese oxides (wad) coating rocks, etc., tend to collect silver. Iron oxides may do likewise if there is some arsenic or antimony in the environment. Analyses of these oxide coatings may, therefore, indicate the presence of silver mineralization in an area. The same can be said for humic precipitates in some areas and for aluminous and siliceous precipitates in others.

## Biogeochemical Methods

Biogeochemical surveys utilizing the silver content of herbs, trees, etc., do not seem to have been used extensively as yet for the location of silver deposits. Probably the reason is that the methods are tedious, and the silver contents are too low for normal analytical or spectrographic techniques. Another reason is that lead, zinc, and copper are probably better indicators and are more readily determined analytically. Nevertheless, some research using silver as an indicator in plants and trees seems desirable for those deposits containing native silver and abundant silver sulphides. Nickel, cobalt, and arsenic may also be useful indicators in vegetation growing in the vicinity of the Ni-Co-As type of native silver deposits. Uranium, likewise, if present in the Ni-Co-As-Ag deposits could probably be utilized as an indicator in biogeochemical surveys.

Webb and Millman (1950-1951) noted that silver gives small erratic increases over the background concentration of a variety of savannah trees in proximity to mineralization in the Nigerian lead-zinc belt. The element was also useful as a 'pathfinder' element when used in conjunction with Pb and Zn. Millman (1957) found increased concentrations of silver in both soils and trees over the suboutcrops of tin-copper lodes in Cornwall and Devon, England. Harbaugh (1950), however, noted no apparent correlation of the silver content of blackjack oak and underlying zones mineralized with galena and sphalerite in the Wentworth area, Lawrence county, Missouri (Tri-State mining district). Salmi (1956) considered silver to be a good indicator in bog plants and peat for zinc-lead deposits in the Vihanti ore field of Western Finland. The arsenic content of Douglas fir needles and tips appears to be a useful indicator of certain arseniferous gold and silver deposits, judging from the recent data given by Warren, *et al.* (1964). These and other investigations of the silver and other indicator element content of vegetation, and their relationship to mineral deposits are discussed in more detail in the section on biogeochemistry. The methods and procedures employed in biogeochemical prospecting are discussed at length by Viktorov (1955), Cannon (1960), and Malyuga (1964).

Silver is a fairly uniform micro-constituent of many types of plants and trees, but there appear to be few indicator plants for the element. Lidgey (1897) and Dorn (1937) mentioned that *Eriogonum ovalifolium* (buckwheat family) is a silver indicator, which has led to the discovery of several silver deposits in Montana. Sykora (1959) made brief reference to a number of plant indicators for gold and silver, and Carlisle and Cleveland (1958) gave a list of sampler plants for silver and other elements. There are also some very interesting references to indicator plants for silver in old Chinese writings (Needham, 1959). For instance, it is stated that the *Tshung* plant (the ciboule onion, *Allium fistulosum*) is an indicator of silver. There are no references in the literature to chlorotic effects, if any, induced in plants by soils enriched in silver.

Silver tends to be enriched in the humus layers of the soil (Boyle, *et al.*, 1968), a feature noted by Goldschmidt many years ago. In his detailed study of the soils of the Bathurst area, New Brunswick, Presant (1963) observed a general enrichment in the humic horizons especially over the massive sulphide deposits. Oja (1964) also observed an enrichment of silver in some of the humus horizons he sampled in the 'black slate' silver belt in the Thunder Bay district of Ontario. He reasoned:

> Because humus represents decayed vegetable matter, a single humus sample represents the heavy metal content of pre-existing vegetation growing in the area surrounding the sample site. Through the ability of vegetation to collect and concentrate heavy metals from the entire area probed by the entire root system, a single humus sample, therefore, represents an integrated heavy-metal content representing an area possibly fifty feet in diameter and a depth equal to that to which the plant roots may penetrate.

## Other Methods

A number of other methods may be useful in locating silver deposits. These include panning, radioactive surveys, and lead-isotope variations.

Silver is associated in many deposits with galena, which oxidizes slowly to anglesite and cerussite. Often these two minerals form only crusts on the galena preventing further oxidation. These partly oxidized nodules of galena collect in the soil, eluvium, and in places in the stream beds. The panning of such stream beds, eluvium, or soil may indicate the presence of silver deposits, which can be traced by following the small particles of galena to their source. In some areas the oxidized galena may occur in relatively large masses, enabling one readily to follow the train of float in the soil, rock talus, etc. In other areas the galena may be finely comminuted, requiring microscopic and spectrographic examination of the pannings. Often a simple map indicating the location of each piece of float, the grain count of comminuted galena, or the spectrographic analysis of the soil pannings for lead and silver will reveal the float train and help in locating the source. By the same token a stream map of the area with similar data plotted on it may indicate the locale from whence the galena and silver came.

Chlorargyrite, a mineral with a moderate specific gravity (5.5), is relatively resistant to chemical attack and may collect in soil and eluvium and locally may accumulate in stream bottoms or washes. In some districts native silver may do likewise, although such occurrences are rare. There is hardly any need to point out that native gold in soil, eluvium, and stream gravels may indicate the presence of gold-silver lode deposits in the drainage basins.

According to Gregor'ev and Dolomanova (1951) traces of silver are restricted to those cassiterites that are derived from sulphide deposits. If silver-bearing cassiterites are found among the heavy minerals of stream systems this feature may indicate the presence of sulphide bodies within the drainage basin.

Gossans of all types should be panned carefully for silver and gold. Particular care should be paid to the oxidation products of indigenous gossans, and a search should be made for chlorargyrite, native silver, and argentojarosite or argentian plumbojarosite. Assays and spectrographic analyses are useful in determining the presence of silver and should be done on a routine basis on all gossans. In some indigenous gossans silver and other metals may be nearly completely removed leaving them barren except for traces of silver and other metals. In such cases deep trenching or diamond drilling may reveal the presence of economic silver minerals at depth. Gossans resulting from the transportation of iron and other elements should be analyzed by spectrograph or other geochemical methods for silver, zinc, copper, lead, and other metals. Often such transported (or pseudo) gossans are the result of the oxidation of pyrite in slates, carbonates in sediments, etc. and are not related to metal deposits. In other cases they show a direct relationship to metal deposits, yet they may not be significantly enriched in the metals present in the primary ores. The reason for this behaviour is not clear but seems to be related to the colloidal behaviour of iron hydroxide and the recrystallization processes that go on to make limonite and goethite. During such processes any adsorbed metal seems to be leached out in a number of transported gossans the writer has investigated. It is, therefore, not possible with our present knowledge to tell which transported gossans are related to metal deposits and which are not. Until further research elucidates this problem the cardinal rule with respect to gossans of all types is that they should not be left until all geological and chemical possibilities as regards their origin and possible relationship to metal deposits have been exhausted.

Analyses for silver and other common associated elements in sulphide, vein quartz, and gossan boulders in glacial trains may be a useful approach in glaciated regions of Canada. Such methods have been used successfully in Finland (Okko and Peltola, 1958). Similar studies have been carried out by Lee (1963) using vein quartz fragments, chloritic fragments, and heavy minerals including gold in the glacial materials in the vicinity of the Kirkland Lake gold-silver deposits. The method involves a close study of the glacial features followed by the plotting of the location of the boulders and analyses on geological maps in order to discover the apex of the fan or train that marks the outcrop sites.

Certain native silver Ni-Co arsenide veins and a few silver-bearing sandstone deposits contain uranium. These can often be detected by geiger or scintillometer surveys or by using uranium as an indicator element in rock, soil, stream sediment, or water surveys.

Most salt beds contain only infinitesimal quantities of silver. Despite this generalization there is some evidence to suggest that silver may become enriched in halite (common salt) if the element is available when the halite is precipitated. In this respect it is worth analyzing salt beds if there is any indication of silver or its deposits in the sequence of rocks in which the saline deposits occur. If the salt contains any quantity of silver its presence should be immediately apparent by dissolving the salt in distilled water and noting whether any white curdy precipitate ($AgCl$) forms.

As noted in a previous section the distribution of the silver isotopes in all types of deposits appears to be rather uniform, and there does not seem to be any way of using silver isotope data in prospecting at the present time. Lead isotopic data may, however, be useful in some areas in the search for lead-silver deposits. For instance certain large silver-bearing deposits such as the Sullivan and Broken Hill are characterized by relatively uniform lead isotopic ratios indicating Precambrian (or somewhat younger) ages, whereas satellitic deposits in the general area have variable isotopic ratios that are usually anomalous. The reasons for these differences are unresolved at our present state of knowledge, but they may be due to different modes of concentration and precipitation of the lead minerals. Whatever the causes, if anomalous lead ratios are found in veins in an area, consideration should be given to the possibility of the occurrence of large massive deposits with uniform ratios in the same mineralized belt. The reverse relationship may also be true in places. Admittedly these considerations are highly speculative, but they are worthy of some thought.

The possibility of applying neutron activation analysis of rock or soil *in situ* for the exploration of silver deposits is outlined by Hoyte, Martinez, and Senftle (1967). They describe two types of mobile units suitable for silver exploration. Laboratory and preliminary field tests both indicate that a sensitivity of less than 1 ounce of silver per ton of ore can be achieved with the field units.

## Analytical Methods for Estimating Silver

Silver can be determined in geological materials by a variety of methods, including optical spectrography, atomic absorption spectrography, assay, colorimetric analyses, spot tests, and a number of inorganic analytical methods.

Probably the most rapid and satisfactory way of estimating the silver content of geological materials is by optical spectrograph. The element has a high sensitivity in the arc ($\sim$ 0.5 ppm) using normal routine methods. This sensitivity can be increased with special buffers and techniques to 0.1 ppm or less. In most cases routine spectrographic methods are satisfactory for screening anomalies in geochemical surveys using soils, stream sediments, and rocks. The methods for increased sensitivity are, however, desirable in all types of surveys especially those using biological materials and evaporated residues of spring and stream waters. The spectrograms provide a permanent record of the survey and can be used to determine lead, copper, and other metallic elements with which silver is often associated.

Spectrochemical methods for the determination of silver in geological and biological materials are described and discussed at length by Ahrens and Taylor (1961) and Mitchell (1964).

For natural waters atomic absorption spectroscopy appears to offer a rapid method of detection of silver (Belcher, Dagnall, and West, 1964). The element can be determined without interference from any known ion in the range 0.1 down to 0.01 ppm in aqueous solution following an extraction of the silver as its di-n-butyl-ammonium salicylate into methyl isobutyl ketone. Lai and Weiss (1962) described a method of silver analysis in sea water by cocrystallization of ultramicro quantities of the element with thionalid. Schutz and Turekian (1965) gave the procedures for the determination of silver in sea water by neutron activation analysis.

Silver is readily determined by assay methods, and these are used extensively in the development and production of silver orebodies. With careful control of the fluxes and accurate determination of the silver content of lead oxide (the blank), assay methods can be adapted to the estimation of silver in rocks, gossans, soils, and stream sediments. The sensitivity attainable is about 0.2 ppm Ag. While the assay method is rather laborious it can be used in detailed geochemical prospecting and is recommended where prospecting for silver deposits is carried out in established mining camps.

The most suitable organic reagent for the determination of silver in geological materials is *p*-diethyl—or *p*-dimethylaminobenzylidenerhodanine (rhodanine) which gives a slightly soluble red-violet silver salt precipitate when a slightly acidified silver solution is treated with a solution of the reagent in acetone or other suitable solvent. The reagent is, however, not specific for silver, but in addition reacts with mercury, gold, platinum, palladium, and cuprous salts. Under suitable conditions, however, that can be readily obtained, silver can be estimated in most samples containing these interfering elements. The methods, using rhodanine as a reagent for silver in geological materials, are detailed by Sandell (1959).

Silver also reacts with diphenylthiocarbazone (dithizone) and cupric dithizonate in acid solution yielding the familiar yellow silver keto dithizonate. When shaken with chloroform or carbon tetrachloride the keto dithizonate dissolves giving a yellow solution. Comparison of the hue of this solution with standards permits the determination of silver to be made down to about 1 ppm. The methods are detailed by Sandell (1959) and Bloom (1966).

A spectrophotometric method for the determination of traces of silver using pyrogallol red is described by Dagnall and West (1961). The reagent forms a yellow silver complex, which is stable for at least 24 hours. It is claimed that the method is more reproducible than the standard dithizone method.

Nakagawa and Lakin (1965) described a new field method for the determination of silver in soils and rocks. Briefly, the sample is digested with nitric acid, and the silver is extracted with triisooctyl thiophosphate (TOTP) in benzene and stripped from the organic phase with dilute hydrochloric acid. Silver is then measured indirectly by its catalytic action in the persulphate oxidation of manganous ion to permanganate. The lower limit of sensitivity of the method is said to be 0.01 ppm. The accuracy is equivalent to that of assay methods. About 80 determinations per man day can be made on soils, rocks, and other geological materials.

Lakin, *et al.* (1952) and Almond, *et al.* (1953) have described a method using the chromograph and rhodanine as reagent. The silver is separated from the coloured ions in nitric acid solution by collecting the silver salt of the rhodanine complex at the interface of an amyl alcohol aqueous extract. The silver rhodanine precipitate, in a dispersed state, is filtered through the chromograph to form a confined spot, the intensity of which is a measure of the silver content of the sample.

The chromograph method is suitable for detailed geochemical prospecting, but requires a considerable amount of equipment and skill. It is subject to many factors, and in the writer's experience the reproducibility is not too good. With careful controls and practice in the method fair results can be obtained, however, on soils and stream sediments.

Several other methods for the accurate determination of silver in geological materials are described by Sandell (1959), Furman (1950), and Belcher, Wilson, and West (1964). Most of these are best carried out in a well equipped laboratory, but some can be adapted to geochemical prospecting where a good central field laboratory is employed. Feigl (1958) gives several spot tests for silver, which can be carried out with a minimum of equipment and reagents. Sen and West (1955) review the literature on spot tests for silver and describe a very simple, specific, and highly sensitive test that suffers from few interfering ions. The method uses test papers dipped in a suspension of nickel dimethylglyoximate in potassium cyanide solution. When a drop of neutral solution containing silver is applied to the paper a red fleck of nickel dimethylglyoximate is developed.

Silver in the native state, in natural alloys, and in sulphides, tellurides, selenides, antimonides, arsenides, and sulphosalts can be detected by the familiar chloride test. To make this test place a small amount of the powdered mineral in a test tube or small beaker and add a few millilitres of concentrated nitric acid. Heat to boiling and boil for a few minutes or until the mineral is dissolved. Cool, add a few millilitres of metal-free water, filter, and add a drop or two of hydrochloric acid or a few drops of concentrated sodium chloride solution to the filtrate. The formation of a white curdy precipitate indicates the presence of silver as well as lead and mercury.

To differentiate these metals proceed as follows: expose the solution containing the precipitate to sunlight or any strong light for an hour or so, stirring occasionally. If the precipitate turns a purplish grey, silver chloride is present. Lead chloride is soluble in hot water. Upon heating, therefore, if the white precipitate remains the presence of silver and/or mercury is indicated. Silver chloride is soluble in concentrated $NH_4OH$. If the precipitate dissolves on the addition of $NH_4OH$ in excess the presence of silver chloride is indicated.

The silver halides are practically insoluble in hydrochloric acid, but are readily soluble in solutions of $NH_4OH$, KCN, or $Na_2S_2O_3$, a feature which provides a distinctive test for these minerals. Argentojarosite and argentian plumbojarosite are slowly soluble in nitric acid, and hence silver in these minerals can be determined by the halide test.

*Chapter VI*

# PRODUCTION AND USES OF SILVER

## Production and Consumption

Approximately 90 per cent of the annual world production of silver is obtained as a by-product of lead-zinc, copper, and gold mining. The remaining 10 per cent comes from deposits that are exploited essentially for silver.

The total world production of silver in 1964 was about 250 million ounces. The average annual production during the period 1960–64 was about 245 million ounces. The main producing countries are as follows:

| *Country* | *Annual Production in millions of ounces*[1] (Average 1960–64) |
|---|---|
| Mexico | 42 |
| U.S.A. | 35 |
| Peru | 35 |
| Canada | 31 |
| U.S.S.R. | 26 |
| Australia | 16 |
| Europe (mainly Sweden, Yugoslavia, and Germany) | 15 |
| Asia (mainly Japan) | 14 |
| Bolivia and other South and Central American Countries | 12 |
| Africa (mainly Congo and South Africa) | 10 |
| Others | 9 |
| Total | 245 |

The world silver consumption for 1963 as given by Dunfield (1964)[2] was as follows:

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[1] Data mainly from Patterson (1963), Dunfield (1964), Wemple (1964), Kiilsgaard (1964), Ryan (1965), and numerous other statistical sources. The production of U.S.S.R. is estimated. It may be low.

[2] Excluding U.S.S.R., Poland, East Germany, Czechoslovakia, etc. for which no data are available.

| *Industrial Uses* | *Millions of ounces* |
|---|---|
| United States | 110.0 |
| Canada | 4.4 |
| Mexico | 3.2 |
| United Kingdom | 20.0 |
| France | 13.9 |
| West Germany | 40.5 |
| Japan | 20.0 |
| Other countries | 35.0 |
| Total | 247.0 |
| *Coinage* | |
| United States | 111.3 |
| Canada | 13.4 |
| France | 12.0 |
| Italy | .5 |
| Japan | 5.0 |
| Other countries | 30.0 |
| Total | 172.2 |
| Total world consumption | 419.2 |

The Canadian silver industry is discussed in detail by Patterson (1963) and George (1965).

## Uses

The principal uses of silver centre on its high electrical and thermal conductivity, high corrosion resistance, intrinsic metallic lustre, and the photosensitivity of its halides. Other uses are based on the alloying properties of the element and on the pharmaceutical and germicidal properties of some of its compounds.

About 40 per cent of the annual world consumption of silver goes into the minting of coins. Use of the metal for silverware, ornaments, and jewellery consumes about 30 per cent, and the photographic industry uses another 15 per cent in the form of halides, particularly the bromide. The remaining 15 per cent is used for a variety of purposes. These include electrical conductors and contact points, printed electrical circuits, silver brazing alloys, certain bearing alloys, as a backing for mirrors, and dental alloys. The metal and its compounds are also used as an industrial catalyst, in various pharmaceutical preparations, and as a germicide.

The supply of new silver reaching the market is a little more than half the consumption of the element as shown by the tables above. This situation seems likely to continue for some time since the rate of discovery of new silver deposits is about equal to the depletion of old deposits. An increase in by-product silver from such large deposits as those at Bathurst, N.B., and Timmins, Ontario, may increase the silver supply slightly but a number of the great silver producers such as the Sullivan mine are gradually declining. The uses of silver are increasing annually, particularly in the electronics and photographic industry and in the manufacture of specialized types of seizure resistant bearings for jet and rocket engines and diesel locomotives.

Furthermore, this increase seems likely to continue for many years to come as the new developments in photochromic glasses, bearing sleeves, cold solders, and silver-zinc tape batteries reach the consumer. Silver should, therefore, enjoy an increasing demand in the market place. A dampening influence might occur, however, if governments restricted the use of silver in coinage.[1]

The price of silver per troy ounce in 1964 was 129.3¢ U.S. for New York delivery.

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[1] Recently (1965) the United States Congress approved the desilverization of U.S. quarters, half dollars, and dimes. This became fully effective by the middle of 1966.

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