



GEOLOGICAL
SURVEY
OF
CANADA

DEPARTMENT OF ENERGY,
MINES AND RESOURCES

PAPER 68-58

ELEMENTAL ASSOCIATIONS IN MINERAL
DEPOSITS AND INDICATOR ELEMENTS OF
INTEREST IN GEOCHEMICAL PROSPECTING

R. W. Boyle

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Price \$1.50

Catalogue No. M44-68-58

Price subject to change without notice

ROGER DUHAMEL, F.R.S.C.

Queen's Printer and Controller of Stationery
Ottawa, Canada

1969

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ABSTRACT

This report contains numerous data on the elemental associations in all types of mineral deposits and discusses the use of various indicator elements in geochemical prospecting.

"Success
in prospecting
lies in the sure knowledge
of what to look for and where to look for it."

A. E. Fersman

PERIODIC TABLE

ATOMIC WEIGHTS BASED ON C¹² (1961)

IA		PERIODIC TABLE																O			
H		ATOMIC WEIGHTS BASED ON C ¹² (1961)																He			
1.008																		4.003			
3	Li	4	Be															5	B		
6.939		9.012																10	Ne		
11	Na	12	Mg															13	Al		
22.990		24.31																16	S		
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni		
39.102		40.08		44.96		47.90		50.94		52.00		54.94		55.85		58.93		58.71			
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd		
85.47		87.62		88.91		91.22		92.91		95.94		(99)		101.1		102.91		106.4			
55	Cs	56	Ba	57	La	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt		
132.91		137.34		138.91		178.49		180.95		183.85		186.2		190.2		192.2		195.09			
87	Fr	88	Ra	89	Ac															100	Th
(223)		(226)		(227)																101	Pa
		IIA																			
		3	Li	4	Be																
		6.939		9.012																	
		11	Na	12	Mg																
		22.990		24.31																	
		19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co		
		39.102		40.08		44.96		47.90		50.94		52.00		54.94		55.85		58.93			
		37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh		
		85.47		87.62		88.91		91.22		92.91		95.94		(99)		101.1		102.91			
		55	Cs	56	Ba	57	La	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir		
		132.91		137.34		138.91		178.49		180.95		183.85		186.2		190.2		192.2			
		87	Fr	88	Ra	89	Ac													100	Th
		(223)		(226)		(227)														101	Pa
				IIIA		IVB		VB		VIB		VIIB		VIII		IB		IIB			
												</									

ELEMENTAL ASSOCIATIONS IN MINERAL DEPOSITS AND INDICATOR ELEMENTS OF INTEREST IN GEOCHEMICAL PROSPECTING

INTRODUCTION

The data on elemental associations in mineral deposits and the discussion of the use of these elements in geochemical prospecting contained in this paper are based on the writer's experience over several years during which many types of geochemical surveys have been carried out and considerable research on elemental associations has been conducted. The data will form part of a forthcoming treatise on geochemistry. Because of its importance in prospecting it was deemed appropriate to publish this preliminary general outline which contains all of the facts without any attempt to explain the various elemental relationships, many of which we do not yet understand. The reader will confer a favour by pointing out any discrepancies in the various statements made and by providing further data not contained in this summary.

ELEMENTAL ASSOCIATIONS AND INDICATORS

Concentrations of a single element rarely occur in the earth. More generally a suite of elements is concentrated in a particular deposit because of certain intrinsic chemical properties which depend essentially on their electronic constitution and hence their position in the periodic table. More specifically the migration and concentration of elements are controlled by the Eh-pH conditions, complex phenomena, hydrolytic reactions, colloidal phenomena, biological reactions, adsorption and base exchange reactions, diffusion, solubility in molten silicates, and various other parameters. In addition to these purely chemical features there are others of a mechanical nature which concentrate the resistate minerals during weathering and the formation of placers. Because of all of these interacting processes it is not generally possible to predict a priori what elements will be concentrated together. Fortunately most elemental associations and indicators are known from purely empirical data which have been gathered during the long history of geochemistry. Elements with the most diverse chemical properties are frequently concentrated together; why we do not yet know. In geochemical prospecting, therefore, the empirical data are of fundamental importance as these can be used in a practical way to predict the probable occurrence of elements that

G.S.C. projects 570022, 650438, 670055

Ms. received 24 September, 1968

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may be unsuspected in deposits. By the same token certain elements may serve as indicators of others that are too low in abundance to determine accurately by analysis in various types of geochemical surveys. Thus arsenic in rocks, soils, and vegetation may indicate the presence of gold deposits, and nickel may be indicative of platinum metals in certain terranes.

In the summary that follows the various elemental associates are discussed in some detail, but the data are not comprehensive and do not take into account all of the known elemental associations in nature. They are deemed sufficient, however, for most types of geochemical prospecting.

GROUP IA: HYDROGEN, LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, AND CESIUM

Hydrogen is one of the commonest elements in the earth being bound mainly in water in the hydrosphere and biosphere, in water and hydroxyl groups in rocks, and in the various hydrocarbon substances. Small amounts of hydrogen also occur in the free state in various rocks, in fumaroles and volcanoes, and in natural gases. Commercially hydrogen is obtained by a variety of processes from water, water gas, and the hydrocarbons.

Lithium exhibits its greatest concentrations in pegmatites and certain coarse-grained granites in which it is present as spodumene, lepidolite, petalite, eucryptite, lithiophilite, and amblygonite; also in certain greisen zones and dykes in which it occurs mainly in lepidolite and zinnwaldite. The greisens are frequently associated with tin, tungsten, and molybdenum veins in granitic rocks and gneisses. The element also occurs in commercial quantities in certain brines and other natural waters. It may also occur in certain saline evaporites in considerable quantities, and is also concentrated in wad and other manganese oxides and in some clays and shales. In clays it is usually present as a lithium clay mineral (hectorite).

In pegmatites and coarse-grained granites lithium may be accompanied, in addition to the more common elements such as Na, K, Al, and Si, by Rb, Cs, Be, Sc, rare earths, Y, Nb, Ta, B, Sn, W, Ga, Tl, Mn, P, F, and more rarely by U, Th, Bi, and Mo¹. The most common associates and the best indicators are Rb, Cs, Be, Nb, Ta, B, P, F, and Sn. In greisens the most distinctive associated elements are Rb, Cs, Be, W, Sn, Mo, Bi, Ti, Ga, B, and F.

¹In these and other lists of elemental associates the common gangue elements such as Si, Al, Fe, Ca, etc. are omitted unless they are of importance in geochemical prospecting methods. It should also be understood that not all of the elements may be concentrated with the particular element in question. Omissions of particular elements are frequently the rule rather than the exception.

In brines and saline evaporites such as those in Searles Lake, California, lithium is generally present as the phosphate or chloride and is accompanied by Na, K, B, W, P, F, Br, Cl, I, SO_4 , CO_3 , and S. There are no particular indicators except perhaps B and W. All natural spring, underground, and saline waters should be tested directly for lithium if a source is sought in these materials.

Lithian wad and other manganese dioxides are comparatively rare but may indicate the presence of lithium deposits in the geological terrane, especially where they occur at the orifices of springs. The wads contain a veritable host of elements among which Ba, Sr, Ti, rare earths, As, Sb, W, Mo, Co, and all of the other heavy metals may be represented¹.

Lithium-bearing clays and shales are not common but should be carefully considered as a future source of the element. The lithium mineral in certain clays is hectorite, a lithium clay mineral belonging to the beidellite and bentonite groups. In lithium clays and shales lithium is usually accompanied by higher than average amounts of magnesium, fluorine, and boron, all of which could serve as indicators of the element. In some areas the lithium in clays and shales appears to have been derived from hot springs. Elsewhere, where the clays and shales are associated with saline evaporites, the element may have been absorbed from brines.

Sodium and potassium are closely allied in nature and rarely occur to the exclusion of one another. Both elements are strongly enriched in granitic rocks and pegmatites in which they occur mainly in the feldspars and micas. Commercially, sodium and potassium are obtained from saline evaporites, saline lakes, and underground brines, in which they are usually present as chlorides, nitrates, sulphates, carbonates, or borates. All saline evaporites, saline lakes, salinas, salt flats, caliche, salty earths, and brines should be analyzed directly for the presence of sodium and potassium salts followed by mineral identifications if a source is sought in these materials.

Potassium is strongly adsorbed and exchanged by clay minerals, and hence certain clays and shales may be greatly enriched in the element. Such materials may be utilized as fertilizer components in the future. Direct analysis for potassium is suggested for clays and shales suspected to contain higher than average amounts of the element.

Soda metasomatism is a feature of many types of carbonatites. Higher than average contents of sodium in rocks, soils, tills, waters, and vegetation may, therefore, indicate the presence of these bodies. Sodium is also enriched in the wall-rock alteration zones of many types of gold deposits

¹All wads and manganese oxide deposits should be analyzed during geochemical surveys as a matter of routine. They are great adsorbers of many elements and may, therefore, indicate their presence in the geological terrane in which they occur.

(albitization), and hence the element may be a useful indicator of these deposits. Potassium, likewise, is frequently enriched in the wall-rock alteration zones of certain gold deposits, and both sodium and potassium may be enriched in the alteration zones associated with pegmatites, base metal, and many other types of deposits.

Rubidium follows potassium closely in its geochemistry and is concentrated in most potassium minerals. No rubidium minerals are known. Most of the rubidium of commerce is obtained from lepidolite. Other possible sources are carnallite, pollucite, leucite, zinnwaldite, various potassium micas and feldspars, adularia, and certain varieties of beryl.

Rubidium is concentrated in certain pegmatites and coarse-grained granites; also in greisens that may be associated with tin, tungsten, and beryllium deposits. The element is also frequently enriched in potassium-bearing brines and mineral waters and in potassium-rich saline evaporites. Certain potassium-rich clays and shales may contain above average contents of rubidium.

The most common elemental associate of rubidium in all geological materials is potassium, and it is the best indicator of the element. In pegmatites, greisens, and coarse-grained granites the common associated elements are Li, Cs, Be, Sc, Y, rare earths, Nb, Ta, Mo, W, Sn, Bi, Tl, Ga, B, P, and F. Of these the best indicators are Cs, Li, Ta, Nb, Be, P, and F. In natural waters and saline evaporites rubidium may be accompanied by K, Li, Cs, W, B, Cl, and the various other readily soluble elements such as Na, Ca, Mg, etc.

Cesium is the least abundant of the common alkalis. It forms the mineral pollucite, $16[(\text{Cs}, \text{Na})\text{AlSi}_2\text{O}_6 \cdot n\text{H}_2\text{O}]$, which commonly resembles quartz and may be easily mistaken for it. Other possible sources are lepidolite, microcline feldspar, adularia, certain varieties of beryl, potassium micas, carnallite, and other potassium minerals. The present commercial source of cesium is pollucite.

Cesium follows potassium and rubidium closely in its geochemistry and is concentrated in certain pegmatites and coarse-grained granites where it is present in pollucite, in the potassium and lithium minerals, and in beryl; also in certain greisens associated with tin, tungsten, and beryllium deposits. The element may also be enriched in certain brines and in other natural waters and in potassium-rich saline evaporites. Certain potassium-rich clays and shales may contain above average amounts of cesium.

The most common elemental associates of cesium in practically all geological materials are potassium and rubidium, and both are good indicators of the element. In pegmatites, greisens, and coarse-grained granites the common associated elements are Li, Rb, Be, Sc, Y, rare earths, Nb, Ta, Mo, W, Ga, Tl, Sn, Bi, B, P, and F. Of these the best indicators are

Li, Rb, Be, Ta, Nb, P, and F. In natural waters and brines and in saline evaporites the commonly associated elements are the same as those for lithium and rubidium mentioned above. All brines, mineral waters, and saline evaporites should be analyzed for all of the alkalis on a routine basis since some of these elements may be present in these materials in commercial quantities.

GROUP IB: COPPER, SILVER, AND GOLD

Copper occurs in 8 principal types of deposits: (1) Copper sulphides in shales and their metamorphic equivalents (Kupferschiefer and Zambia types); (2) copper sulphides in sandstones, sandy shales, and conglomerates ('red bed' type); (3) native copper deposits in amygdaloidal basalts and associated quartzites and conglomerates; (4) copper sulphides in or associated with monzonite and other granitic intrusives (porphyry copper type); (5) copper sulphides in skarn-type deposits; (6) massive copper sulphides associated with Ni-Co-Fe sulphides (Sudbury type); (7) massive copper sulphides associated with iron, lead, and zinc sulphides; and (8) copper sulphides, arsenides, etc. in veins, lenses, pods, disseminations, etc. in faults, fractures, drag folds, crushed zones, and shear zones. An unusual occurrence is the presence of copper sulphides in certain carbonatites as at Phalaborwa in South Africa.

In the copper shales the element is associated with a veritable host of chalcophile elements among which the most abundant are Ag, Zn, Cd, Pb, Mo, Re, Co, V, Mn, Se, As, and Sb. Of these the best indicators appear to be Ag, Zn, Pb, Mo, and Co. The common associated elements in the 'red bed' deposits are Ag, Pb, Zn, Cd, V, U, Ni, Co, P, Cr, Mo, Re, Se, As, Sb, Mn, and Ba. Among these Ag, Pb, and Ba are nearly universal and provide the best indicators. Co, Ni, Mo, As, and Sb occur in many deposits and are useful indicators in some districts. U, V, P, Cr, and Se, while present in trace amounts in most deposits, reach high concentrations only within certain metallogenetic provinces.

The native copper deposits in amygdaloidal basalts and associated sediments have few elemental associates. Among the most common are Ag, B, As, and S; less common and local are Pb and Zn. The minerals calcite, epidote, prehnite, datolite, and zeolites are characteristic.

The most common elemental associates of copper in porphyry copper deposits are Mo, Re, and Fe. Other associates frequently of local occurrence are Zn, Pb, Ag, Au, As, and Sb; W is rare.

In skarn-type bodies copper is accompanied by a number of elements among which the most frequent are Fe, Mn, Zn, Pb, Ag, Cd, Mo, W, Au, Sn, Bi, As, and Sb; Co and Ni are rare. B and F may occur in some deposits. The calcium-magnesium-iron silicates are characteristic.

Massive sulphide deposits containing copper such as those at Sudbury have a characteristic suite of elements which accompany the copper. Most frequent are Ni, Co, Fe, and As. Elements in trace amounts include Pt and other Pt metals, Ag, Au, Se, and Te. Pb, Zn, Sn, Bi, and Sb are rare. The best indicators of such deposits are Ni, Cu, and Co.

The massive copper-lead-zinc deposits and the various vein type deposits of copper may be indicated by the following elements: Zn, Pb, Cd, Ag, Fe, As, and Sb. Other elements present in the deposits, often in traces, are Mo, Re, Co, Ni, B, Ga, In, Tl, Ge, Sn, Bi, Se, and Te. Hg is a good indicator of these deposits and has been used effectively in geochemical surveys in some districts.

For the elemental associations of copper in carbonatites see the discussion under the element niobium.

Certain ground and surface waters are enriched in copper, and the wads, limonites, and other precipitates at spring orifices may be enriched in the element as well as in other elements with which copper is associated in deposits. Certain bogs also contain relatively high amounts of copper due to the strong chelating action of humus. All of these geological phenomena may indicate the presence of copper deposits in the terrane in which they occur.

Silver is won from various types of copper, lead, zinc, gold, and nickel deposits. For the indicator and associated elements in these deposits see the discussion accompanying each of these elements. Particularly good indicators of the presence of silver in these deposits are Pb, Zn, Cd, Cu, Mn, Bi, Se, Te, As, and Sb. Manganiferous siderite or calcite is a good indicator mineral in many silver deposits.

Much silver is also obtained from native silver deposits, particularly those containing the nickel-cobalt arsenides (Cobalt type). The characteristic elemental associates of silver in these deposits are Ni, Co, Fe, S, As, Sb, Bi, and U. The last element is restricted to deposits in specific mineral belts. The deposits also contain some Ba, Cu, Zn, Cd, Pb, and frequently a little Hg, the last mainly in dyscrasite and native silver. Among these various elements the best indicators in geochemical surveys utilizing rocks, soils, vegetation, stream sediments, and waters are Ni, Co, As, Sb, and Bi. Where uranium occurs in the deposits it may serve as an indicator element in geochemical surveys, and the veins can also be located by their high radioactivity. The usefulness of Ba, Cu, Zn, Cd, and Pb as indicators of native silver deposits depends on the content in the veins. Mercury may be useful in rock and soil surveys where it occurs in the deposits.

Silver is a constituent of several copper, uranium, and vanadium deposits in sandstones. These deposits are generally referred to as the 'red bed' type. The characteristic elements concentrated in these deposits include U, V, Sr, Ba, Cr, Mo, Re, Fe, Co, Ni, Cu, Ag, Au, Zn, Cd, Pb, P, As,

Sb, S, and Se. Some of these deposits are similar to the 'red bed' sandstone deposits discussed under copper, uranium, and vanadium.

Ground and surface waters are frequently enriched in silver in the vicinity of silver deposits of all types. The waters leaching the deposits may also be enriched in Zn, Cu, As, Sb, U, V, Mo, Se, Ni, and Co. Of these Ni, Co, U, and As are particularly indicative of the native silver nickel-cobalt arsenide deposits, and U, V, Se, and Mo are characteristic of the 'red bed' silver deposits. Wad and other precipitates near the orifices of springs may indicate silver deposits if they contain high contents of Ag, Cu, Pb, Zn, U, V, Cr, Se, Te, Bi, As, Sb, Ni, and Co.

Gold is won from a number of types of diverse deposits among which the following are the most important: (1) gold-silver quartz veins in volcanic and sedimentary rocks; (2) gold-silver telluride or selenide deposits, principally veins, chiefly in or associated with volcanic rocks; (3) gold deposits in skarn bodies; (4) quartz-pebble conglomerate deposits (Rand type); and (5) placers and residual concentrations. In addition to these gold is won from various types of copper, lead, zinc, and nickel deposits. For the associated and indicator elements for the later types of deposits see the discussion accompanying each of the elements mentioned.

The principal associated elements and indicators in the gold-silver-quartz veins are Ag, As, S, and Fe. Some deposits, especially those of Tertiary age, carry considerable amounts of Sb, Pb, Zn, Cu, and Cd. Precambrian deposits tend to have a high Au/Ag ratio much greater than 1, whereas those of Tertiary age have a low Au/Ag ratio, usually less than 1. Many deposits in sedimentary rocks contain B, and a few in all rock types have W, Mo, Te, and Bi. A few deposits in basic and intermediate igneous and volcanic rocks are marked by enrichments of Cr in their wall-rock alteration zones. Gold-quartz deposits in basic and intermediate igneous rocks and in basic and intermediate lavas are generally enveloped by characteristic potassium-rich, desilicated, and carbonated zones. Other deposits of this type are marked by a development of albite in their wall-rocks and hence exhibit a typical soda metasomatism. Adularia is developed in the wall-rocks of some deposits; alunite in others. Silicification and pyritization are widespread in numerous gold-quartz deposits in all types of rocks.

The gold-silver telluride veins are generally marked by enrichments of Ag, Fe, Te, S, and F. In some there are also Zn, Cd, Cu, Sb, As, Hg, Mo, and W. The Au/Ag ratio is generally much greater than 1, although there are certain veins where the ratio is much less than 1. The common associated elements in the gold selenide veins are Se, Ag, Fe, Cu, Pb, Zn, Hg, Sb, and As. The Au/Ag ratios are generally low, usually less than 1 in these deposits.

The elemental associates in the skarn type gold deposits are generally the same as those discussed for similar deposits of copper, lead, zinc,

and tungsten. Frequently there is abundant arsenic and antimony in the gold deposits, and these elements, especially arsenic, provide good indicators of gold and silver in most types of geochemical prospecting surveys.

The principal elemental associates of gold in the quartz-pebble conglomerate deposits are Fe, S, Ag, U, Th, and rare earths. The iron and sulphur are combined mainly in pyrite which is ubiquitous. The Au/Ag ratio is always greater than 1 and averages about 3.1 in the Rand. Other elements associated with gold in the quartz-pebble conglomerate type of deposit are As, Cu, Pb, Zn, Co, and Ni. Of these probably only arsenic is a suitable indicator, although the other elements may serve the same purpose if they are present in some quantity.

The heavy minerals associated with gold in placers and residual deposits are well known and need not be repeated here. Constant scrutiny of quartzites, conglomerates, and other resistate sediments should be maintained so as not to miss fossil placers during geochemical prospecting.

Ground and surface waters are frequently enriched in gold in the vicinity of gold deposits of all types. The waters leaching the deposits may also be enriched in Zn, Cu, Ag, As, Sb, Se, and Te. Of these Ag, As, Sb, Se, and Te are particularly indicative of gold. Wad and other precipitates near the orifices of springs may also indicate gold deposits if they contain high contents of Au, Ag, Pb, Zn, Cd, Cu, Mo, Bi, As, Sb, Se, Te, and W. Certain humic deposits may also be enriched in gold in terranes where gold deposits occur. All of these geological materials should be carefully studied and analyzed during geochemical surveying for gold deposits.

GROUP IIA: BERYLLIUM, MAGNESIUM, CALCIUM, STRONTIUM, BARIUM, AND RADIUM

Beryllium is a typical element of the pegmatites. It is also concentrated in certain types of albitized, fluoriferous, sericitized, and greisenized granites; in certain skarn-type deposits; in some tin and tungsten veins; in certain gold-quartz and manganese-lead-zinc veins, in quartz-albite veins containing berylite, and in veins, segregations, and disseminations containing minerals such as beryl, bertrandite, phenacite, euclase, berylliferous saponite, etc. in certain altered tuffs, limestones, and other rocks. Beryllium may also be enriched in some of the zeolites such as apophyllite in veins and rocks, but such occurrences are rare. During the processes of weathering and sedimentation beryllium tends to follow aluminium and may be slightly enriched in clays, bauxites, and shales. These, however, do not offer possibilities for commercial extraction of the element at the present time.

Beryllium forms numerous minerals, the most important commercially being beryl. The minerals chrysoberyl, gadolinite, bavenite,

bertrandite, phenacite, euclase, helvite, danalite, genthelvite, berylite, herderite, etc. may also provide a source of beryllium if present in sufficient quantities.

The elemental associates of beryllium in pegmatites are Li, Rb, Cs, Sc, Y, rare earths, Nb, Ta, Mo, W, B, Tl, Sn, P, Bi, F, U, and Th. Of these Li, B, Nb, Ta, and F are probably the best indicators in geochemical prospecting surveys, although the others may prove useful in certain areas. The beryllium minerals found characteristically in granite pegmatites are beryl, gadolinite, chrysoberyl, euclase, phenacite, and bertrandite. In nepheline syenite pegmatites the suite comprises melinophanite, leucophanite, eudidymite, epididymite, hambergite, and helvite.

In albitized, fluoriferous, sericitized, and greisenized granites the principal associates of beryllium are F, Li, and B. Sn, W, Mo, and P may also be present, and there may be traces of all of the elements mentioned above that accompany beryllium in pegmatites.

Certain genthelvite deposits with associated phenacite occur in veins and stock works in alkaline muscovite-biotite granites in U.S.S.R. and elsewhere. These deposits are marked by local silicification and biotitization. Associated minerals are sphalerite, pyrite, galena, and molybdenite. The best indicator elements of these deposits appear to be Na, K, Si, S, Zn, Fe, Mn, Pb, and Mo.

Beryllium is a frequent constituent of skarn deposits in which it occurs principally in berylite, helvite, danalite, and vesuvianite (idocrase). In addition minerals such as grossularite, epidote, allanite, and axinite may be beryllium-bearing. Some varieties of allanite for instance may contain up to 4 per cent BeO. The principal associates of beryllium in skarn-type deposits are Fe, Mn, rare earths, P, F, B, Mo, W, Sn, Bi, Ba, Sr, As, Cu, Pb, and Zn. There is often a coherence between zinc, manganese, and beryllium in skarn-type deposits, a feature that is emphasized by the relatively high contents of beryllium in vesuvianite and other minerals at Franklin Furnace, New Jersey. To avoid missing beryllium in skarn deposits bulk samples and mineral concentrates should be analyzed directly for the element.

Certain tin, tungsten, and molybdenum veins and quartz segregations frequently carry some beryl and possibly other beryllium minerals in some cases. Zinnwaldite, the lithium mica, tends to be enriched in beryllium in these deposits. For the associated and indicator elements in these deposits see the discussions under lithium, tin, tungsten, and molybdenum.

Beryllium is not common in gold-quartz veins, but those containing fluorine (fluorite) may contain small quantities of the element. Likewise, certain manganese-lead-zinc veins containing rhodonite, rhodochrosite, other

manganese minerals, sulphides, and helvite may contain small amounts of beryllium, mainly in the helvite.

The betrandite and phenacite deposits in altered tuffs and limestones are generally accompanied by fluorite and frequently by scheelite. The rare alkalis accompany beryllium in some deposits. The best indicators of such deposits appear to be F and W in some places and F, Rb, Cs, and Li in others. Ancillary indicators are Mn, Zn, Pb, Sn, Sc, and rare earths for certain deposits of this type.

There is frequently a coherence between barium and beryllium in nature, a feature that is emphasized by the relatively large deposit of berylite in veinlets of quartz and albite at Seal Lake, Labrador.

Beryllium is present in small quantities in natural waters and in some hot springs. Springs and groundwaters near berylliferous deposits tend to be enriched in the element as well as in Li, Rb, Cs, rare earths, Sn, F, and the other elements associated with beryllium in the deposits. Wad, limonite, and other natural precipitates may indicate the presence of beryllium deposits by their high concentrations of Be, Li, Rb, Cs, Ba, Sc, Y, rare earths, Nb, Ta, Mo, W, B, Sn, and P.

Magnesium is a characteristic element of intermediate, basic and ultrabasic rocks and of sedimentary carbonate rocks, especially those containing dolomite. The magnesium minerals of commerce are olivine obtained from ultrabasic rocks and used for refractories; asbestos also obtained from ultrabasic rocks and used for a great variety of purposes; brucite, the hydroxide, obtained from crystalline limestones, dolomites, and serpentinites and used for refractories and the production of the metal; dolomite obtained mainly from sedimentary deposits; magnesite used in refractories and for the extraction of the metal and won mainly from epigenetic veins and lenses and also from sedimentary deposits; and various salts, particularly the sulphates and chlorides, used for the extraction of the metal and various other purposes and obtained from ocean bitterns, various underground brines and mineral waters, salt lakes, and saline evaporites.

The search for magnesium deposits in rocks should be confined mainly to areas of ultrabasic and basic rocks and to sedimentary terranes containing dolomite or its metamorphic equivalent. There are no particularly diagnostic indicator elements for magnesium deposits except the element itself. High contents of magnesium in soils, tills, and natural waters may reflect the presence of magnesium deposits of all types, but this is only a general guide. Epigenetic magnesite deposits occur in two settings - firstly in limestone or dolomite terranes that exhibit folding and in some places metamorphism and igneous injection; and secondly in terranes of ultrabasic rocks that exhibit extensive carbonatization and serpentinitization with the release of silica which appears as opal, chalcedony, or fine-grained quartz. The latter rocks are frequently marked by higher than normal amounts of Cr,

Ni, and Co in their overlying soils and tills and in their associated stream sediments. Heavy mineral concentrates from the soils and stream sediments in the vicinity of serpentinized and carbonated basic and ultrabasic rocks are also generally enriched in these three elements.

Natural waters and their precipitates, brines, salt lakes, and saline evaporites should be analyzed directly for magnesium, if a source of the element is sought in these materials.

Calcium is a characteristic element of intermediate and basic rocks and of the sedimentary carbonate rocks and evaporites. The calcium minerals and rocks of commerce require little discussion. They include calcium carbonate (calcite) in its various forms obtained from sedimentary carbonate deposits, various salts, principally the chlorides obtained from natural brines and saline evaporites, and the sulphates which occur as gypsum and anhydrite in sedimentary evaporite beds.

Calcium-bearing rocks in a terrane are often indicated by higher than normal contents of calcium in the soils, tills, stream sediments, and natural waters and by the relatively high pH (~ 8.5) of these materials. A high sulphate content that is enriched in the isotope S^{34} in soils, tills, stream sediments, and natural waters may indicate the presence of gypsum and anhydrite in the terrane. Natural waters and their precipitates, brines, and evaporites should be analyzed directly for calcium, if a source of the element is sought in these materials.

Strontium is widely distributed in rocks, particularly in granites, carbonate rocks, and in gypsum and anhydrite. The only minerals of commercial importance are the sulphate, celestite, and the carbonate, strontianite. The former is the more abundant.

Both celestite and strontianite occur in epigenetic veins and lenses and in certain beds that are evidently of sedimentary origin. Both types of deposits are generally found in sedimentary terranes and are particularly associated with carbonate rocks, gypsum, and anhydrite. The elements accompanying strontium in the vein deposits are Ba, Pb, and Ca. In some deposits there is also an association with F which occurs in fluorite. In the bedded deposits the principal associated element is Ca, and there may be traces of Ba and F; also B and native sulphur.

Strontium deposits may be indicated by higher than normal amounts of strontium in soils, tills, stream sediments, natural waters, and vegetation. Barium and lead may also be good indicators in these materials. Sulphate may indicate the presence of celestite deposits, but this compound is only a general guide.

Strontium is a common constituent of many natural waters and their precipitates, brines, and evaporites. These should be analyzed directly for

strontium if a source is sought in these materials. Wads and other non-manganese precipitates at the orifices of springs tend to be enriched in strontium where disseminations and deposits of strontium minerals occur in the rocks.

Barium is widely distributed in igneous and igneous-type rocks particularly in the more acid varieties such as syenites and granites where the element occurs mainly in the potash feldspars. Certain shales and sandstones may be enriched in barium, and the element is often concentrated in small amounts in manganese sediments and precipitates. The only minerals of commercial importance are the sulphate, barite, and the carbonate, witherite; the former is the more abundant. Barite is a common gangue mineral in many types of ore deposits; witherite occurs only rarely as a gangue mineral. Barytocalcite, nitrobarite, and the various silicates, phosphates, and vanadates of barium are generally rare minerals and cannot be considered as commercial sources of the element.

Barite deposits are found in the following forms: (1) as veins and replacements, containing essentially barite with minor amounts of fluorite, calcite, siderite, ankerite, dolomite, quartz, and sulphides; (2) as bedded deposits containing essentially barite with minor amounts of chert, quartz, dolomite, siderite, strontianite, witherite, pyrite, and iron oxides; (3) as disseminated and massive barite forming the gangue of various types of vein and massive sulphide deposits, particularly those containing lead, zinc, copper, and silver. The barite may be won as a by-product in some cases; and (4) residual deposits in unconsolidated materials such as soil, clay, decomposed rocks, and other residuum. The barite in these deposits is derived from deposits of the first three types.

The vein and replacement type barite deposits may occur in igneous, sedimentary, or metamorphic rocks of all types. There is, however, a general tendency for these deposits to occur in limestones, calcareous shales, and sandstones. The bedded deposits are invariably in sequences of limestones, dolomites, and shales.

Witherite deposits generally occur as veins and irregular lenses in sedimentary rocks, particularly limestone, calcareous shales, and sandstone. Some witherite deposits are bedded or elongated lenses in sequences of limestone and shale.

Barite is a frequent associated mineral in certain carbonatites and is present in some rare earth carbonate veins. In the latter it is associated with bastnaesite, the cerium fluocarbonate as at Mountain Pass, San Bernardino County, California. Barite may be commercially recoverable from some of these deposits.

In most types of barium deposits the element is associated with Ca, Sr, Mg, Fe, Mn, and Pb. In some deposits there may also be enrichments of

Zn, Cd, Ag, Au, Cu, V, As, and Sb. In others Hg and Sb accompany the barium. F is a characteristic element in many deposits. Rare earths, Th, and U accompany barium in the rare earth carbonate deposits, and Nb and the other elements commonly concentrated in carbonatites accompany the element in these deposits. (See also the discussion under niobium).

Barium deposits may be indicated by higher than normal amounts of barium in soils, tills, stream sediments, natural waters, and vegetation. Strontium and lead, as well as the other heavy metals mentioned above, may also be good indicators in these materials. Sulphate may indicate the presence of barium deposits, but this compound is only a general guide. Sulphate enriched in the isotope S^{34} may also be a useful guide to some barite deposits. Fluorine may be a useful indicator in certain places.

Barium is a common constituent of many underground brines and their precipitates. Wad and other iron-manganese precipitates at the orifices of springs tend to be strongly enriched in barium as well as in its associated elements where disseminations and deposits of barium minerals occur in the rocks.

Radium is obtained as a by-product of uranium ores. Its associated elements are the same as those discussed under uranium.

GROUP IIB: ZINC, CADMIUM, AND MERCURY

Zinc occurs in seven principal types of deposits. Cadmium generally accompanies zinc and is won from its ores as a by-product. Most zinc-cadmium deposits also contain lead. The types of zinc deposits are: (1) disseminated sphalerite in shales: These deposits generally accompany the copper shales (Kupferschiefer type) and are not generally exploited; (2) disseminations, knots, and concretions of sphalerite in sandstones, quartzites, and shales: These deposits generally contain galena and copper and iron sulphides. Examples are known at Maubach in Germany, in Cape Breton Island, Nova Scotia, and elsewhere; (3) zones of disseminated sphalerite, veins of sphalerite, replacement deposits of sphalerite, pods of sphalerite, etc. in carbonate rocks which often show the effects of dolomitization and silicification. These deposits are commonly known as 'Mississippi Valley' type. They generally contain considerable quantities of lead; copper and silver are minor; (4) skarn-type zinc deposits. These deposits frequently have considerable quantities of lead, copper, silver, and some gold; (5) franklinite-willemite-zincite deposits (Franklin Furnace, New Jersey type). These deposits probably belong in category (4) above as they have frequently been referred to as pyrometasomatic deposits in the older literature. The mineral association is most complex and contains, in addition to the three principal zinc minerals noted above, a large assortment of zinc silicates, manganese silicates, axinite, scapolite, calcite, garnet, rhodochrosite, fluorite, sphalerite, galena, arsenopyrite, chalcopyrite, and loellingite. The deposits at

Franklin Furnace and Sterling Hill, New Jersey occur in crystalline limestone and coarse gneisses of Precambrian (Grenville) age; (6) veins and replacement deposits of sphalerite in various types of rocks. Accompanying minerals are generally galena and iron, copper, and silver sulphides. Barite may be present as a gangue mineral; and (7) massive sulphide deposits containing essentially sphalerite and iron, copper, and silver sulphides. Barite may be present as an important mineral in some deposits.

The most frequent elemental associate of zinc and cadmium is lead. In some deposits there may also be enrichments of Cu, Ag, Au, Ba, As, Sb, Bi, Mo, In, Tl, Ge, Hg, and Sn. Some deposits contain considerable quantities of manganese either in siderite or in silicates. In the franklinite-willemite-zincite deposits the manganese is present in the franklinite and in various manganese silicates.

Zinc and cadmium deposits are generally indicated by higher than normal amounts of zinc and cadmium in soils, tills, stream sediments, natural waters, and vegetation. Lead is also a good indicator in all of these materials with the exception of natural waters. Cu, Ag, Ba, Mn, As, and Sb, may be useful indicators for vein and massive sulphide type deposits in some areas. Skarn type deposits may be indicated by Mo, W, and Bi under favourable conditions, and the franklinite deposits may be marked by higher than normal amounts of manganese in rocks, soils, etc. Mercury is a good indicator of vein and massive sulphide deposits in some areas and has been used effectively in geochemical surveys.

Ground and surface waters in the vicinity of zinc deposits are frequently enriched in zinc and cadmium and their associated chalcophile elements, as are also the wads, limonites, and other precipitates at spring orifices. Certain bogs also contain relatively high amounts of zinc due to the strong chelating action of humic substances. All of these geological phenomena may indicate the presence of zinc and cadmium deposits in the terrane in which they occur.

Mercury is obtained almost entirely from the sulphide, cinnabar, although the native metal occurs in some ores, and the element has been obtained from livingstonite, metacinnabarite, and a few of the other rarer mercury minerals such as calomel.

Cinnabar and the other types of mercury deposits generally occur in fissure veins, stockworks, and as disseminations, impregnations, and replacements along faults or in brecciated zones. The common host rocks are sandstone, limestone, dolomite, calcareous shale, chert, serpentinite, andesite, basalt, trachyte, and rhyolite. Commonly associated metallic minerals are stibnite, realgar, orpiment, arsenopyrite, pyrite, and marcasite. Some veins have a ferberite and/or scheelite-stibnite association; others contain quartz, tourmaline, and cinnabar. Some lead-zinc and copper ores may contain cinnabar, and mercury minerals are often associated with certain

gold-quartz and silver veins. The gangue in most mercury deposits is invariably opal, chalcedony, or quartz, and carbonates. Barite and fluorite are generally restricted to individual deposits. Argillic alteration, silicification (development of opal), pyritization, and sericitization are common. Carbonatization of serpentinite is marked in some deposits.

Mercury deposits are generally indicated by higher than normal amounts of mercury in soils, tills, stream sediments, and vegetation. In some areas antimony and/or arsenic may also be good indicators in these materials. Germanium is enriched in some cinnabar deposits and may be a useful ancillary indicator in soil and stream sediment surveys. The efficiency of other indicators such as Ba, F, W, and B probably depends on local conditions. Zones of extensive silicification (opal) and carbonatization may serve as a general guide.

Mercury is a common constituent of natural waters, particularly hot springs and their precipitates, in the vicinity of certain mercury deposits. These should be analyzed carefully for Hg, as well as for Sb and As, during geochemical surveys designed to locate mercury deposits.

GROUP IIIA: BORON, ALUMINUM, GALLIUM, INDIUM, AND THALLIUM

Boron is widely distributed in igneous, metamorphic, and sedimentary rocks but generally only in small amounts. The element is a characteristic one in pegmatite dykes and in certain mineral veins and other types of deposits. The common boron minerals in rocks, pegmatites, and mineral deposits include tourmaline, axinite, datolite, dumortierite, and danburite, none of which provide a commercial source of the element.

The commercial boron minerals are the hydrated sodium, magnesium, and calcium borates and boric acid. Boric acid occurs as the mineral sassolite; some of the important borates are kernite, tincalconite, borax, ulexite, priceite, boracite, and colemanite.

Boron compounds are obtained commercially from the following sources: (1) brines of saline lakes and marshes; (2) encrustations around playas, salt lakes, and salt marshes; (3) bedded deposits formed in ancient salt lakes, salt marshes, and playas; (4) hot springs and fumaroles; and (5) disseminations, beds, and lenses of borate minerals in potassium salts in marine evaporites, and irregular beds and disseminations of borate minerals associated with salt domes and diapirs.

Deposits (1) to (3) inclusive are generally situated in Cenozoic tectonic-volcanic belts that pass through regions of arid climates. The borates in these deposits are thought by many to have a volcanic hot spring origin, although connate and groundwaters that have leached boron from the

rocks appear to be responsible for some deposits. The hot spring and fumarole deposits all show a close relationship to recent volcanism. The borates, however, may be leached from the rocks and may not, therefore, be of magmatic origin as some have suggested. The borates associated with evaporites may be of any age. They appear in most cases to have been precipitated from seawater.

Two other possible sources of commercial borates should be mentioned. These include seawater which contains up to 4.6 ppm boron and certain types of skarn deposits containing ludwigite-ascharite and kotoite. According to some investigators these minerals are usually associated with magnesium skarns and the associated intrusives are generally enriched in boron, mainly in the plagioclase, a feature that may assist in prospecting for these deposits. Further, the ludwigite-ascharite type of mineralization is generally present in skarns marked by abundant magnetite whereas the kotoite type of mineralization appears in gold-copper (bornite) skarns and contact-metasomatic deposits.

The borates in playas, salt lakes, and salt marshes and those in bedded deposits and present in evaporites are generally always associated with a great variety of Na, K, Li, Mg, and Ca salts. There is also commonly an association with F and Cl. In hot springs and fumaroles boron is generally accompanied by various alkali and alkaline earth salts and by F and Cl. The boron in skarns often shows a correlation with magnesium and may be accompanied by relatively large enrichments of Fe, Mn, Ca, Cu, Au, Zn, Mo, W, F, and the other elements commonly concentrated in skarn.

Boron is a good indicator of all types of borate deposits and can be used effectively in soil, stream sediment, water, and vegetation surveys. According to some investigators certain plants are accumulators of boron, but these can only be differentiated by detailed surveys. Those searching for borate deposits should analyze all playa sediments and encrustations, bedded saline deposits, evaporites, skarns, brines, fumaroles, hot springs and other natural waters and their precipitates directly for boron to determine their possible commercial importance. Fluorine may be a useful indicator of borates in some of these deposits.

Aluminum is obtained commercially almost exclusively from bauxite. Other possible sources are aluminous laterite, clay, and shale, nepheline syenite, and other rocks relatively enriched in the element.

Other commercial minerals of aluminum include the various alums, particularly alunite and cryolite. The natural alums are mainly hydrated double sulphates of potassium, sodium, and ammonium. Most of these are highly soluble and occur as surface evaporation products in arid regions or in sheltered places. Certain springs may be charged with aluminum sulphates and their precipitates may contain the various alums. In dry areas irregular bedded deposits of alum minerals may originate from springs.

Alunite is most commonly associated with acid volcanic or intrusive rocks and is formed generally where these rocks have been highly altered by sulphuric acid vapours or waters. Some alunite deposits may also owe their origin to the alteration of potassic aluminous rocks by sulphuric acid solutions derived from the oxidation of pyrite and other sulphides. Alunite generally occurs disseminated in the rocks or in well-defined veins. Some deposits contain essentially only alunite, others are pervasive alterations associated with gold-silver and other metallic deposits as at Goldfield, Nevada and elsewhere.

Cryolite (Na_3AlF_6) occurs in commercial quantities at only a few places in the world, particularly at Ivigtut, West Greenland and at Miask, Ilmen Mountains, U.S.S.R. At Ivigtut the cryolite is found in a pegmatitic body in porphyritic granite. It is accompanied by microcline, quartz, fluorite, siderite, topaz, pyrite, arsenopyrite, galena, sphalerite, molybdenite, and a number of rare aluminum fluoride minerals. Cryolite is used as an electrolyte in the Hall process for the reduction of aluminum oxide to the metal.

Geochemical prospecting has not been used extensively to locate bauxite deposits although there seems to be no reason why aluminum should not be a good indicator in laterites, soil, water, stream sediment, and vegetation surveys for these deposits. The same can probably be said for alum deposits, particularly alunite. The presence of excess sulphate in soils, stream sediments, and natural waters should serve as a general guide for the location of these deposits. Furthermore, certain plants appear to be aluminum accumulators, and these may be useful in outlining areas rich in alunite and other aluminum minerals. Laterite, bauxite, clay, and other rocks suspected to contain high quantities of aluminum oxide should be analyzed directly for this compound to prove their commercial importance as a source of aluminum.

Those searching for cryolite deposits should find aluminum and fluorine to be good direct indicators in soil, water, stream sediment, and vegetation surveys. Pb, Zn, As, Mo, and the other elements associated with cryolite may serve as secondary indicators.

Gallium is a rare metal and forms one known mineral, gallite, CuGaS_2 , which is rare. The element is enriched in certain deposits of sphalerite, in some copper shales, in bauxite, and in certain coals. Tin ores in some areas, particularly Bolivia, contain relatively high amounts of the element. The sulphide mineral germanite, $\text{Cu}_3(\text{Fe, Ga, Zn, Ge})(\text{As, S})_4$, may contain up to 1.85 per cent Ga. The element is obtained commercially from sphalerite ores, from the residues of the copper ores of the Kupferschiefer, from bauxite, and from the flue dusts of certain coals.

The elements accompanying gallium in deposits are the same as those discussed under zinc, copper, tin, and aluminum. Materials and residues suspected to contain commercial quantities of gallium should be analyzed directly for the element.

Indium forms four known minerals, all of which are very rare: native indium, In; roquésite, CuInS_2 ; indite, FeIn_2S_4 ; and dzhalindite, $\text{In}(\text{OH})_3$. The element is often enriched in dark sphalerite and is found in trace amounts in many sulphides and in various tin and tungsten minerals, particularly chalcopyrite, galena, stannite, cassiterite, and wolframite. Industrially, indium is obtained from zinc flue dusts and the residues of zinc refining.

The elements accompanying indium in deposits are the same as those discussed under zinc, lead, copper, tin, and tungsten. Materials and residues suspected to contain commercial quantities of indium should be analyzed directly for the element.

Thallium is a rare metal that exhibits a slight enrichment in some potassic feldspars in pegmatites; also in galena, a number of sulphides, a variety of lead sulfosalts in various polymetallic deposits, and various potassium salts. The element also forms the rare minerals crookesite $(\text{Cu, Tl, Ag})_2\text{Se}$; lorandite, TlAsS_2 ; hutchinsonite, $(\text{PbTl})_2(\text{Cu, Ag})\text{As}_5\text{S}_{10}$; vrbaitte, $\text{Tl}(\text{As, Sb})_3\text{S}_5$; and avicennite, Tl_2O_3 ; none of which are of commercial importance. Industrially, thallium is obtained as a by-product of the smelting of lead-zinc ores and from the roasting of pyrite for sulphuric acid production. Some thallium-rich arsenical gold ores provide a reserve for the future.

The elemental associates of thallium in deposits are mainly K, Fe, Mn, Pb, Zn, Cd, Cu, As, Sb, Ag, Au, In, Ga, Ge, Sn, S, and Se. Materials and residues suspected to contain commercial quantities of thallium should be analyzed directly for the element.

GROUP IIIB: SCANDIUM, YTTRIUM, RARE EARTHS, THORIUM, AND URANIUM

Scandium is a rare metal closely associated in nature with yttrium and the rare earth metals. It is widely diffused in rocks of all types, particularly in those containing an abundance of ferromagnesian minerals. The element also occurs in a great variety of minerals in higher than average amounts. These include cassiterite, wolframite, tantalite-columbite, euxenite, monazite, eschynite, keilhauite, zinnwaldite, beryl, lepidolite, biotite, wilkite, zircon, garnet, and allanite. Three scandium minerals are known: thortveitite, $(\text{Sc, Y})_2(\text{Si}_2\text{O}_7)$, found in certain complex pegmatites; sterrettite, $\text{Sc}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$, found sparingly in brecciated zones in phosphate rocks; and a variety of beryllium-bearing sterrettite, called kolbeckite, found only rarely

in quartz-wolframite veins. Some varieties of beryl (bazzite) are relatively rich in scandium, containing up to 10 per cent Sc.

Scandium oxide and metal are obtained from thortveitite ore, yttrium and rare-earth metal ores, and from the residues of wolframite and cassiterite concentrates. The resource of scandium in various uranium ores and phosphate deposits is very large.

The common elemental associates of scandium in its deposits are Li, Rb, Cs, Be, Y, rare earths, Ti, Zr, Hf, Nb, Ta, Mo, W, Fe, B, Sn, Bi, U, Th, P, and F. Of these the best indicators are Y, rare earths, U, Th, W, Sn, Ta, Nb, P, and F. Scandium should prove useful as an indicator of its deposits, and those of the rare earths, in soil, till, stream sediment, and vegetation surveys. Other good indicator elements in such surveys are the rare earths and yttrium. All pegmatites and greisenized, sericitized, and fluoriferous granitic and other types of rocks, rare earth and uranium-thorium deposits of all types, tin and tungsten deposits, and phosphate deposits, should be analyzed carefully for scandium if a commercial source for this element is sought.

Yttrium, lanthanum, cerium, and the other rare earth metals are widely diffused in all types of igneous, sedimentary, and metamorphic rocks. Concentrations occur, however, only in certain pegmatites, in certain vein-like deposits, in some skarns, in certain quartz-pebble conglomerates, in phosphorites, and in placers.

The principal types of deposits of these metals are as follows:

(1) Pegmatites and coarse-grained granitic rocks: The common minerals in these deposits are monazite, thorite, uraninite, cerite, allanite, euxenite, pyrochlore, samarskite, fergusonite, gadolinite, yttrifluorite, xenotime, thortveitite, gagarinite, wiikite, and thalenite. The elements commonly enriched with Y and the other rare earths in pegmatites are Li, Rb, Cs, Be, Sr, Ba, Sc, Ti, Zr, Hf, Nb, Ta, Mo, W, B, Sn, Bi, U, Th, P, and F. There is a marked and nearly constant affinity with thorium, phosphorus, and fluorine.

(2) Skarn deposits: In these the minerals apatite, fluorite, garnet, monazite, allanite, epidote, vesuvianite, scheelite, and sphene are the principal carriers of the rare earth elements and thorium. Few of these deposits are of commercial importance. The principal elements associated with the rare earths in skarn deposits are F, P, Ti, Th, Sc, and the numerous other elements concentrated in skarn.

(3) Monazite 'veins' or 'lodes': The principal example of this unusual type of deposit is in South Africa near Nieuwe Rust, VanRhynsdorp Division. The orebody is an irregular 'vein' in a shear zone in altered granite of Precambrian age. The main minerals are apatite, monazite, zircon,

and iron and copper sulphides. Its origin is obscure. The elements concentrated are rare earths, Th, Zr, P, Fe, and Cu.

(4) Rare earth carbonate veins and masses: The principal example of this type of deposit is near Mountain Pass, San Bernardino County, California. The orebody consists of bastnaesite, the cerium fluocarbonate, barite, apatite, pyrite, galena, chalcopyrite, fluorite, carbonates, parisite, monazite, allanite, cerite, and sahamalite. The elements concentrated include rare earths, Th, Ba, Sr, Pb, Cu, P, and F. The deposit exhibits certain affinities with carbonatites.

(5) Fluorite and apatite veins and lodes: Some varieties of fluorite and apatite are enriched in the rare earths. Their potential as a commercial source is unknown. (See also the discussions under fluorine and phosphorus).

(6) Carbonatites: These deposits frequently contain higher than average amounts of rare earths and thorium in a variety of titanium, niobium, and other minerals. (See further the discussion under niobium). Carbonatites are not generally considered as a primary commercial source of rare earth elements, but the elements can be recovered as by-products in some cases.

(7) Pyritic quartz-pebble conglomerates: The principal examples of these deposits are the Elliot Lake uranium pyritic quartz-pebble conglomerates of Ontario where the rare earths and thorium occur in a brannerite-uraninite-monazite mineral assemblage. The principal elements concentrated are U, Th, Sc, Y, rare earths, Fe, As, and S. Similar deposits, although not as rich in thorium and rare earths, occur in the Rand of South Africa and at Jacobina in Brazil. These deposits are greatly enriched in Au and Ag and contain some uranium.

(8) Phosphorites: Most of these deposits contain traces of rare earths, as well as scandium, uranium, and thorium. The potential by-product reserve of these elements in the phosphorites is enormous. (See also the section on phosphorus.)

(9) Placers: These have long been a source of rare earths and thorium minerals of which the most important are monazite and xenotime. Associated minerals often of commercial importance in beach, stream and other types of placers include ilmenite, leucoxene, magnetite, cassiterite, rutile, zircon, staurolite, garnet, and gold.

The best indicators of rare earths deposits in geochemical surveys utilizing soils, tills, stream sediments, and vegetation are the elements themselves particularly yttrium, lanthanum, and cerium. Phosphorus and fluorine are also excellent indicators, and many of the associated elements in the deposits noted above can probably be used under certain conditions. The

use of some of these elements, however, such as Ba, Sr, Ti, Nb, U, and Th should be preceded by adequate testing for their suitability in any given area.

Thorium is widely distributed in most rocks but only in trace amounts. The deposits of thorium are essentially the same as those mentioned above for the rare earths and below for uranium. The elements accompanying thorium are, likewise, the same as those for the rare earths and uranium in most deposits. Thorium may be indicated by its radioactivity, and the element can be used as an indicator of its deposits in most types of geochemical surveys.

Uranium is widely diffused in igneous, sedimentary, and metamorphic rocks, being enriched in the more acidic igneous and metamorphic rocks, in the black carbonaceous shales, and in phosphorites.

The principal types of uranium deposits are as follows:

(1) Certain granitic rocks: These may contain higher than normal amounts of uranium and thorium. Most are not of commercial importance at present but provide a large reserve of uranium and thorium ore for the future. Such bodies are indicated by their higher than normal radioactivity and by enrichments of U, Th, rare earths and frequently P, F, and Zr.

(2) Pegmatites and other coarse-grained feldspar-quartz-mica-pyroxene segregations and migmatites: The principal uranium minerals are uraninite, uranothorite, euxenite, pyrochlore, and fergusonite. Such bodies are marked by their higher than normal radioactivity and by enrichments of U, Th, Sc, Y, rare earths, and frequently Fe (hematite), Nb, Ta, Mo, Ti, Zr, Hf, P, and F.

(3) Calcite-fluorite-apatite, calcite-fluorite-apatite-biotite-pyroxene, and calcite-biotite-apatite veins and segregations: These deposits are common in the Grenville Province of the Precambrian of Eastern Canada. The principal radioactive minerals are uraninite, uranothorite, allanite, beta-fite, zircon, and fergusonite. These bodies are marked by their higher than average radioactivity and by enrichments of U, Th, rare earths, P, F, Nb, Ta, Ti, Zr, and Hf.

(4) Veins, lodes, pipes, and disseminations: These deposits may occur in practically any rock type although most are present in sedimentary rocks, gneisses and schists, and granitic bodies. The principal primary radioactive mineral is uraninite (variety pitchblende). In some deposits the accompanying minerals are calcite, hematite, quartz, pyrite, chalcopyrite, and a few selenides. The principal enriched elements in these deposits are U, Ca, Mg, Fe, S, Cu, and Se; thorium and rare earths are only slightly enriched in the ores in contrast to the uranium deposits in granitic rocks, pegmatites, etc. In other deposits the accompanying minerals comprise calcite, quartz, hematite, native silver, chalcopyrite, pyrite, galena, sphalerite,

arsenopyrite, abundant nickel-cobalt arsenides, native bismuth, and various antimonides and sulphosalts. The characteristic elements concentrated in these deposits include U, Ca, Mg, Fe (hematite and pyrite), S, As, Cu, Ag, Pb, Zn, Ni, Co, Bi, Sb, and Hg.

Pitchblende veins, lodes, pipes, and disseminations are frequently marked by characteristic coloured ochres in shades of yellow, orange, and green. The ochres consist of various secondary uranium minerals such as gummite and uranophane and various secondary iron, cobalt, and nickel minerals including limonite, erythrite, and annabergite. Few Canadian pitchblende deposits are deeply oxidized, but one, the Gunnar deposit in northern Saskatchewan, contains uranophane down to considerable depths.

(5) Sandstone deposits: These occur in porous beds, in rolls and pinch-outs, in fractures and brecciated zones, in zones containing abundant coalified wood, and in various other sites amenable to precipitation of minerals from circulating waters. The principal primary uranium mineral is uraninite which is associated with a variety of copper and vanadium minerals. Near the surface a host of secondary uranium, vanadium and copper minerals are usually developed. The characteristic elements concentrated in these deposits are numerous and diverse and include U, V, Sr, Ba, Cr, Mo, Fe, Co, Ni, Cu, Ag, Au, Zn, Cd, Pb, P, As, Sb, S, and Se. Some of these deposits are similar to the 'red bed' sandstone deposits discussed under vanadium, copper, and silver.

(6) Pyritic quartz-pebble conglomerates: These deposits are the same as those discussed under (7) in the section on rare earths. The principal primary uranium minerals are brannerite and uraninite. The principal elements concentrated are U, Th, Sc, Y, rare earths, Fe, As, and S: in some deposits Au and Ag are enriched and are won from the deposits.

(7) Carbonatites: Some of these deposits contain small amounts of uranium. (See the further description under niobium.) Carbonatites are not considered to be a commercial source for uranium at the present time, although the element could probably be obtained from some deposits as a byproduct.

(8) Black shales: Certain black carbonaceous shales are considerably enriched in uranium and a host of other elements, particularly those of chalcophile character, including Ag, Zn, Cu, Pb, Ni, Co, and other elements.

(9) Phosphorites: In some areas these rocks are enriched in uranium, rare earths, and a great variety of other elements, particularly those of chalcophile character such as Ag, Pb, Zn, Cu, etc. (See also the discussion in the section on phosphorus.)

(10) Coal and lignite: Some varieties of coal and lignite contain higher than average amounts of uranium.

(11) Placers: Monazite placers and others containing minerals such as xenotime, fergusonite, etc., may contain small amounts of uranium. (See also the description under rare earths.) Few placers are of economic importance for uranium.

Uranium is an excellent indicator of its deposits in practically all types of geochemical surveys, including those based on radioactivity. Depending on the types of deposits and the elements concentrated in them as outlined above, there are also a number of other indicator elements which can be used effectively in geochemical prospecting for uranium. These include Th, rare earths, P, F, Co, Ni, As, Sb, V, Ag, Cu, and a number of others noted above. Some of these are useful in soil and stream sediment surveys. Others may be useful in water surveys. Selenium indicator plants and the selenium content of certain plants may be useful in locating deposits of the sandstone type. Carbonates, quartz, and fluorite, coloured or darkened by radioactive bombardment are good indicators of uranium (and thorium) in certain veins and other types of deposits.

GROUP IVA: CARBON, SILICON, GERMANIUM, TIN, AND LEAD

Carbon is concentrated in coal, petroleum, natural gas, various solid hydrocarbons, and several types of carbonaceous and graphitic shales and schists. Graphite veins and lodes are common in certain sediments.

Hydrocarbon analyses are particularly useful in geochemical prospecting for petroleum and natural gas.

Silicon is the most abundant electropositive element in the rocks of the earth's crust. The deposits of silicon are so well known that they need little discussion here. Briefly they comprise:

(1) Silicates of all types used for a great variety of purposes too numerous to mention here. The silicates of commercial importance not discussed under the other elements above and below include feldspar, mica, nepheline, pyrophyllite, kyanite, andalusite, sillimanite, dumortierite, talc, wollastonite, and asbestos.

(2) Quartzite, sandstone, and silica sand used for flux, for production of silica brick, and for a great variety of other purposes.

(3) Bentonite and bleaching clay.

(4) Clay for brick and ceramics.

(5) Sand and gravel.

(6) Diatomite.

(7) Quartz and quartz crystal.

Prospecting for these types of deposits is guided mainly by geological principles. Where the content of silica is a consideration direct analyses for this element will decide the commercial importance of a deposit.

Germanium is a relatively rare semimetallic substance that forms several rather uncommon minerals of which the best known are argyrodite, Ag_8GeS_6 , germanite, $\text{Cu}_3(\text{Fe, Ge})\text{S}_4$, and renierite, $\text{Cu}_3(\text{Fe, Ge})\text{S}_4$. None of the germanium minerals form deposits of commercial importance. The element is also a trace to minor constituent in various sulphides and sulphosalts, particularly sphalerite, cinnabar, enargite, pyrargyrite, and some tin-bearing sulphides.

Industrially, germanium is obtained from sphalerite concentrates and germanium-bearing sulphide ores during smelting and electrolytic reduction. A potential source of commercial germanium is certain coals and lignites which contain relatively large amounts of the element in some places.

The elements accompanying germanium in deposits are the same as those mentioned for zinc, mercury, silver, tin, copper, arsenic, antimony, and the other elements in polymetallic deposits. Ores, coal, lignite, and smelting residues suspected to contain germanium in commercial quantities should be analyzed directly for the element.

Tin is a common metal that forms several minerals of commercial importance, including cassiterite, stannite, teallite, cylindrite, and franckite. Cassiterite is the most important industrial source of tin.

Deposits of tin are varied and include the following:

(1) Pegmatites and coarse-grained granitic masses: The principal mineral is cassiterite. The main associated minerals are wolframite, scheelite, tantalite-columbite, bismuth, arsenopyrite, beryl, fluorite, tourmaline, lepidolite, spodumene, petalite, triphylite, amblygonite, and molybdenite. The characteristic elements concentrated are Sn, W, Ta, Nb, Bi, As, Be, B, F, Li, Rb, Cs, and Mo. There is a nearly constant association of tin and tungsten in pegmatites. The association with lithium is also marked.

(2) Skarn deposits: Few of these are commercial sources of tin. The principal mineral is cassiterite. Associated minerals are the calcium-magnesium-iron silicates, wolframite, scheelite, fluorite, tourmaline, axinite, ludwigite, hulsite, paigeite, danburite, vesuvianite, scapolite, galena, sphalerite, arsenopyrite, copper sulphides, pyrrhotite, molybdenite, and magnetite. The elements concentrated include, Sn, W, B, F, Be, Cu, Pb, Zn, As, Mo, and Fe. There is generally a close association between Sn, W, B, and F in most skarn deposits.

(3) Veins, lode deposits, and disseminations in greisen and sericitized zones: Some of these deposits contain essentially cassiterite with some pyrite, pyrrhotite, copper sulphides, molybdenite, arsenopyrite, wolframite, scheelite, bismuth, bismuthinite, galena, and sphalerite; rarely beryl. The gangue minerals are invariably quartz, fluorite, zinnwaldite and other lithium-bearing micas, topaz, tourmaline, axinite, apatite, specularite, magnetite, ilmenite, and chlorite. The characteristic elements concentrated are Sn, W, Mo, Li, Rb, Cs, Be, Sc, Fe, Cu, Zn, Cd, Pb, B, As, Bi, S, P, and F. Other veins contain much cassiterite with stannite, cylindrite, teallite, and a great variety of copper, iron, zinc, lead, and silver sulphides, arsenides, and sulphosalts. In these the elements concentrated are the same as those mentioned above with the addition of Ag, Au, Ga, In, Tl, Ge, and Sb. Lithium does not seem to be concentrated in the latter veins to the extent that it is in the former.

(4) Cassiterite pipes: These are unusual types of deposits that take the form of chimneys and pipes frequently in granitic rocks, gneisses, and sedimentary rocks. Some are developed in limestones and bear a certain relationship to the skarn deposits. Examples of those in granitic rocks and sediments are common in New South Wales and in the Potgietersrust district of the Transvaal, South Africa. The principal mineral in the pipes is cassiterite. In granitic rocks and sediments the associated minerals are mainly sericite, tourmaline, fluorite, various sulphides, specularite, and chlorite. In the pipes in limestone, described from the Kinta Valley, Malaya, arsenopyrite, tremolite, fluorite, calcite, and hydrated borates are common. There is a close association of Sn, B, F, and sometimes As in the cassiterite pipes. W is enriched in some of the pipes.

(5) Massive sulphide deposits: Some of these contain traces of tin in cassiterite and as a constituent of sphalerite, galena, and other sulphides. A few such as the Sullivan deposit in British Columbia have small amounts of tin ore often associated with extensive tourmalinized zones. None of these deposits can be considered as important commercial sources of tin. The best indicators of tin in massive sulphide deposits appear to be B, Bi, In, Tl, Cd, Ge, Sb, and As.

(6) Placers: Both eluvial and alluvial placers provide most of the world's supply of tin. The principal mineral is cassiterite with smaller amounts of wolframite and the numerous other minerals commonly found in placers. Deposits of this type are developed extensively in Malaya, Indonesia, Thailand, Congo, and Nigeria.

Tin is a good indicator of its deposits in most types of soil, stream sediment, and vegetation surveys. The natural compounds of the element are relatively insoluble, and hence water surveys are not suitable for geochemical prospecting for tin deposits. Depending on the types of deposits and the concentration of elements in them other indicators of tin are generally effective in most types of geochemical surveys. These include particularly W, Li,

B, Be, and F. For the polymetallic types of tin deposits Cu, Pb, Zn, Ag, Cd, As, Sb, and Bi may be useful indicators.

Wad, limonite, humic, and other precipitates at the orifices of springs may be enriched in Sn, W, and Li, as well as in other elements associated with tin in its deposits. These may serve as useful indicators in some areas.

Lead is obtained from a variety of deposits most of which also contain Zn, Cd, and Cu. These deposits are discussed under these elements and need not be repeated here. The most common elemental associates of lead are Zn, Cd, Ag, Cu, Ba, Sr, V, Cr, Mn, Fe, Ga, In, Tl, Ge, Sn, As, Sb, Bi, Se, Hg, Te, and more rarely B and F. All of these elements can be used as indicators of lead deposits in geochemical surveys, but the best are Zn, Cd, Ag, Cu, Ba, As, and Sb. The natural compounds of lead are relatively insoluble, and hence water surveys utilizing lead are rarely effective. All precipitates, especially those containing manganese, at spring orifices should, however, be analyzed for lead since these often indicate the presence of lead deposits in the environment in which they occur.

GROUP IVB: TITANIUM, ZIRCONIUM, AND HAFNIUM

Titanium is widely diffused in most rock types being present in the largest amounts in basic rocks. Numerous titanium minerals are known, but those of commercial importance include only rutile, anatase, leucoxene, brookite, and ilmenite. Titaniferous magnetite and sphene are common, but they are not generally used as an ore of titanium. Their deposits provide a titanium reserve for the future.

Titanium is notable for the large number of unusual and generally complex types of primary deposits. Some of these are associated with gabbroic bodies especially anorthosites; others are affiliated with alkali syenites and/or carbonatites. Several complex deposits contain an unusual assortment of minerals of which apatite is most common. Titanium minerals are also concentrated in residual deposits and placers, and the element is a constituent of certain bauxites and laterites.

The elements most commonly concentrated in primary titanium deposits are mainly Ti, Fe, Ca, F, and P. Some contain minor amounts of Fe, Cu, and other sulphides. The residual and placer deposits contain mainly rutile, ilmenite, magnetite, and other common resistate minerals concentrated during weathering processes.

Titanium is a good indicator of its deposits in soil, till, and stream sediment surveys. Its use in vegetation is uncertain, although it is known that some plants tend to concentrate higher than average amounts of titanium. The natural compounds of titanium are all relatively insoluble, and hence the use

of the element in water surveys is generally not effective. Precipitates at spring orifices, however, are frequently enriched in titanium in terranes where deposits of the element are present. The use of ancillary indicators in geochemical prospecting for titanium deposits has not received much attention. It would seem that phosphorus may be a good indicator for certain deposits and iron for others. Panning of all streams, placers, beach deposits, and dunes followed by mineralogical and spectrographic analyses can be used to outline residual and placer deposits and may also be a useful guide to the location of primary deposits.

Zirconium and hafnium are two elements that invariably occur together in nature and are obtained commercially from the same sources. Zirconium forms several minerals but only zircon, the silicate, and baddeleyite, the oxide, provide an industrial source for the element. Hafnium forms no known minerals but is a constant constituent of both zircon and baddeleyite.

The principal commercial source of zirconium and hafnium is zircon and baddeleyite in beach sands, dune sands, stream placers, and eluvial deposits. The principal minerals accompanying the zirconium minerals are ilmenite, leucoxene, rutile, staurolite, tourmaline, sillimanite, kyanite, and quartz. Most of these minerals, including zircon, derive from the deep weathering of granite, granitic pegmatites, and other rocks in which zircon is an accessory mineral. The baddeleyite deposits of Brazil occur mainly in alluvial and eluvial deposits and consist of fibrous baddeleyite, amorphous ZrO_2 , zircon, and altered zircon. These minerals are derived mainly from the deep pervasive weathering of a carbonatite complex comprising augite syenite, foyaite, phonolite, nepheline syenite, and other alkaline rocks. Some baddeleyite and amorphous ZrO_2 also apparently occur in vein-like masses in these deeply weathered rocks.

Disseminations and concentrations of zircon, eudialyte, catapleiite, l  venite, baddeleyite, and other zirconium minerals frequently occur in nepheline syenite bodies and in their pegmatites; also in certain masses of apatite and in pyroxene-mica-apatite veins or 'pegmatites'. Some of these minerals could perhaps be obtained as byproducts of the mining of these bodies.

Recently baddeleyite has been produced from carbonatites, especially at Phalaborwa, South Africa. For further discussion of these deposits see the section on niobium.

Zirconium is a good indicator of its deposits in soil, till, and stream sediment surveys. Its use in vegetation surveys has not been investigated extensively, although it is known that some plants near zirconium deposits contain higher than normal amounts of the element. Zirconium is a nearly constant constituent of natural waters, and some spring waters are relatively enriched in the element. There are no data, however, on the effectiveness of hydrogeochemical surveys for locating zirconium deposits. Spring precipitates should, however, be carefully analyzed for zirconium as these usually

are enriched in the element in terranes containing zirconium deposits. Heavy mineral surveys of beach, dune, stream, and residuum should be effective in outlining possible zircon and baddeleyite placers. Furthermore, zircon usually contains some thorium and a little uranium, the disintegration products of which give most zircon sands and placers a slightly higher radioactivity than that normally found in sands and gravels.

Zirconium and hafnium are accompanied by Ti, Nb, Ta, Be, P, F, and rare earths in nepheline syenites and their pegmatites and by Ti, Th, rare earths, P, and locally Sn and W in placer deposits. Each of these diagnostic elements may serve as indicators of zirconium under favourable conditions. The elements characteristically concentrated in carbonatites (see the section on niobium) may also be useful in indicating zirconium deposits in these deposits.

GROUP VA: NITROGEN, PHOSPHORUS,
ARSENIC, ANTIMONY, AND BISMUTH

Nitrogen is concentrated in three materials in the earth - in the atmosphere, in coal, and in certain nitrate deposits. It is obtained commercially from all three. Most of the commercial nitrogen compounds are obtained by "fixing" atmospheric nitrogen. A smaller amount of nitrogen compounds are recovered from byproducts of the coke industry as aqua ammonia or ammonium sulphate. Considerable quantities of nitrates are still obtained from nitrate deposits, particularly those in Chile. A little nitrogen gas is obtained from certain nitrogen-bearing natural gas wells. Some nitrogenous fertilizer materials are obtained from guano, byproducts of meat and fish plants, cotton seed and other seed mills, and processed sewage.

The principal types of nitrate deposits are cave, playa, and caliche deposits. Only the latter are of commercial importance. They occur in very arid regions, generally bordering salars and playa mud flats, and consist of beds and irregular lenses a few inches to several feet thick often overlain by loose sand and gravel. The nitrates are associated with a large number of other salts which frequently show a gradation in chemical composition downward in the regolith. At the top sodium sulphate, gypsum, sodium chloride, bloedite (Mg, Na, sulphate) and rarely ulexite (Ca, Na, borate) predominate. This zone grades into an intermediate one containing sodium chloride, various sulphates and increasing amounts of the chlorides and nitrates of sodium, potassium, and magnesium. Below this zone lies the 'caliche' of commerce. Here the principal cementing salts are sodium nitrate, potassium nitrate, sodium chloride, anhydrite, gypsum, mirabilite, thenardite, bloedite, epsomite, and a suite of rarer salts containing nitrate, chlorate, iodate, and boron. The salts concentrated in the nitrate deposits are mainly those of the elements Na, K, Li, Mg, Ca, Sr, Ba, Cr, Mn, B, N, Cl, Br, and I.

Those searching for nitrate deposits should be guided mainly by geological principles and should analyze all materials suspected of containing commercial nitrates. Groundwaters and springs high in soluble nitrates may be useful guides under certain conditions. Bromine, iodine, and boron analyses may be useful in testing caliche, waters, and other materials for concentrations of these elements associated with nitrate deposits.

Phosphorus is widely distributed in all rocks but generally only in small amounts. The basic rocks tend to have the highest contents of the element. The most common and commercial phosphate minerals are those of the apatite series, amblygonite, and monazite. Less common are xenotime, vivianite, pyromorphite, wavellite, cacoenite, lazulite, and the various uranium phosphates.

Phosphorus is concentrated in a great variety of deposits and is also won as a byproduct of various industrial processes. The principal commercial sources of phosphates are the massive apatite deposits associated with alkaline rocks such as nepheline syenite and the sedimentary phosphorites.

Briefly the types of phosphate deposits are as follows:

(1) Apatite veins, pockets, and segregations in or associated with metamorphic pyroxenites and other granitized sediments (Grenville type).

These deposits are irregular veins, chimneys, and segregations of apatite frequently in a gangue of calcite, pyroxene, and phlogopite. The country rocks are metamorphic pyroxenites, crystalline limestones, or biotite gneiss. The principal elements concentrated in these deposits are Ca, Mg, Fe, Si, Al, Fe, S, rare earths, Ti, Zr, P, F, Cl, and C (graphite).

(2) Apatite lenses, disseminations, veins, etc. in or associated with alkaline syenites, carbonatites, and similar complexes. Apatite is the principal mineral, and it is frequently mixed with nepheline, various other alkali silicates, aegirite, titaniferous magnetite, magnetite, sphene and pyrochlore. The characteristic elements concentrated in these deposits are mainly Na, Ca, Sr, Ba, Fe, Ti, V, Nb, Ta, rare earths, Zr, Th, U, P, and F. (See also the section on niobium.)

(3) Marine phosphorites: These are categorized as shell phosphates and chemically or organically precipitated phosphorites. Only the latter are exploited commercially. The principal mineral of importance in them is colophonite, a microcrystalline variety of apatite. The phosphorites occur in beds from a few inches to a few feet thick and are interbedded with mudstone, limestone, phosphatic mudstone, and shale. Where such beds are weathered and leached they give rise to pebble- and other types of residual rock phosphate deposits.

Phosphorites generally contain a large number of diverse elements among which U, V, F, Se, As, rare earths, Cr, Ni, Zn, Mo, and Ag are most commonly enriched. In most places these appear to have been precipitated with the phosphorites; elsewhere they may be adsorbed from circulating groundwater.

Phosphorus is a good indicator of phosphate deposits in most types of soil, till, and stream sediment surveys. Increased contents of phosphates in groundwaters and in springs may also be useful in certain areas for outlining zones containing apatite and phosphorite deposits. All sedimentary rocks should be scrutinized carefully for phosphorites, and suspected sections should be analyzed directly for their phosphorus content when searching for commercial deposits. The various elements noted above that are concentrated in phosphorites and other apatite deposits may be useful as ancillary indicators of phosphorus in all types of geochemical surveys.

Arsenic is widely diffused in most rocks but only in amounts of a few parts per million. Most of the arsenic in rocks is present in sulphides particularly pyrite or in accessory minerals such as apatite. The common minerals of arsenic are native arsenic, realgar, orpiment, niccolite, loellinite, cobaltite, arsenopyrite, and a great variety of sulphosalts of which the most common are tennantite and enargite.

Most of the arsenic of commerce is obtained as a byproduct of the smelting and reduction of lead, copper, silver, and gold ores. The principal types of deposits in which arsenic is a constituent are as follows:

- (1) Skarn deposits: Arsenic is generally associated with Cu, Pb, Zn, Au, Ag, Mo, and Fe in these deposits, and less commonly with W, Sn, Bi, Sb, and Te.
- (2) Polymetallic deposits of various types: The elements concentrated with arsenic are generally Pb, Zn, Cd, Cu, Ag, Au, Ni, Co, Bi, Fe, Sn, Mo, W, U, Se, Te, Sb, Ga, In, Tl, and Ge.
- (3) Realgar-orpiment deposits: These are rare and constitute veins, pockets, and disseminations in various types of rocks. The elements associated with arsenic include S, Sb, Ag, Pb, Cu, Fe, Au, F, and rarely Hg.

Geochemical surveys are not generally mounted to discover arsenic deposits, but the element is a particularly useful indicator of various other types of deposits particularly those of gold, silver (Cobalt type), copper, lead, and zinc. Under certain conditions it may be useful in locating nickel and cobalt deposits and those of tin and tungsten. Arsenic responds well in all types of soil, stream sediment, and vegetation surveys and is also useful in ground, spring, and stream water surveys. All precipitates, especially those containing limonite and wad, should be carefully analyzed for arsenic as these

usually reflect the presence of arsenic (and hence the possible presence of other elements) in the terrane in which they occur. Arsenic tends to be enriched more in limonite precipitates than in wad.

Antimony is present in most rocks in only a few tenths of a part per million, mostly in sulphides and particularly in pyrite. Commercially the element is obtained from stibnite ores and their oxidation products and as a byproduct of the smelting and reduction of the ores of lead, zinc, copper, silver, and gold. The element forms numerous minerals of which the most important are stibnite, tetrahedrite, and the oxides valentinite, senarmontite, and cervantite.

Briefly, the deposits of commercial importance containing antimony can be listed as follows:

(1) Polymetallic deposits: In these antimony is present in stibnite, native antimony, and various sulphosalts among which tetrahedrite is predominant. Some deposits are deeply weathered and contain many secondary antimony oxides and other antimony minerals. In these deposits antimony is associated with Cu, Pb, Zn, Cd, Ag, Au, Ni, Co, Bi, Fe, Sn, Mo, W, U, Se, Te, Sb, Hg, Ga, In, Tl, and Ge.

(2) Stibnite deposits: These are mainly quartz veins, quartz stockworks, or siliceous replacement deposits with stibnite in seams, nests, and vugs. The principal associated minerals are pyrite, marcasite, barite, calcite, and kaolinite. Some contain realgar, orpiment, native sulphur, cinnabar and a few have some ferberite, FeWO_4 . Others have small amounts of scheelite, arsenopyrite, sphalerite, silver-bearing sulphosalts, gold, electrum, gypsum, and alunite. The principal elements concentrated in these veins are Sb, Si, Fe, Mn, Ba, Hg, W, As, Zn, Ag, Au, and Ca.

Geochemical surveys are not generally carried out to discover antimony deposits, but the element is a particularly useful indicator of various other types of deposits especially those of silver, copper, gold, lead, and zinc. Under suitable conditions it should also be particularly useful for locating the stibnite type of deposit. Antimony responds well in all types of soil and stream sediment surveys and is also useful in ground, spring, and stream waters, especially where these form limonite, manganese, and other precipitates. These precipitates generally reflect the presence of antimony (and hence the possible presence of other elements) in the terrane in which they occur. There is little information on the use of antimony in vegetation surveys, although it is known that some plants take up considerable amounts of antimony in the vicinity of antimoniferous deposits.

Bismuth occurs only in very small amounts in rocks, generally less than 0.1 ppm. Most of the bismuth of commerce is obtained from a variety of polymetallic deposits, especially those containing molybdenum, tin, tungsten, copper, lead, silver, and gold. The most common primary ore

minerals of bismuth are native bismuth and bismuthinite; of less importance are cosalite, galenobismutite, and tetradymite. The principal secondary or supergene minerals are bismutite and bismite.

The principal types of deposits in which bismuth is a constituent are:

(1) Pegmatites, aplites, pipes, and stockworks; these generally occur in granitic bodies or in high grade metamorphic schists and gneisses. The common bismuth minerals are native bismuth, bismuthinite, and cosalite; rarely bismutotantalite. Accompanying minerals in addition to quartz, feldspar, and mica are molybdenite, cassiterite, wolframite, and scheelite; also beryl, tantalite-columbite, spodumene, lepidolite, and uraninite in some deposits. The characteristic elements concentrated with bismuth are Li, Rb, Cs, Be, Sc, rare earths, Cu, Ti, Nb, Ta, Mn, Mo, W, B, Sn, U, Th, and As.

(2) Skarn deposits: In these the bismuth is associated with Cu, Pb, Zn, Sn, W, Mo, Ni, Au, Ag, and the various other elements concentrated in skarn. The Gaspé copper deposits Gaspé, Quebec, produce bismuth from copper-molybdenum ores in skarn.

(3) Bismuth in tin and tungsten deposits: A large part of the world's production comes from this source. The principal minerals are bismuth and bismuthinite. The elements with which bismuth is closely associated in these deposits include Sn, W, Sb, Ag, Fe, As, Pb, Mo, Cu, Zn, Ba, P, and B.

(4) Bismuth concentrations in complex nickel-cobalt-arsenide deposits: The minerals of importance are bismuth and bismuthinite associated with native silver, calcite, nickel-cobalt arsenides, dyscrasite, and uraninite. The elements concentrated in these deposits are Bi, U, Fe, Co, Ni, Mo, Cu, Ag, Zn, Cd, Pb, Hg, As, and Sb.

(5) Bismuth concentrations in lead-zinc-silver and copper deposits. The element is obtained as a byproduct of these ores.

(6) Bismuth concentrations in gold deposits: Bismuth occurs in the native form, in maldonite, in various bismuth tellurides, and in goldfieldite, cosalite, and bismuthinite. There is usually insufficient bismuth to warrant recovery of the metal.

(7) Cosalite deposits: Cosalite is found in a variety of deposits particularly in veins, but also in skarn deposits and certain pegmatite-like bodies. In places it is abundant enough to constitute a bismuth ore. The usual associated minerals are quartz, various lead, zinc, copper sulphides and sulphosalts, and cobaltite.

(8) Secondary (supergene) bismuth deposits: These are derived from the preceding types of deposits and contain bismuthite, bismite, arsenobismite, and corroded native bismuth and bismuthinite. Some of these deposits have been worked for bismuth in the past.

Geochemical surveys are not generally mounted to discover bismuth deposits, but the element is often a good indicator of various types of deposits, particularly those containing Sn, W, Mo, U, Cu, Pb, Zn, Au, and Ag. Bismuth responds well in geochemical surveys using soils and stream sediments. Because of its relative insolubility it is immobile in soils and weathered residuum and remains close to the deposits. Spring precipitates also reflect the presence of bismuth in terranes in which it occurs in deposits.

GROUP VB: VANADIUM, NIOBIUM, AND TANTALUM

Vanadium is widely dispersed in most rock types but only in small amounts. The basic rocks are usually highest in the element. Vanadium forms a large number of minerals of which the most common are the sulphide patronite, carnotite, roscoelite (vanadium mica), descloizite, and vanadinite. Titaniferous magnetite also contains some vanadium, the amount ranging from 0.1 to 1 per cent V_2O_5 .

Vanadium can be obtained commercially from the following types of deposits:

(1) Titaniferous magnetite deposits associated with gabbros and anorthosites: The principal ore mineral is magnetite. The characteristic elements concentrated are V, Ti, Fe, and P.

(2) Vanadium-bearing uranium deposits in sandstone; these are widespread in the Western United States. The principal minerals are carnotite, roscoelite, montroseite, vanoxite, corvusite, and various other vanadates. Uranium and copper minerals are also common. The elements concentrated in these deposits are numerous and diverse and include U, V, Sr, Ba, Cr, Mo, Fe, Co, Ni, Cu, Ag, Au, Zn, Cd, Pb, P, As, Sb, S, and Se. Some of these deposits are similar to the 'red bed' sandstone deposits discussed under uranium, copper, and silver.

(3) Deposits associated with asphalt and other solid hydrocarbons: The best known deposit of this type occurs at Minas Ragra, Peru, where calcium vanadate and patronite fill cracks and fissures in shale and are associated with masses of asphalt material. The characteristic elements concentrated in these deposits are V, S, C, Ni, Fe, and Ca.

(4) Vanadium in various polymetallic deposits: These are generally copper, copper-lead-zinc, or lead-zinc deposits the oxidized parts of which

yield descloizite, vanadinite, mottramite and other lead, zinc, and copper vanadates. These deposits provide rich vanadium ores in places. These oxidized ores are generally enriched in Cu, Pb, Zn, V, Mo, Ag, Au, and As.

(5) Vanadium in phosphorites and vanadiferous shales: These deposits provide a large reserve of vanadium for the future. Few are now commercially exploited. (See the discussion on phosphorites under phosphorus.)

(6) Vanadium in sedimentary iron ores: Certain sedimentary iron ores are enriched in vanadium. The characteristic accompanying elements are Mn and P.

(7) Vanadium in petroleum: Vanadium can be obtained from petroleum residues and flue dusts.

(8) Vanadium in coal ashes: Some coal ashes are rich in vanadium.

(9) Placers containing vanadiferous titaniferous magnetite.

Vanadium is a good indicator of its deposits and responds well when using geochemical surveys based on soils, tills, and stream sediments. Little work has been done on vegetation surveys and those using natural waters. It is known, however, that stream and spring precipitates tend to be enriched in vanadium in terranes containing vanadium deposits. Analyses of titaniferous magnetite obtained during heavy mineral surveys may be a useful guide to vanadiferous magnetite deposits. The various elements listed in the discussion above may indicate the presence of vanadium deposits. The effectiveness of any of these elements is, however, relatively unknown.

Niobium is a rare metal that is concentrated in certain pegmatites, albite granites, carbonatites, and the residual, eluvial, and alluvial placers derived from these bodies. The principal minerals of niobium are pyrochlore, fergusonite, the columbite-tantalite series, the tapiolite-mossite series, betafite, the euxenite-polycrase series, niobian perovskite, samarskite, the eschynite-priorite series, and niocalite. Most of the niobium of commerce is obtained from columbite-tantalite and pyrochlore.

The principal deposits of niobium are as follows:

(1) Granitic pegmatites and certain coarse-grained and fine-grained muscovite granites: These usually contain columbite-tantalite, fergusonite, euxenite-polycrase, samarskite, or eschynite-priorite accompanied generally by cassiterite, wolframite, beryl, spodumene, and other lithium minerals. The characteristic elements concentrated in these deposits include Nb, Ta, Sn, W, Li, Be, Ti, Rb, Cs, rare earths, U, Th, B, Zr, Hf, and W.

(2) Albite-biotite granites and albite-riebeckite granites: The principal minerals in these bodies are tantalite-columbite, pyrochlore, cassiterite, zircon, thorite-orangite, xenotime, monazite, cryolite, and topaz. The elements concentrated include Nb, Ta, Sn, W, Zr, Th, U, rare earths, P, Al, and F.

(3) Carbonatites: These alkaline rocks form rings and elongated complexes and contain a most diverse assemblage of minerals including various alkaline silicates, carbonates, biotite, magnetite, apatite, barite, baddeleyite, pyrochlore, betafite, niobian perovskite, niocalite, monazite, and various rare earth phosphates and carbonates. Some contain economic concentrations of copper minerals. The elements concentrated in carbonates are Na, K, Fe, Ba, Sr, rare earths, Ti, Zr, Hf, Nb, Ta, U, Th, Cu, Zn, P, S, and F.

(4) Residual, eluvial, and alluvial deposits derived from the preceding three types. The principal minerals obtained are tantalite-columbite, pyrochlore, cassiterite, zircon, baddeleyite, xenotime, and monazite.

Niobium is relatively immobile in most natural settings, and hence the element is an excellent indicator of its deposits in soil, till, and stream sediment analyses. Water analyses are not generally effective although precipitates from springs in niobian areas frequently report high values in niobium. Plant analyses may be useful in certain areas, as some plants appear to take up considerable amounts of niobium. Heavy mineral surveys of soils and stream sediments are particularly useful if prospecting is carried out in areas containing pegmatites, granites, or carbonatites. The various elements accompanying niobium in deposits mentioned above can perhaps be used as indicators for niobium deposits, although there is little detailed information on their effectiveness. Some investigators have found that Zn, Pb, Mo, V, Sn, Li, Rb, Ba, and Sr are reliable indicators of niobium deposits using stream sediments.

Tantalum is a rare metal that generally accompanies niobium in its deposits. The principal minerals of tantalum are the same as those for niobium. The foregoing discussion on niobium applies, therefore, to most geochemical surveys organized to search for deposits of tantalum.

GROUP VIA: OXYGEN, SULPHUR, SELENIUM, AND TELLURIUM

Oxygen is the most abundant element in the earth's crust and occurs combined in many forms. Industrially oxygen gas is obtained from the atmosphere by liquifaction processes.

Sulphur is widely diffused in the rocks of the earth's crust being concentrated mainly in the sulphides. It is also a major constituent of many

sulphates, sulphosalts, and a host of other complex minerals. Industrial sulphur is obtained principally from native sulphur deposits and from natural gases containing hydrogen sulphide.

The principal deposits of sulphur and its compounds are:

- (1) Gypsum and anhydrite deposits.
- (2) Massive sulphide and other deposits containing pyrite, pyrrhotite, and the other sulphides. The element is obtained from the smelter gases.
- (3) Native sulphur deposits associated with the cap rocks of salt domes and diapirs.
- (4) Native sulphur deposits associated with gypsum deposits and probably of biogenic sedimentary origin.
- (5) Native sulphur deposits associated with solfataric activity and probably in part of volcanic origin.
- (6) Sulphur in coal; the element is obtained from the coal gases during coking or burning processes.
- (7) Sulphur in sour natural gas and petroleum. Most of the sulphur is present as H_2S , but some is contained in the organic petroleum base. The sulphur is obtained by oxidation of H_2S and during petroleum refining processes.

Those searching for sulphur deposits should be guided by geological principles, and all materials considered to contain sulphur should be analyzed directly for the element. Natural gases should, likewise, be tested directly for their sulphur content. Springs and solfataras containing sulphur may be good indicators of native sulphur deposits in volcanic areas.

Selenium is widely diffused in rocks but in only small amounts. The element is generally concentrated in the sulphides. Numerous selenium minerals are known, but none forms commercial deposits. Most of the selenium of commerce is obtained from refining processes of polymetallic ores, especially copper and nickel.

Geochemical surveys are not generally mounted to discover selenium deposits, but the element is often a useful indicator for several types of deposits. These include uranium deposits of the 'red bed' sandstone type, gold-silver selenide deposits, and various types of polymetallic ores, especially those containing copper, mercury, and silver. Some plants are selenium accumulators and are indicative of selenium in the rocks, especially where selenium accompanies uranium as in the Western United States.

Tellurium occurs in rocks in only a few tenths or hundreds of parts per million. The element forms a number of tellurides, especially with gold, silver, lead, bismuth, and mercury. Tellurates and tellurites are also known. Commercial tellurium is obtained from refining processes of polymetallic ores, especially those containing copper, nickel, and lead.

Geochemical surveys are not generally carried out to discover tellurium deposits. The element may, however, be a relatively good indicator of certain deposits containing silver, gold, and bismuth.

GROUP VIB: CHROMIUM, MOLYBDENUM, AND TUNGSTEN

Chromium is widely diffused in most rocks, being present in the highest amounts in the basic and ultrabasic igneous varieties. The only ore mineral of chromium is chromite, and practically all commercial deposits of the mineral are associated with ultrabasic rocks, and occur as masses, lenses, and disseminations. Many of these ore bodies are closely connected with serpentinization of the ultrabasic bodies.

Chromium is a good indicator of its deposits in practically all types of geochemical surveys with the exception of those based on natural waters. Nickel and cobalt are suitable indicators in soil and stream sediment surveys in some areas; perhaps also in water and vegetation surveys, although there are no suitable data on their effectiveness. Heavy mineral surveys of soils and stream networks followed by mineralogical and spectrographic analyses are particularly useful in prospecting for chromite deposits where there has been some weathering. Even in glaciated regions this method offers considerable success if used judiciously. Wad, limonite, and other precipitates at the orifices of springs are generally enriched in chromium in the vicinity of chromite deposits.

Molybdenum is a trace constituent of most rocks at the parts per million range. It is slightly enriched in acid igneous rocks and in black shales. Several minerals of molybdenum are known, but only molybdenite is of commercial importance at present. Deposits of powellite, $\text{Ca}(\text{Mo}, \text{W})\text{O}_4$, and wulfenite, PbMoO_4 , have been worked in the past.

The principal deposits of molybdenum are as follows:

(1) Pegmatites and aplites: In these deposits molybdenum occurs as molybdenite associated with quartz, feldspar, cassiterite, wolframite, scheelite, fluorite, beryl, tourmaline, bismuth, bismuthinite, copper sulfides, sphalerite, and pyrite. The characteristic elements concentrated are Mo, W, Re, Cu, Sn, Be, B, F, Zn, Bi and Fe. Few of these deposits are of commercial interest.

(2) Quartz veins, quartz pegmatites, quartz segregations, and stockworks: The economic mineral is molybdenite associated with bismuth, bismuthinite, pyrite, chalcopyrite, sphalerite, galena, scheelite, wolframite, topaz, tourmaline, apatite, and fluorite. The characteristic elements concentrated are Mo, W, Re, Bi, Fe, Cu, Zn, Pb, F, P, and S.

(3) Skarn deposits: The molybdenite in these is generally associated with scheelite, bismuth, bismuthinite, copper sulphides, gold, magnetite, pyrite, galena, sphalerite, pyrrhotite, cobaltite, and a great variety of calcium-magnesium-iron silicates. In other deposits typical of the Grenville Province of the Precambrian of Eastern Canada the molybdenite occurs with pyrrhotite, pyrite, and chalcopyrite in metamorphic pyroxenites probably derived from crystalline limestones. The characteristic elements concentrated in the skarn deposits include Mo, W, Re, Bi, Fe, Cu, Au, Ag, Co, Ni, Be, Ti, Zn, Cd, B, As, and S.

(4) Disseminated deposits principally in monzonite but also in various granites, diorites, schists, etc.: Some of these constitute the so called 'porphyry copper' ores from which molybdenite is won as a byproduct. Others contain only molybdenite as the economic mineral. The characteristic elements concentrated in these deposits include Mo, Re, Cu, Ag, Be, Fe, W, Zn, As, B, and F.

(5) Copper shales and 'red bed' sandstone deposits: These carry some molybdenite in places, but the amounts are low. They are not at present a commercial source for molybdenum. For the accompanying elements in these deposits see the discussion of these deposits under the sections on copper and silver.

Molybdenum is an excellent indicator of its deposits and can be used in all types of geochemical surveys utilizing soils, tills, stream sediments, waters and their precipitates, and vegetation. The best ancillary indicator elements of molybdenum appear to be Cu, W, and Bi. The other elements noted above as being concentrated in molybdenum deposits can probably be used in certain areas.

Tungsten is widely diffused in most rocks but only in the parts per million range. Acid rocks such as granites and pegmatites have the highest contents of tungsten. Many minerals of tungsten are known, but the most important commercial ones are scheelite, wolframite, huebnerite, and ferberite.

Geologically tungsten deposits can be classified as follows:

(1) Pegmatites and aplites: The principal minerals are wolframite, huebnerite, and ferberite with subsidiary scheelite. The main associated minerals are cassiterite, beryl, and lithium minerals. The principal elements concentrated are W, Mo, Re, Sn, Cu, As, Nb, Ta, Bi, Li, Be, Rb, Cs, B, F, and Mn.

(2) Skarn deposits: The principal tungsten minerals are scheelite, wolframite, huebnerite, and ferberite. The associated minerals are copper, iron, lead, and zinc sulphides, arsenopyrite, pyrite, borates, tourmaline, magnetite, gold, bismuth, and various calcium, iron, and magnesium silicates. The main elements concentrated are W, Mo, Re, Bi, Cu, Pb, Zn, Fe, S, As, Au, Ag, B, and F.

(3) Veins: There is great variation in these deposits. Some contain essentially cassiterite and wolframite with copper, iron, lead, and zinc sulphides. Others are tungsten-molybdenum veins, scheelite-quartz-gold veins, tungsten-silver-gold veins, tungsten-copper veins, and tungsten-silver-copper-lead-zinc veins. The elements concentrated are likewise varied and include Li, Rb, Cs, Be, B, U, Mo, Re, W, Mn, Fe, Cu, Ag, Au, Zn, Cd, Ga, In, Tl, Ge, Sn, Pb, As, Sb, Bi, and S.

(4) Placers derived from the preceding three types of deposits: The principal minerals won from these deposits are cassiterite, wolframite, tantalite-columbite, and scheelite.

(5) Certain alkaline brines or evaporite deposits in present-day lakes or ancient lakes in arid regions. The brine of Searles Lake in California contains about 70 ppm WO_3 . Similar brines in arid regions of U S S R. are enriched in tungsten. Such deposits are not exploited at the present time because of difficulties in extracting the tungsten. They provide, however, a large reserve for the future. In the brines and evaporites the tungsten is generally closely associated with As and Mo and also with Li in places. (See also the section on lithium).

Tungsten is an excellent indicator of its deposits and can be used in all types of geochemical surveys based on soils, tills, and stream sediments. Tungsten compounds are relatively insoluble in natural settings, and hence water surveys are generally not effective. Exceptions to this may prevail where the waters are alkaline since the element exhibits an increased mobility under such conditions. Spring precipitates, especially those containing manganese, are often enriched in tungsten in terranes containing its deposits. Vegetation surveys may also be useful since some plants take up considerable amounts of the element. Good ancillary indicators of tungsten include Sn, Mo, and Bi. The effectiveness of the other elements noted above that are concentrated with tungsten are relatively unknown.

GROUP VIIA: FLUORINE, CHLORINE, BROMINE, AND IODINE

Fluorine is a trace constituent of most rocks occurring mainly in apatite and in the micas, amphiboles, and tourmaline where it substitutes for the OH groups.

The principal minerals of fluorine are fluorite and cryolite, Na_3AlF_6 . Fluorite is the principal commercial mineral containing fluorine. Cryolite is mined, however, at Ivigtut in Greenland and in the Miask area, U.S.S.R.

Fluorite deposits are widespread and occur in various rock types. The principal concentrations are in veins and various types of replacement deposits in limestone; also in granites and other igneous-type rocks. Less important deposits are lenses and irregular masses of calcite and fluorite, mainly in the Grenville rocks of the Precambrian of Eastern Canada. Still other deposits are bedded replacements mainly in limestone. The common associated minerals in fluorite deposits are calcite, marcasite, pyrite, chalcidony, quartz, barite, galena, and sphalerite; less commonly copper sulphides, cassiterite, and wolframite. The elements commonly concentrated in fluorite deposits are Ca, F, Fe, S, Si, Ba, Pb, and Zn. Sn, W, and Cu accompany the fluorite in some deposits.

A large reserve of fluorine occurs in the phosphorites and in the apatite of various types of deposits discussed under phosphorus.

There are relatively few data on geochemical prospecting for fluorite deposits. Fluorite is relatively immobile in natural settings and appears to remain close to its deposits suggesting that analyses for fluoride should probably be effective in soil geochemical surveys. Fluoride analyses of stream sediments may also be effective. Waters leaching fluorite deposits are generally enriched in fluorine suggesting that hydrogeochemical methods may also be useful under certain conditions. Plants also tend to take up excess fluorine indicating that vegetation surveys may be useful in some places for locating fluorite deposits.

Little is known about the effectiveness of the ancillary indicator elements accompanying fluorite deposits. It would seem that Ba, Pb, Zn, and possibly Cu, Sn, and W could be used depending on the types of deposits sought.

Chlorine is obtained mainly from sodium chloride or halite deposits and from brines of underground and surface origin. The sea is an enormous reservoir of chlorine.

Geochemical surveys are generally not mounted to discover halite deposits. Those searching for such deposits should be guided by geological principles. The presence of brine springs or of brines in drillholes may be a useful guide to the presence of halite deposits.

Bromine is obtained mainly from the sea, from underground brines, from surface saline deposits, and from evaporite salt deposits. There is an inexhaustible source in the sea. Those searching for bromine sources should analyze brines, surface saline deposits, and evaporite salt deposits directly for the element.

Iodine is obtained as a byproduct of Chilean nitrates, from natural brines and mineralized waters, and from the ash of kelp. Some coals also have small quantities of iodine, and some saline soils are enriched in the element. The Chilean nitrates contain iodine in the form of the minerals dietzeite $4[\text{Ca}_2(\text{IO}_3)_2\text{CrO}_4]$, and lauterite, $4[\text{Ca}(\text{IO}_3)_2]$. (See also the section on nitrogen).

Those searching for sources of iodine should analyze brines, mineralized waters, natural salts, coals, caliche, and saline soils directly for the element.

GROUP VIIB: MANGANESE AND RHENIUM

Manganese is widely distributed in rocks in minor amounts. The basic igneous rocks contain the most manganese, and the element is highly concentrated in certain types of manganese sediments.

Manganese ores are of several types including veins and lenses of various manganese oxides and manganese siderite in rocks of diverse types; nodules and masses of manganese oxides in porous limestone beds and brecciated zones; sedimentary deposits of various manganese oxides in sedimentary terranes; sedimentary deposits of various manganese oxides associated with iron formations; manganese shales; metamorphosed sedimentary deposits consisting of a variety of manganese oxides; and residual deposits derived from all of the foregoing types of deposits.

Manganese deposits and areas are generally reflected in the soils, tills, and stream sediments by the occurrence of black manganese oxides and wad. Practically all types of geochemical surveys can be used to outline these areas. Manganese also occurs in some abundance in the waters draining manganese areas and deposits, and spring and stream precipitates are generally greatly enriched in manganese in terranes containing deposits and manganese shales. The vegetation, likewise, generally reflects the presence of manganese by the high contents of the element in the ash of plants.

Rhenium is a trace constituent of certain niobium, tantalum, tungsten, rare earth and platinum group minerals. It is frequently enriched in molybdenite in amounts up to 2,500 ppm. Three poorly differentiated minerals of rhenium are known, dzhezkazganite, $\text{CuReS}_4(?)$, rhenium sulphide, $\text{ReS}_2(?)$, and rhenium oxide, $\text{Re}_2\text{O}_7(?)$. None of these minerals are of commercial importance. The element is produced commercially as a byproduct of the Kupferschiefer copper ores and from the treatment of flue dusts and residues obtained from the roasting and smelting of molybdenite ores. The elements accompanying rhenium are the same as those discussed under molybdenum, niobium, tantalum, tungsten, rare earths, and platinum group metals.

GROUP VIII: IRON, NICKEL, COBALT
AND PLATINUM METALS

Iron is widely diffused in most rocks, being concentrated mainly in the basic varieties and in certain ferriferous sedimentary rocks.

Iron ores are of several types, including veins, and massive lenses of various iron sulphides, particularly pyrite and pyrrhotite, iron oxides, and siderite; skarn deposits of magnetite; sedimentary deposits of various iron oxides in sedimentary terranes; deposits associated with the great iron formations of Precambrian and later ages; iron shales and sandstones; metamorphosed sedimentary deposits consisting of a variety of iron oxides and silicates; and residual deposits of limonite and other iron oxides derived from weathering of the foregoing types of deposits or from the weathering of basic and intermediate rocks and iron-bearing sediments. The last type of deposits constitute the lateritic ores found in tropical regions.

Iron deposits and iron-bearing rocks are generally reflected in the soils, tills, and stream sediments by the occurrence of limonite and other iron oxides. Practically all types of geochemical surveys can be used to outline these areas. Iron also occurs in some abundance in the waters draining iron-bearing areas and deposits, and spring and stream precipitates are generally greatly enriched in limonite and other iron oxides in terranes containing deposits. The vegetation, likewise, generally reflects the presence of iron by the higher contents of the element in the ash of the plants. Heavy mineral surveys may be a good guide to magnetite deposits and other types of iron deposits.

Nickel is widely dispersed in rocks of all types, being concentrated particularly in those of basic and ultrabasic igneous origin. The element forms a number of minerals of which the most important industrially are pentlandite, nickeliferous pyrrhotite, millerite, niccolite, chloanthite, and garnierite.

The following types of nickel deposits can be distinguished:

(1) Massive sulphide lenses containing essentially pentlandite, pyrrhotite, pyrite, and chalcopyrite: These are generally, though not always, associated with basic igneous rocks. The type deposits are those at Sudbury, Ontario. The principal elements concentrated are Ni, Co, Fe, Cu, Ag, Au, Pt metals, Se, Te, As, and S.

(2) Veins and lenses of sulphides containing millerite, gersdorffite, chalcopyrite, pyrrhotite, and pyrite. The characteristic elements concentrated are Ni, Co, Fe, Cu, and S.

(3) Veins containing niccolite, chloanthite, and various other nickel-cobalt arsenides and sulphides: Associated minerals are native silver, arsenic, calcite, bismuth, galena, sphalerite, chalcopyrite, and various other minerals. The characteristic elements concentrated are Ni, Co, Ag, Fe, Cu, Pb, Zn, As, Sb, S, Bi, and U. (See also the discussion on silver.) Commercially, only small amounts of nickel are obtained from these deposits. Cobalt is obtained from some deposits.

(4) Lateritic nickel-cobalt deposits: These originate from the weathering of basic and ultrabasic rocks containing nickel and cobalt. The principal mineral is garnierite. The characteristic elements concentrated are Ni, Co, Fe, and Cr.

Nickel is a good indicator of its deposits in practically all types of geochemical surveys. The element responds well, and its deposits are generally reflected in soil, till, stream sediment, water, and vegetation. Precipitates at the orifices of springs are also generally enriched in nickel in the terrane in which deposits occur. The ancillary indicators of nickel deposits are Cu, Co, As, Pt, and Cr. The latter element may be particularly useful in deeply weathered terranes.

Cobalt forms a number of primary minerals the most important of which are cobaltite, smaltite, linnaeite, carrollite, skutterudite, safflorite, and glaucodot. Secondary or supergene ore minerals are asbolite, heterogenite, sphaerocobaltite, and erythrite. Commercially much cobalt is also obtained from the various primary nickel minerals in massive sulphide deposits.

Cobalt follows nickel closely, and considerable amounts of the element are obtained commercially from the nickel deposits described above. In addition to these, large amounts of cobalt are also obtained from certain bedded copper shales, from native silver nickel-cobalt arsenide deposits, from certain oxidized and primary copper sulphide veins, from certain veins containing lead-zinc ores, and rarely from veins mined essentially for gold (gold-cobalt type).

The elements accompanying cobalt are diverse and depend essentially on the types of deposits. Grouped these include (massive nickel copper deposits) Ni, Co, Pt, Fe, Cu, Ag, Au, Se, Te, and S; (native silver nickel-cobalt arsenide deposits) Ni, Co, Ag, Fe, Cu, Pb, Zn, As, Sb, S, Bi, and U; (copper-cobalt sulphide ores) Cu, Co; (lead-zinc cobalt ores) Pb, Zn, Cd, Ag, Co; (gold-cobalt deposits) Co, Au, Ag; and (laterites) Ni, Co, Fe, and Cr.

Cobalt is a good indicator of its deposits and can be used in practically all types of geochemical surveys including those based on soil, till, stream sediments, water, and vegetation. Spring precipitates containing manganese are generally highly enriched in cobalt in terranes containing

cobalt deposits. The use of the various ancillary indicator elements depends upon the type of deposit sought. Those most indicative of cobalt in a general way are Ni and Cu.

The platinum metals include platinum, ruthenium, rhodium, palladium, osmium, and iridium. All are found closely associated with one another. The principal minerals carrying these metals are native platinum, various platinum metal alloys and intermetallic compounds, sperrylite, PtAs_2 , cooperite, PtS , braggite (Pt, Pd, NiS), laurite RuS_2 , and stibiopalladinite Pd_3Sb . A number of other rare platinoid minerals containing tellurium and bismuth are known. The only rocks slightly enriched in platinum metals are dunites and certain basic rocks.

The principal types of deposits of the platinum group are:

(1) Minor concentrations in nickel-copper ores of the Sudbury type: These deposits are associated with basic rocks and contain the platinum mainly as sperrylite. Other platinum metal minerals are usually present, and there may be some solid solution of platinum metals in the various sulphides. The principal associated elements are Ni, Co, Cu, Fe, Te, As, Ag, and Au.

(2) Hortonolite-dunite pipe deposits: These deposits are unique and occur mainly in South Africa where the peculiar rock type is supposedly a differentiate of the Bushveld Igneous Complex although it crosses the stratification of the complex. Some investigators have suggested that the hortonolites are pegmatite analogues of the complex. The principal platinum mineral is the native metal, and the characteristic elements concentrated are Pt metals and Cr.

(3) Disseminated platinum metal minerals in sulphide and chromite segregations: These deposits are also unique to South Africa where they occur in the famous Merensky Reef, a supposedly differentiated lower part of the Bushveld Complex. In the oxidized zone the main mineral is native platinum with much palladium and minor quantities of rhodium, osmium, iridium, gold, and silver. In the primary zone the minerals are chromite, magnetite, pyrrhotite, pentlandite, chalcopyrite, cubanite, millerite, and nickeliferous pyrite. The platinum metals in the primary zone are said to be largely in solid solution in the pyrite, pyrrhotite, and pentlandite. This early view may not be correct since the platinum group metal arsenides and sulphides noted above and other platinum minerals including the native metal have been recognized in most concentrates. The principal elements concentrated are Pt metals, Ag, Au, Cr, Fe, Cu, Ni, Co, and S.

(4) Skarn deposits associated with basic and ultrabasic rocks: These deposits appear to develop where basic and ultrabasic rocks intrude carbonate rocks. Some are in shear zones and fractures in other types of rocks underlying or overlying ultrabasic and basic bodies of rock. Examples

are known in South Africa and elsewhere. The principal platinum minerals are sperrylite and cooperite; associated minerals are copper and nickel sulphides. The principal elements concentrated are Pt metals, Ni, Co, Fe, and Cu.

(5) Concentrations of platinum metals in various types of copper, lead, silver, and gold veins and lodes: The platinum metals are generally won as a byproduct. The oxidized zones of some of these deposits are enriched in platinum metals.

(6) Unusual platinum concentrations in pegmatites and quartz veins: These are rare although examples are known in Colombia, U.S.S.R., South Africa, and Ontario. Their origin is an enigma.

(7) Witwatersrand quartz-pebble conglomerate: Small amounts of osmiridium containing mainly osmium and iridium and minute amounts of platinum, ruthenium, rhodium, and gold are obtained from the gold ores of the Rand.

(8) Placers: The principal platinum metal mineral is native platinum. The deposits generally occur in regions of ultrabasic rocks. The associated minerals are chromite, magnetite, and ilmenite.

Little work has been done on geochemical prospecting for the platinum metals. Those searching for such deposits should concentrate on areas containing ultrabasic rocks and nickel-cobalt deposits, especially of the Sudbury type. All types of copper deposits should be carefully scrutinized for platinum metals. Probably the best attack is to make heavy concentrates of the soils and stream sediments, followed by mineralogical and spectrographic analyses. Chromite may be a good indicator for platinum metals in some areas. Other good indicators would appear to be Ni, Co, and Cu.

GROUP O: HELIUM, NEON, ARGON,
KRYPTON, XENON, AND RADON

This group contains the inert gases, all of which are found in the atmosphere and in trace amounts in rocks. Some, especially helium, are obtained from certain natural gases held in the rocks. The others are obtained from liquefaction of the gases of the atmosphere. Those searching for these gases in various natural gases should analyze them directly for the various members of the group.

The radon content of water, till, and soil may indicate the presence of uranium and thorium deposits in certain areas.