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

(Revised)

R.W. BOYLE

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

ABSTRACT

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

RÉSUMÉ

Cette révision d'un rapport précédent portant le même titre contient de nombreuses données sur les associations d'éléments dans tous les types de gîtes minéraux et traite de l'utilisation, en prospection géochimique, des divers éléments indicateurs.

INTRODUCTION

This is a revised edition of Geological Survey of Canada Paper 68-58 which has been long out-of-print. Since publication of the first edition considerable new data on elemental associations in mineral deposits have been obtained by the writer both from the literature and from his experience over several years during which many types of geochemical surveys have been carried out and considerable research on elemental associations in mineral deposits has been conducted. The data are being prepared for a forthcoming treatise on geochemistry. Because of its importance in prospecting, however, 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 to the author any discrepancies in the various statements made and by providing further data not contained in this summary. The writer wishes to thank the many individuals who responded to this request when the first edition was published.

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, complexation phenomena, hydrolytic reactions, colloidal phenomena, biological reactions, adsorption and base

Table 1. PERIODIC TABLE

ATOMIC WEIGHTS BASED ON C^{12} (1961)

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
1 H 1.008																	2 He 4.003
3 Li 6.939	4 Be 9.012											5 B 10.81	6 C 12.011	7 N 14.007	8 O 16.00	9 F 19.00	10 Ne 20.183
11 Na 22 990	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.064	17 Cl 35.453	18 A 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (99)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)															
				58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
				90 Th 232.04	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (245)	97 Bk (249)	98 Cf (249)	99 Es (254)	100 Fm (252)	101 Mv (256)	102 No (253)	103 Lw (257)

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exchange reactions, diffusion, solubility in molten silicates, and various other parameters. In addition to these purely chemical features there are others of a physical 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 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 in mineral deposits 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 such as those that exist in normal soils, natural waters, plants, etc. 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 the various states of water in the hydrosphere and biosphere, in water and hydroxyl groups in minerals, and in the various solid and liquid hydrocarbon substances. Small amounts of hydrogen also occur in the free state in various rocks, in fumaroles and volcanoes, and in natural gases; in the atmosphere the element is rare, averaging about 0.1 ppm (parts per million). Commercially, hydrogen can be obtained from water or acids by a variety of reduction reactions; *viz.* reaction of an active metal such as sodium with water, reaction of a metal and acid; reactions of hydrides with water; electrolysis; and by reduction of water by carbon (water gas or producer gas reaction). From hydrocarbons, hydrogen can be obtained by various thermal and thermochemical cracking processes.

There are three naturally occurring isotopes of hydrogen; H^1 (protium), H^2 (deuterium), and H^3 (tritium) whose approximate percentage abundance[1] in natural materials are respectively: 99.985%, 0.015%, and 1×10^{-15}%. The isotopes of hydrogen are commonly symbolized as H, D, and T. Heavy water (D_2O) is used extensively as a moderator in nuclear power plants; it can be obtained commercially in a number of ways - by electrolysis enrichment, by exchange reactions involving H_2S and H_2O followed by electrolysis or fractional distillation, by fractional distillation, and by various diffusion processes in cascade.

The deuterium content of natural materials varies significantly, but sources greatly enriched in the isotope have not yet been identified. Such sources may, however, exist especially in geochemical situations where exchange reactions between H_2S and H_2O have prevailed or where diffusion or sublimation processes have been active. The products of these reactions and processes are mainly deep stratal waters, metamorphic and diagenetic waters such as appear in some hot and cold springs, the deep waters of fiords and seas, glacial ice, certain types of petroleum, and so on. A 5 per cent natural enrichment in deuterium in large volumes of source materials would confer a significant energy advantage in the commercial production of heavy water.

Tritium, the radioactive hydrogen isotope, is used extensively as a tracer in hydrological work. In hydrogeochemical prospecting surveys the isotope should thus prove useful in tracing the paths and sources of elements in ground and stratal waters.

Hydrogen is produced as a result of the radiolysis of water. Natural ground and stratal waters pervading or migrating through radioactive deposits containing uranium and thorium may become enriched in elemental hydrogen. In this respect hydrogen can be considered as an indicator of uranium and thorium deposits and also of hydrocarbon deposits enriched in these two radioactive elements.

Lithium exhibits its greatest enrichment in pegmatites, granitic dykes, and certain coarse-grained granites in which it is present in spodumene, lepidolite, petalite, eucryptite, triphylite-lithiophilite, amblygonite; and various other rarer lithium-bearing minerals; 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, gneisses, and metasediments. The element also occurs in commercial quantities in certain brines and other natural waters. It may also be present in certain clay-rich 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 montmorillonite (hectorite). The element is relatively rare in carbonatites, but in some of these deposits it may occur in amounts up to 100 ppm.

In pegmatites, granitic dykes, 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, Ti, Zr, B, Sn, W, Ga, Tl, Mn, P, F, and more rarely by U, Th, Bi, (As), (Sb), and Mo[2]. 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.

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[1] Throughout the text the isotopic abundance figures are quoted from W.H. Sullivan, Trilinear chart of nuclides, U.S. Atomic Energy Commission, 1957.

[2] In 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. Elements quoted in brackets are generally only rare associates or indicators.

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^{2-}, CO_3^{2-}, 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. One of the richest sources of lithium in the world are the underground brines of Silver Peak, Nevada, an old silver mining area. These brines are some seven times as rich in lithium as the brines of Great Salt Lake, another large source of lithium.

Lithium 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 represented[1].

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 montmorillonite group. In lithium-bearing clays and shales the element 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. Hydrothermally altered tuffs in some districts may carry above normal contents of lithium, accompanied by elements such as Cs, Rb, Be, and F. Examples are known in Juab County, Utah near the berylliferous deposits in the Spor-Topaz district and elsewhere in the county.

Lithium is relatively mobile in most natural settings, although it is the least mobile of the alkalis in some situations, a feature that derives from the small size of its ion which gives it a high charge density thus influencing its adsorption characteristics, solubilities of some of its salts, etc. Natural waters in the vicinity of lithium deposits tend to be enriched in the element as do also clay-rich soils. Many species of plants take up lithium, and some such as those in the Solanaceae (potato, tomato, tobacco, etc.) and Ranunculaceae (buttercup, columbine, etc.) families appear to be accumulators. Other plants such as some of those in the Cupressaceae (cypresses and junipers), Liliaceae (lily), and Gramineae (grasses) families tend to avoid soils with high amounts of available lithium, and still other plants are quite passive to the element. From these general data it would appear that water, soil, stream sediment and plants are good sampling media in geochemical surveys. Resistate mineral surveys of soils and stream sediments should be useful in prospecting for lithium deposits in pegmatites, coarse granites, granitic dykes, and greisens since the various lithium minerals are commonly accompanied by resistate minerals such as lithium micas, cassiterite, tantalite-columbite, wolframite, bismuth, etc. which can serve as indicators. Lithogeochemical surveys do not seem to have been extensively employed in the search for lithium deposits. Some granitic rocks and metasediments carry higher than average amounts of lithium and hence may indicate the presence of lithium deposits of the pegmatite, granite, and greisen type. Systematic analyses of stratigraphic sections of clay beds, shales, tuffs, etc. may serve to identify favourable beds or sequences of beds in which lithium is enriched. Finally our work on drill cores and chip samples in the vicinity of lithium deposits of the pegmatitic type indicates a general increase in the content of the element in the wall-rocks as the deposits are approached.

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. Nepheline syenites and carbonatites are enriched in both sodium and potassium but the K/Na ratio varies widely in the rocks that make up these complexes, commonly from 0.3 to 8. The fenitization process associated with many carbonatites generally involves significant introductions of both sodium and potassium, particularly the former. Most of the sodium and potassium in nepheline syenites and carbonatites is present in the feldspathoids, feldspars, micas, amphiboles, and pyroxenes; sodium and potassium carbonates have been observed in recent carbonatite volcanics in Tanzania and elsewhere in the carbonatite regions of Africa. Commercially, sodium and potassium are obtained from saline evaporites, saline lakes, alkaline lakes and marshes (sodium) and underground brines, in which they are usually present as chlorides, nitrates, sulphates, carbonates, or borates. All saline evaporites, saline lakes, salinas, salt flats, alkaline lakes, 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.

Both sodium and potassium are essential to life, and hence both elements are found in plants and animals. Sodium is enriched compared with potassium in animals; the reverse is generally the case in plants. Most plants are sensitive to high concentrations of sodium and potassium salts (halite, sylvite, etc.) and avoid areas where these salts are readily available. Other plants, the halophytes, frequent salt marshes, lakes, pans and regions of salty earths.

Salt precipitates at the orifices of springs carrying sodium and potassium may be indicative of deposits of halite, sylvite, and other K or Na salts in the underlying bedrocks. Similarly, springs and their precipitates and associated pans, enriched in sodium and potassium salts, particularly sodium carbonate (nahcolite, trona, gaylussite, etc.), may indicate the presence of young carbonatites as in the carbonatite regions of Tanzania in Africa and elsewhere in the world. Such precipitates commonly carry unusual elements such as Ba, Sr, Ce, Nb, etc., all indicators of carbonatites. *See* also the section on niobium. Many of the springs associated with carbonatites are highly charged with CO_2.

Potassium is strongly adsorbed by clay minerals, and hence certain clays and shales may be greatly

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

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 as noted above. 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 and other metallic deposits (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. Use of the K_2O/Na_2O ratio may be useful in assessing proximity to gold, silver, copper, and base metal mineralization in many types of epigenetic deposits since this ratio increases significantly and consistently as mineralization is approached where potash metasomatism is manifest. Where albitization or soda metasomatism is prevalent the ratio remains constant or decreases.

Potassium has a natural radioactive isotope, K^{40}, whose abundance is approximately 0.0119 per cent of the total amount of the element present. K^{40} decays in a complex manner by negative beta-emission, K-capture, and gamma emission. Because of these phenomena rocks and zones enriched in potassium are slightly radioactive and can be detected by radiometric methods.

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 and carnallite. Other possible sources are pollucite, leucite, zinnwaldite, various potassium micas and feldspars, adularia, and certain varieties of beryl.

Rubidium is concentrated in certain pegmatites, granitic dykes, and coarse-grained granites; also in greisens that may be associated with tin, tungsten, and beryllium deposits, and in potash-rich alteration zones associated with gold, silver and base metal mineralization. The element is also frequently enriched in potassium-bearing brines (up to 600 ppm) and mineral waters and in potassium-rich saline evaporites. Certain potassium-rich clays and shales may contain above average contents of rubidium.

Plants and animals have no essential requirements for rubidium, but the element is commonly enriched in plants whose ashes contain high contents of potassium. Some species of fungi are greatly enriched in rubidium. It might be possible to use rubidium effectively as an indicator of pegmatites, rare element granites, greisens, potash-enriched zones associated with gold, silver and base metal mineralization, etc. in biogeochemical surveys utilizing plants as the sampling media.

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, Ni, Zr, Mo, W, Sn, Bi, Tl, Ga, B, P, F and more rarely by U, Th, Bi, (As), (Sb), and Mo. Of these the best indicators are Cs, Li, Ta, Nb, Be, Sn, 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. In some clays, shales, and tuffs, the last often hydrothermally altered, rubidium enrichments are commonly accompanied by higher than normal amounts of Li, Cs, Be, rare-earths, and F.

Data are limited on the effective use of rubidium in lithogeochemical surveys. Granites, and metasediments containing pegmatites, granitic dykes, and greisens are commonly slightly enriched above normal in rubidium. We have also noted that rubidium tends to increase in the wall-rocks of rubidium-bearing pegmatites as these bodies are approached. The aureoles are, however, commonly narrow. In potash-rich alteration zones associated with gold, silver, and base metal deposits there is often a progressive increase in the rubidium content towards mineralization. Rubidium tends to collect (with potassium) in clay-rich soils, a feature that enhances its use in pedogeochemical surveys for the location of deposits in which the element occurs in significant amounts. Rubidium is one of the most mobile of the alkalis and is found in enriched amounts in natural waters near its deposits. This feature ensures its application in hydrogeochemical and stream sediment surveys. The statements made with respect to lithium as regards resistate mineral surveys apply also to rubidium.

Rubidium has a naturally occurring radioactive isotope, Rb^{87}, whose abundance is approximately 27.85 per cent of the total amount of the element present. Rb^{87} is a negative beta emitter and thus adds a modicum of radioactivity to rocks and metasomatic and alteration zones enriched in rubidium (potassium).

Cesium is the least abundant of the common alkalis. It forms the mineral pollucite, $(Cs,Na)AlSi_2O_6 \cdot nH_2O$, which commonly resembles quartz and may be easily mistaken for it. Other possible sources are lepidolite, microcline feldspar, adularia, certain varieties of beryl (vorobieite), rhodizite (a complex Be borate), cesium-kupletskite (a complex Nb silicate) 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, granitic dykes, 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, shales, and altered tuffs may contain above average amounts of cesium.

Plants and animals have no essential requirements for cesium, but the element is commonly enriched in plants whose ashes contain high contents of potassium and rubidium. It might be possible to use cesium effectively as an indicator of cesium-rich pegmatites and granitic rocks in biogeochemical surveys utilizing plants as the sampling media.

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, granitic dykes, greisens, and coarse-grained granites the common associated elements are Li, Rb, Be, Sc, Y, rare-earths, Nb, Ta, Ti, Zr, W, Ga, Tl, Sn, B, P, and F and more rarely U, Th, Bi, (As), (Sb), and Mo. Of these the best indicators are Li, Rb, Be, Ta, Nb, Sn, 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.

Data are limited on the effective use of cesium in lithogeochemical surveys. Rock sampling over large areas may outline belts of granitic rocks and pegmatites enriched in cesium, but in general the cesium contents of most rocks are low, and significant differences are often difficult to identify without a prohibitive amount of sampling. We have noted that cesium tends to increase in the wall-rocks of cesium-bearing pegmatites as these bodies are approached. The aureoles are, however, narrow. The potash-rich alteration zones associated with gold, silver, and base metal deposits often exhibit a progressive increase in the content of the element towards mineralization. Cesium tends to collect (with K and Rb) in clay-rich soils, a feature that enhances its use in pedogeochemical surveys for the location of deposits in which the element occurs in significant amounts. Cesium is one of the most mobile of the alkalis and is found in enriched amounts in natural waters near its deposits. This feature ensures its application in hydrogeochemical and stream sediment surveys. The statements made with respect to lithium as regards resistate mineral surveys apply also to cesium.

GROUP IB: COPPER, SILVER, AND GOLD

Copper occurs in 9 principal types of deposits as follows:

1. Disseminated copper sulphides in shales and their metamorphic equivalents (Kupferschiefer and Zambia types).
2. Disseminated copper sulphides in sandstones, sandy shales, and conglomerates ('red bed' type).
3. Native copper deposits in amygdaloidal basalts and associated quartzites and conglomerates.
4. Disseminated copper sulphides, arsenides, etc. in or associated with monzonite, various acid porphyries, and other granitic intrusives (porphyry copper type).
5. Copper sulphides in skarn-type deposits.
6. Massive and disseminated copper sulphides associated with nickel, cobalt, and iron sulphides in or near basic igneous rocks such as gabbros and norites (Sudbury type).
7. Massive and disseminated copper sulphides associated with iron, lead, and zinc sulphides in volcanic and/or sedimentary terranes.
8. Copper sulphides, arsenides, etc. in veins, lenses, pods, disseminations, etc. in faults, fractures, drag folds, crushed zones, and shear zones.
9. An unusual occurrence is the presence of copper sulphides in certain carbonatites as at Phalaborwa in South Africa, where the orebody averages about 0.7% Cu.

In certain of the copper shale deposits (e.g. Kupferschiefer) copper 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. In some copper shale deposits (e.g. White Pine, Michigan) the only associated elements exhibiting significant enrichments are Ag, Co, and Ni. The common associated elements in the 'red bed' deposits are Ag, Pb, Zn, Cd, Hg, 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 B, Zn, Pb, Ag, Hg, Au, As, and Sb; W is rare. Te is enriched in some regions.

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, Te, 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 associated with basic igneous rocks 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, Bi, Se, and Te. Pb, Zn, Cd, Sn, Bi, and Sb are rare. The best indicators of such deposits are Ni, Cu, Co, and As.

The massive copper-lead-zinc deposits in volcanic and sedimentary terranes and the various vein type deposits of copper in all types of geological environments 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 Au, Mo, W, 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. The Archean massive sulphide bodies rich in copper are commonly low in lead. Barium is enriched in some of the massive and vein type copper deposits.

In carbonatites copper is generally present in chalcopyrite, bornite, cubanite, and chalcocite. Some of these minerals are late in the various stages of formation of the carbonatites. Elements associated with the copper stage are Fe, S, Pb, Ni, Co, Zn, Cd, Au, and Ag. Some bodies exhibit enrichments of W and Bi with Au. For the other elemental associates in carbonatites see the discussion under the element niobium.

Copper has been used as an indicator of its deposits and others in which it occurs as a minor constituent in practically all types of geochemical surveys including lithogeochemical, pedogeochemical, hydrogeochemical, stream sediment, and biogeochemical. Only some specific features of interest need be mentioned.

Certain ground and surface waters are greatly 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 near cupriferous rocks and deposits also contain relatively high amounts of copper due to the strong chelating and organometallic binding action of humus. All of these geological phenomena may indicate the presence of copper deposits in the terrane in which they occur. Copper is necessary to life, and plants take copper up readily. Their ashes are commonly enriched in the element in the vicinity of cupriferous rocks and deposits. Some plants are accumulators of copper, and some are apparently indicators of environments rich in the element (e.g. kachim, pink, mint, basil, copper mosses, California poppy, and thrift plants). Some plants exhibit chlorotic symptoms where excessive amounts of copper are available in soils or waters; other plants show deficiency symptoms where insufficient amounts of the element are available for normal metabolic functions. Coal and lignitic fragments in sandstones, arkose, and shale may be greatly enriched in copper and many of its associated elements. This phenomenon should serve to draw attention to the fact that copper mineralization has been active in a particular terrane.

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, Hg, Tl, Cu, Au, Ba, 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.

Silver is a useful indicator element of its deposits, and of those in which it occurs in minor amounts, in practically all types of geochemical surveys. Only some of the major features of interest need be noted here.

Silver tends to be enriched in the wall-rocks of its deposits, and there is commonly a significant and consistent increase in the element as ore is approached. In soils overlying its deposits silver tends to be highly enriched in the A horizon, and there are generally significant enrichments in the B and C horizons. 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. Stream sediments enriched in silver and in its characteristic associated elements have been widely and effectively used in geochemical surveys for gold, silver, and base metal deposits. Silver is not an essential element to life, but most plants take up excess amounts of silver in the vicinity of argentiferous deposits and are thus useful as sampling media in biogeochemical prospecting. Coal and lignitic fragments in sandstones, arkose, conglomerates, and shales may be greatly enriched in silver and many of its associated elements. This phenomenon should serve to draw attention to the fact that silver mineralization has been active in a particular terrane.

Gold is won both from deposits mined essentially for the element and as a byproduct of the mining and treatment of nickel, copper, zinc, lead, and silver ores. The following types of primary (endogene) and secondary (exogene) deposits, exploited mainly for gold, can be distinguished:

1. Auriferous skarn-type deposits.
2. Auriferous pegmatites, coarse-grained granitic bodies, and porphyry dykes and sills. These are comparatively rare.
3. Gold-silver and silver-gold veins, stockworks, lodes, mineralized pipes, and irregular silicified bodies in fractures, faults, shear zones, sheeted zones, and breccia zones essentially in volcanic terranes.
4. Auriferous veins, lodes, sheeted zones, and saddle reefs in faults, fractures, bedding plane discontinuities and shears, drag folds, crushed zones, and openings on anticlines essentially in sedimentary terranes; also replacement tabular and irregular bodies developed near faults and fractures in chemically favourable beds.
5. Gold-silver and silver-gold veins, lodes, stockworks, silicified zones, etc. in a complex geological environment, comprising sediments, volcanics, and igneous or granitized rocks.
6. Disseminated and stockwork gold-silver deposits in igneous, volcanic, and sediment-

ary rocks.

  (a) Disseminated and stockwork gold-silver deposits in igneous bodies.
  (b) Disseminated gold-silver occurrences in volcanic flows and associated volcaniclastic rocks.
  (c) Disseminated gold-silver deposits in volcaniclastic and sedimentary beds: (1) Deposits in tuffaceous rocks and iron-formations, and; (2) Deposits in chemically favourable sedimentary beds.

7. Gold deposits in quartz-pebble conglomerates and quartzites.
8. Eluvial and alluvial placers.

The quartz-pebble conglomerate deposits provide the bulk of the world's production of gold, almost 67 per cent. The other deposits, mainly the various vein and disseminated types, and eluvial and alluvial placers now provide the remaining 33 per cent of the production.

For the elemental associates of gold in deposits from which the element is won as a byproduct see the discussions under nickel, copper, zinc, lead, silver, platinum, and niobium.

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 minor to trace amounts of antimony and bismuth in the gold deposits, and these elements, especially arsenic, provide good indicators of gold and silver in most types of geochemical prospecting surveys.

The deposits in categories 2 to 6 are invariably quartz veins, irregular bodies, saddles, and stockworks; quartz-sulphide veins and impregnation zones; silicified and pyritized zones; and disseminated gold-sulphide zones. The principal associated elements and indicators in these deposits are SiO_2, Ag, As, Sb, S, and Fe; additionally Cu, Ba, Zn, Cd, Hg, B, Tl, U, Sn, Pb, Bi, Se, Te, Mo, W, F, Co, Ni, and (Pt) depending on the metallogenic belt in which the deposits occur. Some deposits, especially those of Tertiary age, carry considerable amounts of Se, Sb, Pb, Zn, Cu, Hg, 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. There are numerous exceptions to this generalization. Many deposits in sedimentary rocks and some in volcanic terranes 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, pyritization, and arsenopyritization were widespread in numerous gold-quartz deposits in all types of rocks.

Two well-defined types of auriferous veins are recognized in certain metallogenic belts - gold-silver telluride veins and gold-silver selenide veins. 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-silver 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 principal elemental associates of gold in the quartz-pebble conglomerate deposits are Fe, S, Ag, U, Th, and rare-earths. In some deposits U, Th and rare-earths occur only in traces (e.g. Tarkwa, Ghana). The iron and sulphur are combined mainly in pyrite which is ubiquitous in some deposits; in the Tarkwa deposits the iron occurs mainly in the oxide form. The Au/Ag ratio is always greater than 1 and averages about 9 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 eluvial and alluvial placers are familiar and need not be considered in any detail here. The most frequent associated heavy minerals are magnetite, hematite, ilmenite, pyrite, arsenopyrite, garnet, zircon, and monazite; in addition cassiterite, platinoids, native bismuth, amalgam, native copper, cinnabar, scheelite, wolframite, barite, galena, stibnite, and sulphosalts are present in some areas. None of these minerals are specific indicators of gold, but some such as arsenopyrite, native bismuth, scheelite, stibnite, and sulphosalts are suggestive of the presence of gold. Constant scrutiny and analysis of quartzites, conglomerates, and other resistate sediments should be maintained during prospecting so as not to miss fossil gold placers.

The use of gold as an indicator of its deposits in lithogeochemical surveys has been attempted in a number of countries, chiefly in U.S.S.R. The results have been mixed and confusing. Some investigators claim that intrusive bodies, mainly granitic, are enriched in gold in auriferous belts; others claim that no such relationship exists. Sampling of country rocks is even more inconclusive, judging from the various papers on the subject. Analyses of shear and breccia zones, fault gouge, altered (chloritized, sericitized, alunitized, pyritized) zones, and silicified zones for gold is often effective in outlining areas where gold mineralization may exist. In this type of work the indicators in addition to the metal itself are Ag, Cu, Zn, Cd, Hg, B, Pb, As, Sb, Bi, Se, Te, Mo, W, F, Co, Ni, and U. The most specific of these are Ag, As, Sb, Bi, and Te; the other indicators are generally characteristic of local conditions or particular metallogenic belts.

Soils tend to be enriched in gold in the vicinity of auriferous deposits. Residual soils generally show the greatest enrichments; those developed on foreign material such as till may or may not be enriched depending on the depth of the primary material. Soils developed on till and other types of foreign overburden over 5 feet in depth rarely reflect the presence of auriferous deposits. Sampling of the foreign overburden at or near bedrock, however, commonly gives good anomalous patterns with high contrast over auriferous deposits. The indicators of gold deposits utilizing soil and overburden (till, etc.) samples are the same as those mentioned above for rocks. The most specific indicators are Ag, As, Sb, and Te.

Ground and surface waters are frequently enriched in gold in the vicinity of auriferous deposits of all types. Analyses for gold in natural waters are, however, tedious and costly, involving neutron activation methods which are not particularly applicable to geochemical prospecting in most areas. Waters leaching auriferous deposits, however, commonly contain a number of elements associated with gold among which the following are often enriched: Cu, Ag, Zn, Cd, Hg, U, As, Sb, Se, Te, Mo, F, Co, and Ni. Of these Cu, Ag, As, Sb, and Te are particularly indicative of gold. Wad limonite, and other precipitates near the orifices of springs may 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.

The gold content of stream sediments is useful in outlining auriferous zones. The various indicators, particularly Cu, Ag, As, Sb, and Te, are commonly used with greater effect since the anomalies are more marked and give higher contrast.

Gold analyses of heavy minerals separated from soils and stream sediments are particularly effective in locating and outlining auriferous bedrock deposits as well as eluvial and alluvial placers. Other types of deposits such as auriferous base metal sulphides and porphyry copper stockworks are also commonly indicated by the gold content of stream sediments, soils, and their heavy minerals. The heavy mineral work should be made quantitative by selecting and panning a standard amount of soil, glacial overburden, or stream sediment. Good elemental indicators of gold in heavy mineral work are Ag, As, Sb, Bi, W, (Pb), (Pt), (Hg), and (Sn).

Plants tend to take up gold from soils and overburden in the vicinity of auriferous deposits. Little work has been done on biogeochemical prospecting for gold, but what has been done is promising. Specific indicators of gold deposits in plant ash surveys appear to be Ag, Cu, As, Sb, Bi, W, Se, and Te.

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

Beryllium is a typical element of the pegmatites and some coarse-grained granites but is also found in a diverse number of other occurrences. It is commonly concentrated in certain types of albitized, fluoriferous, sericitized, and greisenized granitic rocks; also in greisen zones in metasediments and in certain schists and gneisses often with fluorine minerals such as topaz and fluorite. Beryllium is enriched in certain skarn-type (taconite) deposits; in some tin, tungsten, and molybdenum quartz veins; in small amounts in certain gold-quartz and manganese-lead-zinc veins; in certain fluorite-bearing veins and stockworks commonly in limestone but also in other rocks; 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. Certain carbonatites also carry enriched amounts of beryllium in both the fenitized zones (up to 1,000 ppm at Alnö in Sweden) and in separate masses or disseminations of barylite. Beryllium may also be enriched in minerals such as cordierite (up to 2% BeO) in metasedimentary rocks and veins, in certain types of zircon, in sodalite and nepheline and in willemite in zinc deposits of the type of Franklin Furnace, New Jersey, U.S.A. The element is also found in higher than normal amounts 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 aluminum and may be slightly enriched in clays, bauxites, and shales; also in residual manganese deposits. Some coal ashes have relatively high enrichments of beryllium.

Beryllium forms numerous minerals, the most important commercially being beryl. The minerals chrysoberyl, gadolinite, bavenite, bertrandite, phenacite, euclase, helvite-danalite, beryllonite, bromellite, hambergite, rhodizite, genthelvite, barylite, herderite, swedenborgite etc. may also provide a source of beryllium if present in sufficient quantities. Minerals such as allanite, alvite, aminoffite, bavenite, fergusonite, idocrase, milarite, tengerite, etc. may carry 1 per cent or more Be.

The elemental associates of beryllium in pegmatites and certain coarse-grained granites 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, silicified, and greisenized granites the principal associates of beryllium are F, Li, Rb, Cs 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. In greisen zones in metasediments beryllium is accompanied by the same suite of elements as in greisenized granites.

Certain genthelvite deposits with associated phenacite occur in veins and stockworks 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 (tactites) in which it occurs principally in barylite, helvite-danalite, phenakite, bromellite, euclase, and vesuvianite (idocrase). In addition minerals such as grossularite, epidote, cordierite, 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, Sc, 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, willemite, 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 quartz veins and segregations frequently carry some beryl or helvite, phenakite, bertrandite and other beryllium minerals in some areas. Zinnwaldite, the lithium mica, tends to be enriched in beryllium in these deposits. Topaz is a common mineral in some of 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.

Certain types of fluorite-bearing veins, stockworks, and replacement deposits developed in fractures and brecciated zones commonly in limestones or calcareous shales carry beryllium, generally in bertrandite, beryl, phenakite, or chrysoberyl. Associated minerals are fluorite, hematite, calcite, quartz, chert, often opal, and topaz. Scheelite occurs in some of these deposits. The fluorite is commonly purple and some of the deposits are weakly radioactive. Most deposits occur near quartz-feldspar porphyry and granitic stocks. The principal associated and indicator elements are F, W, Mn, and (U). Ancillary indicators are Rb, Cs, Li, Zn, Pb, Sn, Sc, and rare-earths in certain deposits of this type.

Beryl and most of the other beryllium minerals are commonly closely associated with quartz in one form or another. In some areas, however, beryl may occur in carbonate veins often with barite and fluorite. The emeralds of Colombia occur mainly in bituminous limestones commonly in carbonate veins. Helvite is sometimes found in a variety of manganiferous veins bearing rhodonite, rhodochrosite, pryite, galena, sphalerite, etc.

There is frequently a coherence between barium and beryllium in nature, a feature that is emphasized by the relatively large deposit of barylite in veinlets of quartz and albite at Seal Lake, Labrador. Such occurrences are invariably related to carbonatites or other types of alkali-rich intrusives highly fluxed with fluorine and chlorine. The fenites and various rocks associated with carbonatites may contain a variety of beryllium minerals in small amounts. For the various elements associated with beryllium in carbonatites see the discussion under niobium.

Emeralds, beryl, and a number of other beryllium minerals are relatively resistant to weathering and tend to collect in eluvial and alluvial placers, particularly where the weathering has been deep and prolonged. Some of the placers represent more than one cycle of erosion and deposition. Beryllium mineral placers are rarely commercial except for the gem varieties.

Beryllium is a good indicator of its deposits in most types of geochemical surveys. Other specific and useful indicators of F, Li, Rb, Cs, Sn, W, and a variety of other elements commonly accompanying beryllium such as Ba, Sr, B, Sc, Y, rare-earths, U, Th, Nb, Ta, P, Ti, Mo, and Mn. Fluorine is almost universal in beryllium deposits and is the best specific indicator.

Lithogeochemical surveys should prove useful in locating and outlining fluoriferous, greisenized, sericitized, and silicified zones in granitic rocks and metasediments enriched in beryllium. Similarly soil and overburden surveys would appear to be useful in locating most types of deposits enriched in beryllium. In this type of work fluorine analyses of the soil and overburden materials would seem to be the most effective way of outlining the deposits. The A horizons commonly respond best and give the highest contrast anomalies, but the other horizons are also responsive in most areas. The method is most effective where the soils are residual or where the foreign overburden is thin (<10 feet).

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. Fluorine is a particularly good indicator in hydrogeochemical surveys for beryllium in our limited experience. Wad, limonite, and other natural precipitates near the orifices of springs 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.

Stream sediment surveys using Be, F, and the various other indicators mentioned above are effective in locating berylliferous zones according to some investigations described in the literature. Beryl and the other berylliferous minerals have a relatively low specific gravity (2.7-3.5) and appear, therefore, in the light fractions of the sediments. They may be accompanied, however, in many berylliferous districts by heavy minerals such as cassiterite, tantalite-columbite, wolframite, scheelite, and pyrochlore which can serve as indicators.

Plants take up beryllium from soils enriched in the element, and limited investigations described in the literature suggest that biogeochemical surveys using beryllium as indicator are useful in outlining zones rich in berylliferous pegmatites and other types of deposits. Fluorine should, likewise, prove of value as an indicator in plant ash surveys run to locate beryllium deposits.

Certain low-ash coals are slightly enriched in beryllium, their ashes containing up to 4,000 ppm Be. Some of these coal ashes may provide a commercial source of the element in the future.

Beryllium has one stable isotope Be^9, an important property of which is the ease with which it emits photoneutrons when bombarded by gamma rays having an energy greater than 1.66 Mev from a source such as radioactive Sb^{124}. This is the basis of the berylometer, a useful field and laboratory instrument for the detection of beryllium. The sensitivity of this instrument depends essentially on the length of counting; for normal periods it is about 5 ppm Be.

Magnesium is a characteristic element of intermediate, basic and ultrabasic igneous and metamorphic rocks and of sedimentary carbonate rocks, especially those containing dolomite. Certain carbonatites contain within their complexes masses of medium- to coarse-grained dolomite or dolomitic limestone (dolomitic sövite). The principal magnesium minerals of commerce are olivine obtained from ultrabasic igneous rocks and used for refractories; asbestos and talc also obtained from ultrabasic rocks (serpentinites) and altered meta-dolomites 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. Other magnesium minerals of commercial importance include serpentine (ornamental stone), biotite and phlogopite (for ceramic and electrical purposes), glaucophane, amphibole, and pyroxene (for roofing granules, aggregate, etc.), and spinel and garnet (gems and abrasives).

The search for magnesium deposits in rocks should be confined mainly to areas of ultrabasic and basic igneous and metamorphic 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 and breunnerite (ferroan magnesite) deposits occur in two settings - firstly in limestone or dolomite terranes that exhibit folding and in some places metamorphism, dolomitization, and igneous injection; and secondly in terranes of ultrabasic rocks that exhibit extensive carbonatization and serpentinization 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, stratal 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 igneous rocks and of the sedimentary carbonate rocks and evaporites. Certain carbonatites contain within their complexes masses of nearly pure medium- to coarse-grained calcium carbonate (sövite). 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. Other calcium minerals of commercial importance include the various feldspars, pyroxenes, amphiboles, epidote, wollastonite, garnets, and zeolites. These have various uses. Calcium minerals such as fluorite, apatite (phosphate rock), and scheelite are discussed under the sections on F, P, W, etc.

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, stratal 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. Some carbonatite complexes are enriched in strontium. 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 in faults and fractures and in stratiform deposits consisting of irregular lenses, pods, and strings of concretions. Both types of deposits are generally found in sedimentary terranes particularly in "red bed" sequences, in evaporite basins, and in volcanic sedimentary basins often with abundant tuffs. Examples of the first two environments are numerous including the Enon deposit in Nova Scotia (celestite; Lower Windsor Formation), Port au Port Peninsula, Newfoundland (celestite; Upper Missisipian Codroy Formation), Yate district, Gloucestershire, England (celestite; Keuper Marl), Germany (celestite; Zeckstein); and U.S.S.R. (celestite; Permian of the Russian Platform). The stratiform bodies appear to be of sedimentary or diagenetic origin in some places; in others they are obviously replacement bodies formed after lithification of gypsum, anhydrite, marl and other carbonate rocks. The vein-type bodies appear to have been precipitated from stratal waters, the strontium and other accompanying constituents being derived from the piles of evaporites, carbonate rocks, and shales in which the deposits usually occur.

Celestite is a common constituent of the cap rocks of salt domes and is also found in certain sulphur deposits which seem to have been derived by the reduction of gypsum and anhydrite. So far as is now known to this writer these types of deposits are not commercial.

The elements accompanying strontium in the vein-type deposits are Ba, Pb, Zn, Ca, Fe, S, and F. These minerals are combined mainly in barite, galena, sphalerite, anhydrite, gypsum, pyrite, hematite, and fluorite. In the bedded deposits the associated elements are much the same except that in some of the deposits there are small amounts of boron in borates and often some native sulphur.

Strontium deposits may be indicated by higher than normal amounts of strontium in samples from stratigraphic sections of sedimentary basins, in soils, tills, stream sediments, natural waters, and vegetation. Barium, lead, zinc, and fluorine may also be good indicators in these materials. Sulphate may indicate the presence of celestite deposits, but the presence of 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 nonmanganese 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, in which the element occurs mainly in the potash feldspars. Barium is also commonly enriched in the various syenitic rocks of alkaline complexes and carbonatites; also in the carbonate masses of the latter. Certain shales and sandstones may be enriched in barium, and the element is often concentrated in small amounts in manganiferous sediments and precipitates. Some coals are relatively rich in barium. 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 mineral 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 and witherite 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.
(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 types of barite deposits 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. Numerous deposits of this type are in "red bed" sequences or in series of rocks containing evaporites, e.g. Walton, Nova Scotia.

The bedded deposits are invariably in sequences of limestones, dolomites, and shales. Some of these deposits may be of sedimentary origin, although most are probably of replacement origin. The large bedded deposits at Magnet Cove in Arkansas are apparently of replacement origin related in some manner or other with the Magnet Cove alkali syenite-carbonatite complex.

The disseminated and massive barite bodies accompanying or intimately mixed with various types of vein and massive sulphide bodies are widespread, examples being found at the Buchans mine in Newfoundland, the Meggen deposit in Germany, and other deposits in Eastern Europe and elsewhere. The vein-type and discordant massive deposits are epigenetic; those in stratiform bodies have been the subject of prolonged debate. Some investigators hold to a sedimentary or volcanic exhalative origin, others to a replacement origin. The latter is more probable.

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. These types of deposits are rare.

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. Some of the bedded deposits associated with alkali syenite-carbonatite complexes such as at Magnet Cove in Arkansas provide large commercial sources of barite. Witherite is rare in most carbonatites, and no commercial deposits of the mineral are yet known in these complexes.

The residual deposits of barite are widespread in many parts of the world. They derive from all of the deposits aforementioned. Most are lumps, balls, and irregular masses in the highly weathered residuum forming the regolith on limestones, sandstones, evaporites, carbonatites, etc.; also in karsts, sink holes, and solution cavities on these rocks.

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 rock samples from stratigraphic sections, fractured zones, shear zones, and faults, and in samples of soils and 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 is a useful indicator in certain places. Barite and witherite have high specific gravities (4.5 and 4.3 respectively) and tend to collect in the heavy fractions of soils, weathered residiuum, and stream sediments. Panning of these materials is a satisfactory method of locating deposits of barite and witherite or deposits containing them as gangue minerals.

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. Some varieties of carbonate sinters at the orifices of hot and cold springs also contain both barite and fluorite.

Coalified plant fragments and thin coal seams commonly contain high contents of barium and other associated elements in districts containing barium deposits. Analyses of these materials for barium and its associated elements will often give positive indications that barium mineralization has been active in a district.

<u>Radium</u>, the highly radioactive member of Group IIA, occurs in nature as the isotopes Ra^{223}, Ra^{224}, Ra^{228}, Ra^{225}, Ra^{226}, being daughter products in the actinium, thorium, neptunium, and uranium families respectively. The isotope Ra^{226} derived from U^{238} is the principal isotope and has the longest half-life of all the radium isotopes, some 1,622 years.

The chemistry of radium is essentially similar to that of barium but only in the exogene cycle is it associated with this element as in manganiferous precipitates and certain types of sediments. Generally speaking radium is associated mainly with primary uranium deposits and is extracted commercially from ores of this element. The content of radium in uranium ores is variable and depends on the uranium content and the age of the deposit. The ratio Ra/U is approximately 3.4×10^{-7} by weight in ores older than 500,000 years.

Radium is particularly useful as an indicator element of the presence of uranium (and thorium). Because of its intense radioactivity it can be detected by suitable counters. Its daughter elements (e. g. radon) are, likewise, highly radioactive and can also be detected by suitable counters. Radium and its daughter elements tend to be enriched in the rocks, gossans, soils, glacial materials, natural waters and their precipitates, stream sediments, vegetation, and bogs and swamps in the vicinity of uranium (and thorium) deposits. Some gossans overlying uranium deposits are intensely radioactive, especially if they contain radio-barite $(Ba,Ra)SO_4$, and various other insoluble sulphates, carbonates, wad, limonite, etc. Groundwaters and springs in the vicinity of uranium deposits are commonly greatly enriched in radium, generally some 10 times that of normal waters. Brines associated with petroleum are often enriched in radium, the element apparently being derived partly from the uranium in petroleum and partly from uranium in the reservoir rocks. Many hot springs are relatively rich in radium (and radon) for reasons that are not entirely clear. Evidently the radium is leached from the rocks through which the hot waters circulate. The sinters of hot springs are, likewise, often rich in radium, and some contain radio-barite, radio-calcite, radio-strontianite, radio-celestite, radio-fluorite, radio-pyromorphite, and radio-opal. Precipitates from the brines of oilfields contain a similar suite of minerals in some places. In places radium-bearing wad and limonite are encountered, and radium-bearing humic material is often present in bogs.

Radium may be enriched together with uranium, barium, molybdenum, and many other elements in thin coal seams and coalified plant fragments in certain sandstones, arkoses, and conglomerates. A high radioactivity of these hydrocarbon substances is an indication that uranium mineralization may have been active within a terrane. A high radioactivity of certain solid hydrocarbons such as thucholite, albertite, etc. signals the same phenomenon.

A word of caution about the use of radium and its daughter elements (e.g. radon) as indicators of uranium (and thorium) deposits is necessary. High radium (and radon) contents in various earth materials are not necessarily indicative of uranium (or thorium) deposits. On the contrary many are often the result of chemical enrichments associated with granites, pegmatites, black shales, gneisses, and many other rocks containing only low contents of uranium (and thorium). Furthermore, it should be recognized that thorium and uranium are members of the actinide series (Group IVB and VIB respectively) whereas radium is a member of the alkali earth group (Group IIA) and radon is an inert gas. All have different geochemistries, from which it follows that the daughter elements (radium, radon, etc.) may become markedly separated from their parents in groundwater systems and during weathering and other exogene processes. This feature should always be kept in mind during the interpretative phase of geochemical prospecting, particularly in relating radium (and radon) anomalies to possible uranium (and thorium) deposits. This is the reason that certain radium (or radon) anomalies are found without corresponding uranium (or thorium) anomalies. Similarily uranium anomalies may exist without noticeable radioactivity. In this case the uranium mineralization or enrichment is young and is said to be out of radioactive equilibrium with its daughter products. Radioactive equilibrium is reached at about 500,000 years at which time the Ra/U constant is about 3.4×10^{-7}.

GROUP IIB: ZINC, CADMIUM, AND MERCURY

<u>Zinc</u> occurs in eight principal types of deposits. <u>Cadmium</u> generally accompanies zinc and is won from its ores as a byproduct. 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 (minor zinc), 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 and sulphosalts. Barite may be present as a gangue mineral.
7. Massive sulphide deposits containing essentially sphalerite and iron, copper, and silver sulphides and sulphosalts. Barite may be present as an important mineral in some deposits. Some of these deposits occur in volcanic terranes; others in sedimentary terranes; and still others in mixed volcanic and sedimentary terranes. Deposits of Precambrian Archean age commonly lack lead; younger deposits are generally enriched in lead.
8. Irregular masses and replacement bodies of smithsonite, calamine, hydrozincite, or willemite. These commonly occur in carbonate rocks and generally represent reprecipitation of zinc and other constituents derived from the oxidation of primary disseminations of sphalerite in carbonate and other rocks. The bodies may occupy the same locale as the primary disseminations or they may be slightly removed laterally or vertically (downward) from the primary ores. Examples of these types of orebodies are widespread in the Tintic district, Utah (smithsonite), in the Beltana district of South Australia (willemite), and in the Moresnet district of Belgium (calamine).

In addition to the above types of commercial deposits the elements zinc and cadmium are commonly concentrated in a number of other deposits, two of which are of interest. Some phosphorites are enriched in cadmium (up to 50 ppm) and in zinc. Certain carbonates are, likewise, enriched in zinc (and lead). In fact both sphalerite and galena may occur in veins and late-stage (replacement) bodies in carbonatites.

The most frequent elemental associate of zinc and cadmium is lead. In some deposits there may also be enrichments of Fe, Cu, Ag, Au, Ba, Sr, B, F, As, Sb, Bi, Mo, Ga, In, Tl, Ge, Hg, Co, Ni, 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. The "Mississippi Valley" type deposits have few elemental associates accompanying zinc, lead, and cadmium. Only Mg, Si, and Fe are enriched in most orebodies in the dolomitized, silicified, and pyritized (marcasite) parts. In some deposits there may be slight to moderate enrichments,of Cu, Ag, Ni, Co, Ba, and occasionally Sb. F is enriched in some deposits; Hg is generally low in most deposits. The bodies of secondary (supergene) zinc minerals such as smithsonite and willemite are characterized by few elemental associates of zinc. There is commonly some Cd and a little Pb; rarely Sb, As, Co, Ni, Cu, and Ba in any quantity other than traces or minor amounts.

Zinc and cadmium deposits are generally indicated by higher than normal amounts of zinc and cadmium in soils, tills and other glacial materials, 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. Fluorine is a useful indicator of certain types of deposits, mainly those in carbonate rocks.

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 organic binding (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.

Coalified plant fragments and thin coal seams in sandstone, arkose, and shale may be enriched in zinc and cadmium which are often present in small amounts of sphalerite. Analyses of coal fragments can be utilized to ascertain if zinc (and cadmium) mineralization, as well as lead, silver, and barite mineralization, have been active in a sedimentary terrane.

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, mercurian tetrahedrite and tennantite, 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, chalcopyrite, 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, particularly coloradorite (HgTe) and tiemannite (HgSe), may occur in certain gold-quartz and silver veins. The native silver in the Cobalt-type Ni-Co arsenide deposits is often enriched in mercury (up to 4.7%). The gangue in most mercury deposits is invariably opal, chalcedony, or quartz, and carbonates. Barite and fluorite are generally restricted to individual deposits. Native sulphur is abundant in some deposits, and gypsum occurs in others. Argillic alteration, silicification (development of opal), pyritization, and sericitization are common. Carbonatization of serpentinite is marked in some deposits. Introduction of bituminous substance into the fractures, faults, and breccia zones and into the adjacent wall-rocks is common in some deposits.

Most of the mercury deposits of the world occur in mercuriferous belts that correspond to zones of instability or dislocation of the earth and are often marked by the presence of hot springs and other volcanic or thermal activity. One of these belts (Pacific belt) follows the Cordilleras of the

Americas and the eastern flank of the Australasian and Asian continents; another belt (Mediterranean belt) follows the line of Alpine (Tertiary) folding from Spain and North Africa through the Mediterranean to Indonesia and eastward where it apparently coalesces with the first belt. A number of mercury occurrences and deposits are located outside these belts. Examples are a number of deposits that lie in the Tien Shan and Sayan mountains and northeastward through the Baikalides to the Pacific belt; the Gortdrum deposit in Eire where mercurian tetrahedrite is abundant; Clyde Forks, Ontario where mercurian tetrahedrite and cinnabar occur in Precambrian rocks; and a number of deposits in Arkansas where cinnabar is disseminated in Pennsylvanian sandstones and shales. All of these deposits have one point in common; all are located in zones marked by deep faulting and shearing. Probably deep faulting is common to all mercury occurrences whether in the mercuriferous belts or not.

Most mercury deposits are of Cenozoic age, although there are exceptions to this generalization. The grade of the deposits ranges from 0.5 to 6 per cent Hg, the last figure being that for the famous Almaden mine in Spain.

A survey of the elemental associates of mercury in its deposits indicates that the following elements are particularly characteristic: As and Sb; others that may be enriched in individual deposits include Cu, Ag, Au, Sr, Ba, Zn, Cd, B, Tl, Ge, Pb, Bi, Se, Te, Mo, W, and F. Some deposits in serpentinites have relatively high concentrations of Ni in minerals such as nickelian pyrite and millerite.

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 of mercury deposits 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, 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. A high mercury content in spring waters and precipitates may be indicative of thermal zones.

Cinnabar is relatively resistant to oxidation, and the mineral has a high specific gravity (8.0). From these facts it follows that the mineral is a particularly good indicator of mercury deposits using the heavy mineral fractions of soils, glacial materials, and stream sediments. Similarly, native mercury can be used as an indicator, but care must be taken to ensure that the metal is natural and not present as a contaminant. A high mercury content of placer gold or the presence of the mineral arquerite (Ag,Hg) in the heavy minerals of stream sediments may signal the presence of mercury deposits.

Mercury tends to be concentrated in certain viscous and solid hydrocarbons (albertite, gilsonite, anthraxolite, bitumen, etc.) in faults, fractures, and porous rocks. The presence of these mercuriferous materials is a good indication that mercury mineralization has been active in an area.

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. Dumortierite is used in ceramics.

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 bedded evaporites, 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 botanical 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.

In addition to being a good indicator of its own deposits, boron is also a most useful indicator of a great variety of other deposits in which it is often enriched. The following types of mineral deposits are characterized by the development of boron minerals or boron metasomatism:

Deposit	Characteristic Boron Minerals
Pegmatites (simple and complex types containing various rare elements such as Li, Nb, Ta, Sn, etc.); high temperature quartz veins	Tourmaline, dumortierite
Skarns (including those containing Be, Fe, Cu, Zn, Pb, Sn, Bi, rare-earths, Mo, and W)	Tourmaline, axinite, danburite, dumortierite, kotoite, ludwigite, nordenskiöldine
Greisenized, sericitized, and albitized granites and similar rocks containing Be, Sn, and W	Tourmaline, dumortierite
Tin-tungsten veins and lodes	Tourmaline, axinite, dumortierite
Gold-quartz veins and lodes	Tourmaline
Polymetallic (Cu, Pb, Zn, Ag, etc.) veins and lodes	Tourmaline, axinite, dumortierite
Porphyry Cu and Mo deposits	Tourmaline, dumortierite (only certain deposits)
Native copper deposits in basalts, conglomerates and sandstones	Datolite, axinite
Native silver deposits	Datolite (rare), axinite
Mercury deposits	Tourmaline (rare)
Bedded borates	Borates
Hot springs and stream jets	Boric acid (sassolite), borates

Weathering, oxidation and leaching of endogenic deposits yields soluble borates and the boron resistate minerals, mainly tourmaline and axinite. Both the soluble borates and boron resistate minerals collect in the soils and in nearby stream sediments. Near bedded borate deposits, the natural waters may be greatly enriched in soluble borates. Vegetation in the vicinity of boriferous deposits may become enriched in boron and may also exhibit endemic characteristics.

Geochemical surveys based on soils, stream sediments, water, heavy minerals, and vegetation using boron as an indicator are useful in searching for the types of deposits noted in the table above.

Analyses of tourmaline and other boron minerals obtained in heavy-mineral surveys suggest that these minerals may indicate certain types of deposits in a terrane. Thus, tourmaline from lithium pegmatites is generally enriched in Li, Cs, and Rb; and tourmaline from tin deposits is enriched in Li and Sn.

Difficulties may be encountered in interpreting geochemical surveys based on boron as an indicator of mineral deposits where the country rocks contain abundant tourmaline, dumortierite, or other boron minerals, resulting mainly from metamorphism, igneous intrusion, or migmatization.

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

Other commercial minerals of aluminum include corundum, emery, cryolite, dawsonite, topaz, and particularly alunite. The natural alums are mainly hydrated double sulphates of potassium, sodium, and ammonium. Some of these such as potash alum, soda alum, etc., 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, $KAl_3(SO_4)_2(OH)_6$, 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. Large deposits of alunite are known in Italy, Mexico, U.S.S.R., and at Cedar City, Utah, U.S.A.

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 if found in an irregular massive 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. *See* also the section on fluorine.

Dawsonite, $NaAlCO_3(OH)_2$, is a basic carbonate of sodium and aluminum. It occurs in a variety of settings; in veins and impregnations, and in extensive beds. In the latter form it occurs extensively in the Green River Formation of the western United States. Topaz, $Al_2SiO_4(OH,F)_2$, is a possible source of alumina and fluorine (see the section on fluorine).

Corundum, Al_2O_3 , occurs in the common form and as a gem (ruby, sapphire). It occurs extensively in certain pegmatite dykes; also in limestone and dolomite, gneiss, schists, nepheline syenite, syenite, granite, and peridotite where high temperature metamorphic conditions have prevailed as in the Grenvillian rocks of southeastern Ontario. Emery is a mixture of corundum and magnetite or corundum, spinel, and magnetite. Many of the large emery deposits (Turkey, Naxos in Greece, and Kyzul-Kum desert in Kazakstan, U.S.S.R.) are lenticular masses in limestone near intrusives. Those in the Cortland area of New York are in the Manhattan quartz-mica schist near the contact of the basic Cortland complex. Elsewhere in the United States emery is associated with basic intrusives in gneisses and schists. Placer corundum and emery occur in the Transvaal and Malagasy Republic. Corundum and emery are used mainly as abrasives. The deep red and blue corundum (ruby and sapphire) are valued gems.

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 also 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, corundum pegmatites and syenites, emery deposits, 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.

Bedrock corundum and emery deposits are commonly reflected by relatively large amounts of corundum, magnetite, and spinel in the heavy and resistant concentrates from soils and stream sediments in their vicinity.

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, and some pegmatites contain enrichments of the element. The magnetite of certain contact metamorphic deposits may contain up to 0.06% Ga (600 ppm). The sulphide mineral germanite, $Cu_3(Fe,Ga,Zn,Ge)(As,S)_4$, may contain up to 1.85 per cent Ga. The range of gallium in sphalerite is 5 - 4,000 ppm. Gallium 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.

During oxidation of gallium-bearing deposits the element is relatively mobile as simple and complex sulphates, chlorides, nitrates, and organic ligands (humates, oxalates, etc.). On this account the element may be a relatively good indicator of lead, zinc, and certain copper and tin deposits in hydrogeochemical and stream sediment surveys. In the soils and gossans associated with these deposits gallium tends to be coprecipitated and retained in the hydrous iron, manganese, and aluminum precipitates (limonite, wad, Al-colloids, etc.)

Indium forms four known minerals, all of which are very rare: native indium, In; roquésite, $CuInS_2$; indite, $FeIn_2S_4$; and dzhalindite, $In(OH)_3$. 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, digenite, geocronite, boulangerite, 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.

During oxidation of indium-bearing deposits the element is relatively mobile in slightly acid to alkaline environments as simple and complex sulphates, chlorides, nitrates, and organic ligands (humates, oxalates, etc.). On this account the element may be a relatively good indicator of lead, zinc, and certain copper, tin, and tungsten deposits in hydrogeochemical and stream sediment surveys. In the soils and gossans associated with these deposits indium tends to be coprecipitated and retained in the hydrous iron and manganese precipitates (limonite and wad); in gossans indium is also commonly highly enriched in various arsenates and antimonates (e.g. beudantite and bindheimite).

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 sulphosalts in various polymetallic deposits, and various potassium salts. The element also forms the rare minerals crookesite $(Cu,Tl,Ag)_2Se$; lorandite, $TlAsS_2$; hutchinsonite, $(PbTl)_2(Cu,Ag)As_5S_{10}$; vrbaite, $Tl(As,Sb)_3S_5$; and avicennite, Tl_2O_3; none of which are of commercial importance. Thallium is enriched in the sericite of the wall-rock alteration zones of various deposits, especially gold-quartz veins and lodes; the element is also concentrated in the precipitates from certain thermal springs and in some volcanic sublimates. Industrially, thallium is obtained as a byproduct 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, Bi, Ag, Au, In, Ga, Ge, Sn, S, and Se. Material and residues suspected to contain commercial quantities of thallium should be analyzed directly for the element.

During oxidation of thallium-bearing deposits the element is relatively mobile in acidic and neutral solutions. On this account the element may be a relatively good indicator of lead, zinc, silver, gold, and other deposits in which it is enriched, utilizing hydrogeochemical and stream sediment surveys. In the soils and gossans associated with these deposits thallium tends to be coprecipitated and retained in the hydrous iron and manganese precipitates (limonite and wad); also in significant amounts in jarosites, where these are formed, and in beudantite and bindheimite.

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, wiikite, zircon, garnet, and allanite. Three scandium minerals are known: thortveitite, $(Sc,Y)_2(Si_2O_7)$, found in certain complex pegmatites; sterrettite, $Sc(PO_4).2H_2O$, 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. Some of the minerals of carbonatites including baddeleyite, pyrochlore, alkalic pyroxenes and amphiboles, and kimzeyite are rich in scandium with contents ranging from 700 - 4,000 ppm 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, La, 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, La, 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, carbonatites, 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 some carbonatites, 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, yttrofluorite, xenotime, thortveitite, gagarinite, wiikite, thalenite, and thucholite. The elements commonly enriched with Y, La, Ce 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, uraninite, stillwellite, caryocerite, rinkite, thucholite, epidote, vesuvianite, scheelite, and sphene are the principal carriers of Y, La, the rare-earth elements, and thorium. Few of these deposits are of commercial importance. The principal elements associated with Y, La, and the rare-earths in skarn deposits are F, P, Ti, U, 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, Van Rhynsdorp 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: Some of these are closely associated with carbonatites. The principal example of this type of deposit is near Mountain Pass, San Bernardino County, California. The orebody consists of bastnaesite (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) Calcite-fluorite-apatite, calcite-fluorite-apatite-biotite-pyroxene, and calcite-biotite-apatite veins and segregations: These deposits are common in the Precambrian Grenville Province of Eastern Canada. For details of these deposits see the section on uranium and fluorine.

(6) 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 discussion under fluorine and phosphorus).

(7) Carbonatites: These deposits frequently contain higher than average amounts of rare-earths and thorium in a variety of titanium, niobium, and other minerals, particularly calcite, dolomite, bastnaesite, pyrochlore, perovskite, apatite, monazite, sphene, zircon, allanite, zirconium-garnet, and fluorite. (*See* further the discussion under niobium). Carbonatites are generally enriched in the cerium subgroup of rare-earths as compared with the yttrium subgroup. Carbonatites are not generally considered as a primary commercial source of rare-earth elements, but the elements can be recovered as byproducts in some cases.

(8) 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. The yttrium group of rare-earths predominates in the deposits. 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 uranium in amounts ranging from 70 - 960 ppm U.

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

(10) 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 Y, La, and rare-earth deposits in geochemical surveys utilizing soils, tills, stream sediments, and vegetation are the elements themselves. Phosphorous 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 yttrium, lanthanum, and the rare-earths and below for uranium. The elements accompanying thorium are, likewise, the same as those for yttrium, lanthanum, 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 except those based on water analyses.

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 (>5 ppm U; >15 ppm Th). 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, Y, La, 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) Skarn and hornfels deposits: These are relatively rare. The uranium-bearing minerals are mainly allanite, uraninite, and monazite; occasionally thucholite. There is commonly much magnetite, garnet, and various other typical skarn minerals. The characteristic elements associated with uranium are mainly Th and rare-earths, and there are the usual elements such as Mo, Bi, W, Cu, Zn, etc. commonly found in skarn and hornfels deposits.

(4) 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, betafite, 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.

(5) 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); davidite is an important ore mineral in some deposits; brannerite is rare in commercial quantities in these deposits. 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, Mo, 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, 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, Mo, 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, copper, and nickel minerals including limonite, malachite, azurite, erythyrite, and annabergite. Few Canadian pitchblende deposits are deeply oxidized, but one, the Gunnar deposit in northern Saskatchewan, contains uranophane down to considerable depths.

(6) 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, Sc, rare-earths, Be, Ga, Ge, Li, 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.

(7) Pyritic quartz-pebble conglomerates: These deposits are the same as those discussed under (8) in the section on rare-earths. The principal primary uranium minerals are brannerite and uraninite. The principal elements concentrated are U, Th,

Sc, Y, La, rare-earths, Fe, As, and S: in some deposits Au and Ag are enriched and are won from the deposits.

(8) Carbonatites: Some of these deposits contain small amounts of uranium mainly in apatite, zircon, pyrochlore, monazite, perovskite, sphene, and baddeleyite; also less frequently in thorianite, thorite, cerite, allanite, and eschynite. (*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.

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

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

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

(12) 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, Mo, 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. Analyses of heavy mineral concentrates from soils and stream sediments for uranium and thorium may indicate the presence of certain types of uranium deposits. Bogs in the vicinity of uranium deposits are often greatly enriched in uranium, and some may be radioactive. Analyses of coal fragments in sandstones and bituminous matter and solid hydrocarbons (thucholite) in all types of rocks for uranium will generally give a clue to whether or not uraniferous mineralization has been active in an area.

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 high grade metasediments. The gem and abrasive varieties of carbon, namely diamond and bort are residents of kimberlite pipes and also frequently occur in placers, both modern and fossil. The carbonates and carbonate rocks are so common they require no discussion.

Hydrocarbon surveys of ground and stratal waters, springs, soils and glacial materials, and ocean and lake sediments have been increasingly used in prospecting for petroleum and natural gas with moderate success.

Graphite veins and lodes are sometimes indicated by higher than normal contents of graphite in soils and glacial materials; also in stream sediments. The work involves examination of these materials by microscopic methods since there is no chemical way of differentiating graphite as such.

Diamonds are particularly resistant to weathering and go into the eluvium and alluvium where they can be recovered by washing and collection on a greased mat. Common associates in placers are quartz, gold, platinum, zircon, magnetite, rutile, brookite, ilmenite, hematite, andalusite, diopside, chrysoberyl, topaz, corundum, tourmaline, and pyrope. None of these are specific mineral indicators except pyrope, chrome diopside, and picroilmenite (Mg ilmenite) which are particularly characteristic of most kimberlites.

Kimberlites and carbonatites appear to be genetically connected, the kimberlites being an intermediate phase between ultrabasic rocks and carbonatites as regards their trace and minor element compositions. Thus, kimberlites tend to be enriched in Mg, Fe, Mn, Ni, Co, Cr, and Ti as well as in Ba, Sr, Rb, P, Nb, Zr, rare-earths, and some of the other elements commonly found in carbonatite complexes. From this it follows that elements such as Ni, Co, Cr, Ba, Nb, etc. are useful indicators of diamondiferous kimberlites utilizing soils, glacial materials, stream sediments, vegetation, and probably water as sampling media.

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, for glass making 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 and radiolarite.

(7) Chert and flint.

(8) Quartz and quartz crystal.

(9) Geyserite and siliceous sinter associated with hot springs.

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

Germanium is a relatively rare semimetallic element that forms several rather uncommon minerals of which the best known are argyrodite, Ag_8GeS_6, germanite, $Cu_3(Fe,Ge)S_4$, and renierite, $Cu_3(Fe,Ge)S_4$. None of the germanium minerals form deposits of commercial importance, although in some deposits, e.g. Tsumeb, Southwest Africa, and Mansfeld, Germany (Kupfer-Schiefer), they may be present in sufficient amounts to make recovery of germanium as a byproduct feasible. Germanium is also a trace to minor constituent in various sulphides and sulphosalts, particularly sphalerite, cinnabar, enargite, tetrahedrite-tennantite, pyrargyrite, and some tin-bearing sulphides. Magnetite may be enriched in germanium in some deposits; siliceous sinters and opal are concentrators of the element in places.

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 beds. Certain magnetite ores have low concentrations of germanium in 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 franckeite. 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, Sc, rare-earths, 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, euxenite, 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) Disseminations and quartz (opal) stockworks in rhyolite flows, quartz-feldspar porphyries, ignimbrites, etc. that are commonly sericitized and opalized: The principal tin minerals are wood-tin and concretionary cassiterite associated with opal, chalcedony, hematite, bismuth, bismuthinite, rarely wolframite, and topaz. The elements concentrated are mainly Sn, SiO_2, Bi, Fe, (W), and F. Few of these are economic sources of tin. Examples are widespread in the Tertiary rhyolites and ignimbrites of Mexico. The Mount Pleasant deposit in southern New Brunswick also falls into this class. This deposit occurs in intensely fractured and altered rhyolitic volcanic rocks, tuffs, pyroclastics, and porphyries where zones of silicification, chloritization, epidotization, greisenization, and fluoritization contain a veritable host of minerals including cassiterite, stannite, molybdenite, wolframite, scheelite, fluorite, topaz, kaolinite, sphalerite, pyrite, chalcopyrite, galena, roquesite, arsenopyrite, bismuthinite, and bismuth. The elements concentrated in this deposit include Li, Rb, Cs, Cu, Ag, Zn, Cd, Sc, Y, rare-earths, B, In, Sn, Pb, Ti, P, As, Bi, Nb, Ta, S, Mo, W, F, and Fe.

(5) 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, Australia, 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.

(6) Massive sulphide deposits: Some of these (e.g. Kidd Creek deposit, Timmins, Ontario) 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 large commercial sources of tin, but some supply important amounts of the metal as a byproduct. The best indicators of tin in massive sulphide deposits appear to be B, Bi, In, Tl, Cd, Ge, Sb, and As.

(7) 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 found in placers. Deposits of this type are developed extensively in Malaya, Indonesia, Thailand, Zaire, and Nigeria.

Tin is a good indicator of its deposits in most types of soil, glacial overburden, 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, Nb, Ta, P, 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 or near 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.

Cassiterite has a high specific gravity (7.0) and a marked resistance to chemical attack, features that ensure its preservation in soils, glacial material, and sediments in streams, rivers, lakes, and the sea. Heavy mineral surveys utilizing soils, glacial materials, and sediments of all types as sampling media are particularly effective in locating primary tin lodes and their derived placers.

Lead is obtained from a variety of deposits most of which also contain Ag, Zn, Cd, and Cu. These deposits have been 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 the 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. Many of the lead minerals such as galena, cerussite, and anglesite have a high specific gravity (6.4 - 7.5) and are relatively resistant to chemical weathering. They tend therefore, to collect in soils, glacial overburden, and stream sediments near lead deposits. On this account heavy mineral surveys utilizing soils, glacial materials, and stream sediments are often useful in locating primary lead deposits.

Natural lead is composed of four isotopes, Pb^{204}, Pb^{206}, Pb^{207}, and Pb^{208}, whose proportions vary in natural minerals according to a number of factors too complicated to discuss briefly here. One of the factors concerns the steady increase in the absolute abundance of the last three isotopes as a result of decay processes in the uranium, actinium, and thorium families. Because of this, lead minerals in uranium- and thorium-bearing deposits are enriched in the so-called radiogenic lead isotopes. Lead minerals in other types of deposits, likewise, have characteristic lead isotopic compositions, and it can be said that in a general way that lead isotopes "fingerprint" certain types of deposits. Isotopic analyses of lead minerals obtained from small prospects, soil and glacial till anomalies, and heavy concentrates of stream sediments may, therefore, give valuable clues to the type of mineralization within a district (e.g. uraniferous, "Mississippi Valley" type, etc.), and may actually suggest types of mineralization unsuspected in a mineral belt. This subject is pursued at length by a number of authors in the book "Geochemical Exploration" (Spec. Vol. 11, Can. Inst. Mining Met., 1971, Editors R.W. Boyle and J.I. McGerrigle).

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. There are in addition a large number of relatively rare minerals that contain titanium such as rinkite, perovskite, brannerite, pyrochlore, euxenite, etc. Some of these are ores of Nb, rare-earths, Th, and U.

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. In these bodies the commercial minerals are rutile, brookite, and leucoxene. In some deposits ilmenite and perovskite can probably be recovered as a byproduct. Several complex deposits contain an unusual assortment of minerals of which apatite is most common. An example is the remarkable rocks, referred to as nelsonites, that occur in Nelson County, Virginia; these are rich in rutile, ilmenite, and apatite. The gangue is quartz, plagioclase, pyroxene, and hornblende. 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, rivers, 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 an alkalic 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, låvenite, 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. The Ilimaussaq alkalic complex in Greenland contains zones with up to 25 per cent eudialyte.

Carbonatite complexes are generally enriched in zirconium and hafnium, the principal minerals of these elements being zircon, zirconian garnet (kimseyite), and baddeleyite. At Phalaborwa, South Africa, baddeleyite is won as a byproduct of copper mining.

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 elements. 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, PHOSPHOROUS, 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, S, 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, the apatite series, amblygonite, and monazite. Less common are xenotime, vivianite, pyromorphite, wavellite, cacoxenite, lazulite and the various uranium phosphates. Turquoise, the aluminum-copper phosphate, is a valued semi-precious gem.

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, S, rare-earths, Ti, Zr, P, F, Cl, and C (graphite).

(2) Apatite lenses, veins, and disseminations in or associated with gabbros and anorthosite (nelsonites). These deposits commonly have much rutile and ilmenite (*see* also the section on titanium).

(3) 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.) When these bodies are deeply weathered large residual concentrations of apatite may occur overlying the complexes or in their near vicinity. Solution and redeposition of the phosphorus during weathering may give rise to concentrations of collophane, dahlite, francolite, gorceixite and other supergene phosphates.

(4) 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 collophane, 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 have been adsorbed from circulating groundwater.

(5) Bog phosphate deposits. Certain bog iron ores and peats may be greatly enriched in phosphorus mainly in vivianite, the hydrous iron phosphate and wavellite, the hydrous aluminum phosphate. Most of these deposits are small and often low grade.

(6) Guano deposits: There are two types of these deposits: insular (and coastal) guano and cave guano. Insular and coastal guano have been mined on many islands and coasts in the Pacific, Indian, and Atlantic oceans. Cave guano is of restricted occurrence, and few commercial deposits are known. Some of the insular and coastal guano deposits (guano-derived rock phosphates) have a complex history involving the interaction of the extracts from surface deposited guano with underlying calcareous and other rocks. This has yielded calcium phosphate (collophane) over large areas with lesser amounts of aluminum and iron phosphates. Such deposits are found on Nauru and Ocean Island in the Gilbert group, on the island of Makatea in the Society group in the Pacific, and on Christmas Island in the Indian Ocean. Fossil equivalents of guano-derived rock phosphates are known in various parts of the world (e.g. Japan, Tanzania).

(7) Residual and reworked (placer) deposits: These deposits are extremely varied and result from a combination of both mechanical and chemical reworking processes involving all of the foregoing types of deposits. In some places lean rock phosphates have been enriched solely by the weathering out and reconcentration of phosphatic nodules. In other places there has been much solution and reprecipitation of phosphatic material on weathered and liberated nodules and irregular masses. The phosphates concentrated in this manner include the aluminum, iron, and calcium phosphates. Residual and reworked phosphate deposits occur in Senegal (aluminum and iron phosphates), Central Tennessee (calcium phosphate), some of the Florida "hard rock" deposits (calcium phosphate), and the Florida land pebble phosphates (calcium phosphate).

(8) Miscellaneous sources of phosphate: These include phosphatic chalks, phosphatic nodules on the ocean floors, and byproduct phosphates from steel plants, amblygonite and monazite reduction, meat and fish packing plants, and sewage.

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 part 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, loellingite, 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) Copper shale, argillite, and schist deposits (Kupferschiefer-White Pine-Zambia type): Most of the arsenic is present in pyrite, copper sulphides, and various other sulphides. Contents of arsenic range from traces to 5,000 ppm. The White Pine, Michigan ores are relatively low in arsenic (<5 ppm) according to our analyses of typical material.

(2) Copper (uranium, vanadium, silver) sandstone deposits ('Red bed' type): Most of the arsenic is present in pyrite and various other sulphides. Arsenic contents range from 5 to 5,000 ppm. The uranium deposits in the Gas Hills and Shirley Basin of Wyoming contain from 5 to 300 ppm As. Copper deposits in red beds in the Pennsylvanian rocks of New Brunswick and Nova Scotia have arsenic contents ranging from 100-225 ppm As. Similar deposits in Triassic rocks at Alderly Edge, Great Britain contain from 800-1,500 ppm As. Some vein and lode type deposits in this category are greatly enriched in arsenic (e.g., Walton, Nova Scotia), containing up to 0.65% As in the ores. Most of the arsenic in these deposits is present in arseniferous pyrite, tennantite, and proustite.

(3) Lead-zinc deposits in carbonate rocks (Mississippi Valley-Pine Point type): These generally contain only traces of arsenic, mainly in pyrite. Most ores from these deposits contain less than 5 ppm As.

(4) Pyritiferous quartz-pebble conglomerates and quartzites enriched in one or more of gold, silver, uranium, thorium, and rare-earths (Witwatersrand-Blind River type): Arsenic contents range from 50 to 8,600 ppm or more according to our analyses of typical ore. Most of the arsenic is present in the pyrite and arsenopyrite with small amounts in minerals such as pentlandite, pyrrhotite, and cobaltite.

(5) Native copper deposits in or associated with amygdaloidal basalts (Keweenaw, Michigan type): The arsenic content of these deposits is low, averaging about 5 ppm As in the ore according to our analyses. Most of the arsenic is present in copper arsenides (domeykite, algodonite), in a few Ni-Co arsenides, and in the native copper. The native copper may contain up to 0.5% As.

(6) Skarn type deposits: The arsenic in these deposits is generally associated with Cu, Pb, Zn, Cd, Au, Ag, Mo, and Fe, and less commonly with W, Sn, Bi, Sb, Te, Ni, and Co. The principal primary arsenic minerals in these deposits are arsenopyrite and native arsenic. Certain skarn-type gold deposits are greatly enriched in these minerals, examples being the Nickel Plate Mine in British Columbia (arsenopyrite) and deposits in the Bau gold district of Sarawak (native arsenic and arsenopyrite). In these deposits the arsenic content may be as much as 20 per cent in some ore shoots.

(7) Pegmatites and pegmatite-like bodies enriched in one or more of Sn, W, Nb, Ta, Bi, Mo, and U: Most of the arsenic is present in arsenopyrite; only rarely in minerals such as native arsenic and loellingite. The arsenic content is generally low in most deposits, but in some may average 500 ppm As or more in the ores.

(8) Massive bodies, mantos, lodes, veins and stockworks: These comprise several types, all more or less enriched in sulphides. The principal types are:

(a) Massive nickel-copper sulphide bodies commonly associated with basic rocks (Sudbury type): In these bodies arsenic is associated with Fe, Ni, Co, Cu, Ag, Au, Pt metals, Te, Se, Bi, and S. The principal arsenic minerals are niccolite, maucherite, gersdorffite, arsenopyrite, and the platinum metal arsenide, sperrylite. The arsenic content of the ores varies over a wide range from mere traces to low percentages.

(b) Massive Cu-Zn-Pb sulphide bodies in volcanic and sedimentary terranes (Noranda-Flin Flon-Bathurst type): In these bodies arsenic is associated with Cu, Zn, Pb, Cd, Ag, Fe, and Sb; also with Sn, Bi, Se, and Te in some bodies. Most of the arsenic occurs in arsenopyrite, pyrite, tennantite, enargite, and various other arsenic-bearing sulphosalts. Most deposits average about 800 ppm As, but there may be wide divergences from this value. The great Boliden deposit in Sweden, for instance, contained up to 12.5% As.

(c) Veins, lodes, and stockworks principally in granitic rocks and associated sediments and greatly enriched in one or more of Sn, W, Bi, and Mo:

There is a great variation in these deposits. Some contain essentially cassiterite and wolframite with Cu, Fe, Pb, and Zn sulphides. Others are wolframite-scheelite molybdenum veins, scheelite-quartz-gold veins, wolframite-scheelite-silver-gold veins, wolframite-scheelite-copper veins, and wolframite-scheelite-silver-copper-gold-zinc veins.

The elements concentrated are, likewise, varied and include Li, Rb, Cs, Be, B, F, U, Sc, rare-earths, Mo, Re, W, Mn, Fe, Cu, Ag, Au, Zn, Cd, Ga, In, Tl, Ge, Sn, Pb, As, Bi, and S. Many of these deposits have wall-rock alteration zones marked by extensive tourmalinization and greisenization. Most of the arsenic in the deposits and their alteration zones is present in arsenopyrite and pyrite. The ores vary widely in their arsenic content, some containing only traces (ppm) whereas others may report several percent.

(d) Various polymetallic veins, stockworks, mantos, and lodes containing essentially Cu, Ag, Pb, Zn, and Fe sulphides and sulphosalts: Most of the arsenic in these deposits occurs in arsenopyrite, pyrite, and a great variety of sulphosalts. Enargite, the copper-arsenic sulphosalt, is an important ore mineral in some deposits. Arsenic contents range from traces to percentages.

(e) Veins greatly enriched in Ni, Co, As, Sb, Ag, Bi, and U (Cobalt-Great Bear Lake-Jáchymov type):

Marked concentrations of a variety of Ni-Co-Fe arsenides and native silver occur in these veins. Also present in some deposits are native arsenic, arsenopyrite, and various arsenic-bearing sulphosalts. Pitchblende is characteristic of some deposits (Great Bear Lake, Canada; Jáchymov, Czechoslovakia). The arsenic content of these deposits ranges between 2 and 50 per cent or more.

(f) Gold-quartz veins, stockworks, silicified zones: The principal arsenic minerals are arsenopyrite, arsenic-bearing pyrite, and a great variety of sulphosalts. Native arsenic and the arsenic sulphides are relatively rare in most of these deposits but occur in some abundance in a few. Arsenic contents range from a few ppm to percentages in the ore shoots and their associated wall-rock alteration zones. Pyritic gold-quartz veins and silicified zones devoid of arsenopyrite normally contain from 100 to 500 ppm As, mainly in the pyrite. Those with marked concentrations of arsenopyrite and sulphosalts (e.g. Yellowknife, Canada) have arsenic contents up to 3 per cent or more.

(g) Realgar-orpiment deposits:

These are relatively rare and constitute veins, pockets, and disseminations in various types of rocks. Relatively large deposits of this type are known in Yugoslavia, U.S.S.R., Turkey, and China. The elements associated with arsenic in these deposits include S, Sb, Ag, Pb, Cu, Fe, Au, and rarely Hg.

(9) Mercury deposits: These are mainly fissure veins, stockworks, disseminations, impregnations, and replacement bodies along faults or in brecciated zones in a great variety of rocks. The principal economic mineral is cinnabar. The commonly associated arsenic minerals are realgar, orpiment, arsenopyrite, and arseniferous pyrite and/or marcasite. Some deposits such as those in the Ukraine and other parts of U.S.S.R., in Turkey, and Alaska (Red Devil Mine) are greatly enriched in arsenic. Others, including the great Almaden mine in Spain, Pinchi Lake in British Columbia, the California deposits, and those in Italy at Idria and elsewhere, contain only moderate to low contents of arsenic in the ores. Precipitates from hot springs enriched in mercury (e.g., Sulphur Bank, Steamboat Springs, U.S.A.; New Zealand; Kamchatka, U.S.S.R.) invariably contain high amounts of arsenic.

(10) Disseminated bodies in various rocks: Two general types can be distinguished as follows:

(a) Disseminated gold deposits, mainly in sedimentary rocks: A characteristic example is Carlin, Nevada. Here probably also belong certain gold deposits in tuffs and other rocks, examples being the Madsen gold deposit in the Red Lake district of Ontario, the gold-bearing arsenopyrite occurrences in the Contwoyto Lake area, Northwest Territories, and the Passagem de Mariana deposits in Brazil. The arsenic content of these deposits varies widely. In the Carlin ores an average of 480 ppm As is reported, but locally the arsenic contents range up to 1 per cent or more. Similar arsenic contents are characteristic of the other deposits noted in this category, according to our analyses. Arsenopyrite and arseniferous pyrite are the most abundant arsenic minerals in these deposits; orpiment, realgar, and sulphosalts occur in the Carlin and similar deposits in Nevada.

(b) Disseminated (porphyry) copper and/or molybdenum deposits: The arsenic content of these deposits is generally low, especially the molybdenum type. Some disseminated copper deposits carry considerable amounts of enargite and tennantite. In both the copper and molybdenum types the pyrite is slightly to moderately arseniferous. Arsenic contents in these deposits are variable, depending mainly on the amount of enargite present. Most deposits probably average about 100 ppm As.

Arsenic enjoys a widespread distribution in mineral deposits and is not confined to any particular metallogenic epoch or province. A few features of its distribution are, however, of interest. Most gold deposits in volcanic belts ranging in age from Precambrian to Tertiary age are greatly enriched in arsenic. A similar relation holds for many gold deposits in the greywacke-slate-graphitic schist assemblage throughout the world. One also sees great concentrations of arsenic in the rich native silver veins (Cobalt-Jâchymov type), some of which contain uranium. These veins tend to occur in well-defined metallogenic provinces characterized by various types of other deposits that frequently contain marked concentrations of arsenic. As an example may be cited that part of Ontario and Michigan characterized by diabase and gabbroic intrusions and amygdaloidal basalts, including Cobalt, Gowganda, South Lorrain, Sudbury, Silver Islet, and the Keweenaw Peninsula. Another example is the great Bohemian massif in Central Europe.

Enargite, the copper arsenic sulphide, appears to be concentrated principally in deposits younger than Precambrian. It is particularly abundant in deposits either in or adjacent to the circum-Pacific volcanic belt, appearing often in commercial amounts in porphyry copper, massive sulphide, and various polymetallic deposits in Chile, Peru, Western United States, Japan, Philippines (Luzon), and elsewhere. In the other great mobile volcanic belt of the globe - the Mediterranean and its eastern extension - the mineral appears abundantly in deposits at Bor, Yugoslavia, and elsewhere.

Proustite, the silver arsenic sulphide, occurs in deposits of all geological ages, but is relatively rare in Precambrian deposits, especially those of Archean age. The mineral is most abundant in deposits of Paleozoic, Mesozoic, and Tertiary age, particularly the last two.

Primary realgar and orpiment deposits are relatively rare. None are known that are of Precambrian age as far as the writer can ascertain. Most deposits are young, generally of Late Mesozoic, Tertiary, or Quaternary age.

Geochemical surveys are not generally mounted to discover arsenic deposits, but the element is a particularly useful indicator of various other types of deposits that are enriched in the element as noted above, 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, near springs, 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. Arsenopyrite, native arsenic, and some of the arsenic-bearing sulphosalts tend to weather slowly and pass into the eluvium and stream sediments near their parent deposits. Heavy mineral surveys using arsenic as indicator may, therefore, be useful in locating a variety of deposits in which these particular minerals are concentrated. Similarly particles of arseniferous limonite, wad, scorodite, beudantite, etc., tend to collect in eluvium and stream sediments near deeply oxidized deposits containing various arsenic minerals.

As noted above spring precipitates, particularly those enriched in limonite, wad, and humic matter, are frequently enriched in arsenic in mineralized areas containing arseniferous deposits. Such precipitates clearly mark the main zones of gold and Pb-Zn-Ag mineralization at Keno Hill; the zones of native silver mineralization at Cobalt, Ontario; and the areas containing barite and Pb-Zn-Cu-Ag sulphides and sulphosalts at Walton, Nova Scotia. Care should be taken in interpreting high arsenic contents of springs and their precipitates. Some of those issuing from terranes of pyritiferous rocks are enriched in arsenic, the element presumably being derived from arseniferous pyrite in the rocks. The high arsenic contents of the precipitates from thermal springs may also be related to phenomena other than the presence of mineral deposits. Rocks through which the thermal waters percolate should, however, be examined for the presence of orpiment and realgar deposits, since precipitation of arsenic may have taken place at suitable places along the courses of the thermal waters.

Bogs, muskegs, and marshes near zones mineralized with arsenic are frequently enriched in the element as a result of adsorption, precipitation by H_2S of bacterial origin, chelation, and other organometallic binding reactions. Such bogs may overlie deposits, or their distribution pattern may take the form of halos or partial halos about mineralized zones.

In rocks containing coal fragments, carbonized plants, or thin coal seams the general presence of mineralization may be indicated by higher than normal amounts of arsenic in the coaly materials. At Walton, Nova Scotia the pyritized coal and plant fragments in the grey sandstone beds contain exceptionally high contents of arsenic (up to 6,000 ppm in the coal) near faults, fractures, and bedding planes. Marked enrichments of Ba, Sr, Cu, Pb, Ag, Sb, Mo, Ni, and Co also occur in the coaly fragments. Similar enrichments of arsenic, copper, and other metals have been noted in coal fragments in the vicinity of cupriferous Pennsylvanian sandstones in a number of areas in New Brunswick (up to 225 ppm As in the coal). Arsenic is also enriched in coaly and lignitic fragments picked from sandstones by the writer from uraniferous areas in the Shirley Basin in Wyoming. These may contain up to 1,600 ppm As in the coal where mineralized with uranium, but more generally the values range from 22 to 50 ppm in the coal. The average for normal coal (not in mineralized areas) is about 4 ppm As in the coal, although much higher values are recorded from some seams and fragments in sandstones. If coal samples are used in prospecting, not only arsenic should be analyzed for, but also other elements such as Ag, Cu, Pb, Zn, Ba, Sb, and Hg, which may occur in deposits in the red beds, etc. By judicious screening, those samples which indicate mineralization can be separated from those that are ordinary natural collectors of stray fluxes of As, Sb, etc., in circulating stratal waters.

A number of inorganic and organic compounds such as arsine and dimethylarsine have a relatively high volatility and should occur in low concentrations in soil gases and in the air overlying arseniferous deposits, particularly where bacterial activity is marked. Similar volatile compounds probably also occur in ground and spring waters associated with arsenic-bearing deposits. Bogs enriched in arsenic may, likewise, be marked by higher than normal contents of volatile species of the element. There are no data on the application of atmogeochemical surveys using volatile arsenic compounds as indicators for the location of mineral deposits, a gap in our knowledge which should be filled by suitable research.

Antimony is widely diffused in many types of mineral deposits in trace, minor, and major amounts. It tends to be concentrated in those deposits containing sulphides, either as separate antimony minerals or as a minor or trace constituent of a great number of sulphides and sulphosalts. The common antimony minerals in endogene (primary) mineral deposits are native antimony, stibnite, and a great variety of sulphosalts of which the most common are tetrahedrite, jamesonite, boulangerite, bournonite, polybasite, and pyrargyrite. The most common supergene antimony minerals in deposits are kermesite, senarmontite, stibiconite, nadorite, and bindheimite. In some deposits pyrargyrite may be of supergene origin.

Much of the antimony of commerce is obtained as a byproduct of the smelting and reduction of lead, copper, silver, and gold ores. Some stibnite veins and their supergene minerals are mined essentially for antimony. The principal types of deposits in which antimony is a constituent are as follows:

(1) Copper shale, argillite, and schist deposits (Kupferschiefer - White Pine - Zambia type): Most of the antimony is present in pyrite, copper sulphides, and various other sulphides. Contents of antimony range from <5 to 300 ppm. The White Pine, Michigan ores are relatively low in antimony according to our analyses of typical material; all samples contained less than 1 ppm Sb.

(2) Copper (uranium, vanadium, silver) sandstone deposits ('Red bed' type): Most of the antimony is present in pyrite and various other sulphides. Antimony contents range from <5 to 500 ppm. The uranium deposits in the Gas Hills and Shirley Basin of Wyoming contain from <1 to 90 ppm Sb. Most of the ores contain less than 1 ppm Sb; the replacements of carbonized wood contain the highest amounts of the element. Copper deposits in red beds in the Pennsylvanian rocks of New Brunswick and Nova Scotia have antimony contents ranging from <1 to 24 ppm Sb, with an average of about 6 ppm. Similar deposits in Triassic rocks at Alderly Edge, Great Britain contain from 60 to 450 ppm Sb. Some vein and lode type deposits in this category are greatly enriched in antimony (e.g. Walton, Nova Scotia) averaging 0.05% Sb in the ores. Most of the antimony in these deposits is present in galena, pyrite, tennantite, chalcopyrite, and proustite.

(3) Lead-zinc deposits in carbonate rocks (Mississippi Valley - Pine Point type): These generally contain only traces of antimony, mainly in galena and sporadic tetrahedrite. Most ores from these deposits contain less than 5 ppm Sb.

(4) Pyritiferous quartz-pebble conglomerates and quartzites enriched in one or more of gold, silver, uranium, thorium and rare-earths (Witwatersrand-Blind River type): Antimony contents range from 1 to 4 ppm according to our analyses of typical ore. Most of the antimony is present in the pyrite, arsenopyrite, and galena with small amounts in minerals such as cobaltite and tennantite.

(5) Native copper deposits in or associated with amygdaloidal basalts (Keweenaw, Michigan type): The antimony content of these deposits is low, averaging less than 1 ppm Sb in the ore according to our analyses. The small amounts of antimony are probably present in copper arsenides (domeykite, algodonite), in rare Ni-Co arsenides, and in the native copper.

(6) Skarn type deposits: The antimony in these deposits is generally associated with Cu, Pb, Zn, Cd, Au, Ag, Mo, As, and Fe, and less commonly with W, Sn, Bi, Te, Ni, and Co. The principal primary antimony-bearing minerals in these deposits are tetrahedrite-tennantite, jamesonite and other sulphosalts, and stibnite. Certain skarn-type gold and polymetallic deposits are slightly enriched in antimony, contents up to 500 ppm being present in some ores. Some deposits such as those in the Bau gold district in Sarawak are rich in stibnite and contain percentages of antimony.

(7) Pegmatites and pegmatite-like bodies en-

riched in one or more of Sn, W, Nb, Ta, Bi, Mo, and U: In these deposits antimony is commonly concentrated in minerals such as tantalite-columbite, pyrochlore-microlite, stibiotantalite and related Nb-Ta minerals; also in small amounts in pyrite, arsenopyrite, bismuthinite, and native bismuth; only rarely in native antimony, allemontite, and stibnite. The contents of antimony in the ores rarely exceed a few tens of parts per million Sb.

(8) Massive bodies, mantos, lodes, veins, and stockworks: These comprise several types, all more or less enriched in sulphides. The principal types are:

(a) Massive nickel-copper sulphide bodies commonly associated with basic rocks (Sudbury type): In these bodies antimony is probably largely associated with arsenic minerals such as arsenopyrite, gersdorffite, niccolite, etc. and perhaps with the platinoids. Small amounts seem to occur in all of the sulphides and bismuth minerals. The antimony content of the ores range up to 22 ppm according to our analyses.

(b) Massive Cu-Zn-Pb sulphide bodies in volcanic and sedimentary terranes (Noranda-Flin Flon-Bathurst type): In these bodies antimony is associated with Cu, Zn, Pb, Cd, Ag, Fe, and As; also with Sn, Bi, Se, and Te in some bodies. Most of the antimony occurs in galena, stibnite, tetrahedrite-tennantite, enargite, various other sulphosalts, chalcopyrite, pyrite, and arsenopyrite. Most deposits average about 50 ppm Sb, but there may be wide divergences from this value.

(c) Veins, lodes, and stockworks principally in granitic rocks and associated sediments and greatly enriched in one or more of Sn, W, Bi, and Mo: There is great variation in these deposits. Some contain essentially cassiterite and wolframite with Cu, Fe, Pb, and Zn sulphides. Others are wolframite-scheelite molybdenum veins, scheelite-quartz-gold veins, wolframite-scheelite silver-gold veins, wolframite-scheelite copper veins, and wolframite-scheelite silver-copper-gold-zinc veins.

The elements concentrated are, likewise, varied and include Li, Rb, Cs, Be, B, F, U, Sc, rare-earths, Mo, Re, W, Mn, Fe, Cu, Ag, Au, Zn, Cd, Ga, In, Tl, Ge, Sn, Pb, As, Sb, Bi, and S. Many of these deposits have wall-rock alteration zones marked by extensive tourmalinization and greisenization. Most of the antimony in the deposits and their alteration zones is present in pyrite and arsenopyrite, rarely in native antimony, stibnite, or jamesonite. The ores generally contain only a few to a few tens of parts per million Sb.

(d) Various polymetallic veins, stockworks, mantos, and lodes containing essentially Cu, Ag, Pb, Zn, and Fe sulphides and sulphosalts: Most of the antimony in these deposits occurs in tetrahedrite, jamesonite, boulangerite, galena, arsenopyrite, pyrite, pyrargyrite, and a great variety of other sulphosalts. Antimony contents range from 0.05 to 0.5 per cent.

(e) Veins greatly enriched in Ni, Co, As, Sb, Ag, Bi, and U (Cobalt-Great Bear Lake-Jáchymov type): Marked concentrations of a variety of Ni-Co-Fe arsenides and native silver occur in these veins. Also present in some deposits are native antimony, dyscrasite, allargentum, pyrargyrite, and other antimony-bearing sulphosalts. The native silver is commonly greatly enriched in antimony. Pitchblende is characteristic of some deposits (Great Bear Lake, Canada; Jáchymov, Czechoslovakia). The antimony content of these deposits commonly ranges between 0.03 to 3 per cent.

(f) Gold-quartz veins, stockworks and silicified zones: The principal antimony minerals are stibnite, tetrahedrite, and a great variety of sulphosalts. Native antimony is relatively rare in most of these deposits but occurs in small amounts in a few. Antimony contents range from a few ppm to low percentages in the ore shoots and their associated wall-rock alteration zones. Pyritic gold-quartz veins and silicified zones devoid of stibnite and other antimony minerals normally contain from <1 to 15 ppm Sb, mainly in the pyrite. Those with marked concentrations of stibnite and sulphosalts (e.g. Yellowknife, Northwest Territories; West Gore, Nova Scotia) have antimony contents up to 0.15 per cent or more.

(g) Realgar-orpiment deposits: These are relatively rare and constitute veins, pockets, and disseminations in various types of rocks. Relatively large deposits of this type are known in Yugoslavia, U.S.S.R., Turkey, and China. The elements associated with arsenic in these deposits include S, Sb, Ag, Pb, Cu, Fe, Au, and rarely Hg. The antimony contents in these ores are not known to the writer. Some are evidently greatly enriched in the element.

(h) Stibnite deposits: These are mainly veins, stockworks, and siliceous replacement deposits along faults and shear zones or in porous and chemically favourable rocks such as sandstones, conglomerates, and carbonate rocks. Some of the replacement bodies are tabular masses along faults; others are stratiform, although they generally intersect or ramify across the bedding. The stibnite in all of these deposits commonly occurs as seams, nests, vug fillings, or in massive lenses and irregular bodies. Associated minerals in some deposits are few and include only quartz, pyrite, marcasite, barite, calcite, and kaolinite. In some deposits of this type calcite may exceed quartz as a gangue mineral (e.g. Shiu Chow vein, China), but quartz is the predominant gangue in nearly all stibnite deposits. Some low temperature stibnite deposits are characterized by the presence of native antimony, realgar, orpiment, native sulphur, gypsum, alunite, and cinnabar. Other deposits have some wolframite (ferberite), and the higher temperature, deep-seated deposits commonly are marked by the occurrence of native antimony, scheelite, arsenopyrite, sphalerite, silver-bearing sulphosalts, gold, and electrum. The elements concentrated in stibnite veins are variable depending apparently on whether they were formed under near surface or deep conditions. The low temperature (near surface) deposits exhibit enrichments of Sb, Si, Fe, Mn, Ba, Sr, As, Ca, and Hg. The deep-seated deposits may have these elements in addition to marked enrichments of Ag, Au, Cu, Zn, Cd, Pb, Bi, and W. The antimony content ranges from minor amounts to several tens of per cent in the ores.

(9) Jamesonite and other types of massive and disseminated sulphosalt deposits. These are relatively rare, the classic examples being at Zimapan in Mexico. There, the deposits occur as replacements (or skarn) in limestone and contain essentially jamesonite, pyrrhotite, pyrite, and sphalerite in a gangue of quartz, calcite, amphibole, apatite, danburite, albite, fluorspar, and garnet. Elsewhere, sulphosalt deposits are replacements or vein deposits containing one or more of the sulphosalts -

jamesonite, boulangerite, livingstonite, berthierite, semseyite, tetrahedrite-tennantite - in a gangue mainly of quartz, calcite, pyrite, and other base metal sulphides.

(10) Mercury deposits: These are mainly fissure veins, stockworks, disseminations, impregnations, and replacement bodies along faults or in brecciated zones in a great variety of rocks. The principal economic mineral is cinnabar. The commonly associated antimony mineral is stibnite. Some deposits such as those in the Ukraine and other parts of U.S.S.R., in Turkey, and Alaska (Red Devil Mine) are greatly enriched in antimony; others, including the great Almaden mine in Spain, Pinchi Lake in British Columbia, the California deposits, and those in Italy at Idria and elsewhere, appear to contain relatively low contents of antimony in the ores. Precipitates from hot springs enriched in mercury (e.g. Sulphur Bank, Steamboat Springs, New Zealand, and Kamchatka, U.S.S.R.) invariably contain high amounts of antimony.

(11) Disseminated bodies in various rocks: Two general types can be distinguished as follows:

(a) Disseminated gold deposits, mainly in sedimentary rocks: A characteristic example is Carlin, Nevada. Here probably also belong certain gold deposits in tuffs and other rocks, examples being the Madsen gold deposit in the Red Lake district of Ontario, the auriferous arsenopyrite occurrences in the Contwoyto Lake area, Northwest Territories, and the Passagem de Mariana deposits in Brazil. The antimony content of these deposits varies widely. In the Carlin ores the antimony ranges from 5-450 ppm in the ores. Similar antimony contents are characteristic of the other deposits noted in this category, according to our analyses. Stibnite and sulphosalts are the most abundant antimony minerals in these deposits; stibnite, and sulphosalts also occur in the Carlin and similar deposits in Nevada.

(b) Disseminated (porphyry) copper and/or molybdenum deposits: The antimony content of these deposits is generally low, especially in the molybdenum type. Some disseminated copper deposits carry some tetrahedrite-tennantite and enargite with traces to minor amounts of antimony. In both the copper and molybdenum types the pyrite is slightly antimoniferous in places. Antimony contents in these deposits are variable, depending mainly on the amount of sulphosalts and enargite present. Most deposits probably contain from 5 to 100 ppm Sb; peripheral deposits with lead and zinc sulphides contain up to 500 ppm Sb or more.

(12) Hot spring deposits: The siliceous sulphide precipitates at a number of hot springs carry relatively large amounts of antimony mainly in the form of stibnite; also as amorphous or adsorbed sulphide(?) material. Examples of these deposits are found in the Taupo thermal zone, New Zealand; Kamchatka, U.S.S.R.; and Steamboat Springs, U.S.A. The Sb content of the precipitates may range up to 30 per cent (Taupo).

(13) Supergene (residual and transported) deposits: Stibnite, native antimony and the sulphosalts of antimony weather slowly and often become armoured to oxidation by antimoniferous supergene products such as kermesite. In this form they accumulate in the oxidized parts of the primary deposits, in the eluvium, and are often transported short distances to accumulate in hollows and karsts in the bedrocks. Such deposits are widespread in Mexico, Bolivia, China, and elsewhere. Karst deposits are particularly characteristic of some parts of the antimony belts of China. Some of the supergene deposits consist of intensely weathered and oxidized stibnite and sulphosalt veins and replacement deposits and now contain mainly clay, opal, chalcedony, limonite, kermesite, valentinite, senarmontite, cervantite, stibiconite, nadorite, and bindheimite with residual nodules and lumps of stibnite, native antimony, jamesonite, and other sulphosalts.

Antimony enjoys a widespread distribution in mineral deposits as shown above, and the element is not confined to any particular metallogenic epoch or province. A few features of its distribution are, however, of interest. Many gold deposits in volcanic belts ranging in age from Precambrian to Tertiary are greatly enriched in antimony. In this respect the element is much like arsenic. Certain gold deposits in greywacke-slate-graphitic schist assemblages throughout the world are, likewise, often enriched in antimony. One also sees great concentrations of antimony in the rich native silver veins (Cobalt-Jáchymov type), some of which contain uranium. Antimony is also commonly enriched in most of the rich lead-zinc-silver deposits of the world, there being a particular intimate association between lead (manifest by the common occurrence of jamesonite and antimoniferous galena) and silver (manifest by the common occurrence of minerals such as freibergite and pyrargyrite). Most of the large economic stibnite deposits are younger than Precambrian and are mainly restricted to sedimentary terranes containing phyllites, limestones, and black schists. The relationships to the pyritiferous black schists, invaded by granitic rocks, particularly porphyries, are intimate and remarkable in the antimoniferous belts of Turkey, Bolivia, and China.

Antimony is a good indicator of deposits in which it is highly concentrated, and in addition is a useful indicator of various other types of deposits in which it is a minor constituent, particularly those of silver, copper, gold, lead, zinc, and mercury as noted above. Antimony responds well in all types of soil and stream sediment surveys and is also a useful indicator in ground, spring, and stream waters. In antimoniferous belts the limonite, manganese, siliceous and other precipitates at the orifices of springs generally report high amounts of antimony. Hot springs with antimony-rich precipitates may signal the occurrence of stibnite or other antimony deposits at depth. There is little information on the use of antimony in vegetation surveys, although it is known that some plants take up considerable amounts of the element in the vicinity of antimoniferous deposits. Stibnite and the various other antimony minerals weather slowly and tend to pass into the weathered residuum, eluvium, and ultimately into the stream sediments as small nodules. Heavy mineral surveys of soils and drainage sediments, utilizing antimony as indicator, may, therefore, be useful in locating or outlining various types of antimoniferous deposits. Finally, antimony-rich fragments of coal or thin coal seams in sandstones and shales may signal the general presence of various types of mineralization in a terrane. (*See* also the section on arsenic).

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 element is also a trace constituent of a great variety of minerals from some of which, e.g. galena, tetrahedrite-tennantite, enargite, jamesonite, it is won as a byproduct of metallurgical processes. The principal secondary or supergene minerals of bismuth are bismutite and bismite.

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

(1) Pegmatites, aplites, mineralized quartz pipes, and stockworks: These generally occur in granitic bodies, acid porphyries, or in high-grade metamorphic schists and gneisses. The common bismuth minerals in these deposits 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, As, P, and F.

(2) Greisen zones, dykes, and irregular bodies developed mainly in granitic rocks, quartz porphyries, or metasediments; also feldspathized zones in granitic rocks and metasediments: These deposits contain mainly bismuth and bismuthinite as the economic minerals. The characteristic minerals and elements in these deposits are the same as those mentioned in (1) above.

(3) Disseminations of bismuth, bismuthinite, and other bismuth minerals in highly altered rhyolitic flows, quartz-feldspar porphyries, tuffs, ignimbrites, etc. The characteristic deposit of this type is at Mount Pleasant, southern New Brunswick. For a description of this deposit and the elements concentrated in it, see the section on tin.

(4) 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 principal bismuth minerals are bismuth, bismuthinite, cosalite, tetradymite, joseite, and other bismuth tellurides. The Gaspé copper deposits Gaspé, Quebec, produce bismuth from copper-molybdenum ores in skarn.

(5) Bismuth in tin, molybdenum, 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, B, and F. (*See* also the sections on tin, molybdenum, and tungsten.)

(6) Bismuth concentrations in complex nickel-cobalt-arsenide deposits: The minerals of importance are bismuth and bismuthinite associated with native silver, carbonates, 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. (*See* also the sections on silver, cobalt, and uranium.)

(7) Bismuth concentrations in lead-zinc-silver and copper deposits: The bismuth is obtained as a byproduct of these ores, the element being present mainly as a trace or minor constituent of galena, tetrahedrite-tennantite, enargite, jamesonite, and various other sulphosalts and sulphides. Native bismuth, bismuthinite, matildite, cosalite, tetradymite, and other bismuth tellurides occur in some of these deposits.

(8) Bismuth concentration 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.

(9) 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.

(10) 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. The general low solubility of most of the common bismuth minerals and the rapid hydrolysis of soluble bismuth salts with consequent precipitation of insoluble products permits collection of minerals like native bismuth, bismuthinite, bismite, and bismutite in soils, eluvium, and stream sediments. Heavy mineral surveys employing analyses of bismuth on the panned concentrates of these materials are particularly useful in locating primary bismuth concentrations.

GROUP VB: VANADIUM, NIOBIUM, AND TANTALUM

Vanadium is widely dispersed in most rock types but only in small amounts. The basic rocks usually contain the highest amount of the element. Vanadium forms a large number of minerals of which the most common are the sulphide patronite, carnotite, tyuyamunite, montroseite, roscoelite (vanadium mica), descloizite, pucherite, 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 and in places with carbonatites: The principal ore minerals are magnetite. The characteristic elements concentrated are V, Ti, Fe, and P. (*See* also the section on niobium.)

(2) Vanadium-bearing uranium deposits in sand-

stone: These are widespread in the western United States and elsewhere. The principal primary minerals are roscoelite and montroseite, and the secondary (supergene) minerals are carnotite, vanoxite, corvusite, and various other vanadium oxides and vanadates. Both primary and secondary (supergene) 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, in asphalt, and in tar sands: 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 and lake 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 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. Perovskite bearing complexes provide a reserve for the future.

The principal deposits of niobium are as follows:

(1) Granitic and syenitic 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, Sb, Bi, Li, Be, Ti, Rb, Cs, rare-earths, U, Th, B, Zr, Hf, P, and F.

(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 and their fenitized zones 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, fluorite, and various rare-earth phosphates and carbonates. Some contain economic concentrations of copper minerals. The elements commonly concentrated in carbonatites are Na, K, Fe, Ba, Sr, rare-earths, Ti, Zr, Hf, Nb, Ta, U, Th, Cu, Zn, P, S, and F. Some complexes are marked by higher than average contents of Ag, and Pb and others by low concentrations of Be and Li and sometimes Mo and W.

(4) Bauxites and laterites: Certain deposits of bauxite, bauxitic clays, and laterite are slightly enriched in niobium, especially those covering or derived from alkalic igneous rocks (up to 0.1% Nb or more). Vermiculite deposits derived from the weathering of phlogopite in carbonatite complexes and their fenitized zones may contain enrichments of pyrochlore, perovskite, and other niobium minerals.

(5) Eluvial and alluvial deposits derived from the preceding 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 surveys. Water analyses using niobium as indicator are generally not effective, but precipitates from springs in niobian areas frequently report high contents of niobium and its associated elements. Areas with carbonatites of Recent and Tertiary age are commonly indicated by alkaline warm and hot springs charged with CO_2 and enriched in Na, K, Ca, Mg, Cl, HCO_3^-, SO_4^{2-}, F (fluoride) and H_2S. Some of the waters are radioactive due to the presence of radium and radon. Older carbonatite areas may be indicated by travertine and limonitic deposits and by beds of alkali salts accompanied by fluorides, phosphates, barite, etc. in former lake basins. 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 Cu, Zn, Pb, Mo, V, Sn, Li, Rb, Ba, Sr, Be, rare-earths, and P are reliable indicators of niobium deposits using soils and stream sediments as sampling media.

Tantalum is a rare metal that commonly accompanies niobium in granitic and syenitic pegmatites, coarse- and fine-grained granites, albite-biotite and albite-riebeckite granites, and greisen zones in granitic rocks and metasediments. Some carbonatites are relatively enriched in tantalum, the element accompanying niobium in its various minerals. The tantalum of commerce is obtained mainly from columbite-tantalite, wodginite, and other tantalum-bearing minerals in pegmatites and eluvial and alluvial deposits derived from them.

The minerals of tantalum are essentially the same as those of niobium and the geochemistry of the two elements are remarkably similar because of the effects of the lanthanide contraction in the periodic table. 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 sulphides 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 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.

The sulphate content of underground and surface waters, stream sediments, soils, and glacial materials may be used as an indicator of both sulphide- and sulphate-bearing deposits of many kinds. Thus, high sulphate contents in these various materials may be indicative of the presence of oxidizing sulphides and sulphosalts or of deposits such as evaporites, polymetallic sulphide deposits, porphyry-type copper-molybdenum deposits, etc. subjected to leaching by ground or stratal waters.

Sulphur has two common isotopes, S^{32} and S^{34}, whose ratio has been much used in problems dealing with the origin of deposits containing sulphur in its many compounds. In general the primary (hypogene) sulphates in most evaporites, veins, and other sulphate-bearing metallic deposits are enriched in S^{34}; on the other hand sulphates of supergene origin derived from the oxidation of primary sulphides generally reflect the sulphur isotopic ratios of the primary sulphides which are commonly much less enriched in S^{34} than are their accompanying hypogene sulphates. It is thus possible by using S^{34}/S^{32} ratios to differentiate hypogene from supergene sulphates. Furthermore, sulphides (mainly pyrite and pyrrhotite) in the country rocks commonly have different sulphur isotopic ratios than those of their contained epigenetic mineral deposits, and the derived sulphates are, likewise, different isotopically. From this it follows that waters leaching mineralized zones may be differentiated from those leaching barren rocks by sulphur isotopic analyses of their contained sulphates. The same holds true for the sulphur isotopic composition of spring precipitates and in same places for the sulphate component of stream sediments. Finally, sulphur isotopic ratios of primary sulphides may be a clue to proximity to ore bodies during drilling. In some sulphide mineralized belts it has been noticed that the S^{34} content of the sulphides in the wall-rocks and alteration zones increases as the sulphide-bearing ore bodies are approached.

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. A large reserve of selenium exists in the phosphorites and in the sulphide-rich black shales and schists. Some coals contain small amounts of selenium (mainly in the pyrite), and the sulphur of volcanic derivation is commonly enriched in the element.

Certain areas of the earth's crust yield selenium in an available form and thus give rise to toxic vegetation which has a deleterious effect on cattle and other animals (selenosis). It is not clear whether these areas are richer in selenium than other areas or whether the marked availability of the selenium is due to particular natural chemical factors.

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-vanadium-copper-silver-molybdenum deposits of the 'red bed' sandstone type, certain pitchblende-selenide deposits, gold-silver selenide deposits, and various types of polymetallic ores, especially those containing copper, mercury, bismuth, 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 amounts generally measured in tenths or hundredths of parts per million. The shales, particularly the carbonate-bearing and pyritic varieties, carry the largest amounts of tellurium (1-2 ppm). The element forms a number of tellurides, especially with gold, silver, lead, bismuth, mercury, copper, and nickel. These occur in a variety of deposits of which the most common are: quartz-wolframite-bismuth veins and stockworks; quartz-cassiterite-sulphide veins and stockworks; massive nickel-copper-cobalt sulphides associated with basic igneous rocks; various polymetallic massive and vein-type sulphide deposits in volcanic and sedimentary terranes; most types of gold-silver deposits, particularly the skarn, quartz vein, lode, and stockwork types; and volcanic deposits of native sulphur. Tellurates and tellurites are also known in the oxidized zones of gold and various polymetallic deposits. Commercially, tellurium is obtained from refining process of polymetallic ores especially those containing copper, nickel, and lead.

Geochemical surveys are not generally carried out to discover tellurium deposits since the element rarely occurs in deposits in amounts greater than a few tens or hundredths of parts per million. Tellurium may, however, be a relatively good indicator of certain types of deposits containing silver, gold, bismuth, nickel, cobalt, tungsten, tin, molybdenum, and copper, when soils, glacial materials, and stream sediments are used as the sampling media. The mineralization in certain zones containing disseminated (porphyry) copper deposits is frequently enriched in tellurium. Tellurides tend to weather slowly and collect in the eluvium and stream sediments near telluriferous deposits. Analyses of heavy concentrates for tellurium may, therefore, be useful in locating these deposits.

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 ribbons, layers, masses, streaks, lenses, and disseminations. Many of these ore bodies are closely connected with serpentinization and talcification of the ultrabasic bodies. Weathering of the primary deposits commonly gives rise to residual concentrations of chromite as in New Caledonia. There is a slight concentration of chromium in some of the uranium-vanadium 'sandstone type' deposits, the element being present largely in chrome micas (mariposite). Slight concentrations of chromium are also noticeable in certain gold-quartz and polymetallic sulphide deposits in basic and ultrabasic rocks. In these deposits the chromium is present mainly in the chrome micas (fuchsite and mariposite) in the wall-rock alteration zones. Chrome micas may also occur in various green schists of sedimentary origin. The content of chromium in fuchsite ranges up to 3.5 per cent and in mariposite up to 0.7 per cent. The chrome garnet, uvarovite, commonly found in serpentinites and in contact rocks rich in chromium may contain up to 20 per cent Cr. Lead chromate (crocoite) and other chromates occur in some of the oxidized zones of lead and other sulphide deposits traversing basic and ultrabasic rocks.

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 of chromite deposits 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. Some chromium deposits are enriched in arsenic (mainly as nickel arsenides) (e.g. Malaga, Spain), and others contain platinoids. These elements may, therefore, be suitable indicators in some districts. 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. Bodies of ultrabasic rocks containing chromite are commonly denuded of vegetation, their soils supporting only grasses and scattered trees. Whether these deleterious effects on vegetation are due to available chromium or to nickel or magnesium is uncertain.

Molybdenum is a trace constituent of most rocks at the part 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, $Ca(Mo,W)O_4$, and wulfenite, $PbMoO_4$, have been worked in the past.

Molybdenum is concentrated in the following types of deposits:

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

(2) Greisen zones, greisen dykes, and greisenized stockworks mainly in granitic rocks but also in metasediments and acid porphyries. The economic mineral is molybdenite associated with bismuth, bismuthinite, chalcopyrite, sphalerite, galena, beryl, scheelite, wolframite, topaz, tourmaline, apatite, and fluorite. The characteristic elements concentrated are the same as those in (3) below.

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

(4) 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.

(5) Disseminated deposits principally in monzonite but also in various acid porphyries, 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 with wolframite as a byproduct in some deposits. The characteristic elements concentrated in these deposits include Mo, Re, Cu, Ag, Be, Fe, W, (Sn), (Th), (U), (Nb), Zn, (Pb), As, B, F, and (P). Silicification is widespread in many of these deposits.

(6) Carbonatites: Molybdenum is enriched in some carbonatites (e.g. Kenya, Uganda, Tanzania) in amounts up to 500 ppm, the element being present mainly in molybdenite, formed in most places during late stage mineralization processes. No commercial bodies of molybdenum ore are yet known in carbonatites, but the possibility exists for future discoveries of molybdenum deposits in these complexes. There are also old reports of enrichments of molybdenum in amounts up to 2.87% MoO_3 in sodalite from Monte Somma in Italy (molybdosodalite). For the elements accompanying molybdenum in carbonatites see the section on niobium.

(7) Disseminations and stockworks in rhyolite flows, quartz-feldspar porphyries, tuffs, ignimbrites, etc.: Deposits of this type are known in Mexico and at Mount Pleasant, southern New Brunswick. The principal molybdenum mineral is molybdenite which is commonly associated with fluorite, cassiterite, wolframite, scheelite, and native bismuth. For further descriptions of these deposits and their elemental associates see the section on tin.

(8) 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.

(9) Gold-quartz, pitchblende, and various polymetallic deposits: Many of these deposits carry small amounts of molybdenite especially if they contain copper minerals. None have yet been found which contain sufficient primary molybdenite to constitute molybdenum ore, although the element could possibly be won as a byproduct from some deposits.

(10) Oxidized molybdenum deposits: These contain mainly wulfenite, $PbMoO_4$, molybdite, MoO_3, powellite, $Ca(Mo,W)O_4$, and/or ferrimolybdite (hydrated molybdate of Fe). They are formed by the oxidation of polymetallic deposits bearing molybdenite. Few are now of commercial importance, but in the past some yielded small tonnages of molybdenum ore.

The aqueous chemistry of molybdenum is particularly complicated, and the details of its migration and concentration in nature are known only in the barest outline. There is essentially no cationic chemistry of molybdenum, and the soluble species are mainly molybdates or complexes. There are also a variety of indefinite colloidal species of which the familiar molybdenum blue (ilsemannite) is the most spectacular. Under most climatic conditions molybdenum is relatively mobile in an alkaline environment and relatively immobile under acidic conditions. This is the reverse behaviour to that shown by copper, and hence a marked separation of copper and molybdenum may be noticed in some supergene environments. Restrictions on the mobility of molybdenum may be imposed by the presence of lead which binds molybdate as the insoluble wulfenite; in alkaline environments where abundant carbonates are present molybdenum appears to be less mobile, probably because of the formation of the relatively insoluble calcium molybdate (powellite).

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. Some bogs, especially those with abundant manganese are greatly enriched in molybdenum near deposits containing the element. 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. Molybdenite weathers slowly in temperate climates and may collect in eluvium and stream sediments. Powellite, wulfenite, and ferrimolybdite exhibit a similar behaviour. Analyses for molybdenum of heavy mineral separates obtained from soils, eluvium, and stream sediments are, therefore, useful in locating or outlining deposits containing molybdenum. In addition, it should be noted that molybdenite generally accompanies the quartz phase of mineralization. During weathering of deposits the quartz being highly resistant passes, together with its contained molybdenite, into the eluvium and ultimately into the streams and rivers as cobbles and boulders. These should be examined carefully for the presence of molybdenite wherever they are found. Any deep blue stains (ilsemannite) in spring precipitates or on stones in streams should be a signal to the presence of oxidizing molybdenum deposits. Spring waters and mine waters are often greatly enriched in molybdenum blue and have a bluish caste when viewed in bright sunlight. There are records of such waters that carry up to 8,000 ppm Mo in the vicinity of oxidizing molybdenum deposits.

Tungsten is widely diffused in most rocks but only in the tenths or parts per million range. Acid rocks such as granites, pegmatites, and quartz-feldspar porphyries have the highest contents of tungsten. Many minerals of tungsten are known, but the most important commercial primary ones are scheelite, wolframite, heubnerite, and ferberite. There are in addition a number of secondary (supergene) tungsten minerals among which the most common are tungstite, cuprotungstite, powellite, raspite, stolzite, ferritungstite, and anthoinite.

Tungsten deposits can be classified as follows:

(1) Pegmatites and aplites: The principal minerals are wolframite, heubnerite, and ferberite with subsidiary scheelite. The main associated minerals are cassiterite, beryl, fluorite, and lithium min-

erals. The principal elements concentrated are W, Mo, Re, Sn, Cu, As, Nb, Ta, Bi, Li, Be, Rb, Cs, B, Sc, rare-earths, F, and Mn.

(2) Greisen zones, greisen dykes, greisenized quartz stockworks, and sheared feldspathized zones mainly in granitic rocks but also in metasediments and acid porphyries: The economic mineral is generally wolframite; scheelite is relatively rare, but occurs in quantity in some deposits. Associated minerals are bismuth, bismuthinite, chalcopyrite, sphalerite, galena, topaz, tourmaline, apatite, and fluorite. The characteristic elements concentrated are W, Mo, Re, Be, Sc, rare-earths, As, Sn, Li, Bi, Fe, Cu, Zn, Pb, B, P, and F.

(3) Disseminations and quartz (opal) stockworks in rhyolite flows, quartz-feldspar porphyries, tuffs, ignimbrites, etc. that are commonly sericitized and opalized: The principal tungsten mineral is wolframite, rarely scheelite, associated with wood-tin and concretionary cassiterite, opal, chalcedony, hematite, bismuth, and bismuthinite. Few of these are economic sources of tungsten minerals. Examples are widespread in the Tertiary rhyolites and ignimbrites of Mexico. The Mount Pleasant deposit in southern New Brunswick also belongs in this class. For descriptions of these deposits see the section on tin.

(4) Skarn deposits: The principal tungsten mineral is scheelite; wolframite, huebnerite, and ferberite are less common. 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, Sc, rare-earths, Bi, Cu, Pb, Zn, Fe, S, As, Au, Ag, B, and F.

(5) Veins mainly with a quartz gangue: There is great variation in these deposits. Some contain essentially cassiterite and wolframite with small amounts of copper, lead, zinc, and iron sulphides. Others are wolframite-molybdenite veins, scheelite-gold-quartz veins, scheelite-wolframite gold-silver veins, scheelite-(wolframite) copper veins, and scheelite-wolframite silver-copper-lead-zinc-veins. The characteristic elements of these deposits are likewise varied and include Li, Rb, Cs, Be, B, Sc, rare-earths, U, Mo, Re, W, Mn, Fe, Cu, Ag, Au, Zn, Cd, Ga, In, Tl, Ge, Sn, Pb, As, Sb, Bi, P, S, and F.

(6) Disseminations and veinlets of scheelite in talc (soapstone) bodies: The origin of these occurrences of scheelite are uncertain. They occur in parts of North Carolina and are described by E.H. Bentzen and L.S. Wiener (Econ. Geol. v. 68, no. 5, p. 703-707, 1973).

(7) Carbonatite complexes: Some alkalic rocks associated with carbonatite complexes are enriched in tungsten in amounts up to 10 ppm or more. Scheelite is reported to occur in some quantity in a carbonatite-like complex with copper minerals in Mauritania. For the elements associated with tungsten in carbonatites see the section on niobium.

(8) Manganese ores: Tungsten is commonly enriched in certain manganese ores particularly those rich in barium (psilomelane). According to Fleischer et al. (Econ. Geol. v. 40, p. 82-83) some of these ores are of hydrothermal origin; others are of secondary (supergene) origin. There are references in the literature to the presence of tungsten in wads in amount up to 0.5 per cent WO_3.

(9) Travertine and siliceous deposits associated with warm and hot springs: Some of these contain small amounts of tungsten mainly in manganese oxide layers, streaks, and spots. Records in the literature show amounts of tungsten up to 4 per cent.

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

(11) 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).

The aqueous chemistry of tungsten is much like that of molybdenum and is particularly complicated. Only the general outlines of the natural migration of the element as soluble species are known. There is essentially no cationic chemistry of tungsten, the soluble species being mainly polytungstates or complexes. There are also a variety of indefinite colloidal (?) species of which the most spectacular are the tungsten blues analogous to the molybdenum compounds. In general, the natural primary tungsten minerals, scheelite and wolframite, are much more resistant to weathering and solution in contrast to the common primary molybdenum mineral, molybdenite. Tungsten is, therefore, generally less mobile than molybdenum. Under conditions of extreme weathering such as occurs in the tropics the primary tungsten minerals weather slowly with the formation of a variety of secondary products of which tungstite and ferritungstite are the most common. Some of the tungsten may pass into solution as tungstate under alkaline conditions, but the element does not seem to migrate far in this state since it is strongly adsorbed by hydrous manganese and iron oxides (wad and limonite).

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 as noted above, 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. Some bogs especially if enriched in manganese commonly contain high amounts of tungsten in the vicinity of tungsten deposits. 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. Those which are most common in tungsten deposits, including B, F, As, Li, and Cu, are useful indicators in some districts.

Both wolframite and scheelite are resistant to weathering and tend to collect in the eluvium near their deposits and in the nearby stream sediments. Heavy mineral surveys utilizing analyses for tungsten in the concentrates from eluvium, soils, and stream sediments are an excellent way to locate primary deposits and placers of both scheelite and wolframite. Scanning of heavy concentrates by ultra violet light will generally indicate the presence of scheelite but not wolframite.

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 and O^{2-}.

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 occurs in the Miask area, U.S.S.R. and elsewhere. Topaz, the aluminum fluosilicate is a common mineral in pegmatites, veins, and greisens containing tin, tungsten, molybdenum, and beryllium. It also occurs in quantity in some gold deposits as at the Brewer mine, near Jefferson, Chesterfield County, South Carolina. The mineral is a pleasing gem if crystalline, flawless and coloured. The massive varieties can be utilized for the production of mullite in ceramics and for the synthesis of CaF_2. There are a host of other fluoriferous minerals that are of economic interest but only for their cationic components. These comprise fluosilicates, fluocarbonates and other complex minerals of lithium, beryllium, zirconium, niobium, and the rare-earths, including such minerals as amblygonite, fluolepidolite, zinnwaldite, euclase, lavenite, wohlerite, leucophanite, cryolithionite, fluocerite, yttrofluorite, and bastnaesite. Villiaumite, the sodium fluoride, is common in some alkaline syenites.

Fluoriferous deposits have a widespread distribution occurring in various types of rocks. The following types of deposits can be recognized:

(1) Fluorite-bearing granitic bodies, rhyolites, and quartz-feldspar porphyries. The fluorite occurs as disseminations and patches in the matrix of the rocks. Examples in granitic rocks are common, one good one being the post-kinematic granites in the Nueltin Lake area, Northwest Territories, Canada. Few if any of these deposits can be considered as commercial sources of fluorite at the present time.

(2) Greisen zones, greisen dykes, feldspathized zones, sericitized zones, and silicified zones mainly in granitic rocks but also in various schists and gneisses. Fluorite and topaz are common accessory gangue minerals in these deposits which are mined mainly for tin, molybdenum, and tungsten. They are not recovered commercially (*see* also the sections on lithium, tin, molybdenum, and tungsten).

(3) Carbonatites: Many of these complexes are rich in fluoride, but the mineral is not generally recovered. The mineral is commonly a late stage mineral in these complexes. Associated fluorides in some carbonatites are cryolite, weberite, and other aluminofluorides. The fluocarbonates, particularly bastnaesite and parisite, that occur in some carbonatite complexes and in associated carbonate masses (e.g. Sulphide Queen mine, Mountain Pass, San Bernardino County, California) comprise a large reserve of fluorine. For the elements associated with fluorine in carbonatites see the section on niobium.

(4) Calcite-fluorite-apatite veins and masses: These unusual deposits are common in the high grade metamorphic terranes of the Precambrian Grenville Province of Canada. Their origin is enigmatic. Some of these deposits contain essentially calcite and fluorite, others have abundant apatite, and still others have these three minerals with biotite, scapolite, pyroxenes, uraninite, and various rare-earth minerals. None have been exploited for fluorite, but some contain up to 20% CaF_2. The elements characteristically concentrated in these deposits are Ca, F, P, U, Th, Zr, Ti, Mo, and rare-earths. *See* also the sections on rare-earths and uranium.

(5) Cryolite deposits: The mineral cryolite is relatively rare; it occurs in some carbonatite complexes and in a large lense-like mass at Ivigtut, Greenland. There, the mass occurs in a granitic rock in gneiss and appears to be associated in some manner or other with the many alkaline rocks and carbonatite complexes in southwestern Greenland. Minerals associated with the cryolite are siderite, argentiferous galena, molybdenite, chalcopyrite, pyrite, arsenopyrite, fluorite, topaz, and a number of rare fluorides. Those searching for cryolite deposits should confine their efforts to districts of alkali-rich rocks and carbonatite complexes.

(6) Veins, lodes, pockets, pipes, mantos, disseminations, and stockworks carrying mainly fluorite: These deposits have a widespread distribution and occur in many rock types, being particularly common in carbonate rocks, shales, sandstones, and in granites, rhyolites, quartz porphyries, and other acidic igneous rocks. The fluorite is commonly massive, well crystallized, often banded and is accompanied by small amounts of galena, sphalerite, pyrite, marcasite, chalcopyrite, barite, carbonates, and quartz. Some deposits in granitic rocks carry minor amounts of cassiterite, wolframite, molybdenite, and scheelite. The elements accompanying fluorine in these deposits are Ca, Fe, S, Si, Ba, Sr, Pb, and Zn; some deposits have Sn, W, Mo, and Cu. These deposits comprise one of the main sources of commercial fluorite.

(7) Bedded, layered, and irregular stratiform deposits mainly in limestones and sandstones: In these deposits the fluorite appears to replace the carbonate rocks or the cement in the sandstones. Associated minerals are carbonates, pyrite, marcasite, sphalerite, galena, and barite. The characteristic elements accompanying fluorine are Fe, Zn, Pb, Sr, and Ba. These deposits are mined extensively in some countries.

(8) Phosphorites and other types of phosphate deposits: Large reserves of fluorine are present in these deposits mainly in the form of fluorapatite (*see* the section on phosphorus).

(9) Miscellaneous sources of fluorine: Fluorite is a gangue mineral in many types of vein deposits including gold deposits (e.g. Cripple Creek, Colorado), and polymetallic deposits, especially lead-zinc deposits, tin deposits, tungsten deposits, and molybdenum-copper deposits. The mineral can probably be recovered as a byproduct from some of these deposits. Topaz is a gangue mineral in a large number of pegmatites, veins, and greisens containing tin, tungsten, molybdenum, and beryl minerals.

(10) Spring deposits: The travertines of both hot and cold springs sometimes contain fluorite,

although rarely in quantities that are commercial. Associated minerals are carbonates, barite, pyrite, opal, limonite, and wad.

(11) Residual deposits: Under certain weathering conditions fluorite disintegrates and dissolves only slowly and tends to collect in the weathered residuum and eluvium near its primary deposits. Some of these residual deposits have been exploited in the past.

In recent years considerable work has been done on the migration of fluorine and its use as an indicator of its deposits and of those in which it is an accessory element. It has been shown that fluorine is an excellent indicator of fluorite deposits using soils, glacial materials, waters (ground and surface), and stream sediments. Plants also tend to take up excess fluoride where available, indicating that vegetation surveys are useful in some places for locating fluorite and other fluoriferous deposits. Since many deposits have associated positive primary fluoriferous halos, the element is also useful in the various types of lithogeochemical surveys. Some of the halos associated with fluoriferous pegmatites in granites are of a negative character, that is fluorine exhibits impoverishment in the granitic rocks surrounding the pegmatites. Good indicators of most low temperature fluorite deposits are Ba, Sr, Pb, Zn, and Cu. High temperature fluoriferous deposits may be indicated by Sn, W, Mo, Nb, Ta, and rare-earths. On a regional basis the water extractable fluorine in granitic rocks may prove useful as an indicator of mineralization in some districts (S.E. Kesler, et al., Bull. Can. Inst. Mining Met., v. 66, no. 730, p. 56-60, 1973).

Fluorine is a persistent constituent of almost all types of mineral deposits, occurring in amounts from traces to minor and major amounts. The element is, therefore, almost the universal indicator of mineralization. The other elements of almost universal occurrence in mineral deposits are boron and sulphur. These three elements used in conjunction with one another provide a formidable array of indicators in geochemical prospecting for practically all types of deposits. Where one element fails to serve another will in most cases.

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.

Some nepheline syenites are enriched in chlorine, the element being present mainly in sodalite. Certain serpentinized ultrabasic bodies are rich in chlorine (up to 0.8% in the serpentine) as are also numerous granitic intrusives (up to 0.5% in the biotite). In the serpentinized bodies, the chlorine is largely present in serpentine and asbestos probably replacing the OH groups; its source is most probably the marine sediments that enclose most of these rocks. In the granitic rocks the bulk of the chlorine is present in micas, commonly biotite, where it substitutes for the OH groups. In all rocks there is always some chlorine in NaCl in liquid inclusions. Certain coals are rich in chlorine with amounts up to 1 per cent Cl.

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.

Chloride brines, both cold and hot, issuing from springs and present in faults are common in regions of epigenetic mineral deposits containing gold, silver, and the various base metals. They are particularly abundant in Tertiary and Quaternary volcanic regions, but also occur in older rocks, some even of Precambrian age. The relationship of these brines to the epigenetic deposits is uncertain, but some investigators think that the metals are transported as chlorides. Whatever the relationship, the occurrence of high amounts of chlorides in ground and spring waters should be taken as an indication of mineralization in volcanic and associated sedimentary terranes. Along the same line it has been suggested that the chlorine content of intrusives can be used as an indicator of mineralization (G. Stollery et al., Econ. Geol. v. 66, p. 361-367, 1971; W.T. Parry, Econ. Geol. v. 67, p. 972-975, 1972). Thus, fecund intrusives rich in chlorine in a district may be a general guide to the presence of associated magmatic-hydrothermal deposits. The water-extractable chlorine in granitic rocks appears, however, to be of little use as an indicator of plutons that have associated mineralization (S.E. Kesler et al., Bull. Can. Inst. Mining Met., v. 66, no. 730, p. 56-60, 1973). High chloride contents in ultrabasic and basic intrusives and in waters leaching zones of these bodies may be suggestive of the presence of asbestos and nickel-cobalt-copper sulphide deposits, the latter due to the redistribution of nickel, cobalt, copper, etc. during serpentinization and other hydration processes.

In hot arid regions chlorine tends to concentrate in the oxidized zones of silver, copper, mercury, and lead deposits where the element is bound as the relatively insoluble calomel, HgCl, chlorargyrite, AgCl, and Hg chlorides, double chlorides, bromides, iodides, and oxychlorides. Some of these minerals collect in the soils, eluvium, and nearby stream sediments where leaching has not been too extensive.

Bromine is obtained mainly from the sea, stratal brines, bitterns, 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.

The geochemistry of bromine in epigenetic deposits and their associated primary halos and host rocks is not well known. The element occurs in igneous-type rocks in amounts ranging from 0.5-2 ppm, in sediments in amounts up to 50 ppm increasing generally with the amount of organic matter, and there is some evidence that slight concentrations take place in a variety of epigenetic sulphide and other mineral deposits. In hot arid regions bromine tends to concentrate in oxidized zones of silver, copper, mercury, and lead deposits where the element is bound as the insoluble bromargyrite, AgBr, and as a minor constituent in a great variety of Ag, Cu, Pb, and Hg chlorides, double chlorides, iodides, and oxychlorides.

Iodine is obtained as a byproduct of Chilean nitrates, from natural brines and mineralized waters, oil field 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, $Ca_2(IO_3)_2CrO_4$, and lauterite, $Ca(IO_3)_2$ (*see* also the section on nitrogen).

Those searching for sources of iodine should analyze brines, mineralized waters, oil field waters (some of which contain up to 150 ppm I as in Java), natural salts, coals, caliche, and saline soils directly for the element.

The geochemistry of iodine in epigenetic deposits and their associated primary halos and host rocks is not well known. The element occurs in igneous-type rocks in amounts ranging from 0.05-0.5 ppm, in sediments up to 1 ppm increasing generally with the amount of organic matter, and there is some evidence that slight concentrations take place in a variety of epigenetic sulphide and other mineral deposits. Certain 'porphyry copper' and massive sulphide deposits are said to be relatively enriched in iodine. Some sulphide deposits, however, appear to be lower in iodine content than their host rocks. In hot arid regions iodine tends to concentrate in the oxidized zones of silver, copper, mercury, and lead deposits where the element is bound as the insoluble iodargyrite, AgI, and as a minor or trace constituent in a great variety of Ag, Cu, Pb, and Hg chlorides, double chlorides, bromides, and oxychlorides.

The use of iodine as an indicator of epigenetic mineral deposits requires detailed study since some of the results quoted in the literature.
dictory as to the effectiveness of 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 manganiferous sediments.

Manganese ores are of several types including veins and lenses of various manganese oxides and manganiferous 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; manganiferous shales; metamorphosed sedimentary deposits consisting of a variety of manganese oxides; and residual deposits derived form all of the foregoing types of deposits. Parts of the ocean floor are covered by manganese nodules and irregular masses which are not only a vast major reserve of the element, but they also contain variable amounts of metals such as Cu, Co, Ni, Mo, and W which can probably be removed economically.

Manganiferous 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 manganiferous deposits, and spring and stream precipitates are generally greatly enriched in manganese in terranes containing deposits and manganiferous shales. The vegetation, likewise, generally reflects the presence of manganese by the high contents of the element in the ash of plants. Manganese bogs are particularly common in manganiferous regions.

In passing it should be remarked that manganese is a general indicator of certain types of lead-zinc-silver deposits and gold veins. In the former (e.g. Keno Hill, Yukon; Coeur d'Alene, Idaho) siderite is one of the principal gangue minerals and manganese is markedly concentrated. In the gold deposits the gangue minerals are rodochrosite, rhodonite, and other manganese minerals such as johannsenite and alabandite, these minerals are particularly characteristic of deposits of Tertiary vintage.

Hydrous manganese oxides in soils, spring precipitates, and stream sediments tend to concentrate many elements mainly those that form cations or cationic complexes. This feature is partly due to adsorption processes promoted by the negative charge which the colloidal hydrous manganese oxides carry and partly due to coprecipitation processes. The list of elements concentrated by hydrous manganese oxides is long and practically includes all of the metals and some of the non-metals as well. The following elements exhibit a marked concentration by hydrous manganese oxide (wad): Li, Sr, Ba, Ra, Mo, W, Co, Ni, Cu, and Ag.

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 3,000 ppm or more. Sulphides such as pyrite, chalcopyrite, bornite, sphalerite, and galena may contain up to a few ppm Re in some deposits. Three poorly differentiated minerals of rhenium are known, dzhezkazganite, $CuReS_4$(?), rhenium sulphide, ReS_2(?), and rhenium oxide, Re_2O_7 (?). None of these minerals are of commercial importance. Rhenium is enriched in molybdenite deposits, in some porphyry copper-molybdenum deposits, in copper-bearing sandstones (e.g. Dzhezkazgan, U.S.S.R.), and in a few other types of Cu, Pb, Zn, and U deposits. Some coals contain traces of rhenium. 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, copper, niobium, tantalum, tungsten, rare-earths, and platinum group metals. Selenium and tellurium often show a correlation with rhenium in some deposits.

Rhenium has not been used much as an indicator of deposits in which it occurs mainly because the element is difficult to determine accurately at the concentrations it occurs in natural materials (0.005 ppm). Some cupriferous and uraniferous sandstones, however, may average about 25 ppm Re. Where enrichments of rhenium are encountered in weathered residuum, soils, glacial materials, and stream sediments, molybdenum, tungsten, copper, and a variety of other polymetallic sulphide deposits should be suspected in the terrane. Enriched amounts of rhenium in plant ash may also indicate the presence of rhenium-bearing rocks and deposits. A.T. Meyers and J.C. Hamilton (U.S. Geol. Surv. Prof. Paper 424-B, p. B-286-B-288) found from 50 to 500 ppm Re in the ash of a number of plants growing in the uraniferous sandstone regions of the western United States.

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 and hematite; 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. In addition to these types we may add the hematite and magnetite masses and disseminated bodies commonly found in carbonatite complexes. Some of these are now worked for iron ores; magnetite is recovered from others as a byproduct of copper and niobium mining. Bog iron ores, consisting of limonite, goethite, hematite, and other indefinite iron minerals, are no longer an important source of iron, although some are still worked in places for ocher.

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 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. Bog iron ore deposits may be indicators of terranes rich in iron but are not necessarily indicators of iron deposits. Many derive from the weathering of pyrite, iron carbonates, and iron silicates in ordinary rocks. Others indicate the presence of massive sulphide deposits rich in pyrite. Care should be taken during prospecting to discover the source of iron in limonite-cemented conglomerates, limonite-rich precipitates, bog iron ores, and other accumulations of secondary iron-rich materials.

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, gersdorffite, garnierite, nepouite, and nickeliferous serpentine (serpophyte).

The following types of nickel deposits can be distinguished:

(1) Massive sulphide lenses and disseminated deposits containing essentially pentlandite, pyrrhotite, pyrite, and chalcopyrite commonly with small amounts of platinoid minerals. There is great variety in these deposits; most occur in or near basic and ultrabasic sills, sheets, lenses, lopoliths, stocks, dykes, and flows; others may be somewhat removed from basic and ultrabasic igneous rocks but in a terrane where they are present. The type deposits are those at Sudbury, Ontario. The principal elements concentrated are Ni, Co, Fe, Cu, Au, Ag, Pt metals, Se, Te, As, and S. Some deposits in this classification contain the nickel in a very dispersed state in three principal ways: as a substitution of magnesium in various minerals, e.g. olivine and serpentine; in finely divided nickel sulphides; and in Ni-Fe alloys. These bodies are not generally economic.

(2) Veins and lenses of sulphides containing millerite, gersdorffite, chalcopyrite, pyrrhotite, and pyrite. The characteristic elements concentrated are Ni, Co, Fe, Cu, and S. Some of these deposits are intimately associated with basic and ultrabasic rocks; others exhibit only a general relationship.

(3) Veins containing niccolite, gersdorffite, 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) Residual (supergene) nickel-cobalt deposits: These are of two types not readily separated from each other. One type contains the nickel essentially in garnierite, nepouite, and nickeliferous serpentine (serpophyte), and the other (laterites) contains nickel mainly in a complex of hydrous iron, manganese, and nickel oxides and indefinite supergene silicates. Both types are often found together and are gradational or intermixed. Some of these deposits occur at the present erosion surface; others are fossil and represent ancient buried erosion surfaces. The characteristic elements concentrated are Ni, Co, Fe, Mn, 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. Some bogs, especially those rich in manganese, are often enriched in nickel (and cobalt) in regions containing nickel deposits. The ancillary indicators of nickel deposits are Cu, Co, As, platinoids, and Cr. The last element may be particularly useful in deeply weathered terranes. Heavy mineral surveys of soils, glacial materials, and stream sediments utilizing Ni, Co, and Cr as indicators are generally effective in locating zones of nickel mineralization.

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. There is also commonly some substitution of cobalt for nickel in many of the nickel minerals.

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 (Zambia), 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, Mn, 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. Bogs enriched in manganese behave similarly. 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. Heavy mineral surveys of soils, weathered residuum, and stream sediments can be used effectively to locate cobalt deposits in some terranes.

Cobalt is a particularly good indicator of a number of types of deposits in which it occurs as a minor constituent, mainly because it has a relatively high mobility under normal weathering conditions. The deposits indicated by cobalt include those of copper (shales and some vein type deposits), nickel-copper (massive sulphide deposits), uranium (vein types and disseminated types in shales and some sandstones), native silver-Ni-Co arsenide vein type deposits, certain Pb-Zn veins and lodes, and certain types of cobaltiferous gold deposits.

Cobalt and nickel are commonly enriched in coal fragments and thin coal seams in sandstones and shales in the vicinity of "red bed" deposits. Both elements may, therefore, serve as indicators of general mineralization in red bed environments. See also the section on arsenic.

The platinum metals include ruthenium, rhodium, palladium, osmium, iridium, and platinum. 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,Ni)S, laurite RuS_2, and stibiopalladinite Pd_3Sb. A number of other rare platinoid minerals containing Te, As, Sb, Sn, Hg, and Bi are known. The only rocks slightly enriched in platinum metals are ultrabasic rocks such as dunites, peridotites, and serpentinites.

The principal types of deposits in which the platinum group metals are concentrated include:

(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. A number of 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, As, Ag, and Au. There are also minor enrichments of Te, Bi, Sn, and Sb commonly associated with the platinoid metals. The grade of these deposits is roughly 0.005 oz/ton Pt (0.17 ppm) and 0.008 oz/ton Pd (0.27 ppm). Some of the Noril'sk ores in U.S.S.R. are exceptionally rich in platinoids (up to 0.3 oz/ton or 10 ppm).

(2) Hortonolite-dunite pipe deposits: These rocks 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 associated with sperrylite and cooperite, and the characteristic elements concentrated are Pt metals and Cr.

(3) Disseminated platinum metal minerals in pegmatitic pyroxenite with sulphide and chromitite segregations in basic and ultrabasic layered intrusions, dykes, and lenses: These deposits are common in 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. The grade of the Merensky Reef is roughly about 0.25 oz/ton platinoids (8 ppm), 0.20 per cent Ni, and 0.10 per cent Cu.

(4) Skarn deposits associated with basic and ultrabasic rocks: These deposits appear to develop where basic and ultrabasic rocks, particularly the latter, intrude carbonate rocks. Some are in shear zones and fractures in other types of rocks underlying or overlying ultrabasic bodies of rock. Examples are known in South Africa and elsewhere. One deposit in Sumatra was a skarn in limestone near a granite contact. It was characterized by much garnet and wollastonite and enrichments of Pt metals, Au, Ag, and Cu. Serpentinites occurred nearby. The principal platinum minerals in the skarn deposits are sperrylite, cooperite and stibiopalladinite; associated minerals are copper and nickel sulphides. The principal elements concentrated are Pt metals, Ni, Co, Fe, and Cu; sometimes Au and Ag.

(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. There is commonly a close association between copper and platinum metals in these deposits. If there is no copper in the deposits the platinoids are either rare or absent. Some of the cupriferous platinoid-rich ores are arseniferous or antimoniferous. Most of these deposits occur in or near peridotites, serpentinites, or other ultrabasic rocks in later shear zones, faults, or crushed zones. There is ample evidence to support the thesis that the platinoids (and the Cu, Ag, Au, etc.) were extracted from the basic and ultrabasic and their intruded rocks by some process of metamorphic secre-

tion. An excellent example of this possibility is provided by the Cuniptau mine near Goward, Ontario. The oxidized zones of some of these deposits are enriched in platinum metals in places, commonly in plumbojarosite, scorodite, and similar minerals. One good example of this occurred in the Yellow Pine district, southern Nevada (U.S. Geol. Surv. Bull. 620, p. 1-44, 1915).

(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. Some of those in South Africa occur in brecciated quartz lodes occupying faults of post-Karroo age in felsite and felsite tuff comprising part of the Bushveld igneous complex. Various platinoid minerals including native platinum, are associated with specularite, chrome chlorite, and sericite.

(7) Slight concentrations in uraniferous veins and other deposits: The Nicholson mine and some other prospects in the Uranium City uraniferous belt of Saskatchewan contain small concentrations of platinoids. There, the platinoids appear to be associated with selenides. This association - platinoids-Se - is a common one noticeable at Sudbury; Tilkerode, Harz; Artonvilla mine, Messina, South Africa (Econ. Geol. v. 69, p. 257-262, 1974) and elsewhere.

(8) Porphyry (disseminated) copper ores: Some of these contain small amounts of platinoids, mainly palladium.

(9) Copper shales and schists (Kupferschiefer-White Pine-Zambia type): Some of these contain trace amounts of platinoids associated with the copper and Ni-Co minerals. Rich copper sections of the Kupferschiefer run about 1 ppm Pt and 1 ppm Pd respectively.

(10) Witwatersrand quartz-pebble conglomerates: 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.

(11) Coals: Certain varieties of coal contain traces of platinoids. Reference is made in the literature to the presence of platinoids in the range 0.05 to 1 ppm in the ash of various coals.

(12) Gossans and residual deposits: Most gossans on massive sulphide bodies and disseminations in basic and ultrabasic igneous rocks contain enriched amounts of platinoids. Some laterites on these rocks are, likewise, enriched in these metals in Ethiopia and elsewhere. Chromite commonly accompanies the platinum nuggets and residual sperrylite in these deposits. Platinum is also reported in the bauxite of Tungar Hill and Dhangawan in India; its nature is not known.

(13) Spring deposits: There are reports of traces of platinum in some spring deposits in New South Wales, Australia.

(14) Placers: Native platinoids pass directly from their deposits into eluvial and alluvial placers. The various platinoid minerals, including sperrylite and the sulphides, sulphide-arsenides, antimonides, tellurides, and selenides, may do, likewise, although under conditions of intense weathering they tend to liberate the metals which accrete in the oxidized zones and in the eluvium to give dust, small nodules, and nuggets of platinoids which ultimately collect in eluvial and alluvial placers. These types of placers are invariably found in terranes of ultrabasic and basic rocks especially serpentinites. The native platinoids and various platinoid minerals in placers are accompanied by chromite, chrome magnetite, ilmenite, native gold, and the various other minerals often found in placers. The famous platinum sands of Choco, Columbia carry about 0.5 oz platinoids/ton and about the same amount in gold. Native lead is also found in these placers.

Little published material is available on geochemical prospecting for the platinum metals. Those searching for such deposits should concentrate on areas containing layered ultrabasic rocks, differentiated ultrabasic dykes and lenses, and nickel-cobalt deposits, especially of the Sudbury type. All types of copper deposits should be carefully scrutinized for platinum metals especially those in or near ultrabasic rocks. Probably the best attack is to make heavy concentrates of the soils, glacial materials, and stream sediments of an area followed by detailed mineralogical and spectrographic analyses. Chromite is a good indicator for platinum metals in some areas. Other good indicators would appear to be Ni, Co, Cu, and V. There is also commonly a coherence of the platinum metals with one or more of the following elements: Ag, Au, Sn, Pb, As, Sb, Bi, Te, Se, Hg, and P. Some of these may be useful in lithogeochemical, pedogeochemical, hydrogeochemical (water and stream sediment), heavy mineral, and biogeochemical surveys run to discover platinoid deposits. The platinoids may be useful in differentiating gossans that indicate economic Ni-Cu deposits from those that are developed on barren sulphides or rocks. In Australia for instance the economic Ni-Cu deposits are marked by gossans enriched in the platinoids.

GROUP 0: 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 natural gases held in the rocks. The others are obtained from liquefaction of the gases in the atmosphere. Those searching for these inert gases in various natural gases should analyze them directly for the various members of the group.

Radon, the radioactive member of the series, is composed of the three isotopes Rn^{222}, Rn^{219}, and Rn^{220} derived respectively from decay process in the uranium, actinium, and thorium families. The longest lived of these isotopes is Rn^{222} (3.8 days). The radon content of water, till, and soil can be used as an indicator of uranium and thorium deposits in certain areas.

Helium consists of two isotopes He^3 and He^4. The latter is constantly produced, as alpha particles, in the decay process associated with uranium, thorium, and samarium. He^3 derives from the decay of tritium, and its abundance is exceedingly low ($1.3 \times 10^{-4}\%$). Concentrations of helium in natural waters, rocks, soils, etc. may signal the presence of uranium and thorium deposits.