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PROSPECTING FOR GOLD AND SILVER DEPOSITS

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Geochemical methods for the discovery of blind mineral deposits

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THE GEOCHEMISTRY OF ANTIMONY AND ITS USE AS AN INDICATOR ELEMENT IN GEOCHEMICAL PROSPECTING

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ABSTRACT

Boyle, R.W. and Jonasson, I.R., 1984. The geochemistry of antimony and its use as an indicator element in geochemical prospecting. J. Geochem. Explor., 20: 223—302.

The geochemistry of antimony is reviewed, and the use of the element as an indicator in geochemical prospecting for various types of mineral deposits is outlined.

Antimony is widely diffused in many types of mineral deposits, particularly those containing sulphides and sulphosalts. In these and other deposits, antimony commonly accompanies Cu, Ag, Au, Zn, Cd, Hg, Ba, U, Sn, Pb, P, As, Bi, S, Se, Te, Nb, Ta, Mo, W, Fe, Ni, Co, and Pt metals. Under most conditions antimony is a suitable indicator of deposits of these elements, being particularly useful in geochemical surveys utilizing primary halos in rocks, and secondary halos and trains in soils and glacial materials, stream and lake sediments, natural waters, and to a limited degree vegetation. Some of the natural antimony compounds (e.g. stibine, dimethylstibine) are volatile, but methods utilizing gaseous antimony halos for geochemical prospecting have not yet been developed.

INTRODUCTION

Antimony is an ancient element and is mentioned in the Old Testament (II Kings, 9, 30), "and she painted her face (with stibium)". The reference is to the use of stibnite as a cosmetic for darkening the eyes. Pliny Secundus called the element *stibium*, and in a latin translation of Geber, the alchemist, it is termed *antimonium*. The element was prepared and its compounds described by Basil Valentine (probably Tholde) in his treatise "The Triumphal Chariot of Antimony" written in the 15th century.

Antimony is widely diffused in nature and is concentrated in many types of mineral deposits, particularly those containing sulphides and sulphosalts. It accompanies many elements in their deposits including Cu, Ag, Au, Zn, Cd, Hg, Ba, U, Sn, Pb, P, As, Bi, S, Se, Te, Nb, Ta, Mo, W, Fe, Ni, Co, and Pt metals. Antimony is, therefore, an ideal indicator in geochemical prospecting surveys for some twenty elements of commercial importance.

In preparing this outline of the geochemistry of antimony we have consulted most of the literature available on the element up to the end of 1982.

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This we have supplemented with our own data and research on the geochemistry of antimony extending over a period of some thirty years. During the compilation of the tables on the normal or background abundance of antimony in the various earth materials we encountered considerable difficulty in deciding which analytical data in the literature should be used in our calculations because of the different analytical procedures employed, rock nomenclature, possible presence of antimony mineralization, and so on. These problems are familiar to all geochemists who attempt to calculate normal or background abundance figures. We have been selective in our compilation, utilizing only those data which in our opinion have been obtained by reliable modern analytical procedures on earth materials which seemed to us from the descriptions of the samples to be well removed from the effects of antimony mineralization. Admittedly, this is a subjective procedure, and we would stress the fact that our abundance figures are only estimates at best. All of our data sources are given in the Selected Bibliography at the end of the paper.

GENERAL GEOCHEMISTRY AND MINERALOGY

Antimony is the fourth member of Group VA of the periodic system, which also includes nitrogen, phosphorus, arsenic, and bismuth. In some of its chemical reactions antimony behaves much like arsenic and bismuth.

In nature three oxidation states are possible for the element — the metallic or covalent (0) state, and the (III) and (V) states. The metallic state is not uncommon for the element in certain types of mineral deposits. The (III) and (V) states are common in a variety of complex minerals and in dissolved salts in natural waters. The (III) state is also represented in the gaseous compound SbH_3 (stibine) which may occur under certain natural conditions. Because of the multiple oxidation states of the element and the tendency to form soluble complexes and complex compounds, the geochemistry of antimony is intricate and not well characterized. A generalized cycle of antimony interconversions in nature is shown in Fig. 1. The elements most frequently associated with antimony in nature are arsenic and sulphur.

Antimony has two stable isotopes in nature, the conventional abundances being as follows (Lederer and Shirley, 1978):

^{121}Sb 57.3%

^{123}Sb 42.7%

No authenticated differences in the isotopic composition of antimony have yet been found in nature. Radioactive antimony isotopes are commonly noted in the atmosphere after thermonuclear explosions. The half life of most of these isotopes is short (e.g. ^{124}Sb - 60.2 d; ^{125}Sb - 2.71 y).

Native antimony is relatively common in certain types of mineral deposits despite the fact that the element has a marked chalcophile character forming sulphides and a great variety of sulphosalts, particularly with the metals Cu, Ag, Zn, Hg, Pb, and Fe. The most common of these sulphosalts is tetrahedrite-

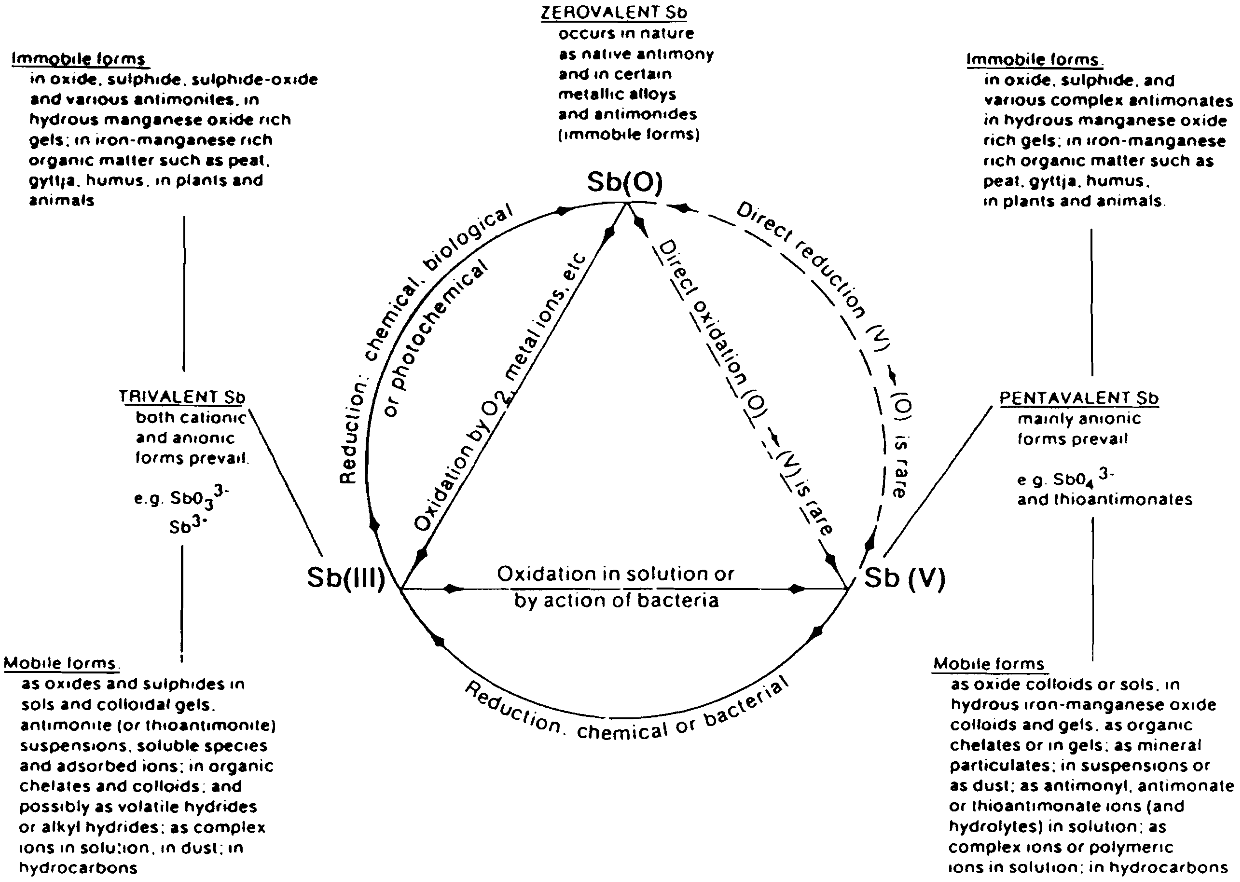

Fig. 1. Cycle of antimony interconversions in nature.

tennantite. Antimony forms oxides and complex oxides in nature, and there are a large number of natural antimonites and antimonates and other complex oxygen-salts of the element. The biophile character of antimony is manifest by its presence, usually in small amounts, in a variety of living organisms and their fossil equivalents.

The principal antimony minerals are given in Table I. Only the most common antimonites and antimonates are given. The principal antimony minerals in endogene (hypogene) deposits are native antimony, stibnite, tetrahedrite, jamesonite, boulangerite, and pyrargyrite. The other sulphosalts of the element are relatively rare. The common supergene antimony minerals, formed as a result of oxidation of the hypogene sulphides, sulphosalts, etc., are senarmontite, stibiconite, kermesite, and bindheimite.

Antimony is found as traces and minor quantities in many of the native elements, in practically all the common sulphides, and in a great variety of secondary oxidation products, particularly in sulphates, arsenates, etc. The element is also a trace or minor constituent in a number of complex niobates and tantalates.

The principal carriers of antimony in rocks and in many types of mineral deposits are arsenopyrite and pyrite. The latter mineral may contain up to 100 ppm or more Sb, the element being apparently present in lattice sites

TABLE I

Antimony minerals

Native elements and intermetallic compounds:			
Antimony	Sb	Allemontite	$SbAs + As$ or Sb
Stibarsen	$SbAs$	Paradocrasite	$Sb_2(Sb,As)_2$
Sulphides, antimonides, arsenides, tellurides, etc.			
Stibnite	Sb_2S_3	Geversite	$PtSb_2$
Metastibnite	Sb_2S_3	Insizwaite	$Pt(Bi,Sb)_2$
Wakabayashilite	$(As,Sb)_{11}S_{18}$	Stibiopalladinite	Pd_5Sb_2
Cuprostibite	$Cu_2(Sb,Tl)$	Genkinite	$(Pt,Pd)_4Sb_3$
Horsfordite	Cu_5Sb	Isomertieite	$Pd_{11}Sb_2As_2$
Allargentum	$Ag_{1-x}Sb_x$	Mertieite — I	$Pd_{11}(Sb,As)_4$
Dyscrasite	Ag_3Sb	Mertieite — II	$Pd_8(Sb,As)_3$
Stistaite	$SnSb$	Arsenopalladinite	$Pd_8(As,Sb)_3$
Breithauptite	$NiSb$	Testibiopalladite	$Pd(Sb,Bi)Te$
Sudburyite	$(Pd,Ni)Sb$	Hexatestibiopanickelite	$(Ni,Pd)_2SbTe$
Stumpflite	$Pt(Sb,Bi)$	Vincentite	$(Pd,Pt)_3(As,Sb,Te)$
Nisbite	$NiSb_2$	Tellurantimony	Sb_2Te_3
Seinajokite	$(Fe,Ni)(Sb,As)_2$	Montbrayite	$(Au,Sb)_2Te_3$
Aurostibite	$AuSb_2$	Borovskite	Pd_3SbTe_4
Sulphosalts:			
Skinnerite	Cu_3SbS_3	Fuloppite	$Pb_3Sb_8S_{15}$
Permingeatite	Cu_3SbSe_4	Plagionite	$Pb_5Sb_8S_{17}$
Famatinite	Cu_3SbS_4	Heteromorphite	$Pb_7Sb_8S_{19}$
Chalcostibite	$Cu_6Tl_2SbS_4$	Semseyite	$Pb_9Sb_8S_{21}$
Gruzdevite	$Cu_6Hg_3Sb_4S_{12}$	Boulangerite	$Pb_5Sb_4S_{11}$
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	Robinsonite	$Pb_4Sb_6S_{13}$
Hakite	$(Cu,Hg,Ag)_{12}Sb_4(Se,S)_{13}$	Zinkenite	$Pb_6Sb_{14}S_{27}$
Giraudite	$(Cu,Zn,Ag)_{12}(As,Sb)_4(Se,S)_{13}$	Playfairite	$Pb_{16}Sb_{18}S_{43}$
Freibergite	$(Ag,Cu,Fe)_{12}(Sb,As)_4S_{13}$	Launayite	$Pb_{22}Sb_{26}S_{61}$
Goldfieldite	$Cu_{12}(Sb,As)_4(Te,S)_{13}$	Dadsonite	$Pb_{21}Sb_{23}S_{55}Cl$
Paakkonenite	Sb_2AsS_2	Ardaite	$(Pb,Fe)_{20}Sb_{12}S_{34}Cl_8$
Getchellite	$AsSbS_3$	Bournonite	$PbCuSbS_3$
Miargyrite	$AgSbS_2$	Meneghinite	$Pb_{13}CuSb_7S_{24}$
Aramayoite	$Ag(Sb,Bi)S_2$	Giessenite	$Pb_{16}Cu_2Bi_{12}Sb_3S_{60}$(?)
Polybasite	$(Ag,Cu)_{16}Sb_2S_{11}$	Freieslebenite	$PbAgSbS_3$
Pyrargyrite	Ag_3SbS_3	Andorite	$PbAgSb_3S_6$
Pyrostilpnite	Ag_3SbS_3	Ramdohrite	$PbAgSb_3S_6$
Samsonite	$Ag_4MnSb_2S_6$	Diaphorite	$Pb_2Ag_3Sb_3S_8$
Stephanite	Ag_5SbS_4	Fizelyite	$Pb_5Ag_2Sb_8S_{18}$
Owyheeite	$Ag_2Pb_5Sb_6S_{15}$	Incaite	$(Pb,Ag)_4FeSn_4Sb_2S_{13}$
Arsenpolybasite	$(Ag,Cu)_{16}(As,Sb)_2S_{11}$	Cylindrite	$Pb_3FeSn_4Sb_2S_{14}$
Antimonpearceite	$(Ag,Cu)_{16}(Sb,As)_2S_{11}$	Potosiite	$Pb_5Au(Te,Sb)_4S_{5-8}$
Billingsleyite	$Ag_7(Sb,As)S_6$	Franckeite	$(Pb,Fe)(Bi,Sb)_2S_4$
Livingstonite	$HgSb_4S_8$	Nagyagite	$Pb_5Au(Te,Sb)_4S_5n_8$
Tvalchrelidzeite	$Hg_{12}(Sb,As)_8S_{15}$	Sakharovaite	$(Pb,Fe)Bi,Sb)_2S_4$
Gerstleyite	$Na_2(Sb,As)_8S_{13} \cdot 2H_2O$	Ustarasite	$Pb(Bi,Sb)_6S_{10}$
Galkhaite	$(Cs,Tl)(Hg,Cu,Zn)_6(As,Sb)_4S_{12}$	Kobellite	$Pb_5(Bi,Sb)_8S_{17}$
Chalcothallite	$Tl_2(Cu,Fe)_6SbS_4$	Tintinaite	$Pb_5(Sb,Bi)_8S_{17}$
Vrbaite	$Tl_4Hg_3Sb_2As_8S_{20}$	Jamesonite	$Pb_4Fe3b_6S_{14}$
Rohaite	$TlCu_5SbS_2$	Parajamesonite	$Pb_4FeSb_6S_{14}$
Weissbergite	$TlSbS_2$	Benavidesite	$Pb_4(Mn,Fe)Sb_6S_{14}$
Parapierrotite	$Tl(Sb,As)_5S_8$	Gudmundite	$FeSbS$
Pierrotite	$Tl_2Sb_6As_4S_{16}$	Berthierite	$FeSb_2S_4$
Chabourneite	$(Tl,Pb)_5(Sb,As)_{21}S_{34}$	Garavellite	$FeSbBiS_4$
Guettardite	$Pb(Sb,As)_2S_4$	Costibite	$CoSbS$
Twinnite	$Pb(Sb,As)_2S_4$	Paracostibite	$CoSbS$
Veenite	$Pb_2(Sb,As)_2S_5$	Willyamite	$(Co,Ni)SbS$
Geocronite	$Pb_{14}(Sb,As)_6S_{23}$	Ullmannite	$NiSbS$
Jordanite	$Pb_{14}(As,Sb)_6S_{23}$	Tolovkite	$IrSbS$
Sterryite	$Ag_2Pb_{10}(Sb,As)_{12}S_{29}$	Hauchecornite	$Ni_9Bi(Sb,Bi)S_8$
Madocite	$Pb_{17}(Sb,As)_{16}S_{41}$	Tucekite	$Ni_9Sb_2S_8$
Sorbyite	$Pb_{19}(Sb,As)_{20}S_{49}$		

Oxides, hydroxides, oxyhalides, etc.:	
Senarmontite	Sb_2O_3
Valentinite	Sb_2O_3
Cervantite	$Sb^{+3}Sb^{+5}O_4$
Kermesite	Sb_2S_2O
Stibivanite	$Sb_2^{+3}V^{+4}O_5$
Melanostibite	$Mn(Sb^{+5},Fe^{+3})O_3$
Shahovite	$Hg_8Sb_2O_{13}$
Kelyanite	$Hg_{36}Sb_3(Cl,Br)_9O_{28}$
Stibiocolumbite	$SbNbO_4$
Stibiotantalite	$SbTaO_4$
Bystromite	$MgSb_2O_6$
Ordonezite	$ZnSb_2O_6$
Klebelsbergite	$Sb_4^{+3}O_4(OH)_2(SO_4)$
Peretaite	$CaSb_4^{+3}O_4(OH)_2(SO_4)_2 \cdot 2H_2O$
Monimolite	$(Pb,Ca)_3Sb_2O_8$(?)
Sarabauite	$CaSb_{10}O_{10}S_6$
Scheteligite	$(Ca,Y,Sb,Mn)_2(Ti,Ta,Nb,W)_2O_6(O,OH)$
Stenhuggarite	$CaFe^{+3}(As^{+3}O_2)(As^{+3}Sb^{+3}O_5)$
Manganostibite	$(Mn,Fe^{+2})_7Sb^{+5}As^{+5}O_{12}$
Schafarzikite	$Fe^{+2}Sb_2^{+3}O_4$
Tripuhyite	$Fe^{+2}Sb_2^{+5}O_6$
Derbylite	$Fe_4^{+3}Ti_3Sb^{+3}O_{13}(OH)$
Versiliaite	$(Fe^{+2},Zn,Fe^{+3})_8(Sb^{+3},Fe^{+3}As^{+3})_{16}O_{32}S$
Bindheimite	$Pb_2Sb_2O_6(O,OH)$
Nadorite	$PbSbO_2Cl$
Onoratoite	$Sb_8O_{11}Cl_2$
Stibiconite	$Sb^{+3}Sb_2^{+5}O_6(OH)$
Stetefeldtite	$Ag_2Sb_2(O,OH)_7$(?)
Partzite	$Cu_2Sb_2(O,OH)_7$(?)
Lewisite	$(Ca,Fe^{+2},Na)_2(Sb,Ti)_2O_7$
Romeite	$(Ca,Fe^{+2},Mn,Na)_2(Sb,Ti)_2O_6(O,OH,F)$
Stibiobetafite	$(Ca,Sb^{+3})_2(Ti,Nb,Ta)_2(O,OH)_7$
Cesstibtantite	$(Cs,Na,Sb)Ta_2(O,OH)_7$
Bahianite	$Al_5Sb_3^{+5}O_{14}(OH)_2$
Cyanophilite	$Cu_{10}Al_4Sb_6^{+3}O_{25} \cdot 25H_2O$
Silicates:	
Chapmanite	$Sb^{+3}Fe_2^{+3}(SiO_4)_2(OH)$
Holtite	$Al_6(Ta,Sb,Li)((Si,As)O_4)_3(BO_3)(O,OH)_3$
Welshite	$Ca_2Sb^{+5}Mg_4Fe^{+3}Si_4Be_2O_{20}$
Parwelite	$(Mn,Mg)_5Sb(As,Si)_2O_{12}$
Katoptrite	$(Mn,Mg)_{13}(Al,Fe^{+3})_4Sb_2^{+5}Si_2O_{28}$
Langbanite	$(Mn^{+2},Ca)_4(Mn^{+3},Fe^{+3})_9SbSi_2O_{24}$
Yeatmanite	$Mn_7Zn_8Sb_2^{+5}Si_4O_{28}$

Sources:

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substituting for sulphur. The antimony content of some common minerals in rocks and mineral deposits, as determined in our laboratories and compiled from the literature, is shown in Table II.

The terrestrial abundance of antimony and arsenic is of the order of 0.5 ppm and 3 ppm respectively as calculated from the available data. The As/Sb ratio in terrestrial rocks is, therefore, approximately 6.

TABLE II

Antimony content of some common minerals

Mineral	Sb (ppm) range	Remarks
Copper	1—1000	In mineral deposits
Silver	1—5000	In mineral deposits
Gold	1—100	In mineral deposits
Arsenic	Up to 9%	In mineral deposits
Bismuth	1—2000	In pegmatites and mineral deposits
Graphite	0.8—4	In mineral deposits
Pyrite	5—124	In rocks
Pyrite	5—1000	In mineral deposits
Pyrrhotite	<1—2	In rocks
Pyrrhotite	<1—2	In mineral deposits
Marcasite	<10—82	In mineral deposits
Arsenopyrite	170—1160	In mineral deposits
Orpiment	Up to 1.5%	In mineral deposits
Molybdenite	<1—8	In mineral deposits
Galena	3—8000	In mineral deposits
Chalcocite	2—6	In mineral deposits
Chalcopyrite	<1—180	In mineral deposits
Cinnabar	4—16	In mineral deposits
Sphalerite	<5—3800	In mineral deposits
Bismuthinite	Up to 8.8%	In mineral deposits
Gold tellurides (various)	Up to 8%	In mineral deposits
Halite	<2	In evaporites
Fluorite	<1—2	In mineral deposits
Hematite	<1—13	In iron ores and mineral deposits
Magnetite	<1—10	In mineral deposits
Ilmenite	<1—2	In mineral deposits
Limonite	5—2440	In oxidized zones of mineral deposits
Manganese oxides (wad)	<1—35	In oxidized zones of mineral deposits
Calcite	<1	In rocks and mineral deposits
Dolomite	<2	In rocks and mineral deposits
Siderite	<2	In mineral deposits
Cerussite	1—2	In oxidized zones of mineral deposits
Quartz	<1	In rocks and mineral deposits
Silicates (various)	<1	In rocks
Lepidolite	12	In pegmatites (average of 4 analyses)
Pollucite	10	In pegmatites (average of 4 analyses)
Apatite	<1	In mineral deposits
Barite	<1—2	In mineral deposits
Gypsum and anhydrite	<1—1	In evaporites and mineral deposits
Anglesite	2—>1000	In oxidized zones of mineral deposits
Smithsonite	<5	In oxidized zones of mineral deposits
Jarosite	3	In oxidized zones of mineral deposits
Scheelite	<1	In mineral deposits
Wolframite	<1—1	In mineral deposits
Cassiterite	<1—2	In mineral deposits
Uraninite	<1	In mineral deposits
Pitchblende	<1—800	In mineral deposits (admixed antimony minerals?)

Tantalite-columbite	1.4—3	In pegmatites
Pyrochlore	<1	In carbonatites
Fergusonite	23	In pegmatites
Betafite	16	In pegmatites
Euxenite	<1	In pegmatites
Niocalite	<1	In carbonatites
Samarskite	<1	In pegmatites
Ellsworthite (uranpyrochlore)	5	In pegmatites
Priorite	3	In pegmatites
Aeschynite	6	In pegmatites
Wodginite	200	In pegmatites

Sources: Laboratories, Geological Survey Canada, Ottawa. Various literature sources — *see* the Selected Bibliography.

The generalized geochemical cycle of antimony is shown in Fig. 2. Contributions of the element to the atmosphere, hydrosphere, pedosphere, and biosphere also occur as a result of industrial, domestic, and mining activity.

Antimony in the lithosphere

The abundance of antimony in the common igneous, sedimentary, and metamorphic rocks is given in Tables III—V inclusive. Among the igneous rocks (Table III) there appear to be some differences in the antimony con-

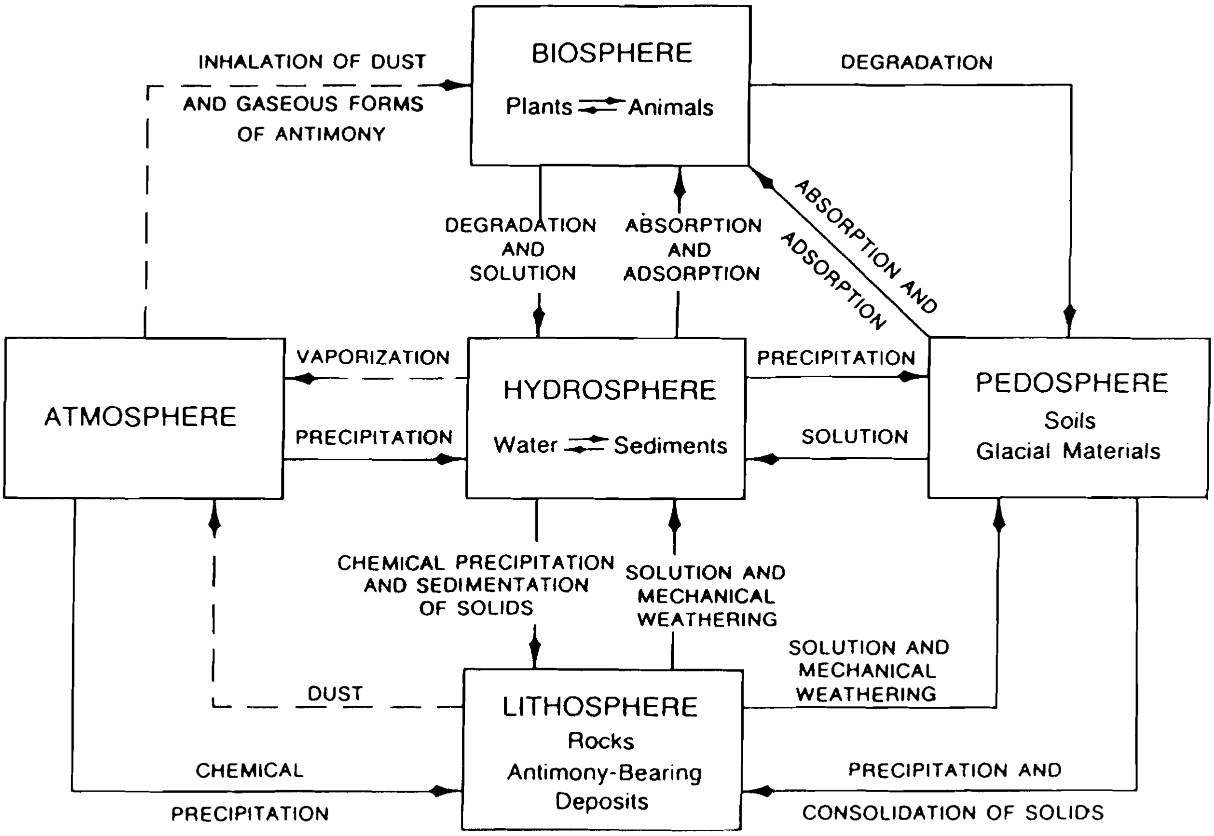

Fig. 2. Generalized geochemical cycle of antimony.

TABLE III

Antimony content of igneous rocks (in ppm)[1]

Rock type	Number of values	Range	$\overline{X}$	S	$\overline{X}_g$	$S_g(\log_e)$
Ultramafic rocks (peridotite, pyroxenite, dunite, kimberlite, etc.)	22	0.005—1.59	0.69	0.54	0.44	1.28
Mafic rocks						
Extrusives (basalt, etc.)	27	0.016—10	1.18	2.21	0.29	1.79
Intrusives (gabbro, diabase, etc.)	69	0.014—2	0.54	0.49	0.27	1.40
Intermediate rocks						
Extrusives (latite, trachyte, andesite, etc.)[2]	15	0.18—5.42	3.39	1.78	2.23	1.28
Intrusives (granodiorite, syenite, diorite, etc.)	25	0.029—3.32	0.99	1.27	0.35	1.51
Felsic rocks						
Extrusives (rhyolite, etc.)[2]	10	2.9—15.0	8.9	4.47	7.8	—
Intrusives (granite, aplite, etc.)	88	0.015—6.2	0.36	0.66	0.24	0.80
Feldspathoid rocks						
(nepheline syenite, phonolite, etc.)	3	0.8—1.39	1.0	—	0.8	—

[1] In this and subsequent tables $\overline{X}$ is the arithmetic mean; S, the standard deviation; X_g, the geometric mean; and $S_g(\log_e)$ the logarithmic standard deviation.

[2] Forgac et al. (in Ilavsky et al., 1980) quote high values for the antimony content of rhyolite-andesite suites from Slovakia. Their values range from 10.7 to 37.5 ppm Sb for 21 samples of andesites giving $\overline{X} = 20.7$, $S = 8.3$, and $\overline{X}_g = 19.2$. The values for rhyolites are given for their 10 samples under Felsic rocks, extrusives (rhyolite, etc.).

TABLE IV

Antimony content of sedimentary rocks (in ppm)

Rock type	Number of values	Range	$\overline{X}$	S	$\overline{X}_g$	$S_g(\log_e)$
Recent sediments:						
Stream, river, and lake silts						
Northwest Territories, Canada, (various localities)[1]	1200	<0.5–6	<0.5	—	—	—
Northwest Territories, Canada (Lake silts — Indin L., Yellowknife — Cameron R. area)[2]	1000	<1.6–9.6	<1.6	—	—	—
Great Lakes (sediments)[7]	26	0.20–1.8	0.75	—	—	—
Yukon (Keno Hill–Galena Hill area)[3]	5900	<2.5–1100	<2.5	—	—	—
New Brunswick (Bathurst area)[4]	3481	<1.0–70	3.8	3.1	3.1	0.6
Nova Scotia (Walton area)[5]	150	<0.05–5	<1	—	—	—
Southeastern Ontario (lake gyttja)[6]	125	<0.5–10	<0.5	—	—	—
Ocean sediments	14	0.1–7.03	1.9	2.28	0.99	1.23
Sandstone, arkose and conglomerate	8	0.22–54	0.59	0.27	0.54	0.48
Shale and argillite	52	0.1–300	1.1	1.3	0.6	1.1
Shales, black shales and pyritic shales (Helikian), N. Labrador, Canadian Shield[8]	75	<1–48	1.7	—	—	—
Limestone, dolomite, etc.	7	0.09–1	0.46	0.28	0.39	0.59
Evaporites						
Gypsum and anhydrite	30	<1	<1	—	—	—

[1] R.J. Allan (pers. commun., 1972)
[2] Nickerson (1972)
[3] Gleeson et al. (1967)
[4] Boyle et al. (1966)
[5] Boyle (1972a)
[6] I.R. Jonasson (unpublished)
[7] Jervis et al. (1973)
[8] W.C. Morgan (pers. commun., 1974)

tent of the various types. The intermediate and felsic extrusive rocks are slightly enriched in the element compared with the other igneous rocks. This seems also to be a feature of the intermediate intrusives. The data are, however, not extensive enough to draw valid conclusions, but it is worthy of note that many mineral deposits in meta-andesites, and in some meta-rhyolites, are commonly enriched in antimony. Among the sedimentary rocks the shales and argillites contain the most antimony (Table IV). This is particularly true of the pyritic types and phosphorites. Iron-rich rocks show wide variations in their antimony content. The sulphide facies of iron formations are commonly enriched in the element, mainly in pyrite. Stream, river, and lake sediments vary widely in their antimony contents, depending essentially on their proximity to antimony-bearing rocks and deposits. Some representative values from Canadian occurrences are given in Table IV. Values higher than 5 ppm Sb are invariably associated with antimony-bearing deposits or pyritic rocks. In recent stream, river, and lake sediments there is often a direct relationship between the antimony content and the iron oxide and organic (carbon) content, the first a result of strong adsorption and absorption processes and the second probably due to chelation and/or metal-organic binding of antimony. Little can be said about the metamorphic rocks (Table V) except that they contain antimony contents similar to the rocks from which they are derived, and that they carry the element mainly in pyrite.

TABLE V

Antimony content of metamorphic rocks (in ppm)

Rock type	Number of values	Range	$\overline{X}$	S	$\overline{X}_g$	$S_g(\log_e)$
Hornfels	1	—	1	—	1	—
Skarn	6	—	1	—	1	—
Quartzite	30	<1—1.5	0.8	0.6	0.7	0.6
Slate and phyllite	25	0.3—1.9	0.9	0.6	0.7	0.7
Schist	25	1—3.1	2.1	1.5	1.8	0.8
Gneiss[1]	18	<1	<1	—	—	—
Amphibolite and greenstone[2]	35	<1—1.5	0.6	0.5	0.3	0.6
Eclogite	1	—	0.3	—	0.3	—

[1] Principally from Grenville Province of Canadian Shield (I.R. Jonasson, unpublished).
[2] Principally from greenstone belts of Canadian Shield.

Extensive studies of the antimony content of rocks in four areas of Canada have been carried out in recent years. These are shown in Tables VI—IX inclusive. Details can be obtained from the papers published by Boyle (1961, 1965, 1972a) and Boyle et al. (1969). The abundance figures in these tables serve to emphasize the fact that sediments, principally the graphitic and pyritic types, contain the largest amounts of antimony, and that most igneous rocks are relatively low in the element. In these studies we have found that the bulk of the antimony in igneous, sedimentary, and metamorphic rocks occurs in pyrite.

Small amounts of antimony minerals may occur in the heavy concentrates of soils and of both eluvial and alluvial placers, especially in those near antimoniferous deposits. In some of the gold placers of Yukon we have noted the presence of the following antimony minerals: jamesonite, bou-

TABLE VI

Antimony content of the rocks of the Keno Hill—Galena Hill area, Yukon, (in ppm)

Rock type[1,2]	Sb content (range)	Sb content (average)
Skarn (6)	1.0	1.0
Greenstone (27)	<1.0—1.0	0.8
Biotite lamprophyre (2)	<1.0—1.0	0.7
Quartz-feldspar porphyry (6)	1—1.5	1
Granodiorite (6)	<1.0—1.0	<1
Graphitic argillite, schist, and phyllite (29)	1.0—7.0	3.1
Quartz-sericite schist (8)	1.0—1.5	1
Quartzite (39)	1.0—6.0	1
Limestone (3)	1	1

[1] All of the rocks are of Precambrian or Early Paleozoic age with the exception of the granodiorite which is probably of Cretaceous age. For further data see Boyle (1965).
[2] Numbers in brackets refer to the number of composite samples analyzed.

TABLE VII

Antimony content of the rocks of the Yellowknife Area, Northwest Territories (in ppm)

Rock type[1,2]	Sb content (average or range)	Remarks
Amphibolite (greenstones)	1	Archean (Keewatin type)
Diabase	<1	Proterozoic
Tuff and sulphide schist	1—25	Archean (Keewatin type)
Argillite and slate	<1	Archean (Timiskaming type)
Greywacke and allied rocks	1.5	Archean (Timiskaming type)
Quartz-sericite schist and gneiss	1	Archean (Timiskaming type)
Granodiorite (Western)	1	Archean (Kenoran)
Quartz-feldspar porphyry	5—10	Archean (Kenoran)
Granite (Prosperous Lake)	<1	Archean (Kenoran)
Pegmatites	<1	Archean (Kenoran)

[1] Five composite samples of each type of rock were averaged.
[2] For further details see Boyle (1961).

TABLE VIII

Antimony content of the rocks of the Cobalt Area, Ontario (in ppm)

Rock type[1,2]	Sb content (average)	Remarks
Basic to intermediate lavas (greenstones)	<2	Archean (Keewatin type)
Lamprophyre	<2	Archean
Granite	<2	Archean (Kenoran)
Syenite	<2	Archean (Kenoran)
Nipissing quartz diabase	<2	Proterozoic
Interflow sediments: graphitic schist, slate, chert, etc.	5	Archean (Keewatin type)
Conglomerate	<2	Archean (Timiskaming type)
Greywacke	<2	Archean (Timiskaming type)
Conglomerate	<2	Proterozoic (Huronian)
Quartzite and arkose	<2	Proterozoic (Huronian)
Greywacke and arkose	<2	Proterozoic (Huronian)
Limestone and dolomite	<2	Paleozoic

[1] Five composite samples of each type of rock were analyzed.

[2] For further details see Boyle et al. (1969).

TABLE IX

Antimony content of the rocks of the Walton Area, Nova Scotia (in ppm)

Rock type[1,2]	Sb content (range)	Sb content (average)	Remarks
Carbonaceous shale and argillite (38)	1—10	2.2	Horton Bluff Formation, Carboniferous (Mississippian)
Quartzite and sandstone (21)	1—2	1	Horton Bluff Formation, Carboniferous (Mississippian)
Argillaceous dolomite (14)	1—1.5	1	Horton Bluff Formation, Carboniferous (Mississippian)
Green and grey shale and argillite (17)	1—2.5	1	Cheverie Formation, Carboniferous (Mississippian)
Red shale and argillite (10)	1—3.5	1	Cheverie Formation, Carboniferous (Mississippian)
Sandstone (26)	1—2	1	Cheverie Formation, Carboniferous (Mississippian)
Limestone (5)	1—2.5	1	Macumber Formation, Carboniferous (Mississippian)
Limestone conglomerate (7)	1—1.5	1	Macumber Formation, Carboniferous (Mississippian)
Anhydrite and gypsum (27)	1	1	Evaporite Formation, Carboniferous (Mississippian)
Sandy Shale (2)	1	1	Tennycape Formation, Carboniferous (Mississippian)
Sandstone and conglomerate (7)	1	1	Wolfville Formation, Triassic
Diabase (2)	1—2	1	Triassic
Basalt (1)	1	1	North Mountain basalt, Triassic

[1] Numbers in brackets refer to the number of composite samples analyzed.

[2] For further details see Boyle (1972a).

langerite, antimoniferous pyrite, antimoniferous limonite and wad, and senarmontite. These minerals have also been identified in stream, river, and lake sediments near antimony-bearing deposits in several other mineralized districts in Canada.

Antimony in the pedosphere

The antimony content of normal soils and glacial materials (Table X) is low except in the vicinity of deposits containing the element. The A horizons of some soils are greatly enriched in antimony compared with the other horizons (Boyle and Dass, 1967), but in general it is usual to find an enrichment of antimony in the B horizons of most normal soils. In soils near antimony-bearing deposits marked enrichments of antimony have been noted in both the B and C horizons. The reason for the enrichment of antimony in the A horizons of some soils is evidently due to chelation processes or some other type of tenacious organic binding. The enrichment in the B horizons is mainly the result of strong adsorption and absorption of antimony by hydrous iron oxides, clay minerals, and wad which predominate in this horizon.

Soils in the vicinity of antimoniferous deposits may contain highly oxidized residual particles of hypogene antimony minerals (e.g. stibnite, boulangerite), and secondary products such as particles of senarmonite, cervantite, and stibiconite, usually in the size range of 5—50 μm. Near some pegmatites tantalite-columbite (stibiotantalite, stibiocolumbite) and other antimony-bearing minerals such as wodginite and betafite (Table II) commonly appear in the heavy concentrates of the soils and weathered residuum.

Antimony in the hydrosphere

The antimony content of natural waters is given in Table XI. Most stream, river, and lake waters are relatively low in the element (average - 0.65 ppb), generally well below the toxic levels of the element. Ground waters tend to have higher concentrations of antimony compared with surface waters. Near antimoniferous deposits groundwaters may be greatly enriched in antimony as shown in the table. Hot springs and cold springs in active volcanic terranes tend to carry relatively large amounts of the element.

The state of antimony in natural waters is uncertain. In the carbonate waters of the Carpathians with HCO_3-Cl-Na and Cl-HCO_3-Na compositions Krainov et al. (1979) consider that the element is present as SbO_3^-, HSb_2O^0, and $Sb(OH)_3^0$, and in the reducing and oxidizing alkaline groundwaters of the mountainous areas of Central Asia, U.S.S.R., Shvartsev et al. (1974) concluded that the principal migration species of antimony are negatively charged coordination complexes comprising oxides, sulphides, fluorides, carbonates, sulphates, and organic compounds. Of these the sulphide complexes $[SbS_3]^{3-}$ prevail in waters enriched in H_2S; in oxidizing waters complexes involving

TABLE X

Antimony content of soils and glacial materials (in ppm)

Soil type	Number of values	Range	$\overline{X}$	S	$\overline{X}_g$	$S_g(\log_e)$
Normal soils (world, various localities)	32	0.18—2.5	0.69	0.51	0.56	0.65
Peaty soils, muck and half-bog soils (Canada, various localities)	13	1.0—3.6	2.1	0.8	2.0	0.4
Normal soils: (Clyde Forks area, E. Ontario)[1]						
A - horizon	40	1—8	3.4	1.9	—	—
B - horizon	40	1—8	3.2	1.8	—	—
C - horizon	39	1—12	3.1	2.3	—	—
Soils and tills near antimoniferous deposits (world, various localities)	261	0.5—10,000+	56	137	14	1.6
Soils: near antimoniferous deposits (Canada, New Brunswick, Bathurst area)[2]						
A - horizon	6	4—38	12	13	8.7	0.84
B - horizon	6	2—91	30	39	12	1.55
C - horizon	2	15—36	26	14	23	0.62

[1] I.R. Jonasson (unpublished).

[2] For further details see Presant (1971).

TABLE XI

Antimony content of natural waters (in ppb)

Water type	Number of values[1]	Range	$\overline{X}$	S	$\overline{X}_g$	$S_g(\log_e)$
Rainwater[2]	2	0.14—0.18	0.16	—	0.16	—
Normal stream river and lake waters	32	0.01—12.1	1.5	2.5	0.65	1.32
Ground waters and mine waters near polymetallic sulphide deposits	328	1.3—5750	—	—	—	—
Carbonate waters, Carpathians U.S.S.R. Background waters in belts of Sb-As mineralization[3]	8	1—10	—	—	—	—
Glacial ice[4]	—	8—91	32	—	—	—
Hot springs and certain mineral waters	41	0.1—1500	226	298	105	1.59
Oil field and saline waters	1	—	<0.4	—	<0.4	—
Oceans and seas	110	0.07—1.6	0.45	0.23	0.42	0.46

[1] Many of these values record averages of specific areas.

[2] Rancitelli and Perkins, (1970).

[3] Krainov et al. (1979).

[4] Values are in parts per trillion (Weiss and Bertine, 1973).

OH, sulphate, and organics are probably the most stable species. Studies carried out by Bowen et al. (1979) using radiotracer ^{124}Sb in river and lake waters indicate that antimony interacts with humic and fulvic acids to form complexes. The Sb(III) and Sb(V) humates are stable in the pH range 7—11 but are largely disassociated below pH 4. Sb(III) does not form a fulvate complex at pH 4 and interacts only weakly at pH 7—9. Sb(V) is not reduced by humic acid to Sb(III) in solution. Recent investigations of the state of antimony in natural waters by Andreae et al. (1981) indicate that most of the element in the waters of rivers (some polluted) and estuaries is present in the Sb(V) state; the remainder (generally less than 10%) is present in the Sb(III) state and in methylantimonials (methylstibonic and dimethylstibnic acids). The methylantimonials are considered to be due to organic (algal) activity.

Antimony minerals, mainly stibnite and occasionally pyrargyrite and other sulphosalts, occur in certain hot spring precipitates, particularly those of a highly siliceous nature (Clarke, 1924; White, 1955; Ritchie, 1961; White et al., 1963; Dickson and Tunell, 1968; Ozerova et al., 1971; Silberman et al., 1979). Weissberg (1969) and Browne (1969, 1971) recorded up to 30% Sb in precipitates from the thermal waters of the Taupo Volcanic Zone, New Zealand. The water from which these precipitates were deposited ranged in content from 0.3 to 1.5 ppm Sb. In a number of thermal waters on North Island, New Zealand, some including those mentioned above, Ritchie (1961) found the Sb content to range from 8 to 900 ppb. This compares with As contents ranging from 0.00 to 8.5 ppm. The As/Sb ratio in the waters was found to range from 1 to 240. Ritchie observed that the antimony content of a thermal spring water may be subject to rapid and wide fluctuations and that no significance can be attached to it. His results show no correlation with either the arsenic or chloride content. In some siliceous precipitates he found antimony to be enriched relative to arsenic. In the literature this feature is also shown by a number of other analyses of siliceous sinters.

Several other investigations of precipitates associated with thermal waters are of interest. Zotov et al. (1972) found the pyrite precipitated from some thermal springs in the Kurile Islands to contain up to 0.13% Sb, apparently replacing the S in the mineral. In the lake-bed evaporites at Kramer, California, small amounts of stibnite and realgar occur in certain layers with the borate minerals. Dickson and Raab (1965) think that these minerals had their origin in hot spring waters charged with sodium borate ($Na_2B_4O_7$).

Jonasson (unpublished) has investigated the antimony (and arsenic) contents of precipitates from 103 hot springs in British Columbia, Canada. These comprise high sulphide, potassium, sodium (trona), calcium (calcite), and normal types. Preliminary results indicate a range in arsenic content from 0.5 to 890 ppm in the precipitates with respective mean values for the various types of waters as follows: 17, 162, 118, 29 and 45 ppm; the antimony contents range from 0.5 to 51 ppm with an overall mean of 2 ppm Sb and respective mean values for the various types of waters as follows: 1.4, 1.4, 0.5, 2.8, and 6.7 ppm. While a wide range of contents is recorded for all classes of springs those with carbonate precipitates are generally enriched in both arsenic and antimony. In most of the precipitates antimony is accompanied by As, and in the precipitates of some springs the association As, Hg, Rb, Cs, Li and B is common.

Antimony is a common trace and minor constituent of limonitic and manganiferous deposits near both hot and cold springs. Some of these contain up to 580 ppm Sb according to our analyses. The highest contents generally occur in mineralized belts, and the hydrous iron oxides (limonite) are invariably enriched several fold compared with coexisting hydrous manganese oxides (wad).

The oceans and seas average about 0.42 ppb Sb. The nature of this antimony is poorly characterized. It may be present as ions in the form of antimonite or antimonate, as dissolved organo-antimony compounds, and in a variety of forms adsorbed to suspended particulate matter. According to Gohda (1975) the antimony in seawater is principally present as Sb(V) in anionic forms, with minimal amounts in the Sb(III) state and associated with suspended matter. Shvartseva (1972) states that the saline waters of Searles Lake, California contain up to 5000 ppb Sb evidently quoting the data of D.E. White.

With respect to pH both acid and alkaline waters contain antimony, mainly because of the amphoteric nature of the element.

Antimony in the atmosphere

There are few data on the content of antimony in the atmosphere. It seems probable that small amounts of antimony are contributed to the atmosphere by volcanic activity, since some hot spring waters in volcanic areas are rich in the element (Table XI). The burning of coal and petroleum products, both containing small amounts of antimony (Table XIII), and the smelting of antimoniferous ores, may also contribute some antimony to the atmosphere. Rancitelli and Perkins (1970) determined the antimony content of the aerosols of the troposphere and lower stratosphere at several sites. The compilation of their results and those of others indicates that at ground level the antimony content of the aerosols ranges from 0.08 to 55 nanograms/standard m^3 air (over the ocean the value is 0.08—1.2; at ground level in Chicago, 1.4—55; and at ground level in Toronto 2.3—7.4) to $n \times 10^{-1}$ nanograms/standard m^3 air at 3 kilometers of altitude, and $n \times 10^{-3}$ nanograms/standard m^3 air at 15 kilometers. A similar decrease was observed for the Fe, Zn, Cr, Co, and Sc content of the aerosols. There are inversions of the concentration of the elements at different levels on the same day, and large variations in the absolute and relative concentrations occur between measurements at a given altitude on different days. Further details should be sought in the original publication. Rancitelli and Perkins (1970) concluded that the relatively high concentrations of antimony in the atmosphere tag it as a pollutant. Rahn and Winchester (1971) observed that most of the elements they determined in their aerosol research of surface air in remote regions of North America were associated with the larger aerosol particles and appear to have soil and soil dust as their main source. They noted a close coherence of Zn and Sb and attributed this to the high volatility of both elements and to their geochemical similarities (chalcophile character, etc.). Details should be consulted in the original work. A small amount of the antimony in the atmosphere is probably contributed as volatile compounds (stibine, dimethylstibine) by bacteria acting on antimoniferous compounds and minerals in the soil, sediments, etc. There is a very small contribution of antimony to the atmosphere as a result of nuclear explosions. (*See* above, under the section on General Geochemistry and Mineralogy).

Antimony in the biosphere

The literature on the antimony content of plants and animals is scarce and scattered. As shown in Table XII the antimony content of marine animals (dry weight) ranges from 0.01 to 0.24 ppm. In terrestrial animals Wester (1965) reported from 0.0007 to 0.01 ppm Sb in fresh (wet) samples of connective tissue of 4 hearts from cattle. In the hair of humans the antimony content ranges from 0 to 4.4 ppm with a mean of about 0.8 (Bate and Dyer, 1965).

TABLE XII

Antimony content of living organisms in ppm (dry weight)

Description	Number of values	Range	$\overline{X}$
Marine[1]	9	0.08—0.24	—
Marine animals[2]	10	0.01—0.05	0.03
Marine alga (*Pelvetia canaliculata*)[3]	1	—	0.19
Phytoplankton[4] (Columbia River, U.S.A.)	5	0.36—2.85	1.3
Cotton plants[5]	—	—	0.52 ± 0.08
Terrestrial plants[6] (near antimoniferous deposits)	20	0.4—200+	—

[1] Gmelin (1943) (after Noddack and Noddack, Ark. Zool. V. 32A, no. 4, p. 32, 1939).
[2] Leatherland et al. (1973).
[3] Abu-Hilal and Riley (1981).
[4] Cushing and Rancitelli (1972).
[5] Rustamov et al. (1973).
[6] Values refer to averages of various mineralized areas.

There are a few published accounts of the antimony content in plants near antimony-bearing deposits. Sainsbury (1957) analyzed four samples of the inner bark of hemlock and found an increase in the concentration of antimony (0.4—4.5 ppm in the bark) with approach to the stibnite deposits of Caamano Point, Cleveland Peninsula, Alaska. Nikiforov and Fedorchuk

(1959) report enriched amounts of antimony in plants growing in the vicinity of Hg-Sb deposits in South Ferghana, U.S.S.R., and Flerova and Flerov (1964) mention that a number of plants (spirea, mint, yarrow, St. John's wort, and vetch) concentrate large amounts of antimony in the vicinity of polymetallic deposits in the Dzungarian Ala Tau region of U.S.S.R. A report by the U.S. Geological Survey (U.S.G.S. Prof. Pap. 501-A, p. A201, 1964) indicates that antimony in fern bush (*Chamaebatiaria millefolium* (Torr.) Maxim.) may be useful in biogeochemical prospecting in the Egan, White Pine, and Schell Creek Ranges, Nevada. The antimony found in thirteen samples of this plant ranged from 8 to 220 ppm in the plant (not ash). Shacklette (1965a) also found 50 ppm antimony in the ash of branches of *Betula resinifera* Britton whose roots were in contact with cinnabar mineralization at the Red Devil mine on the Kuskokwim River, Lower Yukon River District, Alaska. A number of desert plants investigated in U.S.S.R. tend to concentrate relatively high amounts of antimony in the vicinity of antimoniferous mineralization. Those of the *Artemisia*, *Salsola*, and *Astragalus* species have the highest amounts of antimony in some desert regions. Details are given in the section on Biogeochemical Surveys.

In the upper (organic) layer of soil and in the ash of plants Iokhel'son and Popov (1964) detected ^{125}Sb, one of the fission products of nuclear explosions. The activity in the soil ranged from 4 to 7×10^{-3} curie/gram; that in the plant ash ranged from 12 to 132×10^{-3} curie/gram.

The generalized food chains incorporating antimony are shown in Fig. 3.

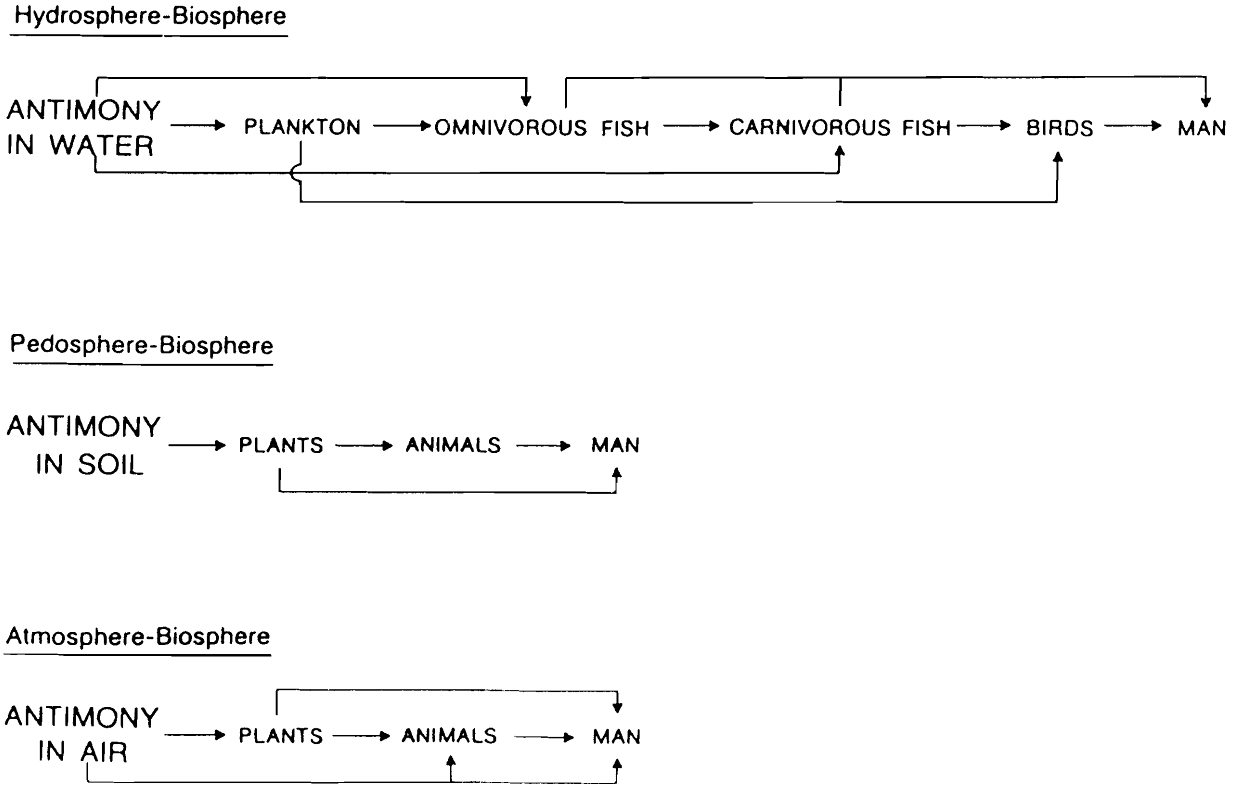

Fig. 3. Generalized food chains for antimony.

Certain types of thionic bacteria (*Thiobacillus ferrooxidans*) are capable of growing by utilizing free CO_2 and oxidizing antimonite ion to antimonate. Such bacteria are particularly active in systems containing oxidizing stibnite (Lyalikova, 1967). In a later study another organism *Stibiobacter senarmontii* was identified by Lyalikova (1978) as an agent in the oxidation of Sb(III) to Sb(V) in oxidizing sulphide deposits containing stibnite. The oxidation of stibnite by bacteria is thus considered by Lyalikova to be a two step process; firstly oxidation of Sb_2S_3 to Sb_2O_3 by *Thiobacillus ferrooxidans*, followed by the oxidation of Sb(III) by *Stibiobacter senarmonitii* to Sb(V), an oxidation state that distinguishes minerals of the stibiconite type.

Algal activity is thought to be the source of the low amounts of methylantimonials in some natural waters (Andreae et al., 1981).

Muskeg, peat, and peaty mucks concentrate antimony when waters containing the element percolate through these materials or debouch into basins containing them. There are three main reasons for the enrichment: (1) organic chelation or other types of metal-organic binding by humus; (2) coprecipitation, adsorption, and/or absorption by hydrous iron oxides as in bog iron ores; and (3) precipitation by H_2S or other sulphide species in sulphides such as pyrite and marcasite. According to our analyses normal bogs contain less than 1 ppm Sb in the peaty materials. Those receiving water containing antimony may report up to 5 ppm or more. Bog iron and manganese ores vary widely in their antimony content, from <1 to 10 ppm Sb or more.

The fossil residues of the biosphere, especially coal, contain relatively high amounts of antimony as shown in Table XIII. In coal we have found that much of the antimony is present in pyrite and occasionally in other sulphides such as arsenopyrite, marcasite, and galena; rarely in sulphosalts such as tetrahedrite. Some antimony is also probably present as an organoantimony compound in certain types of coal. The nature of antimony in petroleum, asphalt and oil shale is not known.

ANTIMONY DEPOSITS

Antimony is widely diffused in many types of mineral deposits in trace, minor, and major amounts. It tends to be concentrated in those deposits enriched in sulphides, either as separate antimony minerals or as a minor or trace constituent of a great number of sulphides, arsenides, and sulphosalts. The common antimony minerals in endogene (hypogene) 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 gold antimonide, aurostibite, $AuSb_2$, is common in certain auriferous deposits, particularly those enriched in antimony. The most common supergene antimony minerals in deposits are kermesite, senarmontite, stibiconite, nadorite, and bindheimite. In some deposits pyrargyrite may be of supergene origin.

TABLE XIII

Antimony content of fossil fuels (in ppm)

Description	Number of values	Range	$\bar{X}$	S	$\bar{X}_g$	$S_g(\log_e)$
Coal[1]	605	<30—3000	—	—	—	—
Canadian coal (Nova Scotia) (ash)	7	1—30	12	—	—	—
Petroleum[2]	10	0.0295—0.1068	0.0553	0.0224	0.0519	0.3714
Petroleum[3]	3	<0.001—0.035	—	—	—	—
Asphalt[4]	4	0.035—11.0	—	—	—	—
Green River oil shale[5]	—	—	0.39	—	—	—

[1] In many of the papers consulted averages of a large number of analyses are given. Hence statistics could not be applied effectively to the data. The average Sb value in coal ash is probably less than 20 ppm. Headlee and Hunter (1953) give <50 ppm Sb_2O_3 as an average of the ash of 596 samples from 16 coal seams in West Virginia. Much antimony is probably lost during ashing of coal unless special care is taken. Kessler et al. (1973) give values ranging from <0.1 to 2 ppm in the whole coal of 13 U.S. composite samples with a mean of 0.65 ppm. Gluskoter et al. (1977) give mean (arithmetic) values of 1.3, 1.6, and 0.58 ppm Sb for whole coal samples from the Illinois, Appalachian, and Western U.S. coal basins, respectively.

[2] Shah et al. (1970).

[3] Colombo et al. (1964).

[4] Colombo et al. (1964).

[5] Cook (1973).

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; only rarely in tetrahedrite and other sulphosalts. 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. Jung et al. (1974) give averages of 10—88 ppm Sb for various mineralized members of the Kupferschiefer. Some of the antimony in the Kupferschiefer is associated with organic (carbonaceous) matter.

(2) *Copper (uranium, vanadium, silver, lead) sandstone deposits ('Red bed' type).* Most of the antimony in the Cu-U-V-Ag types of deposits is present in pyrite and various other sulphides; only rarely in tetrahedrite and other sulphosalts. 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 according to our analyses. 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. In the lead sandstone type of deposits (Laisvall, Sweden; Maubach, Germany; Yava, Nova Scotia) the antimony contents are generally low (<1—20 ppm) and are contained principally in galena; also in tetrahedrite, boulangerite, and other minor sulphosalts. 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 (Boyle, 1972a). 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. Galena concentrates from these deposits contain from 10—100 ppm Sb.

(4) *Pyritiferous quartz-pebble conglomerates and quartzites enriched in one or more of gold, silver, uranium, thorium and rare-earths (Witwatersrand —Elliot Lake 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 the rarer arsenide and sulphosalt minerals such as cobaltite, tennantite, and tetrahedrite.

(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 ores according to our analyses. The small amounts of antimony are present principally in the 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. Pyrite and arsenopyrite are commonly antimoniferous in these deposits. Certain skarn-type gold and polymetallic deposits are slightly enriched in antimony, contents up to 500 ppm being present in some ores. Some skarn 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 enriched 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, stibiobetafite, 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 as a whole rarely exceed a few tens of parts per million.

(8) *Carbonatites.* These deposits are notably low in antimony, generally averaging less than 1 ppm Sb. Those that contain copper sulphides and pyrite in some abundance (e.g. Palabora) may carry a few parts per million, mainly in the sulphides. Others that contain galena carry antimony in this mineral (generally less than 10 ppm).

(9) *Kimberlites (diamond pipes).* These deposits carry only traces of antimony mainly in the small amounts of disseminated pyrrhotite and pyrite.

(10) *Segregations and disseminations of sulphides and platinoid minerals in basic and ultrabasic rocks (Merensky Reef—Insizwa type).* Antimony in these deposits is contained mainly in the various sulphide minerals, including pyrrhotite, pentlandite, chalcopyrite, pyrite, and cubanite, and in the various platinoid minerals. Some of the platinoid minerals are antimonides (e.g. stumpflite, $Pt(Sb,Bi)$; geversite, $PtSb_2$; stibiopalladinite, Pb_5Sb_2); others contain antimony as a trace or minor element (e.g. sperrylite, michenerite) in amounts up to 1000 ppm or more. Overall the sulphide and platinoid mineral segregations (ores) in basic and ultrabasic rocks contain only minor quantities of antimony, generally less than 5 ppm, according to our analyses and those in the literature. There is a close and fairly consistent correlation of antimony with Ni, Co, Cu, As, Bi, Te, Au, Ag, Pt-metals, and probably with Sn and Se in the platinoid-bearing deposits of this type.

(11) *Massive bodies, mantos, disseminations, 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—Norilsk type):* In these bodies antimony is largely associated with arsenic minerals such as arsenopyrite, gersdorffite, niccolite, etc. and with the platinoid minerals. Small amounts (up to 5 ppm) also occur in pyrrhotite, pentlandite, and pyrite. The antimony content of the ores as a whole ranges up to 60 ppm according to our analyses. A selection of ores from the Thompson Nickel Belt, Manitoba are arsenical (10—500 ppm As) but low in antimony (<0.5 ppm Sb). Sudbury ores as a whole tend to be low in antimony (<0.5 ppm Sb) except those marked by developments of arsenopyrite. The ores of the Rankin Inlet Mine, Northwest Territories are slightly enriched in both arsenic (30—60 ppm) and antimony (20—60 ppm).

(b) *Massive and disseminated Cu-Zn-Pb sulphide bodies in volcanic and sedimentary terranes: (1) Noranda—Flin Flon—Bathurst—Rio Tinto (volcanic- or volcanic-sedimentary-hosted) 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-ennantite, enargite, various other sulphosalts, chalcopyrite, sphalerite, pyrite, and arsenopyrite. Most deposits average about 50 ppm Sb, but there may be wide divergences from this value. *(2) Sullivan—Mount Isa (shale-hosted) type:* Most of the antimony in these bodies (1—260 ppm) occurs in galena, stibnite, tetrahedrite, bournonite, boulangerite, jamesonite, chalcostibite, pyrargyrite, and other sulphosalts. Associated elements include Pb, Zn, Cd, Ag, Fe, and As; also Ba, Sn, Bi, Cu, Co, and Ni in some deposits.

In these deposits most of the antimony is concentrated in the footwall mineralized zones or in underlying stringer and breccia ore when present.

(c) *Veins, lodes, and stockworks principally in granitic rocks and their associated intruded sediments and volcanics 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 and Cu, Fe, Pb, and Zn sulphides. Others are wolframite-scheelite-molybdenite 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, Th, 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, arsenopyrite, and galena; in some deposits also in native antimony, stibnite, jamesonite, and other sulphosalts. The ores generally contain only a few to a few tens of parts per million Sb, but some ores may be enriched in the element in amounts up to 1000 ppm Sb.

(d) *Various polymetallic veins, stockworks, disseminations, and lodes in all rock types and containing essentially Cu, Ag, Pb, Zn, and Fe sulphides and sulphosalts:* Most of the antimony in these deposits occurs in tetrahedrite, jamesonite, boulangerite, pyrargyrite, and a great variety of other sulphosalts; also in trace and minor amounts in galena, sphalerite, arsenopyrite, pyrite, and other sulphides. 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, stibarsen, pyrargyrite, and other antimony-bearing sulphosalts. The native silver is commonly greatly enriched in antimony, in some samples up to 1000 ppm Sb or more. Pitchblende is characteristic of certain deposits (Great Bear Lake, Canada; Jáchymov, Czechoslovakia). The antimony content of the deposits in this category commonly ranges from 0.03 to 1.5%.

(f) *Gold-quartz veins, stockworks, and carbonated silicified zones:* The host rocks of these deposits are varied, principally greenstones but also greywacke-slate sequences and granitic rocks. The principal antimony minerals are stibnite, tetrahedrite, and a great variety of other sulphosalts. Native antimony is relatively rare in most of these deposits but occurs in small amounts in a few. Aurostibite, $AuSb_2$, is an economic mineral in some deposits. 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 and arsenopyrite. Those with marked concentrations of stibnite and sulphosalts (e.g. Yellowknife, Northwest Territories, Canada; Antimony Line, Murchison Range, South Africa; West Gore, Nova Scotia, Canada; Costerfield, Victoria, Australia) have ores with antimony contents up to 10 per cent or more. For the disseminated types of gold deposits see (14).

(g) *Thorium and uranium veins, lodes, and stockworks:* The principal minerals in these deposits include one or more of thorite, brannerite, uraninite, and pitchblende with which are generally associated pyrite, chalcopyrite, and molybdenite; some deposits (*see* (e) above) contain a complex assemblage of Ni-Co arsenides, native silver, native bismuth, bismuthinite, etc. The simple type of Th-U and U veins and lodes are generally low in antimony with contents usually less than 10 ppm in the ores as a whole; some of the younger deposits of this type, particularly those associated with calderas and other volcanic phenomena may be somewhat enriched in antimony mainly in galena, tetrahedrite, and silver sulphosalts. The complex Ni-Co arsenide type of pitchblende deposit may contain up to 1.5% Sb.

(h) *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 content in these ores usually does not exceed 0.1%.

(i) *Stibnite deposits:* These constitute 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 (chalcedony), pyrite, marcasite, barite, fluorite, calcite, siderite, dickite, and kaolinite. In certain deposits of this type calcite (or siderite) 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 low- to medium-temperature deposits have some wolframite (ferberite), and the higher-temperature, deep-seated deposits commonly are marked by the occurrence of native antimony, scheelite, arsenopyrite, sphalerite, base metal- and 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 also have these elements in addition to marked enrichments of Ag, Au, Cu, Zn, Cd, Pb, Bi, Be, and W. Uranium (uraninite, coffinite) is a constituent of certain stibnite deposits (e.g. Vardar zone, Yugoslavia; Lake George, New Brunswick, Canada). The antimony content ranges from minor amounts to several tens of per cent in the stibnite deposits.

(12) *Jamesonite and other types of massive and disseminated sulphosalt deposits.* These are relatively rare, the classic example being at Zimapan, Hidalgo, Mexico. There, the deposits occur as replacements in limestone (or skarn) 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, meneghinite, semseyite, tetrahedrite-tennantite — in a gangue mainly of quartz, calcite, pyrite, and other base metal sulphides. The ores of these deposits contain percentages of antimony.

(13) *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, contain relatively low contents of antimony in the ores. Our analyses of minerals from the Almaden Mine, Spain show pyrite to contain up to 115 ppm Sb and cinnabar up to 4.2 ppm Sb. The content of pyrite in the ores is generally low. Precipitates from hot springs enriched in mercury (e.g. Sulphur Bank and Steamboat Springs, U.S.A.; New Zealand; and Kamchatka, U.S.S.R.) invariably contain high amounts of antimony. (*see* (15) below and the section above on antimony in the hydrosphere).

(14) *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 pyroclastics, 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 Morro Velho, Passagem de Mariana, and other similar deposits in Brazil. The antimony content of these deposits varies widely. In the Carlin ores the antimony ranges from 5 to 450 ppm in the ores. Similar antimony contents are characteristic of the other deposits noted in this group according to our analyses. Stibnite and sulphosalts are the most abundant antimony minerals in the deposits of this category; antimoniferous orpiment is present in a number of the Carlin-type deposits (Radtke et al., 1973).

(b) *Disseminated (porphyry) copper and/or molybdenum deposits:* The antimony content of these deposits is generally low, especially in the molybdenum type. Certain disseminated copper deposits carry minor amounts of tetrahedrite-tennantite and others contain 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 sulphides, sulphosalts and enargite present. The ores of most deposits probably contain from less than 1 ppm Sb, with contents up to 100 ppm Sb in the various sulphides; peripheral deposits with lead and zinc sulphides contain up to 500 ppm Sb or more.

(15) *Hot spring deposits.* The siliceous sulphide precipitates at a number of hot springs carry large amounts of antimony mainly in the form of stibnite; also in 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% (Taupo).

The Senator antimony deposits, Kutahya, Turkey described by Bernasconi et al. (1980) represent examples of fossil volcanic vents and hot springs in the throats of which were deposited quartz, cristobalite, barite, pyrophyllite, stibiconite, scorodite, dussertite, orpiment, amorphous meta-stibnite, and stibnite.

(16) *Supergene (residual and transported) deposits; eluvial and alluvial placers.* Native antimony, stibnite, and the sulphosalts of antimony weather slowly and often become armoured to oxidation by antimoniferous supergene products such as kermesite and senarmontite. 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, bindheimite, and residual nodules and lumps of stibnite, native antimony, jamesonite, and other sulphosalts. Ahlfeld (1948) describes an unusual type of oxidized antimony (stibnite) deposit in Argentina in which the surface parts are marked by an abundance of (colloidal) antimoniferous opal associated with the iron antimonate tripuhyite (jujuyite).

Nodules of oxidized native antimony, stibnite, jamesonite, and other sulphosalts tend to collect in alluvial placers frequently with gold, cassiterite, and other heavy resistates. Antimony is also a trace constituent (2—10 ppm) in limonite, wad, pyrite, and other minerals in alluvial placers. None of the alluvial placers contain economic amounts of antimony minerals.

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 large 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 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). With one known exception (the Antimony Line in the Murchison Range, Transvaal, South Africa), most of the large economic stibnite deposits are younger than Precambrian. Furthermore, most stibnite deposits are mainly restricted to sedimentary terranes containing phyllites, carbonaceous 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. Precambrian (Archean) deposits with abundant antimony minerals (stibnite and sulphosalts) (e.g. Antimony Line, Transvaal; Yellowknife, Northwest

Territories) are generally in or near extensive carbonated (shear) zones in volcanics or assemblages of volcanics and sediments, the latter commonly quartzitic, cherty, and graphitic. Many of the stibnite deposits of the world are related to extensive deep-seated fracture systems often bounding graben and uplifted zones of the earth.

Theories of the origin of epigenetic antimony deposits range from late stage hydrothermal, related to magmatic events (Lindgren, 1933), to metamorphic secretion (Boyle, 1979; Perichaud, 1980) and lateral secretion (Roger, 1972).

CHEMICAL FACTORS BEARING ON THE MIGRATION AND CONCENTRATION OF ANTIMONY

Antimony can exist in three oxidation states (0), (III), and (V). The (0) and (III) states are characteristic of endogene (reducing) processes and the (III) and (V) states are a feature of most exogene (oxidizing) processes. Because of the high charges on the (III) and (V) states of antimony, and the rapid base hydrolysis of these (ionic) states in aqueous solutions, the element has only a minor cationic chemistry. As a consequence of this, antimony forms mobile anionic complexes and polymers, mainly with oxygen and sulphur in most natural processes. Some of these complexes involve various acids in which antimony forms the nucleus of an anion, e.g. $[Sb(SO_4)_2]^-$, $[Sb(OH)C_4H_3O_5]^-$. The latter, as potassium antimony tartrate, is one of the most soluble antimony compounds. In the (III) state antimony forms an oxide which exhibits amphoteric properties. Antimony also forms a reactive hydride, stibine, SbH_3, in which the oxidation state of the element is trivalent. All of these features endow the element with a complicated chemistry in natural processes, many aspects of which are not well characterized. The generalized cycle of the most common antimony interconversions in natural environments is shown in Fig. 1.

Endogene processes

In endogene processes antimony and antimony compounds may reach their sites of deposition in fractures, faults, chemically receptive rocks, etc. in the vapour state, in true and colloidal solutions, or by a variety of diffusion mechanisms. The temperature and pressure range of precipitation of the various antimony minerals (stibnite, sulphosalts, etc.) in endogene deposits is highly variable judging from liquid inclusion data and wall rock alteration phenomena. In skarn deposits the range appears to be 350—100°C and 4×10^5—2×10^4kPa (4 kbar—200 bar); in veins, stockworks and similar deposits the range is 300—100°C and 1×10^5—1×10^3kPa (1 kbar—10 bar). The actual chemical forms in which antimony migrates in endogene processes have not yet been fully characterized in natural vapours, solutions, and diffusion currents as far as these writers are aware. We can, therefore, only speculate on the possible migration states from the known chemistry of antimony and from the properties of natural vapours and solutions. Some of the probable migration states and the modes of precipitation of antimony minerals include the following:

(1) *As the element, Sb(O).* Antimony has a relatively low volatility, melting at 630°C and boiling at 1750°C. Because of this, elemental vapour transport would be expected only under high temperature conditions such as might prevail during the formation of deposits such as volcanic sublimates, pegmatites, and skarn bodies. Precipitation of the element in the native form and as stibarsen (allemonite) (SbAs) in these deposits probably takes place mainly as a result of cooling processes. Complex reactions involving S, As, Fe, Cu, Pb, Ag, and other elements with vapour-transported elemental antimony may yield minerals such as stibnite, tetrahedrite-tennantite, etc. More generally, however, most of the element is precipitated as traces in minerals such as pyrite and arsenopyrite.

(2) *As the hydride, SbH_3.* This compound is a gas at normal temperatures and pressures. It is very unstable, highly reactive, easily oxidized, and decomposes above 25°C. It is an unlikely candidate for the transport of antimony in most endogene processes except those taking place at very low temperatures under strongly reducing conditions.

(3) *As volatile compounds.* A number of antimony compounds are relatively volatile below 400°C, including $SbCl_3$, Sb_2O_3, Sb_2S_3 and others. Transport in these forms is conceivable during the formation of skarn bodies and certain veins and lodes. Cooling of the vapours and/or reactions with elements or compounds in the host rocks, groundwaters, etc., may precipitate various antimony minerals.

(4) *As the chloride, $SbCl_3$.* This compound is highly volatile and hydrolyzes readily in the presence of water:

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$$

In certain acid chloride volcanic vapours and acid chloride hot spring waters antimony may be present as the chloride or as various chloride complexes of the type $[SbCl_6]^{3-}$. Reaction of acidic antimony chloride solutions with H_2S produces stibnite:

$$2SbCl_3 + 3H_2S \rightarrow Sb_2S_3 + 6HCl$$

Other reactions to produce antimony minerals are essentially the same as those discussed in (6) below.

(5) *As the sulphate, $Sb_2(SO_4)_3$.* This compound is relatively unstable in water because of base hydrolysis but may exist in some low temperature hydrothermal solutions in a complexed anionic form.

(6) *As polymeric thioantimonites, $[SbS_2]^-$, and thioantimonates.* These appear to range from $[SbS_2]^-$ to $[Sb_{14}S_{27}]^{n-}$, and even higher analogues are possible. Two are of particular interest, $[SbS_3]^{3-}$ and $[Sb_4S_{13}]^{n-}$, from the viewpoint of their probable presence in the common sulphosalts pyrargyrite and tetrahedrite. Other more complicated species are also known involving double and triple complexes with As and Bi. Most of these complex polymers are stable only in neutral and alkaline media, the most soluble being the alkali, magnesium, and calcium species. All have considerable complexation affinities for metal cations; some may also control the redox potential in solution.

Stibnite dissolves in alkali sulphide solutions to give polymeric thiospecies:

$$Sb_2S_3 + S^{2-} \rightarrow 2[SbS_2]^-$$
$$Sb_2S_3 + 3S^{2-} \rightarrow 2[SbS_3]^{3-}$$
$$2Sb_2S_3 + S^{2-} \rightarrow [Sb_4S_7]^{2-}$$
$$Sb_2S_3 + HS^- \rightarrow H[Sb_2S_4]^-$$

Stibnite is likewise soluble in a variety of alkaline solutions (e.g. KOH, Na_2CO_3, $Na_2B_4O_7$):

$$2Sb_2S_3 + HS^- + OH^- \rightarrow [Sb_4S_7]^{2-} + H_2O$$
$$Sb_2S_3 + 6OH^- \rightarrow [SbS_3]^{3-} + [SbO_3]^{3-} + 3H_2O$$

According to Raab and Dickson (1967) the solubility of antimony sulphide is such solutions is controlled largely by the OH^- concentration. They state that natural geothermal fluids, even at low temperatures, need only contain OH^-, produced by numerous natural hydrolysis reactions, to transport considerable quantities of Sb_2S_3. Specific complexing agents are not required. Ovchinnikov et al. (1980) show that Sb_2S_3 is relatively soluble in pure water (1—10 g/l), and more so in water containing NaCl (2.08 *M*) at temperatures above 325°C.

Precipitation of stibnite from dilute solutions and from waters containing NaCl can take place simply by cooling as indicated by the curves given by Ovchinnikov et al. (1980). Similarly, precipitation of stibnite and antimonial sulphosalts from alkali sulphide and alkaline solutions of various types can take place by decreases in temperature, acidification or dilution of the solutions; possibly also by oxidation reactions when rising solutions come into contact with ground waters, resulting in decomposition of the sulphide complexes:

$$[Sb_2S_4]^{2-} + 2O_2 \rightarrow Sb_2S_3 + (SO_4)^{2-}$$

Deposition of these minerals may also be affected by reactions with wall rocks. This may be one of the principal mechanisms by which antimonian arsenopyrite and gudmundite, FeSbS, are formed in skarns and in the wall rock alteration zones of gold and other deposits. The reactions involve an exchange between iron in silicates and alkali in solution, the iron binding the thioantimonite as antimonian arsenopyrite or gudmundite thus liberating alkali which forms such minerals as alkali feldspar, sericite, etc. Schematically the reaction for the potassium species can be written as follows:

Fe(II) silicate + 2K(thioantimonite) → FeSbS + 2K(silicate).

(7) *As various antimony, antimonite, and antimonate species.* In acid media the Sb(III) species can be characterized as $[Sb(OH)_2]^+$; in alkaline media the antimonite and antimonate are respectively $[Sb(OH)_4]^-$ and $[Sb(OH)_6]^-$. In endogene environments with a low oxidation potential the Sb(III) species predominates; where the oxidation potential is high, as in some near surface waters, the Sb(V) species are more stable. Sulphide ion (H_2S, alkali sulphides, etc.), and probably also polymeric sulphide ions, precipitate stibnite and antimonian sulphosalts from antimonite and antimonate solutions under acidic conditions. Complex reactions between antimonites, antimonates, sulphide ion, polymeric sulphide ions, iron, copper, silver, and other elements precipitate a variety of antimony minerals such as gudmundite, tetrahedrite, jamesonite, etc. Native antimony, SbAs compounds (stibarsen and allemontite), and SbAg-compounds (dyscrasite and allargentum) may be precipitated from hydrothermal solutions containing antimonites (or thioantimonites) at temperatures below 200°C in the presence of strong reducing agents. This may account for the presence of native antimony, dyscrasite, and allargentum in medium- to low-temperature deposits such as the native silver-Ni-Co arsenide veins at Cobalt, Ontario.

(8) *As colloidal compounds.* Hydrosols of metallic antimony are readily prepared by reduction methods, and these are stable in the presence of protective colloids in reducing environments. Various sulphide hydrosols of antimony are known of which the most familiar is the $Sb_2S_3\text{-}nH_2O$ sol. Both the metallic and trisulphide sols carry negative charges, the trisulphide sol as a result of the adsorption of SH^- or OH^- ions on its surface. Hydrous Sb(III) and Sb(V) oxide sols can be prepared and numerous organo-antimony sols are known. In endogene environments the metallic and trisulphide sols appear to be possible modes of transportation at low temperatures (100°C), as do also the hydrous oxide sols under certain restricted conditions. Organo sols of antimony seem probable where relatively large amounts of bituminous and carbonaceous residues are present in stibnite and other antimoniferous deposits. Precipitation of antimony minerals from the various colloidal solutions of the element may take place as a result of changes in pH, mingling of oppositely charged electrolyte or colloidal solutions, oxidation-reduction reactions, absorption reactions, and so on.

Summarizing the above brief resume of the possible modes of transport of antimony in endogene processes we see that the element is relatively mobile under both acidic and alkaline conditions. This is substantiated by the presence of antimony in acidic volcanic vapours and in both acidic and alkaline hot spring waters. Most hot spring waters carrying and precipitating relatively large amounts of antimony, however, tend to be neutral or alkaline, a feature which suggests that probably most deposits containing antimony minerals were precipitated from neutral and alkaline media.

Exogene processes

The fate of antimony during the oxidation of antimony-bearing deposits has been extensively studied by the senior author and his colleagues (Boyle, 1965, 1972a, 1972b; Boyle and Dass, 1971). The details are particularly complex and only the salient points can be discussed in the space available here.

As noted above, antimony exists in three principal oxidation states in nature: Sb(0), Sb(III) and Sb(V). The Sb(0) and Sb(III) states are those found in native antimony, in the sulphide, Sb_2S_3 and in the various antimonides and sulphantimonides. The pentavalent state is the most stable in an oxidizing environment, being a constituent of a number of the natural oxides (cervantite, stibiconite) and various complex antimonates. The trivalent state is also present in the hydride stibine, SbH_3, which may occur in highly reducing organic exogene environments.

Oxidation of native antimony, stibnite and the various other antimonides and sulphantimonides yields a variety of supergene antimony minerals depending on the redox conditions and the presence of binding constituents in the oxidizing solutions; the most common of these minerals is cervantite, senarmontite, valentinite, stibiconite, kermesite, bindheimite, romeite, and numerous other antimonites and antimonates. Yellowish and white antimony ochres that are amorphous to X-rays characterize the oxidation zones of many deposits containing abundant hypogene antimony minerals.

Most antimony-bearing deposits contain pyrite, pyrrhotite, or marcasite which on oxidation yield sulphate and usually some free sulphuric acid depending on the redox conditions. The reaction for pyrite is probably as follows:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$

The acid (sulphate) so formed not only renders many of the antimony sulphides and sulphosalts soluble but also provides an acidic milieu for the transport of certain antimoniferous salts (complexes).

Oxidation of primary antimony minerals is a complex phenomenon that yields a variety of products depending on the compositions of the original minerals and reaction products in the oxidizing media. Oxidation of native antimony, allemontite (stibarsen), and stibnite tends to give the oxide in which antimony is present in the (III) state:

$$4Sb + 3O_2 \rightarrow 2Sb_2O_3$$
$$2SbAs + 3O_2 \rightarrow Sb_2O_3 + As_2O_3$$
$$Sb_2S_3 + 6O_2 + 3H_2O \rightarrow Sb_2O_3 + 3H_2SO_4$$

Stibiconite, $Sb(III)Sb_2(V)O_6(OH)$, also commonly appears in the oxidation products of these minerals. Oxidation of tetrahedrite yields the oxide and other soluble antimony (III) species:

$$2Cu_{12}Sb_4S_{13} + 57O_2 + 14H_2O \rightarrow 24CuSO_4 + 8Sb(OH)_3 + 2H_2SO_4$$

or

$$6Cu_{12}Sb_4S_{13} + 171O_2 \rightarrow 72CuSO_4 + 10Sb_2O_3 + 2Sb_2(SO_4)_3$$

Similarily, minerals such as jamesonite yield the Sb(III) sulphate and other sulphates:

$$Pb_4FeSb_6S_{14} + 28O_2 \rightarrow 3Sb_2(SO_4)_3 + 4PbSO_4 + FeSO_4$$

Hydrolysis of the antimony sulphate yields the various oxides, stibiconite, and so on:

$$Sb_2(SO_4)_3 + 3H_2O \rightarrow Sb_2O_3 + 3H_2SO_4$$

Oxidation of stibnite may also yield antimony oxysulphide, the mineral kermesite; ocherous native sulphur commonly appears in this oxidation reaction:

$$2Sb_2S_3 + O_2 \rightarrow 2Sb_2S_2O + 2S$$

Where concentrations of chloride are present in the oxidizing solutions the oxychloride (not known as a mineral in nature) may form, and this may ultimately be dissolved as the trichloride where sufficient chloride ion is present:

$$Sb_2S_3 + 2Cl^- + 7O_2 \rightarrow 2SbOCl + 3SO_4^{2-}$$
$$2SbOCl + 4HCl \rightarrow 2SbCl_3 + 2H_2O$$

The chloride is stable only in acid solutions ($pH<2$); at higher pH's the oxide (senarmontite, valentinite) is precipitated in aqueous solutions:

$$2SbCl_3 + 3H_2O \rightarrow Sb_2O_3 + 6HCl$$

Concentrations of sulphate, either as the acid or as ferric sulphate, slowly dissolve stibnite, yielding antimonyl sulphate or analogous complexes in aqueous solutions:

$$Sb_2S_3 + 3H_2SO_4 \rightarrow Sb_2(SO_4)_3 + 3H_2S$$

The sulphate is stable only in acid solutions ($pH<2$); at higher pH's it hydrolyzes readily with the precipitation of the oxides:

$$Sb_2(SO_4)_3 + 3H_2O \rightarrow Sb_2O_3 + 3H_2SO_4$$

Oxidation of the hydrogen sulphide yields free sulphur which is commonly found intermixed with the various natural antimony oxides in oxidized zones.

Bacteria may play a role in the oxidation of antimonides and antimonites in nature. Lyalikova (1967, 1978) describes a species of bacteria, that is capable of oxidizing antimonite ion to antimonate. (*see* the section on Antimony in the biosphere). Algal (and bacterial) activity are thought to play a role in the production of soluble methylantimonials in natural waters (Andreae et al., 1981).

The solution chemistry of antimony is particularly intricate especially in oxidizing zones of deposits where abundant pyrite is undergoing simultaneous oxidation. The trivalent oxide is amphoteric yielding $[Sb(OH)_2]^+$ ions in acid solutions and antimonite anions, usually written as $Sb(OH)_4^-$ in basic solutions. The cationic complex is particularly prone to hydrolysis on the dilution or neutralization of acidic solutions and the hydrous trioxide, $Sb_2O_3 \cdot xH_2O$, SbOOH, or a variety of basic salts are precipitated depending on the pH of precipitation and the presence of other binding cations. Antimonites, precipitated as a result of the reaction of various cations such as Ca and Fe with antimonite-bearing solutions, are however, relatively rare. Acidification of basic solutions of Sb(III) generally yields the hydrous oxide, $Sb_2O_3 \cdot xH_2O$, from which water may be split out to give the trioxide. In natural environments, precipitates from solutions of Sb(III) are generally complex and amorphous, being mainly composed of phases of the trioxide (senarmontite) and pentoxide and a variety of indefinite hydrous oxides, among which the basic hydrous oxide, stibiconite, may appear. The pentavalent oxide, unknown as a mineral, is acidic dissolving in base to give antimonate anion, usually written as $Sb(OH)_6^-$. Reactions of this complex and/or the various derivatives of antimonic acid with cations, particularly lead and iron, yield a number of insoluble minerals of which bindheimite and tripuhyite are the most common. Bindheimite may also originate as the direct result of oxidation of boulangerite, jamesonite, and other similar lead-bearing sulphosalts; indirectly bindheimite may develop as a result of the alteration of mimetite whereby Sb replaces As followed by structural rearrangements and removal of Cl, etc.

Under very acid ($pH<3$) conditions much antimony is removed from deposits during oxidation processes as the sulphate or other complexes of the Sb(III) ion; similarily at high pH (>8) the element is mobile mainly as the alkali antimonite or antimonate species. Under more normal pH conditions (4—8), when the various oxides are only sparingly soluble, much of the antimony is retained in the oxidized zones in the form of the oxides and various antimonites and antimonates and in an adsorbed or chemically combined state in limonite, wad, clay complexes, and other colloidal materials. There may also be considerable amounts of antimony camouflaged in the various arsenates and a variety of other supergene minerals. In the Keno Hill Pb-Zn-Ag deposits a depletion of antimony was noted in the oxidized zones of some lodes and an enrichment in others compared with the primary ores (Boyle, 1965). At Cobalt, Ontario, antimony is severely depleted in the parts of the veins where intensive oxidation has taken place (Boyle and Dass, 1971). At Yellowknife a general enrichment of antimony in the shallow oxidized zones of some veins is apparent. In some of the gossans overlying the massive sulphide deposits of the Bathurst district, New Brunswick, antimony is considerably enriched (Boyle, 1979). Under conditions of intense leaching by groundwaters antimony is largely removed from gossans and oxidized zones. This effect is particularly marked where wall rocks and gangue have lost most of their carbonates as a result of oxidation, or where they originally contained relatively small amounts of carbonates, minerals that neutralize the downward moving acidic solutions. In such oxidized zones about all that remains is limonite and wad with traces to minor amounts of adsorbed or chemically combined antimony.

Antimony commonly shows an enrichment in supergene sulphide zones. There the element occurs in most of the secondary sulphides such as chalcocite, pyrite, and marcasite, and frequently in the mineral pyrargyrite. The formation of this mineral seems to involve either the reaction of silver-bearing solutions with primary tetrahedrite or complex reactions of silver and antimony solutions with H_2S or sulphide ion as follows:

$$3Ag_2SO_4 + Sb_2(SO_4)_3 + 6H_2S \rightarrow 2Ag_3SbS_3 + 6H_2SO_4$$

Aurostibite, $AuSb_2$, may be of supergene origin in some gold deposits, although this postulate is generally difficult to verify in most deposits. Native antimony seemingly occurs in some oxidized zones and zones of reduction in certain antimoniferous veins as a supergene mineral. Masses of native antimony weighing up to a ton in weight, associated with kermesite and valentinite, were found in the near-surface parts (30—50 m) of the veins at Lake George, New Brunswick (Kunz, 1885), and this mineral can still be found as small nodules in some of the near surface exposures of veins at this site and elsewhere. The conditions under which native antimony is formed probably imply organic reductants, colloidal reactions, or reactions with ferrous salts. Metastibnite, Sb_2S_3, is generally of hypogene origin, but the mineral can apparently also be formed in some secondary sulphide zones where the primary veins are enriched in antimony. The amorphous red sulphide can also be precipitated as a supergene mineral in the oxidation zones of certain stibnite deposits. Clark (1970) mentions such an occurrence at Mina Alacran, Pampa Larga, Copiapo, Chile where the metastibnite occurs as an in situ oxidation product of stibnite. Elements with which antimony is commonly enriched in secondary sulphide zones include Cu, Ag, Au, As, Zn, Cd, and Fe.

The antimony dispersed in the ground waters percolating through oxidized zones of deposits is ultimately dispersed through springs into the drainage systems of an area. A small amount of this antimony is coprecipitated with limonite, wad, and other precipitates at the orifices of these springs or at proximal sites downstream on hillsides and in limonite-wad conglomerates in the bottoms of streams and rivers. The remainder is precipitated mainly by adsorption on the materials of distal downstream drainage sediments or moves in the water systems ultimately to the sea.

The amounts of antimony dispersed into the groundwater systems near oxidizing deposits are generally low; our observations indicate no more than 10 ppb in most mineralized belts, although values up to 800 ppb in highly acid waters are recorded in the literature from Butte, Montana, and contents up to 5000 ppb and more have been recorded in some neutral and alkaline spring waters near stibnite and gold deposits in the Tien Shan, U.S.S.R. (Table XI). Our analyses indicate that from <5 to 500 ppm Sb or more may be present in limonite, wad, and other precipitates at spring orifices, the lower values being in antimony-poor and the higher values in antimony-rich terranes; similar amounts may be present in some limonite-wad conglomerates in stream bottoms near springs leaching zones enriched in antimony. At Keno Hill, Yukon up to 1100 ppm Sb occurs in stream sediments in the vicinity of the antimoniferous Pb-Zn-Ag deposits; at Walton, Nova Scotia amounts up to only 5 ppm were found in stream sediments near the antimony-poor but arsenic-rich Ba-Pb-Zn-Ag-Cu deposits.

GEOCHEMICAL PROSPECTING USING ANTIMONY AS AN INDICATOR

Antimony is a particularly good indicator in most types of geochemical surveys, not only for deposits containing the element as an economic product, but also for many other types of mineral deposits enriched in a great variety of metals. The most common elemental associates of antimony are Cu, Ag, Au, Zn, Cd, Hg, Ba, U, Sn, Pb, P, As, Bi, Nb, Ta, Mo, W, Fe, Co, Ni, Pt metals, Te, Se, and S. There is a marked coherence between antimony and gold in many types of gold deposits, particularly in those in greenstone belts, some of which contain aurostibite, $AuSb_2$, as a subsidiary economic mineral, and in those auriferous deposits that have a polymetallic association. This coherence also extends to silver in all of its deposits and is greatly accentuated in the native silver variety containing nickel and cobalt minerals (Cobalt type) and in the polymetallic variety in which minerals such as tetrahedrite (freibergite) carry much of the silver. There is frequently a close relationship between antimony, arsenic, and bismuth in many deposits. Antimony may accompany Cu, Zn, Hg, As, Pb, Mo, W, Fe, Co, Ni and the Pt metals in most types of their deposits and can often serve as a valuable indicator for these metals.

Certain types of uranium deposits, particularly those enriched in the Ni-Co arsenides (Jáchymov—Great Bear Lake type) are markedly enriched in antimony; also those that are associated with volcanic caldera and have a polymetallic mineral paragenesis. Some uranium deposits in sandstone (Colorado Plateau type) also have higher than average amounts of antimony, mainly in pyrite. Some pegmatites, certain pegmatite-like bodies, and various albitized (feldspathized) zones carrying Nb, Ta, Be, and Sn may be slightly enriched in antimony principally in minerals such as tantalite (stibiotantalite), and columbite (stibiocolumbite). Other types of deposits in which antimony exhibits minor enrichments and which may be indicated by the element are mentioned in the section on deposits.

Antimony can be used as an indicator in practically all geochemical prospecting methods with success. The selection of the method to be employed should be guided by a knowledge of the mobility or fixation of the element in its deposits and their host rocks, in the gossans and oxidized zones of the deposits, in the overlying soils or glacial drift, in the associated ground, spring, and stream waters and their precipitates, in stream and lake sediments, and in the proximal vegetation. Many of the factors bearing on the mobility and fixation of the element in these environments are outlined in preceding sections of this paper. Others will suggest themselves to the exploration geologist as he works a specific area.

One of the particularly advantageous features of antimony as an indicator (pathfinder) for metalliferous deposits is the general low abundance (<0.5 ppm) of the element in most geological terranes of both endogenic and supergenic derivation. When contents exceeding twice this value are encounted, mineralization is generally indicated in which antimony minerals or minerals bearing the element in substitutional positions, are present. In addition the ratio As/Sb is generally relatively uniform in most supergene and endogene environments; decreases in this ratio may, therefore, indicate enhanced concentrations of antimony that may be related to mineralization containing the element.

Analytical methods

Numerous methods of solution extraction of antimony from geological materials are described in the literature; those employed in surveys depend on whether total or partial extraction of the element is desired. If total extraction is employed fusions of aliquots of the samples employing carbonates, borates, or bisulphates, or attack by HF-HNO_3-$HClO_4$ are necessary, and these may have to be prolonged because certain antimony minerals and others carrying the element (e.g. tantalite) are particularly refractory. When partial extractions are employed less rigorous attacks employing reagents such as $4N$ HNO_3 are satisfactory. The total methods extract the total combined antimony from the geological materials and are best suited to lithochemical work and extraction from biological ash; the partial methods, on the other hand, extract the relatively soluble antimony associated with epigenetic mineralization in host rocks and in the oxidation products and secondary minerals in gossans and secondary halos developed both mechanically and hydromorphically in residual soils, till, and other types of overburden.

General treatises and reviews on the analytical chemistry of antimony and their indicator elements, and analytical methods for use in geochemical prospecting surveys, include those by Maeck (1961), Smith (1973), Shapiro (1975), Ward (1975), Stanton (1976), Aslin (1976), Abbey et al. (1977), Reeves and Brooks (1978), Ward and Bondar (1979), Johnson and Maxwell (1981), and Jeffrey and Hutchison (1981).

Antimony is not readily determined by routine optical spectrographic methods except when present in large amounts (>10 ppm), the reason for this being that the element has a relatively low sensitivity in the arc. X-ray fluorescence methods, likewise, have a low sensitivity for antimony, the lowest amount determinable under normal conditions being about 5 ppm. Nemec (1979) describes a spectrographic method using an AC double-arc procedure in which he states a limit of detection of 4 ppm Sb in soils and other geological materials.

Aslin (1976) has reviewed the analytical methods for the determination of antimony in geologic materials. Historically, antimony has usually been determined by colorimetric techniques after an acid leach or potassium pyrosulphate fusion of the samples of geological materials. Brilliant green was used as indicator in one method (Stanton, 1966), and Rhodamine B in another (Ward and Lakin, 1954; Ward et al., 1963). In both methods visual comparison with standards was employed. More recently, atomic absorption methods, employing an air-acetylene flame after extraction of the samples with TOPO (trioctylphosphine oxide) into MIBK (methyl isobutyl ketone), have been used in the determination of antimony in rocks, soils, etc. (Welsch and Chao, 1975).

Aslin (1976) describes the determination of antimony by flameless atomic absorption spectrometry, the method now used by the Geological Survey of Canada and found to be suitable for most geological materials·utilized in geochemical and geochemical prospecting surveys. Antimony is separated from the sample leach solution via hydride formation with sodium borohydride as reductant. The hydrides are passed into a heated quartz cell where an atomic absorption measurement is made. The detection limit, based on 500 mg of digested sample is 80 ng/g (0.08 ppm) for Sb. The advantages of the method are its sensitivity, speed, versatility, simplicity and apparent freedom from interferences.

Thompson et al. (1978) describe a method for the simultaneous determination of As, Sb, Bi, Se, and Te in aqueous solution by generation of their gaseous hydrides and introduction of these hydrides into an inductively coupled plasma source where the atomic line emission from the elements is detected. Detection limits of 1 ng per ml or below can be attained by the method. Interferences from Cu, Fe, Pb, and other elements are discussed. The method was designed for rapid and inexpensive analysis of geological and biological materials used in geochemical surveys.

Methods suitable for the determination of low amounts of antimony (nanogram level) in natural waters have recently been published by Nakahara et al. (1978), Abu-Hilal and Riley (1981), and Andreae et al. (1981). The first investigators utilize non-dispersive atomic fluorescence spectrometry, the second, a spectrophotometric method after preconcentration of antimony, and the third, atomic absorption spectrometry with hydride generation.

Methods using radioactivation analysis can be used for the determination of antimony in practically all types of earth materials; they are particularly useful in analyzing biological samples. Details are given in the papers by Voin et al. (1978), Gladney (1978), and Willis (1981). The limits of detection vary depending on sample size and other factors; a limit as low as 0.5 ppb (0.0005 ppm) can be attained for some types of samples, but for samples utilized in geochemical prospecting the lower limit is 10 ppb (0.01 ppm) Sb.

Care must be taken in ashing biological materials for antimony determinations because of the relatively high volatility of the element and some of its organic and inorganic compounds. A wet ashing procedure is recommended in most cases to prevent loss of antimony. If perchloric acid is used in the digestion procedures of biological samples consideration should be given to possible loss of antimony chlorides at higher temperatures.

Lithochemical methods

Relatively little detailed work has been done using the antimony content of fresh (unsheared and unaltered) country rocks to outline geochemical or metallogenic provinces containing stibnite deposits or deposits in which antimony is present in sufficient amounts to constitute an indicator (e.g. gold and silver deposits). There are well-defined local and regional antimoniferous metallogenic provinces in practically all ages of rocks in the Earth's crust, but we do not know whether antimony analyses of country rocks (volcanics, sediments, intrusives, etc.) reflect these provinces. This is a research problem that should receive attention, particularly from a statistical viewpoint.

Antimony is a relatively mobile element in endogene processes and tends to form broad primary halos and dispersion trains (leakage halos) in the vicinity of various types of antimoniferous deposits. Studies of primary (endogene) antimony halos and trains associated with a variety of mineral deposits have been carried out in numerous countries, a few of which are briefly described below as examples. Most investigations have been concerned with gold deposits, examples being those by Boyle (1961), Erickson et al. (1961, 1964a, b, 1966), Polikarpochkin et al. (1965), Polikarpochkin and Kitaev (1971), Wrucke et al. (1968), Lovering et al. (1968), Obraztsov (1969), Akright et al. (1969), McCarthy et al. (1969), Wells et al. (1969), Grigoryan and Zubov (1971), Stock and Zaki (1972), Chibisov et al. (1973), Atabek'yants (1973), Kudryavtsev et al. (1974), Zlobin and Vyushkova (1977), Voin et al. (1978), and Kudryavtsev and Zubov (1979); a number with lead-zinc-silver, copper, and other polymetallic deposits, Boyle (1965, 1972a), Dvornikov (1965), Yanishevskii (1966), Chan (1969), Karamata (1969), Ovchinnikov and Grigoryan (1971), Erickson and Marsh (1971, 1973), Bektemirov and Kurmanaliev (1972), Ovchinnikov et al. (1972), Cillik (1973), Gott and Botbol (1973), Lovering and Heyl (1974, 1980), Jankovic et al. (1977), Scott and Taylor (1977), and Gott and Cathrall (1979a, 1979b, 1980); some with native silver veins, Boyle et al. (1969), Dass (1970), Dass et al. (1973); uranium deposits, Rossman et al. (1972a, 1972b), Brookins (1978), Della Valle and Brookins (1980), and Boyle (1982b); and a number with antimony, mercury-antimony, and fluorite deposits, Bradshaw and Köksoy (1968), Lukas (1969, 1970), Gapontsev et al. (1971), Terekhova et al. (1971), Yusupov et al. (1971), Tsertsvadze (1972), Stock and Zaki (1972), Vargunina (1972), Bykovskaya (1972a, 1972b), Kamenshchikov et al. (1972), Bektemirov and Kurmanaliev (1972), Protsenko (1972), Suerkulov (1973), Cillik (1973), Baba-Zade et al. (1973), Terekhova and Vershkovskaya (1973), Ovchinnikov (1973), Vershkovskaya and Krapiva (1973), Bykovskaya and Mukimova (1974), Mudrinic (1975), Ivanova (1975), Martinez Ramos and Maldonado (1975), Velichkin et al. (1977), Yablonskaya and Meleshko (1978), Tsertsvadze and Astakhov (1978), and Cerny (1981).

The primary antimony halos associated with gold-quartz veins and silicified bodies tend to be restricted to the visible alteration zones, which are usually only fractions of a metre to a few metres in width. Where extensive chloritization (propylitization) and carbonatization has taken place, however, the halos may be more extensive. At Yellowknife (Boyle, 1961) the halos associated with the deposits in greenstones vary in width from 0.5 to 40 m and completely envelope the orebodies (Table XIV). There is a fairly uniform increase in the antimony content as the orebodies are approached accompanied by a similar increase in arsenic. In the gold-quartz deposits in greywacke and slate at Yellowknife, the antimony halos are restricted, rarely more than a metre in width. The antimony content is low in these halos mainly because the veins contain no sulphosalts or stibnite. Results similar to those described above for gold deposits in a variety of igneous and sedimentary rock types are given for a number of Canadian auriferous mineral belts (Boyle, 1979).

Polikarpochkin et al. (1965) and Polikarpochkin and Kitaev (1971) found well-developed antimony halos associated with the Baley gold-quartz deposits (Eastern Transbaikaliya) which cut a sequence of clastic sediments and volcanics. The concentration of antimony and arsenic in the halos increased upward and was greatest some 200 m above the orebodies. The halos also expanded laterally above the ore zones being in places some 800 m wide. Similar features are reported by Grigoryan and Zubov (1971), Atabek'yants (1973), and Kudryavtsev and Zubov (1979) for other gold deposits in U.S.S.R.

The results and conclusions drawn from the investigations of primary antimony haloes associated with auriferous deposits have been varied and are not readily systematized. Most investigations indicate that the most significant antimony halos in gold deposits are those in which the deposits are enriched in antimony minerals, particularly stibnite and sulphosalts. Many of these deposits also contain aurostibite ($AuSb_2$) as an economic mineral. Widths, extents, and up-dip projections of the primary antimony halos vary widely depending on the types of host rocks, localizing structures, degree of

TABLE XIV

Antimony content (in ppm) of primary halos — gold-quartz deposits, Yellowknife District, N.W.T., Canada[1]

Description of rock[2]	Sb content	As content	Remarks
Greenstone belt:			
Amphibolites	<1	5	Country rock (greenstone)
Chlorite and chlorite-carbonate schist	26	74	Shear zones; width of schist 0.5—40 m
Carbonate-sericite schist	23	6900	Shear zones; width of schist 0.1—3 m
Gold-quartz bodies	0.2%	1.5%	Average values. Most bodies contain sulphosalts and stibnite
Sedimentary area:			
Greywacke, slate, quartzite	<1—1	<5—10	Country rock (Yellowknife Super Group sediments) Ptarmigan vein
Greywacke, slate, quartzite	1	10	Wall rock 0.6—1 m from Ptarmigan vein
Greywacke, slate, quartzite	1	38	Wall rock 0.1—0.3 m from Ptarmigan vein
Altered greywacke, slate, quartzite	3	50—3,500	Contact rock adjacent to Ptarmigan vein
Gold-quartz vein	<1—5	0—500	Most quartz veins are barren of tetrahedrite, stibnite, etc.; mineralized sections may contain higher contents of antimony and arsenic

[1] See Boyle (1961, 1979) and Boyle and Jonasson (1973).

[2] All samples were composites of the rock or ore types.

wall-rock alteration, post-mineralization fracturing, and other geological factors. Each gold belt, and commonly each deposit, has its individual characteristics. Antimony is generally associated with a number of trace elements in the primary halos of auriferous deposits, including Rb, Cu, Ag, Ba, Zn, Hg, B, U, Pb, As, Sb, Bi, Se, Te, Tl, Cr, Mo, W, Mn, Co, and Ni. Some of these elements may be absent or present in only erratic traces in certain deposits. All investigators agree that Sb and As, particularly the latter, are the best universal indicators for use in primary (endogene) halo surveys of auriferous deposits. As, Sb, Hg, and Te commonly show coincident dispersion aureoles in gold deposits, and these aureoles, with the exception of Te in a number of deposits, exceed the width of the auriferous orebodies by factors of three or more. Most primary Sb (and As) halos reproduce the shape of the auriferous orebodies with which they are associated, and most exhibit symmetrical envelopes, although in some deposits asymmetry is marked.

The details of the dispersion of antimony and its various associated trace elements (including gold) in the primary halos of auriferous deposits are complex. Some observers find the lateral dispersion limited to fractions of a metre in some gold districts; in others the lateral dispersion may exceed 100 metres. Commonly the arsenic halo (as well as that for B and a number of other elements, e.g. Ag, Pb) is more extensive laterally than the antimony halo about individual deposits, although no general rule appears to apply at the present time for all auriferous deposits. The vertical dispersion of antimony up-dip of auriferous orebodies in shear zones, fractures, faults, or replaced beds, is commonly much greater than the lateral dispersion for reasons of permeability and porosity. In most districts the leakage halos can be detected at distances measured in tens to hundreds of metres above blind orebodies. Within individual structures a vertical zonation, often complex, and in places erratic, can be detected in the primary halos of auriferous deposits. As a general rule, however, the supra-ore elements include Sb and As with the latter element (and B) usually farther up dip; sub-ore elements include those characterized by less mobility, e.g. Cu, Co, Ni, Sn, and Mo. These data can be often used effectively for the differentiation of halos situated above or below ore bodies (and hence can give an estimate of the level of erosion or penetration point of the drill), if due regard is taken of the geological situation and other factors such as oxidation and secondary enrichment of auriferous deposits.

Primary antimony halos associated with lead-zinc-silver and other types of polymetallic deposits are generally distinct and useful where the mineralization contains antimony minerals (e.g. stibnite and sulphosalts) or antimony-bearing minerals (e.g. antimoniferous galena). At Keno Hill (Boyle, 1965, p. 170) the antimony halos are only a metre or so wide ajdacent to some of the galena-sphalerite-freibergite orebodies in interbedded phyllites and quartzites, or greenstones, whereas they may exceed ten metres adjacent to others, principally those orebodies in massive quartzites. The lateral extent of the halo depends almost entirely on the degree of fracturing in the wall rocks of the orebodies. In nearly all profiles there is a consistent increase in the antimony (and arsenic) content with proximity to orebodies. One interesting feature of some orebodies is an increased content of antimony (and arsenic) in pyrite (separated from the rocks) as the lodes are approached. This effect has been noted at distances up to 30 m or more from some wide lodes in extensively fractured rocks. The pyrite with increased contents of antimony and arsenic is generally, but not always, located in minor fractures related to the main focus of mineralization.

The details of the zonation of antimony halos associated with polymetallic deposits are complex but similar in many respects to those just described for auriferous deposits. All pyritic deposits examined by Ovchinnikov et al. (1972) in the Soviet Union have endogenic halos characterized by the presence of a large number of elements of which antimony is one. Those deposits investigated by Ovchinnikov and Grigoryan (1971) exhibit similar features. These authors stress the point that the halos are generally contemporaneous with the deposition of the ores and not due to later metamorphic effects. In addition the halos are commonly symmetrical with respect to the orebodies and greatly enlarge the target. Antimony usually figures in the supra-ore halos in the vertical zonation sequences. Laterally antimony halos tend to be much more restricted than those of As, Pb, Zn, Ag, and Cu.

Native silver veins, such as those at Cobalt, Ontario, commonly contain antimoniferous minerals (e.g. native antimony, dyscrasite, allargentum, pyrargyrite) and are marked by antimony halos as shown by Boyle et al. (1969) and Dass et al. (1973) at Cobalt. The extent of the antimony halo (and those of other elements) depends essentially on the type of host rock. Veins in Nipissing diabase and Archaean amphibolites (greenstones) have narrow primary antimony halos, seldom more than a metre wide; in greywacke, conglomerate, and quartzite of the Cobalt Group the dispersion is broad, in places more than 30 m.

Trace element halos associated with the varied types of thorium and uranium deposits are discussed in detail in Boyle (1982b). Antimoniferous minerals (sulphosalts, native antimony) occur in many types of thorium and uranium deposits, principally in veins and stockworks with complex mineralogies such as those at Great Bear Lake, Canada, Jáchymov, Czeckoslovakia, and elsewhere. Some sandstone-type uranium deposits have higher than average contents of antimony.

Rossman et al. (1972a, b) studied the distribution of a suite of indicator elements (Mo, Pb, Cu, As, Sb, Bi, Hg, Sn, Tl) in shallow dipping U-Mo (pitchblende) deposits localized in porphyrites (acid tuffs) in a band of alternating volcanic and sedimentary rocks at an unspecified location. The ores are oxidized and leached to varying degrees. Primary halos were noted for all of the indicators, most being broader and more extensive up-dip than U, especially those for Sb, As, Tl, and Hg. The Hg halo exceeded all other indicator elements in its limits. The thallium and bismuth halos are comparable in size.

The linear productivity of uranium in the halos is maximal for the middle and lower parts of the orebodies. An analysis of the change of the linear productivity ratios As/U, Sb/U, Bi/U, and Sn/U with respect to the dip revealed that these ratios decrease regularly as one approaches the orebody. The maximum gradient was found for the As/U ratio.

Brookins (1978) states that uranium abundance by delayed neutron activation analysis indicates at least trends if not halos near orebodies in sandstone terranes in the southern San Juan Basin, New Mexico. Certain of the trends are backed up by concentrations of a number of other trace elements (e.g. rare earths, Ni, Co, Sb, Ta, As) in clay mineral of sulphide separates.

Numerous investigations and surveys of primary (endogene) antimony halos associated with antimony (stibnite), mercury-antimony, fluorite, and barite deposits are mentioned in the literature and referenced above. Antimony halos associated with stibnite and sulphosalt deposits are usually distinctive and well developed; those with mercury-antimony deposits similarily characterized, and those with fluorite and barite deposits commonly weak and only detectable by highly sensitive analytical work. Many of the halos of these types of deposits are zoned laterally and vertically with mercury being the most dispersed element forming the most extensive halos lateral from and vertically above the orebodies. Both Hg and Sb are characteristic of the supra-ore halos associated with stibnite and cinnabar-stibnite deposits. A number of investigators state that antimony halos correspond in shape with the shapes of individual stibnite and/or cinnabar-stibnite orebodies or with clusters of orebodies where the fracturing, shearing, or replacement processes have been homogeneous; elsewhere the shapes of the halos tend to be erratic.

Antimony dispersion patterns at the Costerfield, Victoria, Australia quartz-stibnite-gold deposits are described by Stock and Zaki (1972) and Hill (1980). In the weathered bedrock the former investigators delineated anomalous areas with elongated trends marking the presence of stibnite in the bedrocks. Some of these anomalies had contents greater than 1000 ppm Sb. Hill (1980) noted that the fracture zones containing the stibnite mineralization are outlined by the 20 ppm Sb contours in the weathered bedrock. The Sb/As ratio rises from 0.4 to 150 on passing from unmineralized to mineralized zones, due in part to the preferential concentration of Sb by secondary iron minerals (e.g. limonite). The observed patterns are said to represent a combination of primary distribution, secondary hydromorphic dispersion, and contamination from mining.

Our studies of the primary dispersion of antimony and those described in the numerous investigations referred to in the bibliography show that the element is relatively mobile in primary (endogene) mineralization processes. Antimony finds its way into many subsidiary fractures and may migrate far in advance of the main wave of mineralization. As a consequence the primary antimony halos enveloping deposits and the trains (leakage halos) developed on their upward extensions may be broad, exceeded only by those of mercury in most deposits and arsenic and selenium in certain deposits. On this account it is advisable to test carefully mineralization in all exposed shear zones, fractures, faults, and altered zones (and where present all hot spring sinters, travertines, etc.) for antimony as well as for various constituent metals contained within the deposits. These particular geological features when plotted with their antimony contents may form a pattern which can suggest the locus of underlying mineralization. This technique has been employed successfully by Erickson et al. (1964a, b, 1966), Elliott and Wells (1968), Gott and Zablocki (1968), Wrucke et al. (1968), and others (*see* Selected bibliography) in Nevada, for outlining favourable zones in which gold deposits may occur. Mineralized jasperoid, containing anomalous amounts of antimony and a variety of other elements, has also been found to be a useful sampling media by Lovering (1972), Lovering et al. (1968), and Lovering and Heyl (1974, 1980) for localizing gold, silver, and other types of deposits. It should also be mentioned that one can sometimes snatch fortune from adversity by analyzing drill cores for antimony. Holes which pass above, below, or to one side of orebodies may report higher than average amounts of antimony, and thus give a clue to the location of possible blind orebodies characterized by the presence of antimoniferous minerals that accompany many types of economic orebodies as described in a foregoing section. The use of leakage halos in prospecting is discussed in some detail in a recent paper by Boyle (1982a).

Surveys and investigations utilizing indicator minerals containing anomalous amounts of antimony are relatively few. Minerals such as sulphides, arsenides, and sulphide-arsenides are the best sampling media, but certain oxides, particularly limonite, goethite, and magnetite, may contain higher than average amounts of antimony in the vicinity of deposits containing the element. Our investigations indicate that the lead-zinc-silver lodes at Keno Hill, Yukon are enveloped by a halo of disseminated pyrite and arsenopyrite considerably enriched in antimony. Antimony-enriched arsenopyrite and/or pyrite commonly form a distinctive halo about gold deposits in greenstones as at Yellowknife, Northwest Territories and in the greywackes and slates of the Meguma Group in Nova Scotia. Protsenko (1974) advocates using separates of pyrite as a sampling medium for the determination of the level of erosion and/or position in mineralized zones in the mercury deposits of the Donets Basin, U.S.S.R., principally because the contrast of the antimony (and other element) content is much greater than that obtained by utilizing rock or ore samples. Fewer samples are also required by this method.

Primary (endogenic) lateral zonation of antimony minerals in areally distributed vein-type deposits is evident in some districts although the details of the patterns are commonly complex and not easily interpreted without considerable work (Boyle, 1979, 1982a). In the Keno Hill district (Boyle, 1965; Gleeson and Boyle, 1980a) the richest silver shoots are characterized by abundant freibergite and are localized in faults in the central part of the district, about equidistant from two flanking granitic bodies. On the western limits of the district, and to a limited extent on the eastern limits, jamesonite, boulangerite, and bournonite predominate, and the silver values are low. The reason for this zonation is unclear; it may have resulted from the effects of thermal remobilization of elements attendant on metamorphism of the district, or it may be due to pulsation zoning caused by overprinting of a late antimoniferous mineralization characterized by freibergite on an earlier mineralization typified by jamesonite, boulangerite, bournonite, and meneghinite.

Primary (endogenic) vertical zoning of antimony minerals within individual deposits or groups of deposits is a common phenomenon in some ore districts characterized by gold and polymetallic mineralization (Boyle, 1979, 1982a). Antimony minerals, especially stibnite and sulphosalts, tend to be restricted to the upper parts of vertically extensive mineralized faults and shear zones. This feature is especially evident in many Tertiary gold and polymetallic deposits and is noticeable in certain Precambrian gold deposits. At Yellowknife the gold deposits near the surface are relatively rich in antimony minerals, including stibnite; with depth there is a gradual decrease in these minerals almost to their virtual exclusion at depths of 1500 metres. At Keno Hill, Yukon, the vertical sequence of vein minerals in many of the lead-zinc-silver ore shoots is also marked. Galena predominates at the top of most shoots giving a high lead content. Within a comparatively short distance down the dip (30—70 m) the content of galena decreases and sphalerite is the principal mineral constituent. With increasing depth (150 m) sphalerite decreases in turn, and siderite becomes the predominant mineral. Freibergite also decreases with depth, but its vertical range is much greater than that of galena, a feature which maintains a relatively uniform silver to lead ratio in the lower parts of many of the shoots. On their lower extensions, the shoots are composed mainly of siderite with a considerable amount of freibergite and small quantities of galena and sphalerite. This assemblage gradually gives way to siderite containing pyrite and only small amounts of the ore minerals. In the Coeur d'Alene silver belt Mitcham (1952) states that with qualifications silver-rich tetrahedrite occurs in halos of 150-foot (45-m) radii in the plane of the veins around oreshoots. However, the fact that the mineral may also be found, 5000 (1.5 km) feet away seriously detracts from the value of any particular occurrence as an indicator of an oreshoot. Mitcham rightly concludes, however, that statistical work on the problem of the distribution of tetrahedrite as an indicator might produce useful results.

Most gossans and their underlying oxidized zones developed on antimoniferous deposits tend to be enriched in antimony as a result of a variety of hydrolytic and colloidal reactions involving iron and manganese oxides, silica, alumina, and so on (*see* the section above on Chemical factors bearing on the exogene migration of antimony). On this account gossans of all types should be analysed carefully for antimony. Particular care should be paid to the oxidation products of indigenous gossans, and a search should be made for antimony ochers, senarmontite, cervantite, derbylite, nadorite, etc. In some indigenous gossans antimony and other semi-metals and metals may be nearly completely removed leaving them barren except for traces of these elements. In such cases deep trenching or diamond drilling may reveal the presence of economic antimony minerals and their associates at depth. Transported gossans resulting from the migration of iron and other elements should be analyzed by spectrograph and other geochemical methods for antimony, arsenic, silver, zinc, copper, lead, and other metals. Often such transported (or pseudo) gossans are the result of the oxidation of pyrite in slates, iron carbonates in sediments, etc. and are not related to metallic deposits. In other cases they show a direct relationship to metallic deposits, yet they may not be significantly enriched in the metals present in the primary ores. The reason for this behaviour is not clear but seems to be related to the colloidal behaviour of iron hydroxide and the recrystallization processes that ultimately yield limonite and goethite. During such processes the adsorbed antimony and metals seems to be leached out in a number of transported gossans the writers have investigated. It is, therefore, not possible with our present knowledge to tell which transported gossans are related to metallic deposits and which are not. Until further research elucidates this problem the cardinal rule with respect to gossans of all types is that they should not be abandoned until all geological and chemical possibilities as regards their origin and possible relationship to antimony and other metallic deposits have been exhausted.

Pedochemical methods

Antimony tends to form well-defined secondary dispersion halos and trains in residual soils in the vicinity of antimoniferous deposits, particularly where the B (iron- and clay mineral-rich) horizons are well developed. Soils on glacial materials that are not too thick (<2 m) respond in a similar manner. Glacial clay deposits mask anomalies, as does also a thick cover of till, sand, gravel, etc. In such cases overburden drilling methods to obtain samples above bedrock are usually employed and have proved effective in most glaciated regions.

Pedochemical methods employing antimony as an indicator have been successfully used in many parts of the world, particularly in mineralized belts containing gold (James, 1957, 1972; Webb, 1958; Boyle, 1965; Banister, 1970; Stock and Zaki, 1972; Leonard, 1973; Gustavson, 1975; Coope, 1975; Gustavson and Neathery, 1976; Rus and Turnovec, 1976; Boyle, 1979; and Hill, 1980); in those containing lead-zinc-silver and other polymetallic deposits (Boyle, 1965; Dvornikov 1965; Köksoy and Bradshaw, 1969; Presant, 1971; Gott and Botbol, 1973; Khorin et al. 1974; Taube, 1978; Ryall and Nicholas, 1979; and Gott and Cathrall, 1980); native silver deposits (Boyle, 1966; Boyle et al., 1969; and Boyle and Dass, 1971); and in those characterized by antimony, mercury-antimony, fluorite, or barite deposits (Sainsbury, 1957; Maloney, 1962; Chowdhury et al., 1969; Chakrabarti and Solomon, 1970; Stock and Zaki, 1972; Mechacek and Veselsky, 1972; Boyle, 1972a; Oliveira, 1974; Futamase and Fujiwara, 1974; Rieck, 1975; Lee et al. 1973; Slacik et al. 1977; and Gubac in Ilavsky, 1980). Brief discussions of some of these investigations and surveys follow.

James (1957, 1972) found antimony to be a useful indicator element in soil surveys for gold deposits in Southern Rhodesia, and Webb (1958) remarks on the usefulness of the element in overburden surveys as a pathfinder for gold in some tropical terrains (Southern Rhodesia and West Africa).

Humus-rich forest soil (mull) as a sampling medium in geochemical exploration for gold has been extensively employed in a number of countries, but few investigators have used antimony as an indicator in their humus surveys. Banister (1970) used antimony as indicator in the ash of humus (conifer needle pads) in the Stibnite district, Idaho, characterized by the presence of a number of mercury prospects, gold-silver-antimony, and tungsten deposits (*see* below). Banister outlined several gold-antimony anomalies near Stibnite and noted a reasonably good statistical correlation of antimony with gold and essentially no correlation with silver.

At Costerfield, Victoria, Australia, Stock and Zaki (1972) found that antimony formed a distinct hydromorphic halo in the near surface soils through some six metres of alluvium as a result of upward migration of the element from underlying gold-quartz-stibnite lenses. Later work by Hill (1980) has shown that the secondary antimony minerals, stibiconite and senarmontite, occur as 5—60 μm particles in the soils, and the highest contents of Sb and the highest Sb:As ratio are found in the iron-oxide-rich upper B horizon. The distribution patterns of Sb (and As) in this horizon are similar to and reflect those found in the weathered bedrock but tend to be broader, have higher concentrations (up to 50,000 ppm), and are more affected by erosional and solution processes.

In the West End Creek area, Yellow Pine district, Valley County, Idaho, Leonard (1973) found a gold anomaly near the Yellow Pine Mine by soil sampling. The gold anomaly is accompanied by a silver anomaly and by coincident conspicuous though minor antimony, arsenic, mercury and tungsten anomalies. The gold content of 128 soil samples ranged from <0.05 to 8 ppm, the median value being 0.70 ppm; the antimony contents from <100 to 300 ppm with a mean of less than 100 ppm. The Tertiary mineralization at the Yellow Pine Mine (Stibnite district) consists of disseminated bodies associated with faults and shear zones and containing essentially auriferous pyrite and arsenopyrite, gold, scheelite and stibnite, in a gangue of quartz, feldspar, sericite, and carbonate. There are mercury prospects and mines in the area; these contain cinnabar as the principal mercury mineral.

Coope (1975) found that antimony values strongly reflect the secondary dispersion patterns of lead, and to a lesser extent, show similarity to the zinc pattern in the soils and overburden overlying the Mount Nansen gold prospects in Yukon. There, the mineralization is essentially quartz with gold, galena, stibnite, and sulphosalts, all highly oxidized to scorodite, plumbojarosite, cerussite, antimony ochers, and residual galena and quartz.

Gustavson and Neathery (1976) used antimony in soils to explore for gold in Alabama. They found that Sb, As, and Zn were good pathfinders for lode gold and residual placers in saprolite (residual decomposed rock). Antimony and zinc were found to display a high correlation coefficient at auriferous locations in contrast to non-mineralized areas.

Pedochemical methods utilizing antimony as indicator are particularly applicable in the search for polymetallic and other types of base metal deposits as shown by a number of surveys and investigations in various parts of the world.

Boyle (1965, 1972b) examined the distribution patterns of antimony in the permanently frozen residual soils and glacial materials of the Keno Hill district, Yukon where lead-zinc-silver vein deposits contain freibergite, jamesonite, boulangerite, and bournonite as the principal antimony minerals. The antimony content of the residual soils reflects the presence of the veins as does also a number of other elements as shown in the traverses in Fig. 4. In most places the anomalies are offset a short distance down the slopes. Vertical profiles directly over veins show that antimony increases in content with depth and approach to the highly oxidized deposits. In till and gravel covered areas the near-surface glacial materials have relatively uniform antimony contents, and no anomalies indicate the presence of the veins beneath. Near bedrock in these areas, however, anomalous amounts of antimony occur in the basal till near deposits, indicating that deep sampling (overburden drilling) of till and gravel can effectively locate mineralized vein faults as shown by Van Tassell (1969).

Dvornikov (1965) examined the distribution of antimony (and mercury and arsenic) in the soils overlying the lead-zinc deposits of the Bokovo—Khrustal'sk region (Donbas) and found that the aureoles of the three elements are coincident and correspond to aureoles associated with mineralization in the bedrock. Concentration of antimony was marked in the A horizon of the soils.

Presant (1971) noted high contents of antimony in podzolic soils over the massive Cu-Pb-Zn deposits of the Bathurst-Newcastle area, New Brunswick. The greatest range of values was found in the B horizon, which is usually the location of the maximum mean values. Over some deposits concentrations of antimony were found in the A horizons. Antimony was found to behave like arsenic by increasing downward to a peak value in the B horizon. Presant concluded that the antimony contents of the B and C horizons generally reflect the presence of nearby mineralization. Details should be consulted in his comprehensive report.

Taube (1978) found lead in the C horizon of lateritic soils to be a reliable indicator of the structure (principally faults) in which lead-zinc sulphide mineralization occurs at the Woodcutters Prospect, Northern Territory, Australia. Antimony yielded anomalies along the structure, but these were

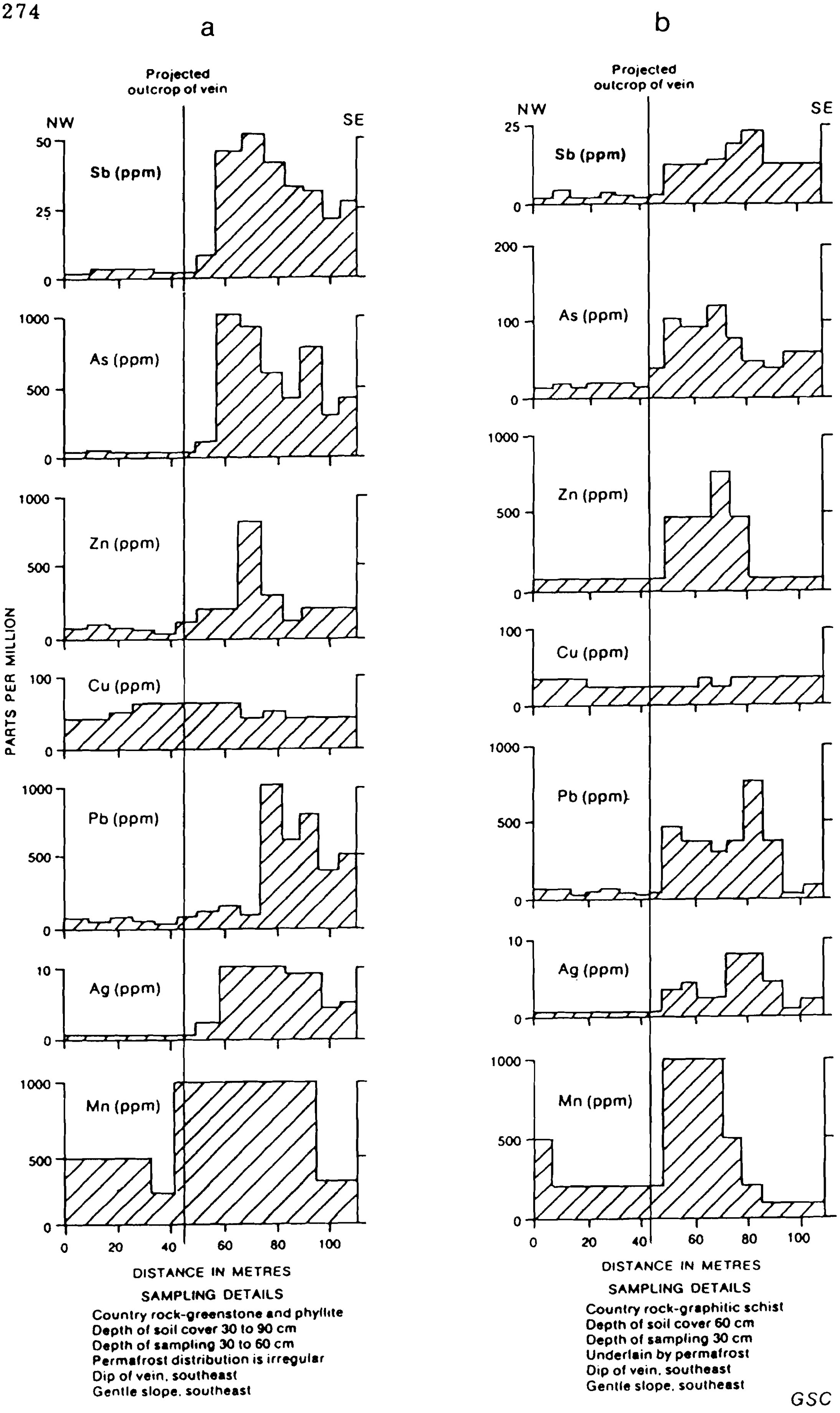

Fig. 4. a. Metal content of soil on traverse D, No. 6 vein, Keno Hill, Yukon. b. Metal content of soil on traverse across Kinman-Porcupine vein, Keno Hill, Yukon.

all too erratic to be considered reliable indicators. At Woodlawn, New South Wales, Ryall and Nicholas (1979) observed that antimony responded in the soils over the massive lead-zinc sulphide ore zone and showed elevated contents in soils over the hanging-wall rock units.

The Coeur d'Alene district in Idaho is one of the premier silver producers in North America, most of the silver being present in tetrahedrite and argentiferous galena in a gangue of siderite, quartz, barite, and pyrite, localized in shear zones and faults in Belt Supergroup quartzites and argillites. Gott and Cathrall (1980) carried out an extensive geochemical survey in this district utilizing some 35 elements as indicators in soil and rock samples. Their investigations show that antimony, silver, lead, manganese, and copper form dispersion patterns and halos that are related to many of the ore deposits within the district, and these same elements were found to be most useful in delineating the known mineral belts that contain most of the orebodies. They considered the dispersion patterns to be probably primary, having only minor modifications due to secondary redistribution of the ore-forming elements. Further details should be sought in their comprehensive report.

Native silver deposits, such as those at Cobalt, Ontario, usually contain a number of antimoniferous minerals, particularly native antimony, dyscrasite, allargentum, and pyrargyrite. During oxidation these minerals contribute some antimony to the soils as shown by Boyle and Dass (1971) at Cobalt. Investigations by Boyle et al. (1969) showed that soils and glacial materials well removed from mineralized zones contain only small amounts of antimony, generally less than 3 ppm. The A_0 and A_1 horizons in these environments are generally enriched in the element compared with the B and C horizons. In the vicinity of mineralized zones the soils developed on till tend to be enriched in antimony. In places the A_0 and A_1 horizons contain more than 20 ppm Sb over or near veins; the B and C horizons generally exhibit a much lower degree of enrichment (Boyle and Dass, 1969). The soils on the glacial clay and the clay itself are not generally enriched in antimony to any degree in the vicinity of the mineralized zones. In areas covered by these materials overburden drilling and sampling of till, etc. near bedrock is recommended during pedochemical surveys.

Pedochemical methods utilizing antimony as indicator have proven useful in geochemical surveys designed to locate stibnite deposits, antimony-mercury deposits, and barite and fluorite deposits containing sulphides and sulphosalts. Sainsbury (1957) found the method particularly applicable for localizing stibnite deposits in southeastern Alaska. He found that antimony was concentrated in two zones in the soils (reworked glacial till and residual materials), one immediately overlying bedrock and the other at the base of the humus layer. In the vicinity of stibnite mineralization the enriched zones in the soils consistently averaged more than 300 ppm Sb, and in some places contents of 1500, 3000 and 10,000 ppm Sb and more were found. Soil sampling also proved useful near Flat, Yukon River region, Alaska according to Maloney (1962). There, the gold-bearing stibnite-quartz veins were reflected in the soils by antimony contents in excess of 20 ppm Sb.

Köksoy and Bradshaw (1969) found that the antimony content of soils marked stibnite mineralization at the Ivrindi Mine in West Turkey. In addition antimony had a similar distribution to mercury in the soils and stream sediments in this mine area. Contents of Sb as high as 1000 ppm were observed over stibnite mineralization, compared to a background of 5 ppm Sb.

In recent years the use of antimony as an indicator of stibnite deposits has proven successful in many parts of the world under a variety of climatic and geological conditions. Chakrabarti and Solomon (1970) proved its usefulness at the Rajburi antimony prospect, Thailand where the soils are mainly lateritic; Mechacek and Veselsky (1972) found that antimony was concentrated in the iron oxide fraction of the soils in the Little Carpathians and recommended its use in geochemical prospecting for antimony deposits in this region; Stock and Zaki (1972) and Hill (1980) found antimony in soils to be particularly useful in localizing stibnite-gold mineralization at Costerfield, Victoria, Australia. (*See* the discussion in the section above under gold deposits). Austria (1971) observed that the antimony content (up to 500 ppm Sb or more) of the B horizon of the podzols over and near the Lake George stibnite deposits in New Brunswick, Canada marked the sites of the veins; Oliveira (1974) noted that the antimony content of soils usually marked antimoniferous (stibnite) veins in Portugal, but also found that low to background values of antimony frequently occurred in soils within close proximity to veins, a feature he attributed to the low mobility of the element in the soil-forming environment; and Rieck (1975) found that the antimony content of lateritic soils marked the sites of stibnite mineralization near Sta. Cruz Cuchilla in Honduras, Central America. Contents as high as 7200 ppm Sb were encountered in some soils in the vicinity of stibnite mineralization localized in silicified sediments. Finally, Gubac (in Ilavsky, 1980) found that the anomalous antimony contents of weathered materials (soils) followed the course of the known stibnite and gold-stibnite veins in the Dumbier zone of the Nizke Tatry Mountains in Czechoslovakia.

The use of antimony as indicator in soils has been employed extensively in the search for mercury-antimony deposits and less so for low temperature deposits containing barite, fluorite, stibnite, etc. The antimony halos in the soils overlying the mercury-antimony deposits are usually marked, but those associated with low-temperature fluorite and barite deposits are commonly not well developed except where the deposits contain stibnite or antimoniferous galena. References to a number of investigations and soil surveys conducted over mercury-antimony deposits are given in the section on lithochemical methods and at the beginning of the present section and need not be repeated.

Summarizing, most investigations and surveys of the antimony content of residual soils show that antimoniferous mineralization is readily outlined if the soils are not excessively thick (<5m); in excess of this depth overburden sampling at or near bedrock usually has to be employed. In glaciated terrains the maximum depth of overburden (till) through which antimony reflects underlying mineralization appears to be about 2 m; over this depth overburden drilling techniques are recommended. The optimum soil horizon for sampling is the B horizon in shallow soils and the C horizon (near bedrock) in deep overburdened areas. The A horizon, when well developed, exhibits enrichment in antimony in the vicinity of antimoniferous mineralization in many parts of the world. Before using this horizon exclusively for sampling, however, pilot surveys are recommended to establish the patterns of distribution of antimony in the horizons of the soil profiles of an area.

Soil anomalies related to antimoniferous mineralization are usually well developed and have a high contrast, features related to the relatively low mobility of antimony during most soil-forming processes. Background values for antimony in soils range from <1 ppm to 3 ppm, with a probable average of 1.0 ppm. Consistent values 4—6 times this average background content should receive attention during most types of soil surveys. When supported by other elemental anomalies as shown in Fig. 4, the certainty of occurrence of mineralization is greatly improved.

Analyses of heavy mineral concentrates obtained from soils, weathered residuum or glacial materials by panning, rocking, sluicing or other methods are effective in some regions for outlining secondary dispersion trains and halos related to antimoniferous deposits. Several techniques can be applied in heavy concentrate studies, including:

(1) The heavy concentrates can be studied mineralogically and the frequency determined and plotted of oxidized nodules of native antimony, stibnite and sulphosalts; supergene antimony minerals such as senarmontite, cervantite, bindheimite, etc.; and the common mineral carriers of antimony and associated minerals of antimoniferous deposits, particularly pyrite, arsenopyrite, galena, cinnabar, realgar, wad, and limonite. Pegmatites can be traced in some regions by plotting the frequency of stibiotantalite and other similar pegmatite minerals that are commonly enriched in antimony.

(2) The whole sample of heavy concentrates or separated fractions such as the magnetic and/or nonmagnetic fractions can be analysed for antimony and the results plotted.

(3) The heavy concentrates or separate mineral fractions such as pyrite, arsenopyrite, magnetite, wad, or limonite can be analyzed for antimony and the elemental indicators of the element such as As, Bi, Zn, Cu, Pb, Hg, etc., and the results plotted.

In all of these techniques the sampling media can be collected on a grid or on lines as the terrain dictates. The work should be quantitative — a standard quantity of soil, glacial materials, etc. should be collected from which all of the heavy minerals are separated and the whole or an aliquot analyzed. The mineralogical and chemical results on the heavy concentrates should then be uniform, but if different sample sizes are used in the survey the mineralogical and chemical results should be calculated to a standard sample size. In practice, the sample size for obtaining the optimum amount of heavy concentrates for mineralogical and chemical work has to be determined in the field since the content of heavy minerals varies widely in soil, eluvium, and glacial materials. Any of the horizons of the soil can be chosen for sampling, but generally the B and C horizons are the best. In glacial terrains, samples taken near the bedrock (in the basal till, sand, gravel, etc.) are generally the most effective in outlining dispersion trains and fans. These commonly contain unoxidized and oxidized particles of the primary antimony minerals, principally stibnite and sulphosalts.

Light mineral associates of antimony minerals obtained from soils, glacial, and allied materials can also be used in tracing secondary dispersion trains and fans related to primary antimoniferous deposits. Particularly useful in this respect is vein quartz, especially the milky, black, drusy, and chalcedonic varieties. By plotting the frequency of vein quartz particles and nodules it is sometimes possible to locate the source of pegmatites and veins. Other minerals such as carbonates, limonite, and wad can also be used as indicators. Before attempting work on light minerals, however, it is desirable to study the nature of the vein or pegmatitic quartz, carbonates, and other associated light vein minerals in the known antimoniferous deposits of a district in order that proper comparisons can be made between the minerals in the secondary dispersion trains and fans and those in the primary deposits.

An extension of heavy and light mineral surveys utilizing large clasts, including mineralized stones and boulders, vein quartz, carbonate, and other gangue stones and boulders, and gossan boulders to locate mineralized zones and deposits is commonly referred to as boulder tracing or in an older terminology, float tracing. The method is an old one having been used successfully for centuries in tracing gold deposits in many countries; more recently boulder tracing has again become especially useful in glaciated countries, particularly Sweden, Finland, U.S.S.R., and Canada. The method is not only applicable to glaciated terrains but may also be employed under all conditions where float appears at or near the surface in the vicinity of deposits. The floats (stones and boulders) located during systematic visual surveys can be analyzed chemically or examined mineralogically. The presence of boulders containing antimony minerals is a direct indication of mineralization; the presence of higher than normal contents of Sb and its indicator elements in boulders (e.g. As, Hg) is circumstantial evidence of mineralization.

The methods of float or boulder tracing to locate stibnite and other antimoniferous deposits are simple. Sample grids can be employed or sampling can be carried out along terrain features such as stream nets, talus slopes, valleys and ridges, etc. In terrains covered with residual soils the apex of the boulder fans or cut-off points of broad trains on gentle slopes mark the sites of the mineralized zones under ideal conditions; in flat terrains the deposits are usually haloed by an irregular distribution of mineralized float.

In glaciated terrains the boulder fans and trains apex or cut-off at the mineralized sites in the up-ice direction as measured from striae or other glacial directional indicators. Under most conditions (residual and glacial) the numbers of boulders and floats generally increase and become more angular in the direction of the mineralized zones.

Hydrochemical methods

These include methods based on waters, drainage sediments, and natural precipitates in springs and drainage systems.

Only a few surveys have been carried out using antimony in water as an indicator of deposits containing the element. The reason is probably because the older analytical methods were tedious, time consuming, and not particularly accurate for the very low contents of antimony in natural waters (<0.5 ppb). With more rapid and accurate methods utilizing carriers, freeze-dry techniques, atomic fluorescence, spectrophotometry, atomic absorption and neutron irradiation, analyses of natural waters should find more favour in prospecting. Descriptions of surveys utilizing antimony as an indicator in surface and/or groundwaters for localizing gold, antimony, and various other types of antimoniferous deposits noted during compilation of this review include those by Polikarpochkin et al. (1960), Sal'e (1965), Vsevolozhskaya (1966), Shvartseva (1972), Adilov et al. (1971, 1976), Makarov (1972), and Shvartseva and Lyan (1976). Kharkar et al. (1968) discuss the concentrations of antimony in a number of river systems in various parts of the world. Average values quoted from their work and that of others range from 0.32 to 4.9 ppb Sb for various stream (river) waters.

The average antimony content of the fresh surface waters of normal terranes is about 0.65 ppb; groundwaters in such terranes are slightly elevated at about 1.5 ppb. In areas mineralized with antimony minerals surface- and groundwaters tend to be enriched in antimony, the contents ranging widely, from 1 to 5750 ppb Sb or more according to the available data. The nature of antimony in the enriched waters is uncertain; probably most of the dissolved element is present in anionic form, as $[SbO_2]^-$ in most neutral and alkaline waters or complexed by chloride, sulphate, hydrogen carbonate, and organic matter in some acidic and alkaline waters (pH 3—8). Shvartsev et al. (1974) also suggest the possible presence at pH 7 of $[SbO_3]^-$ under oxidizing conditions and $[HSbO_2]^0$ under reducing conditions, Sb^{3+} or $[SbO]^+$ under weakly alkaline conditions, and $[Sb_2S_4]^{2-}$ in the presence of complexing sulphide ion in weakly acid, neutral and weakly alkaline reducing waters. Recent data given by Andreae et al. (1981) suggest that most of the antimony in natural waters is present in the Sb(V) state with small amounts in the Sb(III) state and as methylantimonials (*see* also the section on antimony in the hydrosphere).

Sal'e (1965) recorded high contents of antimony (up to 500 ppm Sb) in the surface and sub-surface waters (pH 6.5—7.4) near auriferous deposits in the Kuranakh ore field, Aldan Shield, U.S.S.R. In general he observed that antimony had a much wider dispersion than arsenic in the waters. Vsevolozhskaya (1966) found antimony in water to be one of the best indicators for auriferous deposits and noted that the element is particularly effective in permafrost areas marked by frost-free windows. Shvartsev (1966) noted that antimony has a high migration capacity in humic (muskeg) environments in the vicinity of bornite-chalcocite mineralization in northern Siberia, U.S.S.R. The average Sb content of muskeg (marsh) waters was found to be 1.7 ppb as compared with the waters of soils and other overburden (2.8 ppb) and bedrock waters (3.6 ppb). Adilov et al. (1971) remark that antimony is a good element indicator when ground and stratal waters are used in geochemical prospecting for deep-seated (blind) gold deposits, and Shvartseva (1972) and Shvartseva and Lyan (1976) have shown that antimony in water is an excellent indicator of both stibnite and auriferous deposits. Contents greater than 5000 ppb were present in some spring and sub-surface waters (mainly neutral and alkaline in pH) in the vicinity of these types of deposits in the Tien Shan and elsewhere in U.S.S.R. The dispersion trains in the waters downstream from springs in some of the areas were up to 1.5 km in length.

Spring precipitates, particularly those enriched in limonite, wad, and humic matter, are frequently enriched in antimony in mineralized areas containing antimoniferous deposits. Such precipitates clearly mark the main zones of gold and Pb-Zn-Ag mineralization at Keno Hill (Boyle, 1965; Gleeson et al., 1967; Gleeson and Boyle, 1976, 1980a); the zones of native silver mineralization at Cobalt, Ontario (Boyle et al., 1969; Boyle and Dass, 1971); and the areas containing barite and Pb-Zn-Cu-Ag sulphides and sulphosalts at Walton, Nova Scotia (Boyle, 1972a). Similar conclusions with respect to localization of antimony (stibnite) deposits by high antimony concentrations in spring precipitates are evident from the papers by Shvartseva (1972) and others noted above in the section on water surveys.

Care should be taken in interpreting high antimony contents of springs and their precipitates. Some of those issuing from terranes of pyritiferous rocks are enriched in antimony, the element presumably being derived from pyrite in the rocks. The high antimony 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 stibnite deposits, since precipitation of antimony may have taken place at suitable places along the underground courses of the thermal waters.

Antimony has been used as an indicator in a large number of stream, river, and lake sediment surveys. In these surveys the element is particularly indicative of gold deposits of practically all types, various polymetallic skarn deposits, native silver Ni-Co-arsenide deposits, and antimony-bearing sulphide deposits of all types. Extensive regional stream sediment surveys in the Keno Hill area, Yukon by Gleeson et al. (1967); in the Bathurst district, New Brunswick by Boyle et al. (1966); and in the Walton area, Nova Scotia by

Boyle (1972a) show that antimony clearly outlines or indicates the mineralized zones containing gold, tungsten, and Pb-Zn-Ag lodes (Keno Hill), massive Cu-Pb-Zn and other polymetallic vein deposits (Bathurst) and barite-Cu-Pb-Zn-Ag deposits (Walton). Similar results are evident from the surveys carried out by others in many parts of the world (Alaska: Foster, 1968; Cathrall et al., 1979); (U.S.S.R.: Polikarpochkin et al., 1960; Khorin et al., 1974); Portugal: Oliveira, 1974); (New Brunswick, Canada: Austria, 1971; Chapman, 1977); (Sardinia: Heetveld and Pretti, 1975); (Czechoslovakia: Cillik, 1977); and (United Kingdom and Nepal: Hale, 1981).

Antimony appears to be a suitable indicator in stream sediments for deposits containing the element in various terrains and under a variety of climatic conditions. Judging from the literature and our experience antimony anomalies have marked peaks in stream sediments near the source of the mineralization. This is probably because antimony tends to be strongly chelated or otherwise bound by organic matter in streams and is also effectively co-precipitated and/or adsorbed by colloidal clay complexes and by iron and manganese precipitates which form as a result of oxidation of dissolved iron and manganese near the sites where seeps and springs emerge from the rocks or overburden. The dispersion trains of antimony enrichment above background in the stream networks of most mineralized areas are relatively long (commonly greater than 1 km), although the fall-offs of the high concentrations downstream are often rapid. At Keno Hill we have noted antimony dispersion trains in stream sediments associated with virgin mineralization that range from less than 0.5 to 6 km in length. With respect to iron (limonite) and manganese (ferriferous wad) in stream sediments we should mention in passing that these materials may give false antimony anomalies in stream sediments as a result of scavenging effects. The interpretation phase of stream sediment surveys using antimony as an indicator should, therefore, take into account the iron and manganese oxide (limonite and wad) contents of the sediment, and the background and threshold levels should be adjusted accordingly. From a geochemical and metallogenic viewpoint, however, the writers would urge caution in assuming that anomalous antimony contents in manganiferous and ferriferous sediments are due entirely to the spurious scavenging properties of hydrous iron and manganese oxides. It cannot be assumed a priori that anomalous drainage systems are due to scavenging effects; on the contrary their sediments may be enriched in secondary manganese, iron, and antimony as the result of extensive leaching of deposits containing these elements, as for instance at Keno Hill (Boyle, 1965). The latter feature should always be checked by examining the mineralogy and elemental content of any known antimoniferous mineralization before making corrections to normalize analytical data over a region. In many cases with respect to manganese and iron the ratios Sb/Mn and Sb/Fe, or their reciprocals, may be more meaningful as an indication of mineralization than Sb alone.

In drainage sediments antimony tends to be concentrated in the −100 to

−200 mesh size. Where possible, therefore, sediment surveys should be based on this mesh size.

Drainage sediments report varied contents of antimony. In most regions the background content ranges from <1 to 3 ppm; near antimoniferous mineralization the concentrations may rise to values as high as 1000 ppm or more. There is commonly a positive correlation between antimony and arsenic contents in the drainage sediments of an area, although in a number of districts we have noted that arsenic is more dispersed (mobile). Others have noted the reverse situation in some terranes.

In closing this section we should point out that thermal areas can probably be outlined by higher than normal amounts of antimony in the ground, spring, stream, river and lake waters as well as in the precipitates and sediments associated with these bodies of water. This is predicated on the fact that most natural waters in thermal areas tend to be enriched in antimony (Table XI) as well as in various associated elements such as arsenic and mercury.

Heavy mineral surveys

The heavy (panned) concentrates of soils, glacial materials and drainage sediments frequently contain antimony minerals such as stibnite, sulphosalts, and native antimony near deposits containing these minerals. Most of these primary (endogene) minerals are highly oxidized and have coatings or thick rinds of secondary (supergene) minerals such as senarmontite, cervantite, stibiconite, valentinite, bindheimite, various antimony ochers, anglesite, etc. We have also noted antimoniferous limonite, wad, and pyrite in panned concentrates from soils and drainage sediments. Stibiotantalite, stibiocolumbite, and antimoniferous betafite may also occur in heavy concentrates from soils, eluvium, and alluvium in pegmatitic terrains. Devismes (1978) figures the principal antimony minerals found in eluvium and alluvium in his atlas of detrital minerals and details the methods applicable in prospecting by panned concentrates. Analyses of heavy concentrates indicates that antimony is a satisfactory indicator in heavy mineral surveys for various types of deposits. More research is necessary, however, to define the various problems inherent in such surveys, especially those concerned with differentiating antimony-bearing minerals derived specifically from mineral deposits from those, particularly antimoniferous pyrite, which may come from various country rocks. In this respect statistical mineralogical and X-ray work on the heavy concentrates may give sure clues to the presence of deposits. We have for instance found that stibnite, sulphosalts, and other antimony minerals occur only in high frequencies in the heavy concentrates of drainage sediments, soils, and glacial materials near antimoniferous deposits. When stibnite and/or sulphosalts are found in heavy (panned) concentrates of residual soils and drainage sediments, one can be relatively certain that antimoniferous occurrences lie nearby; with glacial materials, however, a knowledge of the glacial direction and degree of travel of the till, etc. are necessary in order to pinpoint the location of the occurrence(s).

Syrovatskii and Karpenko (1973) noted the presence of large nuggets of native antimony in the gold placers of the Kas'ma River, U.S.S.R., and suggested their use in prospecting for primary deposits of gold in the basin of this river.

Gleeson and Boyle (1980b) carried out a heavy mineral survey utilizing antimony (and a number of other elements) as indicator in the Keno Hill district, Yukon. They noted that the anomalous patterns for antimony follow closely those for arsenic. Above average amounts of antimony in the magnetic fraction of the heavy concentrates occur in a number of streams; some drain areas known to contain lead-zinc-silver lodes, others drain areas where antimoniferous occurrences have not yet been identified.

Biogeochemical surveys

Antimony is a trace constituent of many plants and animals and their fossil equivalents (Tables XII and XIII), but only living plants have been investigated to any extent as a sampling medium in biogeochemical surveys, mostly in U.S.S.R. The methods utilized in geobotanical and biogeochemical surveys are covered extensively by Brooks (1972) and Kovalevskii (1979).

Shacklette (1965a) observed as much as 50 ppm Sb in the ash of branches of *Betula resinifera* Britton (birch) having root contact with the cinnabar-stibnite ores of the Red Devil Mine on the Kuskokwim River, Lower Yukon River district, Alaska. The same investigator (Shacklette, 1965b) examined the antimony content of the ash of bryophytes from various localities in U.S.A.; no antimony was found in any of the samples.

Talipov and Khatamov (1973) found that both Sb (and As) in the *Artemisia* (wormwood) species were good indicators of gold deposits in the northern part of the central Kyzyl-Kum in U.S.S.R. They also noted differences in antimony and other metal accumulations in various plant species such as *Artemisia*, *Salsola* (saltwort) and *Astragalus* (vetch). *Artemisia persica* had the highest Au concentrations during the first part of the growth period, and the highest amounts of As and Sb during flowering. On the other hand the highest concentrations of all these elements in *Prangos pobularia* were noted during flowering, data indicating to the investigators that in using biogeochemical methods in prospecting the time of sampling and analyses of various plants are critical. A review of a number of other papers describing the use of antimony as an indicator in plant analysis methods for locating auriferous deposits is given by Boyle (1979).

Dvornikov and Ovsyannikova (1972) investigated the antimony content of the ash of *Artemisia campestris* L. (wormwood), *Euphorbia virgata* W. and K. (vine spurge), and other shrubs and plants in the vicinity of the Yesaulov lead-zinc deposit (Donbas) and observed that the aureoles of Pb, Zn, Ag, and especially Sb are narrow, with Sb anomalies occurring only directly over the deposit. The highest antimony contents recorded were 8 ppm Sb. Zakharov and Zakharova (1974), likewise, observed relatively narrow halos of antimony in plants (up to 300 ppm) in the vicinity of the cobalt and cobalt-copper deposits of central Tuva, U.S.S.R.

Humus sampling may be effective in localizing antimoniferous deposits as noted by Slacik et al. (1977) in the heavily wooded districts of Czechoslovakia. They noted that samples of thick humus horizons pinpoint antimoniferous mineralization as accurately as soil analyses.

Bogs, muskegs, and marshes near zones mineralized with antimony are frequently enriched in the element as a result of adsorption, precipitation by H_2S of bacterial origin, chelation, and other metal-organic binding reactions. Such bogs may overlie deposits, or their distribution pattern may take the form of halos or partial halos about mineralized zones (Boyle et al., 1971; Boyle, 1982a).

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 antimony in the coaly materials. At Walton, Nova Scotia (Boyle, 1972a) the pyritized coal and plant fragments in the grey sandstone beds contain exceptionally high contents of antimony (up to 110 ppm in the pyrite of the coal) near faults, fractures, and bedding planes. Marked enrichments of Ba, Sr, Cu, Pb, Ag, As, Mo, Ni, and Co also occur in the coaly fragments. The average for normal coal (not in mineralized areas) is less than 1 ppm Sb in the coal (Table XIII), although much higher values are recorded from some seams and fragments in sandstones. If coal samples are used in prospecting, not only antimony should be determined, but also other elements such as Ag, Cu, Pb, Zn, U, Ba, 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 Sb, As, etc. in circulating stratal waters.

Organic matter (bitumen) is a common substance in many antimony, mercury, and antimony-mercury deposits throughout the world. No analyses of these organic materials are available for antimony, but Vol'nov and Yakovets (1978) suggest that the general presence of these materials may be useful as a prospecting indicator for certain mercury, antimony, and antimony-polymetallic deposits.

Atmogeochemical surveys

A number of inorganic and organic compounds such as stibine and dimethylstibine have a relatively high volatility and should occur in low concentrations in soil gases and in the air overlying antimoniferous deposits, particularly where bacterial activity is marked. (*See* also the section on exogene processes). Similar volatile compounds and other methylantimonials probably also occur in ground and spring waters associated with antimony-bearing deposits. Bogs enriched in antimony 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 antimony compounds as indicators for the location of mineral deposits. Frederickson et al. (1971) mention the use of gases such as arsine among other compounds but give no details; probably stibine or other volatile antimony compounds could be utilized in the mass spectrometric method described. Because of the widespread occurrence of antimony in mineral deposits, more research on the distribution and utilization of its volatile compounds is highly desirable. This is further suggested by the recent favourable report by Curtin et al. (1974) with respect to movement of elements into the atmosphere from coniferous trees in subalpine forests. In Colorado and Idaho they found that exudates (volatile materials) from these trees contain antimony in addition to a large number of other elements. As a consequence of these findings they postulated that volatile exudates from vegetation are a medium for the transport of elements in the biogeochemical cycle in subalpine environments and hence, that air sampling and analysis of aerosols derived from volatile exudates may be a useful tool in geochemical exploration.

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WORKSHOP - PROSPECTING FOR SILVER DEPOSITS

SILVER DEPOSITS - AN OVERVIEW OF THEIR TYPES, GEOCHEMISTRY, PRODUCTION, AND ORIGIN.

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Abstract

The general geochemistry of silver is briefly discussed, followed by summary descriptions of the common types of argentiferous deposits and brief discussion of the world production of the metal. A short section on the origin of argentiferous deposits completes the paper.

The epigenetic vein, lode, stockwork and disseminated types of argentiferous deposits originated mainly by metamorphic secretion and/or granitization processes, the source rocks of the silver and its associated elements being mainly in the enclosing volcanic and/or sedimentary piles. Many of the native silver-Ni-Co arsenide veins appear to represent late secretion extracts derived probably by diffusion from a variety of metal-rich rocks such as graphitic, pyritic sediments, volcanics, and diabase sills as at Cobalt, Ontario. The 'red bed' type silver deposits are epigenetic in origin, the silver and accompanying elements being derived from a variety of sources such as underlying metalliferous shales and volcanics. In places the red and black beds of the 'red bed sequences' may be the source of the silver and its associated elements. The argentiferous copper shales (Kuperschiefer type) have a sedimentary signature, but the rich Cu-Ag sections (shoots) appear to have been concentrated from the body of the shales by diagenetic and/or metamorphic fluids.

The oxidation processes in silver deposits are complex and depend essentially on the Eh and pH. Colloidal and coprecipitation phenomena also play a large part. Iron and manganese minerals and carbonates in the gangue and ore greatly influence the reactions that lead to the secondary enrichment of silver. The common supergene minerals of silver are the various halides (chlorargyrite, bromargyrite, iodargyrite) and argentojarosite in the zone of oxidation of argentiferous deposits, and native silver, pyrargyrite, proustite, and argentiferous chalcocite in the zones of reduction.

Most of the world's production of silver (11,500 metric tons) is obtained as a byproduct of copper-silver shale deposits, various types of polymetallic deposits enriched in Pb, Zn, and Cu, gold deposits, Ni-Cu deposits, and porphyry Cu-Mo deposits; a small production (<5 percent) comes from native silver-Ni-Co arsenide-sulphide deposits.

General Geochemistry of Silver

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

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

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

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

Argentiferous Deposits

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

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

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

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

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

The elements with which silver is generally associated in hypogene deposits are mainly chalcophile and include S, Se, Te, As, Sb, Cu, Fe, Ni, Mn, Ca, Co, Bi, Sn, Zn, Cd, Ba, Si, Pb, and Au. With the last two elements there is a marked coherency, and with certain particular reservations most gold and lead deposits are enriched in silver. In certain silver veins and in some silver deposits in sandstones, uranium is an associated element. Tin and silver are frequently associated. Silver and thallium often show a certain degree of geochemical coherence in lead-zinc deposits, a feature that probably has something to do with the fact that the silver and thallous sulphides are somewhat analagous in their precipitation characteristics, and that the silver and thallous halides and halide complexes resemble one another in their solubility relationships and in their reactions in solutions. In deposits, both silver and thallium tend to be concentrated in galena, less commonly in the sulphosalts, and in the rare minerals crookesite and hutchinsonite. Indium and silver also exhibit a geochemical affinity in some zinc-silver-lead deposits, the two elements being concentrated principally in galena, chalcopyrite, tetrahedrite, and sphalerite. Tungsten is likewise frequently found with silver and gold; one need only recall the numerous occurrences of scheelite in the gold-quartz veins of the Canadian Shield, and the common presence of small amounts of both scheelite and wolframite in the polymetallic silver deposits of the Western Cordillera, South America, U.S.S.R., etc. Boron frequently accompanies silver, mainly in deep seated gold deposits, but also in certain galena-sphalerite-pyrite-arsenopyrite veins. Bismuth and silver show a moderate geochemical coherence in a number of deposits, principally in the native silver-cobalt-nickel arsenide type, but also in numerous instances in lead-zinc-silver, mantos, etc. The relationship also seems to extend to various types of deposits containing copper sulphides and molybdenite. Silver is frequently associated with cobalt and nickel, particularly in the Ag-Ni-Co-As vein deposits. The same association, especially for cobalt, extends as well to the Cu-Ag shale type of deposits and to the silver-bearing 'red bed' deposits. In these same two types of deposits, silver, molybdenum, vanadium, and sometimes chromium may show a parallel enrichment. Mercury and silver are often associated, the former element occurring principally in native silver or in gold-silver alloys and amalgams. Chlorine, bromine, and iodine may accompany silver in the oxidized zones of silver deposits in arid regions.

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

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

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

1. Copper-silver shale deposits (Kupferschiefer type).
2. Disseminations in sandstones ('red bed' type).
3. Silver-bearing skarn type deposits.
4. Lodes, veins, etc. dominantly in sedimentary rocks.
5. Silver-gold and gold-silver veins in or associated with volcanic flows, tuffs, etc.
6. Silver deposits in a complex geological environment comprising sedimentary rocks, volcanic rocks, etc.
7. Native silver-Ni-Co arsenide-sulphide deposits in a complex geological environment.
8. Miscellaneous sources: these include all gold deposits, Ni-Cu ores, massive sulphide bodies, polymetallic vein and lode deposits, kuroko ores, porphyry Cu-Mo deposits, and certain types of uranium (pitchblende) deposits.

1. Shale Deposits: Kupferschiefer Type:

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

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

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

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

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

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

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

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

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

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

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

There has been much controversy about the origin of the copper shales. Some investigators maintain that the deposits are essentially syngenetic, others that they are epigenetic. The arguments for an initial syngenetic sedimentary origin for the constituent elements of the cupriferous shales are strong. Thus, the argentiferous copper shales have a sedimentary signature, but the rich Cu-Ag shoots appear to have been concentrated from the body of the shales by diagenetic and/or metamorphic fluids.

2. Sandstone Deposits - 'Red Bed' Type:

In general this category includes a number of important bedded and vein type copper, lead, silver, vanadium, and uranium deposits in many parts of the world. We shall, however, confine our description to generalities, and essentially to those deposits containing silver. In the general category, however, belong the numerous uranium-vanadium-copper deposits of Texas, Oklahoma, New Mexico, Arizona, Colorado, Wyoming, Utah and Idaho; the Silver Reef deposits in Utah; the numerous copper deposits in the Carboniferous sandstones of New Brunswick and Nova Scotia; the barite-lead-zinc-copper-silver deposit near Walton, Nova Scotia; the lead deposit in the Salmon River area, Cape Breton Island, Nova Scotia; the lead deposits of Laisvall and other areas in Sweden; the copper deposits of Corocoro, Bolivia; the Cu-Ag deposits at Negra Huanusha, central Peru; the copper-lead deposits of Alderly Edge, near Manchester, England; the lead deposits of the Kaller Stollen-Maubach area in Germany; and the extensive copper sandstone deposits of Dzhezkazgan, Kazakhstan, U.S.S.R.

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

The ores are generally low grade, but the available tonnages are usually large. The mineralogy of the deposits is varied and depends on the type of deposit. In the bedded copper-silver deposits the principal economic minerals are chalcocite, bornite, chalcopyrite, domekyite, native copper, native silver, chlorargyrite, azurite, and malachite. Similar copper and silver minerals occur in some of the copper-uranium-vanadium deposits, and there are in addition, uraninite, carnotite, vanadinite, and a host of other uranium, vanadium, and copper minerals, many of supergene derivation. The bedded lead-zinc sandstones contain essentially galena and sphalerite with cerussite, pyromorphite, and anglesite in the zones of oxidation. Gangue minerals are sparse in most of the bedded deposits, but some barite, calcite, fluorite, and gypsum may occur. Pyrite and marcasite are found in nearly all of the deposits, in variable amounts. Outcrops of the copper and uranium types are generally marked by blooms of azurite, malachite, and the various secondary uranium and vanadium minerals. The lead-zinc sandstones and quartzites are extremely difficult to recognize in outcrop since they rarely exhibit any marked blooms, iron stain, or other distinguishing features.

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

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

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

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

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

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

The nature of the sediments (viz., channelling, crossbedding, etc.) in most cases suggests an environment of rapid clastic sedimentation on extensive flood plains coursed by numerous meandering streams that migrated from channel to channel. The location of the flood plains has long been a matter of much debate. From the distribution of the sediments some appear to have covered vast stretches of country and must have bordered on shallow inland seas or large lakes. Others, such as those on which some of the Mississippian and Pennsylvanian sandstones in Nova Scotia, Canada, were laid down, appear to have occupied wide intermontane valleys and received sediment from a variety of granitic and metamorphic rocks. Still other sandstones in this category are obviously deltaic deposits formed at mouths of great river systems in inland seas or lakes. All appear to be near-shore shallow-water facies, as witnessed by the nearly universal occurrence in them of carbonized logs, leaves, and other plant remains. Some writers have concluded that the continental sediments containing the 'red bed' deposits in many countries appear to have accumulated in shallow, poorly drained foreland or post-orogenic basins.

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

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

Nearly all the deposits exhibit evidence of epigenetic deposition. While the deposits may be confined to certain members or formations they are seldom restricted to individual beds and rarely show the characteristics of having been deposited during sedimentation processes. Certain uranium deposits, and probably also certain types of enriched copper deposits in this category, the so-called roll-front or ore-roll type, appear to represent down-dip secondary enrichments at reduction fronts of uranium, copper, and other elements leached by descending groundwaters from leanly mineralized sandstone, arkose and conglomerate beds.

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

A great many of the bedded deposits are too low grade at present to be economically exploited. The economic copper deposits average about 3 per cent Cu and the lead-zinc varieties about 3.5 to 4 per cent Pb. The uranium-vanadium deposits generally have a variable and often erratic grade but rarely exceed 1 per cent U_3O_8. The silver content of nearly all of the bedded copper and lead-zinc deposits is low (0.5 - 20 ppm) and usually makes little difference to the value of the ore. A few bedded deposits, however, such as those at Silver Reef, Utah, and Brush Creek, Colorado, are greatly enriched in silver with assays up to 500 ppm or more.

The vein-type deposits and irregular lenses in faults are relatively high grade (up to 500 ppm Ag or more), but their tonnage is generally small. Some of the deposits such as the one at Walton, Nova Scotia, yield much barite, lead, zinc, copper, and silver.

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

1. Most of the deposits occur in continental sediments formed under oxidizing conditions. In some places there is evidence of volcanic activity, and in a number of places there are associated basaltic or other types of basic flows that presently overlie the favourable beds or have been removed by erosion. Such conditions occur at Walton, Nova Scotia, Silver Reef, Utah, and at Dalane, Norway. Since it is well known that basic volcanic rocks are often enriched in copper as well as nickel, cobalt, and silver in some cases, it follows that they could be the source of some of the elements in the deposits. It is evident in some places that the 'red

bed' mineral deposits were formed long after the consolidation of the volcanic rocks, and hence one must call on a later secretion mechanism if the metals in the deposits came from the rocks. In a number of places, a groundwater concentration seems evident.

2. In a number of areas, the 'red bed' deposits are underlain or overlain by black shales or petroliferous shales and limestones. It is again well known that such rocks are greatly enriched in copper, silver, cobalt, nickel, uranium, sulphur, and other elements. These rocks could, therefore, be the source of the elements in the deposits. In fact, such a source seems probable for most of the 'red bed' deposits in the Maritime Provinces of Canada.

3. In a few areas, e.g., Kupferschiefer of Germany and White Pine area of Michigan, the native silver in sandstones is closely associated with the cupriferous shales. In these areas it seems probable that the silver was originally deposited in the cupriferous shales and was later redistributed and concentrated by ground or connate waters in the more porous parts of upper or lower sandstone sequences.

4. The 'red beds' may themselves contain sufficient amounts of copper, silver, cobalt, barium, uranium, etc. to provide a source for the elements in the deposits. During the intense weathering that took place to form the continental sediments it is logical to suppose that enormous amounts of copper, silver, uranium, etc. would be released and ultimately find their way into the basins of sedimentation. There, under the oxidizing conditions that prevailed, much of the copper, silver, and other elements would be adsorbed by the abundant iron and manganese oxides and by the clay portion of the shales. Later during diagenesis and subsequent processes these elements would be readily available for solution and migration in groundwater. The so-called roll-front or ore-roll type of deposit, as well as a number of irregular deposits, in red beds appear to represent down-dip secondary enrichment at reduction fronts of various elements leached by descending groundwaters from leanly mineralized sandstone, conglomerate, etc.

5. There are generally no igneous granitic bodies near the deposits to which one could ascribe a logical magmatic source for the elements in the deposits.

6. Many of the deposits, as they now occur, are definitely epigenetic, indicating that the constituents of the ore and gangue minerals have been introduced into favourable geologic sites, such as porous zones, fractures, etc.

7. Many of the deposits are associated with plant remains, and there are indications that these have been effective in precipitating the ore minerals. In other cases, there is evidence that the ore minerals have been precipitated in porous sandstones or conglomerates. These are generally bleached, indicating a reduction of the iron oxides during the process of precipitation of the ore minerals. In a few areas the deposits

occur along faults or fracture zones, and there are indications of both fracture filling and replacement. A number of deposits contain small amounts of bitumen closely associated with the ore and gangue minerals.

These facts suggest to the writer that the source of the elments lies in the sedimentary pile in which the deposits occur. In some places it seems evident that the elements came from the red beds themselves; in other places they may have been contributed from underlying or overlying black or petroliferous shales. In still other places, a contribution of certain elements from overlying or underlying volcanic flows seems probable. Perhaps the source of the elements for some deposits lies in the collective sequence of sediments and volcanic rocks enclosing the deposits.

The mechanisms whereby the elements have been concentrated appear to be varied and each deposit probably has to be considered as a special problem. Nevertheless some generalizations seem to be justified.

In most cases the medium of transport for the ore and gangue elements appears to have been groundwaters or connate waters. Two mechanisms seem to have operated in the concentration of the elements - mass transport by the waters (flow) and diffusion of ions, hydrated ions, molecules, and gases through the stationary ground or connate water that pervaded all fractures, breccia zones, porous zones, pores and other discontinuities in the rocks. Both mechanisms may have operated depending on the geological setting. Near the surface the mass transport mechanism would probably be the most effective, whereas at depth the diffusion mechanism probably prevailed.

The nature of the dissolved elemental species is a matter of speculation. Judging from the known composition of typical groundwaters the elements probably migrated as the sulphates, hydrogen carbonates, and chlorides. Where H_2S and alkalies were present in solution one can postulate soluble complex sulphides, sulphide-arsenides, or sulphide-antimonides. Our knowledge of the chemistry of silver suggests that this element was probably transported as the sulphate, as the hydrogen carbonate, as the complex ion $(AgCl_2)^-$ in solutions charged with sodium chloride, or as the complex sulphide ion AgS^- or some other soluble silver sulphide-arsenide or sulphide-antimonide ion.

The mode of precipitation of the elements seems likewise to be varied and depends on the geological situation. Some general mechanisms can however be suggested:

1. Reduction of sulphates, chlorides, hydrogen carbonates, etc. by reaction with organic matter (coal fragments, etc.). The reduction may be direct in some cases. In other cases bacteria associated with the organic matter may have effected the reduction. Some of the sulphur to form the sulphides may have been contributed by the plant matter. In still other cases the plant matter seems to have acted only as a catalyst during the breakdown of the various sulphide complexes to form the sulphides.

2. In some deposits it is evident that the plant matter was responsible for the precipitation of pyrite. Later this sulphide was replaced by the copper, silver, and other sulphides. This phenomenon is normal and is in accord with Schürmann's series which gives the order of the solubility of the various sulphides (viz., $Ag < Cu < Pb < Zn < Ni < Co < Fe^{2+}$, etc.).

3. In deposits where plant matter is sparse or lacking, precipitation of sulphides from sulphates may have taken place by the action of sulphate-reducing bacteria at or just below the level of the groundwater table. As the sulphate is isolated from the system as sulphide, say in the porous zones where the bacteria are operating, the concentration of the sulphate component is decreased, causing an upward or lateral diffusion of more sulphate to these zones. By such a process extensive sulphide deposits can be built up.

4. An inorganic precipitation of sulphides may take place where dissolved metal sulphates, chlorides, hydrogen carbonates, etc. come into contact with H_2S diffusing upwards or laterally from black or petroliferous shales. As the metal ions and H_2S are used up they would be replaced by a diffusion of more metal ions and H_2S from the surrounding stagnant water medium. The size, distribution, and form of the deposits would depend, therefore, essentially on the degree of porosity of the rocks and on the distribution of the porous zones.

5. Precipitation of ore and gangue elements in fractures, faults, and breccia zones may result from a variety of mechanisms such a dilatancy, chemical inequilibrium, reaction of metal-bearing solutions with favourable wall-rocks, and mingling of solutions or diffusion currents bearing chemically reactive components.

3. Silver-Bearing Skarn-Type Deposits:

The general features of these deposits are well known and need not be described in detail. Most of the deposits occur in highly metamorphosed terranes in which there has been much granitization and injection of granitic rocks. Some deposits occur near the contacts of the granitic rocks and have long been called 'contact metamorphic'; others are developed in favourable reactive beds or zones some distance from granitic contacts.

Most of the deposits occur in skarn zones or are associated with skarn minerals, developed in limestones, dolomites, or calcareous schists. The form of the deposits is irregular and bunchy, but many of them are tabular, following beds that have been selectively replaced; some have vein-like forms.

The deposits usually contain a characteristic suite of relatively high temperature Ca-Mg-Fe-silicate and carbonate minerals such as garnet, epidote, vesuvianite, diopside, tremolite, scapolite, wollastonite, and crystalline calcite and dolomite. The sulphide minerals are generally chalcopyrite, bornite, pyrite, pyrrhotite, galena, sphalerite, and molybdenite. Magnetite and hematite occur in many of the deposits.

Silver is concentrated mainly in the lead-zinc deposits of this type and is associated principally with the galena and tetrahedrite of the deposits. The well known contact-metamorphic copper types tend to have low contents of silver. In various parts of the world there are also a few skarn-type gold deposits in which silver is present in the free gold or is concentrated with the gold in arsenopyrite, pyrrhotite, or pyrite.

Most of the contact metamorphic and skarn types of deposits are relatively low in silver. A survey of the literature shows that the silver content of most deposits ranges from 5 to 10 ounces to the ton (150 - 320 ppm). A few deposits are of higher grade and may contain up to 30 ounces Ag/ton (960 ppm).

4. Veins, Stockworks, Mantos, and Tabular Bodies, Essentially in Sedimentary Rocks:

Deposits of this type include as their members some of the most productive silver mines in the world. They also include those gold-silver deposits that occur essentially in sedimentary rocks and many great lead-zinc deposits that have a similar setting and which produce large amounts of silver as a by-product.

Many deposits in this category are localized by particular structures such as faults, fractures, shear zones, sheared beds, dragfolds, and breccia zones. Some are controlled by chemically favourable beds, which they replace, often in great detail. Most of the deposits are discordant with the enclosing sediments, but a number have conformable attitudes.

Most of the deposits occur in low-grade metamorphic rocks, but some occur in gneisses, schists, and other high-grade rocks. Porphyries cut the sedimentary rocks in places and sills or flows of basic volcanic rocks may be present. In many areas the sediments may be intruded by granitic rocks or granitized over large areas. Most of the deposits show no obvious relationship to the porphyries or granitic rocks, and in nearly all places where the two are in contact, the veins, lodes, etc. cut the granitic rocks and porphyries in most places and were formed long after their consolidation.

The principal primary silver minerals in deposits of this type are argentiferous tetrahedrite-tennantite, argentite, proustite-pyrargyrite, and argentiferous galena. In a few deposits native silver and dyscrasite occur as primary minerals. Pyrite, sphalerite, and chalcopyrite are the main associated minerals, but in some deposits, nickel-cobalt arsenides, bismuthinite, native bismuth, and pitchblende are abundant. Cassiterite and wolframite are uncommon minerals in these deposits, but are present in some areas. The most common gangue minerals are siderite, calcite, dolomite, quartz, and barite. Fluorite is uncommon in most deposits, but tourmaline may be present in places. Zeolites may occur in a few deposits, but they are generally late minerals and may not be associated with the deposition of silver.

Many of the vein deposits in the low-grade sedimentary rocks are markedly vuggy and crustiform in character. In the higher grade metasediments the structure of the veins tends to be more compact. The tabular deposits generally have compact structures and commonly replace the host rock in the minutest detail.

A characteristic suite of elements exhibits a high frequency of concentration in deposits of this type. These include Pb, Zn, Cd, Cu, Ag, In, Fe, Mn, Mg, Sb, As, S, CO_2 and SiO_2. Less frequent are Ba, F, Sn, Au, Co, Ni, Bi, Se, and Te. Rare are U and W.

The source of the ore and gangue elements in the deposits has long been attributed to granitic magmas, although in many areas granites and allied rocks are not found at the present level of erosion. In other deposits the source of the metals and gangue has been attributed to exhalations from diabasic magmas despite the fact that in nearly all places the evidence shows that the veins cut the diabases from which the exhalations supposedly came. Furthermore, in some areas diabase or other basic rocks are not present. Granitic rocks or diabase do not, therefore, seem to be the source of the elements in the deposits.

During the writer's long association with these deposits he has been struck by the nearly constant presence of black pyritic shales or pyritic argillites and greywackes in their vicinity. This particular association is so marked in districts such as Keno Hill, Yukon, Slocan, British Columbia, and Thunder Bay, Ontario, as to suggest that these rocks may be the source of most of the elements in the deposits. In certain areas diabase may also have contributed some of the elements, especially nickel and cobalt, since nickel-cobalt arsenides are often found in the veins where diabase is present. Diabase need not be present, however, since most black pyritic sediments also tend to be somewhat enriched in both nickel and cobalt.

It can be shown that carbonaceous sediments are enriched in silver, and these rocks are also great reservoirs of sulphur, arsenic, lead, zinc, and numerous other chalcophile elements. They constitute, therefore, an adequate source for all of the elements present in the argentiferous deposits.

It is evident that nearly all of the deposits in this category are either structurally or chemically controlled. In a great many cases the veins and lodes occur in fracture systems in competent quartzites, diabase, greenstones, or even in granitic stocks above, below, or to the flanks of sequences of pyritic sediments. In other cases they are mantos or pipes in limestones, calcareous shales, or argillites below or above which lie the source beds of pyritic sediments.

Considering these features it seems probable that the deposits are largely the result of metamorphic secretion processes. As the faults, fractures, disrupted beds, and other structures dilated they drew in the various elements that constitute the ore and gangue mainly from the enclosing sediments, but also perhaps in certain places from diabase and other rocks. The mode of transport of the ore and gangue elements was probably largely by diffusion, although in certain cases solutions may have been the active transfer agents. The way in which the silver migrates is highly speculative. The element may have travelled as the carbonate or sulphate or as the chloride complex $(AgCl_2)^-$. In the presence of alkalies, the various polysulphide ions offer possibilities for transport, as do also the complex ions of silver combined with sulphur, arsenic, or antimony.

The number of deposits in this category are legion and only a few examples can be cited and briefly described. In Canada the deposits of the Keno Hill - Galena Hill area, Yukon, the Slocan and Ainsworth areas, British Columbia, the Bluebell mine at Riondel, British Columbia, the great Sullivan mine at Kimberley, British Columbia, and the silver deposits in the Thunder Bay district of Ontario are typical examples. In the United States the Coeur d'Alene deposits and those in the East Tintic district, Utah, and Leadville and Aspen districts of Colorado provide further examples. Many of the Mexican deposits belong in this category, especially those in the Santa Eulalia (El Potosi mine) and in the Zacatecas silver districts. In Europe classic examples are found in the Kongsberg district of Norway, in the Clausthal and Freiberg silver districts of Germany, and at Jachymov in Czechoslovakia. It seems probable that the great lead-zinc-silver lodes of Broken Hill and Mount Isa, Australia, belong in this category as do also many of the polymetallic silver-bearing deposits of the U.S.S.R. (Nerchinsk district and elsewhere). The enigmatic Kurokô (black ore) deposits of Japan seem to be best classified in this category.

5. Silver-Gold and Gold-Silver Veins and Lodes in or Associated With Volcanic Flow Rocks:

Representatives of this type of deposit are widespread throughout the folded volcanic terrains of the earth. The deposits occur in rocks of all ages, but the largest number occur in Precambrian and Tertiary rocks.

The favourable host rocks are commonly andesites, latites, trachytes, and rhyolites. In Precambrian rocks such assemblages are usually referred to as 'greenstones'. Deposits in basalts are rare. Many deposits occur in tuffs, agglomerates, and sediments interbedded with the volcanic flows. In the older terrains, the rocks are generally regionally metamorphosed and exhibit the characteristic regional metamorphic facies outward from igneous or granitized centres. The younger rocks generally show the effects of chloritization (propylitization) over broad areas, but locally some of the andesites and rhyolites may be relatively fresh.

In the older rocks the deposits are veins, lodes, stockworks, pipes, and irregular masses generally in extensive fracture and shear zone systems. Some occur in drag-folds. The deposits in the younger rocks are usually confined to fissures, fractures, and faults that often have a limited horizontal and vertical extent. Others, however, are associated with fracture and fault systems that extend for many miles.

The structure of the veins and lodes in the older rocks is generally compact and the minerals are commonly intimately intergrown with one another. Recrystallization and a coarse-grained character are common. The structure of the younger, generally Tertiary, deposits is characteristic. Open cavities are abundant, and filling, crustification, and comb and cockade structures are conspicuous. The vein walls are often irregular, and the vein matter is generally frozen to the walls. Banding and repeated surges of mineralization witnessed by numerous overgrowths are characteristic.

Quartz is the most important gangue in these deposits. In the older rocks the quartz is colourless, white, milky, grey, or black, and forms coarse granular aggregates, intimately intergrown with the other vein minerals. Most of the quartz gives the appearance of being considerably recrystallized. Some varieties have a definite schistose and gneissic appearance. Vugs and crusts of quartz crystals occur in some deposits, but they are rare. The quartz in the younger rocks is characteristically white or light grey, and in some deposits an amethyst colour is often noticeable. It is usually fine grained and often chalcedonic. Some varieties exhibit a delicate colloform banding suggesting colloidal deposition. Several generations are often present, and these cement older brecciated quartz aggregates, ore minerals, and wall-rock fragments.

Other gangue minerals in the older deposits include calcite, dolomite, and ankerite. In the younger deposits, barite and fluorite are also common, and rhodochrosite and rhodonite may be present in places. Adularia is characteristically developed in some Tertiary deposits, and kaolinite, sometimes in abundant amounts, is present in the veins. It may be a product of descending surface waters. Zeolites occur in a few of the younger deposits.

The metallic minerals are varied and seem, in part, to be dependent on the age of the deposits. Native gold is the most common. In the older deposits it tends to be relatively pure with only a little silver, the ratio of Ag/Au ranging between 1:5 and 1:50. The gold of the younger deposits is usually much richer in silver, the ratio Ag/Au approaching 1:1 in some districts. Gold and silver tellurides commonly occur in all ages of deposits, but are particularly abundant in the younger deposits. Both the native gold and gold-silver tellurides tend to be late minerals in the paragenetic sequence of the veins. Gold-silver selenides occur in some of the younger deposits, but these minerals are generally rare.

The principal silver mineral in the deposits is acanthite (argentite). In addition there may be proustite, pyrargyrite, miargyrite, stephanite, polybasite, and tetrahedrite. Native silver is common, but is often an oxidation product. these silver minerals are rare in the older (Precambrian) deposits, but a little silver-bearing tetrahedrite may occur in some veins. Most of the deposits that are rich in silver minerals are in Palaeozoic, Mesozoic, or Tertiary rocks.

Among the other metallic minerals, pyrite, arsenopyrite, argentiferous galena, sphalerite, and chalcopyrite are nearly ubiquitous in all ages of deposits, although the last three minerals are generally present in only small amounts in the Precambrian deposits. Pyrrhotite occurs in some of the older deposits, but is rare in the younger. Stibnite and a variety of sulphosalts are most common in the younger deposits, but also occur in some abundance in certain Precambrian ones. Alabandite is usually restricted to the younger deposits. Molybdenite and scheelite are present in certain Precambrian deposits, but are relatively rare in younger veins, although there are some exceptions to this generalization.

Characteristic types of wall-rock alteration are generally developed adjacent to and in the vicinity of nearly all deposits in this class. In the old Precambrian rocks the most common types of alteration are chloritization, sericitization, carbonatization, pyritization, and silicification. In the younger rocks propylitization (chloritization and pyritization) is especially characteristic, and there may also be a development of adularia, silicification, kaolinization, sericitization, and more rarely alunitization.

Veins in Precambrian greenstones and in certain younger andesites and trachytes are generally flanked by zones of carbonate-sericite schist, which grade imperceptibly into zones of chlorite-carbonate and chlorite schist. In general these alteration zones represent a loss of silica and some of the cafemic elements, and major increases in water, carbon dioxide, sulphur, and potassium. Sodium is generally leached. The reactions to produce the alteration zones are complex and have been discussed in detail by the writer (Boyle, 1961). The most significant feature is the transfer of silica to the vein sites where it probably crystallizes as quartz. By means of detailed chemical profiles it has been shown that most of the vein quartz owes its origin to this process.

Where rhyolites or dacites are present the alteration effects are less marked. Sericitization, pyritization, and silicification are, however, characteristic. Sediments, interbedded with the volcanic rocks, are not markedly affected in most places, although there may be a development of pyrite, sericite, and some carbonate minerals near the veins.

Propylitization is characteristic of many Tertiary deposits. The mineralogical changes include the abundant development of chlorite and pyrite, sometimes also epidote, from the ferromagnesian minerals of andesite and similar rocks. There is also a development of carbonates and some sericite in certain areas. The chemical changes consist of a moderate leaching of potassium and sodium, a decrease of silica and cafemic elements, and additions of water, sulphur, and carbon dioxide in some areas. The propylitization is pervasive, being developed usually adjacent to the veins as well as in great volumes of rock in the general vicinity of the mineralized zones.

The alteration in the younger rhyolites and dacites is usually sericitization and silicification. Alunitization, the development of adularia, and carbonatization may affect all younger rock types. Silicification, without the development of lime silicates, may take place in limestones and limy shales. Sandstones, shales, and argillites are generally little altered.

The elements commonly concentrated in this class of deposits include Ag, Au, Te, Sb, As, Cu, Pb, Zn, Ca, Mg, Fe, Mn, K, SiO_2, CO_2, and S; less common are Mo, W, Se, Ba, and F. The source of these elements is probably in the volcanic pile in which the deposits are developed. Interbedded sediments, tuffs, and agglomerates may also have made a contribution. The manner of concentration is probably similar to that suggested above for deposits in sedimentary rocks.

Numerous deposits belong in this category. At least three types can be recognized. Briefly these are with examples:

1. Gold deposits. Native gold, alloyed with variable, though generally small, amounts of silver, is the principal economic mineral. There may be subordinate amounts of acanthite (argentite), tetrahedrite, sulphosalts, ruby silver, etc. Quartz is the principal gangue.

Numerous examples occur in the greenstone belts of the Canadian Precambrian Shield, including Yellowknife, Red Lake, Porcupine, Kirkland Lake, and western Quebec. Other examples occur in the Canadian Cordillera, as in the Bridge River district where the veins occur in augite diorite. There are many examples in Australia (Kalgoorlie), in U.S.A. (Mother Lode system where the veins cut greenstones), and elsewhere. In all these deposits native gold is the economic mineral. There may be minor amounts of gold-silver tellurides in some deposits. Silver is won as a by-product.

Deposits in Tertiary andesites, rhyolites, and allied rocks are found in various parts of the world. In these, native gold, often greatly enriched in silver (up to 40 per cent or more), is the principal economic mineral. Gold-silver tellurides are generally subsidiary. Examples occur in Roumania (Transylvania), New Zealand (Hauraki), Mexico (El Oro), U.S.A. (Black Mountains, Arizona; De Lamar, Idaho; Rawhide, Nevada), Japan, and elsewhere.

2. Silver-gold-quartz deposits. Most of these deposits occur in rocks younger than Precambrian. Many occur in Tertiary andesites and rhyolites and in underlying Palaeozoic or Mesozoic sediments and volcanic rocks. The principal economic minerals are silver-rich native gold (electrum), argentite, tetrahedrite, ruby silvers, silver selenides, and polybasite. Typical examples are found in the Tonopah district in Nevada where the veins cut Tertiary volcanic rocks and are mineralized with electrum, argentite, polybasite, pyrite, chalcopyrite, galena, sphalerite, silver selenides, and small amounts of scheelite and wolframite in a gangue of quartz, sericite, rhodochrosite, and adularia. Another example is the Comstock Lode in Nevada. This famous deposit was localized in a fault separating intensely propylitized and sericitized Tertiary and older volcanic rocks from Mesozoic rocks. The great bonanzas consisted of crushed quartz and some calcite in which were electrum, gold, pyrite, argentite, polybasite, a variety of other silver sulphosalts, and minor amounts of sphalerite and galena.

Further examples of this type of deposit are common in Mexico, especially in the Pachuca, Hidalgo district and at Guanajuato. In the Pachuca district the fissure veins carry quartz, rhodonite, galena, sphalerite and an abundance of argentite, polybasite, stephanite, and traces of gold. They cut Lower Cretaceous sediments and a variety of Tertiary intrusive and extrusive rocks which exhibit widespread propylitization, chloritization, and silicification. The great lodes of the Guanajuato district, of which the Veta Madre is the most famous, occur in extensive fault zones that cut through pre-Cretaceous shales, sandstones, and conglomerates cut by rhyolite, andesite, prophyry, and monzonite and overlain by Tertiary volcanic rocks. The vein matter is quartz, in part amethystine, carbonate, adularia, pyrite, argentite, native silver, native gold, various silver sulphosalts and minor amounts of galena, sphalerite, and chalcopyrite. The Ag/Au ratio in the ores is about 100/1.

3. Gold-telluride and gold-selenide deposits. These deposits are veins, pipes, and stockworks generally in Tertiary volcanic rocks, although some are known in older rocks. The deposits are mined essentially for gold with silver as a by-product.

Cripple Creek, Colorado, is the best known example of the gold-telluride deposits. The country rocks are Precambrian granites and gneisses broken through by a great mass of Tertiary volcanic rocks probably representing a large volcano. The core of this volcano is composed of tuffs and breccias of latite-phonolite, which are cut by dykes and masses of phonolite, syenite, monchiquite, and vogesite. The deposits are veins, mineralized sheeted zones, replacements in breccia and along fissures, and irregular pipes in mineralized breccia. These cut both the Precambrian and Tertiary rocks, but are best developed in the latter. The principal ore mineral is calaverite, $AuTe_2$, with a silver content generally less than 4 per cent. There is practically no hypogene native gold. Associated with the calaverite are small amounts of sylvanite, petzite, pyrite, sphalerite, galena, tetrahedrite, stibnite, cinnabar, molybdenite, and minor amounts of wolframite (huebnerite). The gangue is quartz, fluorite, carbonate, and roscoelite (the vanadium mica). The vein structure is drusy. The alteration is pyritization, carbonatization, and propylitization. Adularia is developed in some veins. The deposits are now largely exhausted.

The gold-selenide deposits are rather rare. There are, however, examples at Republic in Washington, in the Radjang-Lebong gold field in Sumatra, Indonesia, and at the Kushikino mine, Kagoshima Prefecture, Japan. Most of the deposits are veins, stockworks, and pipes in Tertiary or younger andesites. The principal gangue is quartz and calcite, sometimes adularia, usually in banded and colloform arrangements or in fine-grained intergrown aggregates. The principal ore minerals are native gold often high in silver, electrum, various silver, lead, and copper selenides, such as aguilarite, naumannite, and berzelianite, pyrite, tetrahedrite, chalcopyrite, galena, and sphalerite. The alteration attending the veins is generally silicification, pyritization, or propylitization. The Ag:Au ratio, in the Radjang-Lebong field varies from 1:1 to 90:1.

6. Silver Deposits in a Complex Geological Environment Comprising Sediments, Volcanic, and Igneous or Granitized Rocks:

Deposits in this category combine nearly all the epigenetic features described for the previous categories. The origin of their metallic and other components may lie in the combined group or groups of rocks in which they lie. This category includes numerous gold-silver deposits, silver-gold deposits, argentiferous polymetallic deposits, and the unique native silver-Ni-Co arsenide-sulphide deposits described below.

7. Native Silver-Ni-Co Arsenide-Sulphide Deposits in a Complex Geological Enrvironment:

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

The deposits occur in a variety of rock types and in a number of diverse geological situations. In age they range from Precambrian to Tertiary. Nearly all are short narrow veins containing phenomenally rich concentrations of native silver, together with variable amounts of argentite, freibergite, other silver sulphides and sulphosalts, various cobalt-nickel arsenides, native bismuth, bismuthinite, and native arsenic. A few contain pitchblende. The gangue is invariably calcite with some barite and quartz. The mineralogical textures are characteristic and are familiar to every student of geology and mineralogy. The characteristic elements and compounds concentrated in the veins are Ag, Ni, Co, As, Sb, Bi, U, Hg, S, Ca, Mn, Ba, and CO_3. Examples are numerous in a number of countries. The best known and most productive are those at Cobalt and Silver Islet, Ontario; Great Bear Lake area, N.W.T.; Kongsberg, Norway; Jachymov (Joachimsthal) Czechoslovakia; and others in the Erzgebirge of Saxony and Bohemia.

During the compilation of the data on these deposits the writer has been struck by the frequent reference to the occurrence of basic magnesium-rich rocks in the vicinity of the deposits. In some cases the rocks are diabase or gabbro, in other serpentinites, in still others amphibolites or talc-tremolite schists. These rocks could be the source of the nickel and cobalt in the deposits as has been suggested by a number of investigators. However, this association is not invariable. Some of the deposits seem to be related to granitic intrusions especially monzonites or diorites. Other deposits show no such relationships. A few deposits are enriched where they intersect sulphide-bearing schists (fahlbands), but in others these rocks are not present. A number of deposits occur either in or near black shales or other sediments that could have provided the silver, uranium, arsenic, sulphur, and their other constituent elements, but again this relationship is not invariable. The presence of mercury, a low temperature volatile element, with nickel and cobalt, elements generally found in high temperature deposits, is puzzling, as is also the presence of uranium in some deposits and the virtual absence of this element in others. All these features serve only to point out the enigmatc nature and origin of these deposits. Work by the writer and his colleagues at Cobalt, Ontario, suggests that the native silver veins represent late secretion extracts derived probably by diffusion from a variety of metal-rich rocks, particularly (interflow) graphitic, pyritic sediments, basic volcanics, and diabase sills.

8. Miscellaneous Sources of Silver:

The element is won as a by-product from a great variety of deposits mined essentially for copper, nickel, lead, zinc, and gold. The amount of silver in these deposits is generally low, but in some deposits the content has an influence on the economics of mining the deposits.

Oxidation and Secondary Enrichment of Silver Deposits

Argentiferous deposits, subjected to oxidation, generally become enriched near the surface both as a result of chemical processes involving the migration of silver and by the removal of soluble gangue and sulphides. Where lead occurs in quantity in the silver deposits as galena or other sulphides, there is also a parallel enrichment of this element as a result of oxidation processes. In contrast to copper, however, silver exhibits less tendency to form secondary sulphide zones in veins and other deposits.

The mobility migration, and concentration of silver during the oxidation of silver deposits are strongly influenced by the following factors:

1. The type of deposit and its mineral composition. The nature of the gangue, types of sulphides, and primary silver minerals are the main considerations.

2. Types of enclosing rocks.

3. Climatic factors.

4. Position of the water-table.

5. Organic agencies. Sulphate reducing bacteria may contribute materially to the precipitation of silver in the zones of reduction.

The redox processes in argentiferous deposits are complex and depend essentially on the Eh and pH of the environment of oxidation and reduction. Colloidal and co-precipitation phenomena also play a large part. Iron and manganese minerals and carbonates in the gange, ore, and wall rocks greatly influence the reactions that lead to secondary enrichment of the element. Silver sulphate, Ag_2SO_4, is relatively soluble, in contrast to the analagous gold complex, and the two elements are commonly separated during oxidation of gold-silver deposits; the gold tends to concentrate in the gossans and weathered residuum and silver is leached out especially under acidic conditions. In an environment where ferrous sulphate predominates silver is commonly precipitated according to the reaction: $Fe^{2+} + Ag^+ = Ag + Fe^{3+}$. Soluble manganous ion (Mn^{2+}) has a similar effect. Where chlorides, bromides, and iodides are present in surface oxidizing waters the corresponding insoluble silver halides (chlorargyrite, etc.) are precipitated. In the zones of reduction of oxidized argentiferous deposits, silver is commonly precipitated in a very finely divided form on or in pyrite and in secondary (supergene) sulphide minerals such as chalcocite, covellite, and marcasite. In some reduction zones native silver may predominate and pyrargyrite and/or proustite may be formed. Further details and extensive references describing the redox phenomena in argentiferous deposits are given in Boyle (1968).

World Silver Production

The world production of silver is of the order of 11,500 metric tons. The leading silver-producing countries are U.S.S.R. (14.5%), Mexico (14.2%), Peru (11.4%), Canada (11.0%), United States (10.7%), Australia (7.1%), Poland (6.4%), and other countries (24.7%). Most of the world production of silver, some 85 percent or more, is won as a by-product of base metal ores; the remainder is derived from native silver deposits, and gold deposits.

Origin of Silver Deposits

A number of geologists consider the argentiferous copper shale deposits to be essentially sedimentary in origin; others consider them to be of epigenetic hydrothermal origin. In this writer's opinion the silver in these deposits was initially sedimentary and highly disseminated through the shales (schists) and associated rocks. The silver- and copper-rich sections (shoots) are, however, epigenetic, the silver, copper and associated elements having been mobilized and concentrated during diagenetic and metamorphic processes.

The 'red bed' types of silver deposit are epigenetic in origin, the source of the silver and mode of its concentration being varied. In most red bed terranes the source of the silver appears to be the complex pile of sediments in which the deposits occur; in this pile carbonaceous and pyritiferous shales underlying the deposits appear to be the most probable source rocks. In most deposits the medium of transport for the silver and associated ore and gangue elements appears to have been groundwaters or connate waters. Two mechanisms seem to have operated in the concentration of the elements - mass transport by the waters (flow) and diffusion of ions, hydrated ions, molecules, and gases through the stationary ground or connate water that pervaded all fractures, breccia zones, porous zones, pores and other discontinuities in the rocks. Both mechanisms may have operated depending on the geological setting. Near the surface the mass transport mechanism was probably the most effective, whereas at depth the diffusion mechanism probably prevailed. Precipitation of the silver and associated chalcophile elements has been mainly by reduction, facilitated in many cases by the presence of carbonaceous matter, plant remains, etc.

The writer has concluded from his studies of the various epigenetic vein, lode, stockwork, and disseminated silver deposits that they originated mainly by metamorphic secretion and/or granitization processes, the source of the silver and its associated elements being mainly the enclosing volcanic and/or sedimentary piles in the case of greenstone and most greywacke-slate terrains. Argentiferous deposits, mainly of Cretaceous-Tertiary age associated with young volcanic calderas and basins, probably derived much of their silver from older underlying (basal) volcanic or sedimentary terrains and the remainder from their host propylites. Particularly favourable source rocks are certain basaltic and andesitic rocks, pyritic and pyrrhotitic tuffs, pyritic and graphitic interflow sedimentary beds in volcanic terrains, sulphidic iron-formations, pyritic and graphitic phyllites and schists in sedimentary terrains, and pyritic quartz-feldspar porphyries. It has been shown (Boyle, 1979) that such rocks affected by regional and/or contact metamorphism, extensive carbonatization, and/or granitization are capable of producing the quantities of silver, gold and associated elements present in the deposits of an auriferous/argentiferous mineral belt.

The origin of the native silver-Ni-Co arsenide deposits is conjectural. Some geologists attribute their origin to hydrothermal agencies related to magmatic bodies (granites, diabase, etc.). Work by the writer and his colleagues at Cobalt, Ontario, suggests that the native silver veins there represent late secretion extracts derived probably by diffusion from a variety of metal-rich rocks, particularly (interflow) graphitic, pyritic sediments, basic volcanics, and diabase sills. In other areas, metal-rich sediments (pyritic schists) and volcanics, particularly pyritic volcaniclastics, appear to have been the source rocks.

Literature on Silver

The literature on silver, including that on its history, chemistry, deposits, production, and uses, is voluminous. Silver is the second metal mentioned in practically all of the ancient texts including those of the Hindus, Hebrews, Persians, Greeks, and Romans. More-modern treatises are noted in the following Selected Bibliography.

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WORKSHOP - PROSPECTING FOR GOLD DEPOSITS

GOLD DEPOSITS - AN OVERVIEW OF THEIR TYPES, GEOCHEMISTRY, PRODUCTION, AND ORIGIN

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Abstract

The general geochemistry of gold is briefly discussed, followed by summary descriptions of the common types of auriferous deposits and a brief discussion of the world production of the metal. A short section on the origin of auriferous deposits completes the paper.

The epigenetic vein, lode, stockwork and disseminated types of gold deposits originated mainly by metamorphic secretion and/or granitization processes, the source rocks of the gold and its associated elements being mainly in the enclosing volcanic and/or sedimentary piles. Modern gold placers are of sedimentary origin, the gold being winnowed into pay streaks as the result of both chemical (accretion) and physical (gravity) processes operating during weathering and subsequent sedimentation. The auriferous quartz-pebble conglomerate deposits probably originated as placers, the gold and many of its associated elements having undergone radical chemical re-working during subsequent diagenetic and metamorphic events.

General Geochemistry of Gold

Gold is a member of Group IB of the Periodic Table, which includes copper, silver and gold. In its chemical reactions gold resembles silver in some respects, but its chemical character is markedly more noble. The principal oxidation states of gold are + 1 (aurous) and + 3 (auric). These states are unknown as aquo-ions in solutions, the element being present mainly in complexes of the type $[Au(CN)_2]^-$, $[AuCl_2]^-$, $[Au(OH)_4]^-$, $[AuCl_4]^-$, and $[AuS]^-$. There is only one naturally occurring isotope of gold: ^{197}Au.

In nature, gold occurs predominantly in the native state or as a major constituent of various alloys containing mainly silver, copper or platinum metals. Several gold and gold-silver tellurides are known, of which the most common are sylvanite, calaverite, petzite, krennerite and nagyagite. The antimonide, aurostibite, $AuSb_2$, occurs in some auriferous deposits, and there is also an argentiferous gold selenide, fischesserite, Ag_3AuSe_2, an argentiferous gold sulphide, uytenbogaardtite, Ag_3AuS_2, and a bismuthide, maldonite, Au_2Bi, which is fairly well differentiated. The principal ore minerals of gold are the native metal, aurostibite, and the various tellurides.

The abundance of gold in the upper lithosphere is about 0.005 ppm and the Au/Ag ratio is about 0.1. The average gold content of igneous-type rocks in parts per million is - ultramafic (0.004), gabbro-basalt (0.007), diorite-andesite (0.005) and granite-rhyolite (0.003). The average gold content of sedimentary rocks in parts per million is - sandstone and conglomerate (0.03), normal shale (0.004) and limestone (0.003). Certain graphitic shales, sulphide schists, phosphorites, and some types of sandstones and conglomerates may contain up to 2.1 ppm Au or more.

The average gold content of soils is 0.005 ppm, and the average for natural fresh waters is 0.00003 ppm. Sea and ocean waters contain an average of 0.000012 ppm Au. Gold is a trace constituent of many plants and animals. Some coals are slightly enriched in gold, with 0.05 to 0.01 ppm Au in the ash.

Auriferous Deposits

Gold is won from deposits mined essentially for the metal and as a by-product of the mining and treatment of nickel, copper, zinc, lead, and silver ores. A number of types of deposits, exploited mainly for gold, are listed and discussed briefly below. The classification of these deposits is that suggested by the writer in his monograph on gold (Boyle, 1979), and is based essentially on the general morphology and chemical constitution of a deposit-type and on its geological and geochemical setting, particularly the nature of its host rocks. It is thought that this manner of classification is as factual and as objective as can be devised, and that it is relatively independent of speculative genetic theories.

Two general types of auriferous deposits are recognized-lode (vein) deposits and placers. The enigmatic quartz-pebble conglomerate deposits, the largest known auriferous concentrations on earth, have generally been classified as modified placers, but some geologists have considered them to be of hydrothermal origin and akin to lode deposits.

Gold deposits are of all geological ages. Most of the world gold production has come from deposits of Precambrian age, but considerable production has also been won from rocks of Paleozoic, Mesozoic, and Cenozoic (particularly Tertiary) age.

The following types of auriferous deposits are recognized:

(1) *Auriferous porphyry dykes, sills and stocks; auriferous pegmatites, coarse-grained granitic bodies, aplites, and albitites:*

The indigenous gold content of these granitic rocks is invariably low, of the order of 0.003 ppm. Certain albitites and quartz-feldspar porphyry dykes and stocks with indigenous pyrite and pyrrhotite may contain up to 0.10 ppm Au and 1 ppm Ag, principally in the sulphide minerals. Porphyritic, aplitic and granitic bodies of this type are common in Precambrian, mainly Archean, terranes and in younger rocks throughout the world. Most are of an intrusive nature, probably the anatectic products of deep-seated granitization. None so far are known to be of economic value, although many are probably the sources of the gold, silver and other metals secondarily concentrated in the fractures, faults and shear zones in the porphyry and albitic bodies themselves and in their nearby host rocks (see Type 7A below).

(2) *Carbonatites and carbonatite-related bodies:*

These bodies are complex magmatic and hydrothermal assemblages of rock in which four phases can usually be recognized: (1) an ultramafic followed by an alkalic magmatic phase; (2) a magmatic dyke phase; (3) a (magmatic?) carbonatite phase; and (4) a late hydrothermal phase. The third and fourth phases are marked by extensive replacement processes in some complexes. Most carbonatites are zoned, often in a ring pattern. The late hydrothermal stage is commonly marked by base metal sulphide mineralization that occupies late fractured and faulted parts of the rocks of all zones. In some carbonatites, however, sulphides, mainly pyrite, pyrrhotite, chalcopyrite and molybdenite, are widely distributed as (indigenous) disseminations in the fenites and rocks of all zones of the complexes; in the great Palabora deposit in South Africa the chalcopyrite and bornite occur in a disseminated (indigenous) form in a number of rock types, but the main concentrations are in the fractured transgressive carbonate (sovite) complex and in transgressive carbonate veinlets that cut several rock types.

Carbonatites and carbonatite-related bodies (e.g., carbonate-barite-fluorite-sulphide veins, dykes and disseminations) are characterized by a distinctive suite of elements that includes: Na, K, Fe, Ba, Sr, rare-earths, Ti, Zr, Hf, Nb, Ta, U, Th, Cu, Zn, P, S, and F; more rarely Li, Be and Pb. Most of the rocks comprising carbonatites are low in gold and silver (0.005 ppm Au; 0.1 ppm Ag respectively). The late stage carbonate-sulphide mineralization, however, commonly contains slightly enriched amounts of both gold and silver. The silver is present mainly in galena, tetrahedrite, and other such minerals; the gold is invariably native and occurs in association with pyrite, pyrrhotite, molybdenite, chalcopyrite and other copper sulphides.

Few if any carbonatites are enriched enough in gold and silver to constitute economic orebodies. However, the fact that the sulphide phases exhibit enrichments in the two precious metals suggests that deposits of this type should be considered as possible gold deposits.

The recently discovered Cu-U-Au deposits at Olympic Dam (Roxby Downs) in South Australia and the auriferous quartz-carbonate counterparts of the rare earth carbonate deposits at Mountain Pass, San Bernardino County, California may be carbonatite-related bodies.

(3) *Auriferous skarn-type gold deposits:*

Gold is a frequent constituent of skarn deposits, in which it is commonly more abundant than the literature would indicate. Most skarn deposits yield gold as a by-product of copper and lead-zinc mining, but there are a number of these deposits that are greatly enriched in gold and silver and are mined essentially for the two precious metals.

The general features of skarn deposits are well known and need not be described in detail here. Most of the deposits occur in highly metamorphosed terranes, particularly those containing carbonate rocks or carbonate-bearing pelites, and in which there has been much granitization and injection of granitic rocks. Some deposits occur near the contacts of granitic bodies and have long been called 'contact metamorphic'; others are developed in favourable reactive beds or zones some distance from granitic contacts. The deposits contain a characteristic suite of early-developed Ca-Mg-Fe silicate and oxide minerals and a lower-temperature, generally later, suite of silicate, carbonate, sulphide and arsenide minerals. The gold minerals include native gold and various tellurides. Most of the skarn deposits worked essentially for gold contain much pyrite and/or arsenopyrite.

The elements most frequently enriched with gold in skarn deposits are Fe, S, Cu, Ag, Zn, Pb, Mo, W, As, Bi and Te. There is commonly a positive correlation between Au and Cu in some skarn deposits. The Au/Ag ratio of the auriferous skarn-type ores is variable but is commonly greater than 1.

Auriferous skarn deposits are relatively uncommon in Precambrian rocks, especially in those of Archean age. In the Canadian Shield, skarn deposits carrying by-product gold occur mainly in the Grenville Province, examples being the lead-zinc-silver-gold ores of the Tetreault Mine near Quebec and the New Calumet Mine northwest of Ottawa. Elsewhere in the world auriferous skarn deposits have a widespread distribution in rocks younger than Proterozoic especially in belts of carbonate rocks invaded by diorites, monzonites, granodiorites and granites. Here belong the auriferous skarn deposits at Cable in Montana, the La Luz and Rosita mines in Nicaragua, a number of mines in the Altai-Sayan of U.S.S.R., and the skarn deposits of Bau, Sarawak, and the Suian district of Korea.

(4) 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:

Representatives of this type of deposit are widespread throughout the folded and relatively flat-lying volcanic terranes of the earth. The deposits occur in rocks of all ages, but the largest number occur in those of Precambrian (mainly Archean) and Tertiary age.

The favourable host rocks are commonly basalts, andesites, latites, trachytes, and rhyolites. In Precambrian rocks, such assemblages are usually referred to as 'greenstones'. Many deposits of Precambrian age occur in tuffs, agglomerates and sediments interbedded with the volcanic flows, particularly in banded iron-formations. In the older terranes, the rocks are generally regionally metamorphosed and have the characteristic regional metamorphic facies outward from igneous or granitized centres. The younger rocks generally show the effects of chloritization, carbonatization, hydration, and pyritization (propylitization) over broad zones, but locally some of the andesites and rhyolites may be relatively fresh.

In the older rocks, the deposits are veins, lodes, stockworks, pipes, and irregular mineralized masses generally in extensive fracture and shear-zone systems. Some occur in drag folds. The deposits in the younger rocks are usually confined to fissures, fractures, faults and brecciated zones that cut the volcanic rocks of calderas and generally have a limited horizontal and vertical extent. Others, however, are associated with fracture and fault systems that extend for many kilometers across volcanic sequences and their associated intrusive granitoids.

The mineralization of these particular deposits is characterized essentially by quartz, carbonate minerals, pyrite, arsenopyrite, base-metal sulphide minerals and a variety of sulphosalt minerals. The principal gold minerals are the native metal and various tellurides; aurostibite occurs in some deposits. Characteristic types of wall-rock alteration are generally developed adjacent to and in the vicinity of nearly all deposits in this class. In the old Precambrian rocks, the most common types of alteration are chloritization, carbonatization, sericitization, pyritization, arsenopyritization and silicification. In the younger rocks, propylitization (chloritization and pyritization) is especially characteristic, and there may also be a development of adularization, silicification, kaolinization, sericitization and more rarely alunitization.

The elements commonly concentrated in this class of deposits include Cu, Ag, Zn, Cd, Hg, B, Tl, Pb, As, Sb, Bi, V, Se, Te, S, Mo, W, Mn, Fe, CO_2 and SiO_2; less commonly Ba, Sr, U, Th, Sn, Cr, Co, Ni, and F. Hg and Sb are particularly characteristic of the younger deposits. The Au/Ag ratio of ores is generally greater than 1 in most Precambrian and in some younger deposits; in many Tertiary deposits the ratio is less than 1.

Deposits of this type are widespread in the Precambrian greenstone belts of the world; examples include: Yellowknife, Northwest Territories, Canada; Red Lake and Timmins, Ontario, Canada, Kolar goldfield, India; Kalgoorlie goldfield, Western Australia; and the Cam and Motor, Dalny, and other similar mines in Zimbabwe. Younger representatives are the Mother Lode System of California (Mesozoic); Comstock Lode, Nevada (Tertiary); Goldfield, Nevada (Tertiary); Cripple Creek, Colorado (Tertiary); Sacarimb (Nagyag), Romania (Tertiary); Coromandel gold belt, New Zealand (Tertiary); Emperor Mine, Fiji (Tertiary); Lebong and other auriferous districts, Indonesia (Tertiary); Lepanto Mine, Philippines (Tertiary); Kasuga Mine, Japan (Tertiary), and the Belaya Gora and other similar deposits in the U.S.S.R. far east (Tertiary).

(5) *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:*

These deposits are widespread throughout the world and have produced a large amount of gold and silver; they are often referred to as "Bendigo type". The deposits are developed predominantly in sequences of shale, sandstone and greywacke dominantly of marine origin. Such sequences are invariably folded, generally in a complex manner, metamorphosed, granitized and invaded by granitic rocks, forming extensive areas of slate, argillite, quartzite, greywacke and their metamorphic equivalents. Near the granitic bodies, various types (kyanite, andalusite, cordierite) of quartz-mica schists and hornfels are developed, and these grade imperceptibly into relatively unmetamorphosed slates, argillites, quartzites and greywackes marked by the development of sericite, chlorite and other low-grade metamorphic minerals. Most of the gold deposits are developed in the lower-grade facies. A few economic deposits occur in the granitic batholiths and stocks that invade the greywacke-slate sequences.

The principal gangue mineral in these deposits is quartz; feldspar, mica, chlorite and minerals such as rutile are subordinate. Among the metallic minerals, pyrite and arsenopyrite are much the commonest, but galena, chalcopyrite, sphalerite and pyrrhotite also occur. Molybdenite, bismuth minerals and tungsten minerals are local. Stibnite occurs in abundance in a few deposits, but is relatively rare in most deposits. Acanthite, tetrahedrite-tennantite and other sulphosalts are not common in these deposits. Carbonate minerals, mainly calcite and ankerite, are common, but not abundant. The valuable ore minerals are native gold, generally low in silver, auriferous pyrite and auriferous arsenopyrite. Telluride minerals are relatively rare, and aurostibite is an uncommon mineral in these deposits.

A few deposits in this category are tabular or irregular replacement (disseminated) bodies developed in carbonate rocks or calcareous argillites and shales. The principal minerals in these deposits are quartz, fluorite, pyrrhotite, pyrite, arsenopyrite, sphalerite, galena, chalcopyrite and stibnite.

As a general rule, wall-rock alteration associated with these deposits is minimal, and the quartz veins, saddle reefs and irregular masses are frozen against the slate, argillite or greywacke wall rocks. In places, thin zones of mild chloritization, sericitization and carbonatization are present. Some veins are marked by thick black zones (up to 15 cm wide) of tourmalinized rock. Disseminated pyrite and arsenopyrite are common in the wall rocks of most of these deposits. This pyrite and arsenopyrite is usually auriferous.

The elements exhibiting a high frequency of occurrence in this type of gold deposit include Cu, Ag, Mg, Ca, Zn, Cd, (Hg), B, (In), (Tl), Si, Pb, As, Sb, (Bi), S, (Se), (Te), (Mo), W, (F), Mn, Fe, (Co) and (Ni). Those in parentheses, have a low to very low frequency of occurrence. The Au/Ag ratio in the ores is generally greater than 1.

Deposits in essentially sedimentary terranes are widespread throughout the world. In Canada, examples occur in the Archean Yellowknife Supergroup in the Yellowknife district, Northwest Territories (Ptarmigan, Thompson-Lundmark and Camlaren mines); in the Paleozoic Cariboo Group at Wells, British Columbia (Cariboo Gold Quartz Mine); and widespread in the Ordovician Meguma Group of Nova Scotia. Elsewhere in the world deposits of this type occur in the auriferous Appalachian 'Slate Belt', U.S.A. (Paleozoic); Salsigne Mine, Montagne Noire, France (Paleozoic); Sovetskoe deposit, Yenisey region, U.S.S.R. (Proterozoic); Muruntau deposit, Uzbec S.S.R. (Paleozoic); Bendigo deposits, Victoria, Australia (Paleozoic); and the Pilgrims Rest and Sabie goldfields in the Transvaal System, South Africa (Proterozoic?).

(6) Gold-silver and silver-gold veins, lodes, stockworks and silicified zones in a complex geological environment, comprising sedimentary, volcanic, and various igneous intrusive and granitized rocks:

Deposits in this category combine nearly all the epigenetic features described in categories (4) and (5). Quartz is a predominant gangue, and some deposits are marked by moderate developments of carbonates. The ore bodies constitute principally quartz veins, lodes, and silicified and carbonated zones. The gold is commonly free but may be present as tellurides and disseminated in pyrite and arsenopyrite. The Au/Ag ratio of the ores is variable depending upon the district and often upon the deposit.

The deposits have a widespread distribution throughout the world in rocks ranging in age from Precambrian (Archean) to Tertiary. Examples in Canada include the Precambrian (Archean) deposits in the Kirkland Lake and Little Long Lac-Sturgeon River districts of Ontario and in the Jurassic volcanics of the Rossland gold-copper camp in the West Kootenay district of British Columbia. Elsewhere, gold is won from deposits of this type in Alaska at the Alaska Juneau Mine (Mesozoic); Grass Valley and Nevada City auriferous districts, California (Mesozoic); and the Central City district, Colorado (Tertiary).

(7) Disseminated and stockwork gold-silver deposits in igneous, volcanic and sedimentary rocks:

Three general categories can be recognized in this type:

(A) Disseminated and stockwork gold-silver deposits in igneous bodies.

(B) Disseminated gold-silver and silver-gold 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.

The principal economic element in these deposits is gold, with small amounts of silver. A few deposits yield the base metals, but they are generally not known as base-metal deposits. The grade of the deposits is highly variable. Most are relatively low grade (generally less than 15 g Au/tonne), but are characterized by relatively large tonnages. The elements commonly concentrated in these deposits, omitting those in the common gangue minerals such as quartz, silicate and carbonate minerals, are: Cu, Ag, Au, (Ba), (Sr), Zn, Cd, Hg, B, (Sn), Pb, As, Sb, Bi, V, S, Se, Te, Mo, W, (F), Fe, Co and Ni. Those in parentheses are infrequent or occur only in certain deposits. The Au/Ag ratio of most deposits is greater than 1.

The deposits in category (A) occur in igneous plugs, stocks, dykes and sills that have been intensively fractured or shattered and infiltrated by quartz, pyrite, arsenopyrite, gold and other minerals. Most of the deposits are stockworks or diffuse irregular impregnations. The alteration processes vary with the types of host rock. In granitic (felsic) rock, sericitization, silicification, feldspathization (development of albite, adularia, etc.) and pyritization are predominant; in intermediate and mafic rocks, carbonatization, sericitization, serpentinization and pyritization prevail. Alunitization may occur in both felsic and mafic rocks in places. The Au/Ag ratio in most deposits is greater than 1.

Deposits of this type are common in Canada, particularly in the Canadian Shield and Cordillera. Examples are: The Howey and Hasaga mines at Red Lake, Ontario, in an Archean quartz porphyry dyke; the Matachewan Consolidated and Young Davidson mines in Archean syenite plugs and dykes in the Matachewan district of Ontario; and the Camflo Mine in an Archean porphyrytic monzonite stock near Malartic, Quebec. Elsewhere typical examples occur in the Beresovsk auriferous district, Urals, U.S.S.R. (Paleozoic); Twangitza Mine, Kivu Province, Zaire (Precambrian); and the Morning Star Mine, Woods Point, Victoria, Australia (Paleozoic).

The disseminated gold-silver occurrences in volcanic flows and associated volcaniclastic rocks in Category (B) are relatively common, but commercial deposits of this type have not been worked. Most occurrences are very low grade, commonly less than 0.01 oz Au/ton (0.3 ppm). Silver contents are higher in places, averaging in some cases 3.5 oz Ag/ton (120 ppm).

The disseminated occurrences in Category (B) are in reality large irregular and diffuse zones of alteration manifest mainly in rhyolites, andesites, basalts and their associated volcaniclastic rocks. These zones of alteration constitute silicification, sericitization, epidotization, argillization or alunitization, commonly associated with pyritization and carbonatization. In the mafic and intermediate rocks, the effects are commonly collectively called propylitization. Large volumes of the volcanic country rocks are affected, giving them a bleached and altered aspect. Locally diffuse silicified zones, quartz veins, alunite veins, and pyrite veins and segregations ramify through the altered rocks.

Occurrences of this type are generally enriched in S, Ba, B, Hg, Sb, As, Pb, Zn, W, Mo, Se, Te, and Ag. The Au/Ag ratio is variable, but most occurrences exhibit values less than 1.

The disseminated gold-silver deposits in volcaniclastic and sedimentary beds in category (C) are usually conformable with the sedimentary and volcaniclastic beds, although in some cases their limits may infringe irregularly on overlying or underlying rocks. Some are large and of relatively high grade; others are commonly too low grade or not of sufficient tonnage to merit attention.

Two general categories of these deposits can be recognized: (1) those developed in tuffaceous rocks and iron-formations within volcanic and sedimentary terranes; and (2) those resulting from extensive infiltration or replacement of chemically favourable beds, particularly carbonate rocks or calcareous pelites. The first category is especially common in Precambrian terranes, although there is no reason why they should not occur in rocks of younger age; however, examples of the latter are rare to date. The second can apparently occur in rocks of any age.

Gold deposits in tuffaceous and other volcaniclastic rocks and in iron-formations in volcanic and sedimentary terranes are particularly common in the Archean greenstone and associated sedimentary belts of the Canadian Shield and in other similar rocks throughout the world. Orebodies in tuffaceous rocks are generally large-tonnage, irregular disseminated bodies containing essentially pyrite, pyrrhotite and arsenopyrite, with much secondary fine-grained quartz. Elements exhibiting an enrichment in these types of deposits include Cu, Ag, Zn, Cd, B, Pb, As, Sb, Bi, Te, and S. Less common are Ba, Sr, Sn, V, Mo, W, Co and Ni. The gold is usually free or present in a finely divided state in the sulphide and arsenide minerals. A typical example of this type of deposit is the Madsen Mine in Archean tuff at Red Lake, Ontario. The newly discovered deposits at Hemlo, Ontario may also belong in this category. Auriferous deposits in iron-formations are of two types - disseminated bodies similar to those just described, and zones of quartz veins or stockworks traversing the constituent rock members of the iron-formations. These contain essentially quartz with pyrite, pyrrhotite and arsenopyrite; the gold is generally present in the native state, and the enriched elements are similar to those mentioned for the deposits in tuffaceous and other volcaniclastic rocks. Typical examples of deposits in iron-formations are the Central Patricia Mine and the Pickle Crow Mine in the Archean Crow River greenstone belt of northern Ontario, the Detour Lake mine in northeastern Ontario, and the Cullaton Lake mine in eastern Northwest Territories. Elsewhere deposits in iron formations include probably the Homestake Mine, Lead, South Dakota (Precambrian?); the Morro Velho Mine, Minas Geraes, Brazil (Precambrian); and a number of deposits in the Precambrian (Archean) iron formations of Zimbabwe.

Gold deposits resulting from extensive infiltration or replacement of chemically favourable beds (Category 2) are developed principally in calcareous and dolomitic pelites and psammites and in thin-bedded carbonate rocks invaded by granitic stocks and porphyry dykes and sills; a few occur in porous sandstones. Most deposits are characterized by one or more of silicification, argillization, pyritization and arsenopyritization, and introductions of elements such as Au, Ag, Hg, Tl, B, Sb, As, Te and the base metals. The gold is usually disseminated through the altered rocks in a very finely divided form (<5 μ) and is generally, although not always, rich in silver.

Deposits of this type have a widespread distribution throughout the world and are commonly referred to as Carlin-type because of their occurrence in Silurian silty limestone and dolomitic siltstone in the Carlin - Gold Acres District of Nevada. Similar deposits have been recognized in British Columbia (Specogna), and in U.S.S.R. (Kuranakh).

(8) Gold deposits in quartz-pebble conglomerates and quartzites:

These constitute the largest and most productive of the known auriferous deposits, producing some 50 percent of the annual gold production of the world; some deposits are also economic sources of uranium, thorium, and rare earths. Typical examples are the Witwatersrand deposits in South Africa; other deposits include those in the Tarkwaian System of Ghana and at Jacobina, Bahia, Brazil. The orebodies in the quartz-pebble conglomerate deposits are marked by the presence of abundant pyrite with variable and usually minor to trace amounts of a host of other sulphides, arsenides, sulphosalts and minerals such as uraninite, thucholite, and brannerite. The gold is mainly present as the native metal in a very finely divided form (<80 μ); minor amounts of the element also occur in the pyrite and in the various other sulphides, arsenides, sulphosalts, and so forth. Elements concentrated in the quartz-pebble conglomerate type of deposit are variable. Most orebodies report enrichments of Fe, S, As, Au, and Ag; some are marked by above average amounts of U, Th, rare earths, Cu, Zn, Pb, Ni, Co, and platinoids. The average Au/Ag ratio in the ores is 10.

(9) Eluvial and alluvial placers:

These modern placers produce both gold and silver, the latter metal being present usually as a small percentage content of the gold dust and nuggets. Accompanying heavy minerals commonly include variable quantities of monazite, magnetite, ilmenite, cassiterite, wolframite, scheelite, cinnabar, and platinoid minerals. The Au/Ag ratio in placers is generally greater than 1.

Fossil (lithified) equivalents of both eluvial and alluvial placers are known, but few are economic. Here we exclude the quartz-pebble conglomerates of the Witwatersrand and other similar deposits mentioned in 8 above. These appear to be modified placers, although other origins have been suggested. Placers have been worked for centuries in most countries of the world. The placers of the Pactolus, a tributary of the Gediz (Sarabat) in Anatolia, Turkey, and of the Maritsa (Hebrus) in Thrace were famous in ancient times; in modern times the placers of Colombia, California, Victoria (Australia), Alaska, Yukon, British Columbia, and the far eastern U.S.S.R. have produced large amounts of gold.

(10) Miscellaneous sources:

Gold is won from a number of miscellaneous sources, mainly as a by-product from nickel, copper, and other base metal ores as follows:

(1) Nickel-copper ores associated with basic intrusives - Sudbury type;

(2) Massive sulphide deposits containing essentially Fe, Cu, Pb, and Zn sulphides in volcanic and sedimentary terranes;

(3) Polymetallic vein and lode deposits containing essentially Fe, Cu, Pb, Zn, Ag sulphides in volcanic and sedimentary terranes;

(4) Kuroko (black ore) sulphide deposits. These occur mainly in Japan. Some are greatly enriched in both gold and silver;

(5) Disseminated deposits - porphyry Cu-Mo type. These deposits are relatively large sources of gold (and silver) especially in U.S.A., New Guinea, and the U.S.S.R.; and

(6) Certain types of uranium (pitchblende) deposits (e.g., Jabiluka, Australia).

In these varied deposits, gold usually occurs as the native metal in a very finely divided state, or as tellurides; also in a finely divided form or present as a lattice constituent in pyrite, arsenopyrite, chalcopyrite and other base metal sulphides, arsenides, sulphosalts, and selenides.

Oxidation and Secondary Enrichment of Gold Deposits

The oxidation processes in gold deposits are complex and depend essentially on the Eh and pH. Colloidal and co-precipitation phenomena also play a large part.

Iron and manganese minerals and carbonates in the gangue and ore greatly influence the reactions that lead to the secondary enrichment of the element. Gold is not easily solubilized in nature, and its soluble forms are readily reduced to the metal by a great variety of natural materials. The result of this behaviour is that the only common gold mineral found in the oxidized zones of auriferous deposits is the native metal. In this form, and as an adsorbate or intimate constituent of limonite, wad, scorodite and bindheimite, gold is commonly greatly enriched in the gossans and oxidized rubble of auriferous deposits. In the zones of reduction of oxidized gold deposits, some dissolved gold is precipitated in a very finely divided form on pyrite and in secondary (supergene) sulphide minerals such as chalcocite, covellite, and marcasite. Further details and extensive references describing the oxidation and reduction phenomena in auriferous deposits are given in Boyle (1979).

Gold Production

It is estimated that the total amount of gold won by man from the earth to the end of 1983 is about 3.85 billion (3.85×10^9) troy oz. (120×10^9 grams). Of this amount some 2% was produced prior to 1492, 8% during the period 1492-1800, 20% during the interval 1801-1900, and 70% from 1901-1982 (all figures being rough estimates). In volume the total amount of gold won from the earth would occupy 6300 cubic metres or an 18.5 metre cube, a small volume of metal indeed to have so influenced the toil, trials, tribulations, and destiny of man for 5000 years.

The current world production of gold is about 1338 metric tons (Table 1). Some 50% of this production is derived from quartz-pebble conglomerate deposits, some 20% from non-lithified eluvial and alluvial placers, and the remainder from the various vein and disseminated deposits.

Origin of Gold Deposits

The writer has concluded from his studies of the epigenetic vein, lode, stockwork, and disseminated gold deposits that they originated mainly by metamorphic secretion and/or granitization processes, the source of the gold and its associated elements being mainly the enclosing volcanic and/or sedimentary piles in the case of greenstone and most greywacke-slate terrains. Deposits, mainly of Cretaceous-Tertiary age associated with young volcanic calderas and basins, probably derived much of their gold from older underlying (basal) volcanic or sedimentary terrains and the remainder from their host propylites. Particularly favourable source rocks are certain basaltic and andesitic rocks, pyritic and pyrrhotitic tuffs, pyritic and graphitic interflow sedimentary beds in volcanic terrains, sulphidic iron-formations, pyritic and graphitic phyllite and schists in sedimentary terrains, and pyritic quartz-feldspar porphyries. It has been shown (Boyle, 1979) that such rocks affected by regional and/or contact metamorphism, extensive carbonatization, and/or granitization are capable of producing the quantities of gold and associated elements present in the deposits of an auriferous mineral belt.

Modern gold placers are of sedimentary origin, the gold being winnowed into pay streaks mainly as the result of physical (gravity) processes operating during weathering and subsequent sedimentation. However, during the concentration of gold in placers, chemical accretion phenomena have played a large part in the formation of gold particles and nuggets, first in the oxidized zones of the auriferous deposits, then in the eluvium, and finally to a lesser extent in the alluvium.

The origin of the auriferous quartz-pebble conglomerate deposits has long been debated, two general theories being advanced to explain them - a modified placer genesis and a hydrothermal origin. At present, the geological and geochemical evidence suggests that these deposits are highly modified placers, the gold having been originally deposited as very fine particles (flour gold) over extensive deltas and later radically chemically re-worked into ore shoots during subsequent diagenetic and metamorphic events.

Literature on Gold

The literature on gold, including that on its history, chemistry, deposits, production, and uses, is greater than that for any other element. Gold is the first metal mentioned in practically all of the ancient texts including those of the Hindus, Hebrews, Persians, Greeks, and Romans. More-modern treatises are noted in the following Selected Bibliography.

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WORKSHOP - PROSPECTING FOR GOLD AND SILVER DEPOSITS

(A) Favourable rocks (not in order of importance)

1. Volcanic rocks (basalts, andesites, dacites, rhyolites and their equivalent tuffs and breccias) comprising greenstone, greenschist and propylitic belts: In Archean and some Proterozoic terranes greenstone belts are particularly favourable especially if they have a mixed assemblage of volcanics, tuffs and interflow sediments (cherts, pyritic graphitic slates, and iron formations). In younger rocks similar assemblages are favourable; in Tertiary assemblages propylitic belts invaded by stocks and plugs of dacite and monzonite are particularly favourable.

2. Sedimentary terranes: Greywacke-slate belts, iron formations, carbonaceous-graphitic-sulphidic slates and schists, and carbonate-skarn assemblages. Highly (isoclinally) folded greywacke-slate (turbidite) belts are most favourable especially where dilatant zones on the noses and legs of folds are developed thus yielding saddle reefs, leg reefs, etc. Sulphidic iron formations in Precambrian rocks appear most favourable; similarly carbonaceous-graphitic-sulphidic slates and schists in greenstone belts are particularly favourable. In younger assemblages of rocks sequences of pyritic phyllites, slates and schists interbedded with quartzites and carbonate-bearing rocks (calc-phyllites, slates, etc.) are especially favourable.

3. Sedimentary terranes containing pyritic or hematitic quartz-pebble conglomerates and pyritic quartzites: These constitute the host rocks of the most productive of all gold deposits (e.g., Witwatersrand, S.A.). Two types can be recognized: (1) Pyritic quartz-pebble conglomerates and quartzites (Witwatersrand type), and (2) hematite-ilmenite quartz-pebble conglomerates and quartzites (Tarkwaian type).

4. Recent sedimentary terranes containing modern and fossil placers: Two general types are recognized: (1) Eluvial or near deposit residual type, and (2) alluvial type including stream, river, deltaic, and marine placers. 1st generation placers are usually the richest and most productive although 2nd generation (reworked) placers may, likewise, be rich and productive. Multiple generation placers are usually low grade and contain much microscopic gold. Fossil equivalents of both types of placers noted above may occur in certain sedimentary belts.

5. Igneous rocks: Quartz-feldspar porphyry, syenite, and granite stocks and small batholiths invading greenstone, greenschist and propylitic belts are especially favourable where such bodies are extensively fractured resulting in development of silicified (quartz-pyrite) stockworks(porphyry gold deposits). Similar fractured and silicified bodies invading greywacke-slate belts, iron formations, calc-slate and phyllite assemblages are, likewise, of great prospecting significance for gold. Fractured, shattered, and severely faulted granite, porphyry, and syenite contact zones especially where silicified and pyritized should be carefully prospected.

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(B) Favourable structures (not in order of importance)

1. Carbonated shear and schist zones in greenstone belts: Many gold deposits occur in the folded, crumpled, and dilatant zones of these structures or in faults, fractures and other structures subsidiary to them. The source of the silica to form quartz veins and silicified zones appears in many cases to have been derived from the carbonatization of silicates with fixation of Ca, Fe, Mg, and Mn by CO_3 and release of SiO_2. Gold and other associated elements may be similarily derived.

2. Faults, fractures, sheeted and brecciated zones in propylitic belts: Propylitization of large zones of rocks in Mesozoic and Cenozoic (mainly Tertiary) volcanic centres appears to release silica, sulphur, gold, etc. which concentrates in the dilated faults, fractures, etc. Sediments, volcanics, etc. underlying volcanic centres (caldera) appear to be the source of gold, silver, base metals, etc. in some terranes.

3. Faults, fractures, bedding-plane discontinuities and shears, drag folds, crushed zones and openings on anticlines (saddle reefs) in greywacke-slate assemblages and other sedimentary rocks: Dilatancy is the principle driving mechanism for the concentration of quartz, gold, and other elements in veins, saddle reefs, etc. The source of the quartz, gold, etc. is probably the host sedimentary rocks. Metamorphism plays a large part in the concentrating processes.

4. Fracture zones, shear zones, brecciated (stockwork) zones in igneous rocks constituting dikes, stocks, small batholiths, contact zones, etc.: Dilatancy (fracturing, crushing, brecciation) is the principle mechanism inducing concentration. The source of the gold, quartz, etc. is probably the invaded greenstones, propylites, sediments, etc.

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(C) Chemically favourable rocks (not in order of importance)

1. Carbonate rocks, calcareous shales and schists: Replacement following brecciation or other structural activity is the principal process in both the skarn-type and disseminated (Carlin-type) deposits. Both types exhibit extensive silicification with development of calc-silicates in skarn type and fine-grained quartz (jasperoid) in disseminated type.

2. Porous sandstone, arkose, and conglomerate: Zones characterized by good porosity appear to have localized many of the ore shoots in the quartz-pebble conglomerate and quartzite type of gold deposit.

3. Volanic tuffs, breccias, and iron formations: Many of these rock types appear to have had an initially high content of Au, Ag, S, etc. as a result of original sedimentary (syngenetic) processes. Tuffs are particularly susceptible to shearing with consequent dilatancy in sites where drag folds, crumpling, brecciation, etc. are developed, features that concentrate the gold and silver. Iron formations, likewise, are susceptible to shearing, fracturing, brecciation, etc. with similar results. Ore shoots in tuffs and iron formations are invariably epigenetic, but the source of the gold and its associated elements is probably the pile of tuff beds and iron formations many of which are slightly enriched in gold and silver.

4. Ultrabasic, basic and intermediate igneous rocks: These rocks are particularly susceptible to carbonatization and hydration with consequent formation of extensive carbonatized, chloritized and sericitized shear zones, especially in Precambrian, Paleozoic, and Mesozoic terranes. In Tertiary terranes propylitization is a major feature in these rock types. During the processes of carbonatization, hydration, and propylitization silica is released to form quartz veins and silicified zones in nearby dilatant features. Gold may be similarly released to concentrate with the silica. Ultrabasic, basic, and intermediate basic rocks also have a major influence on the precipitation of gold carried as the alkali sulphide species in carbonated ore solutions. For example when carbonatization takes place K is split out of the complex [KAuS] to form sericite, gold is precipitated, and the S binds with Fe to form pyrite in the wall rock.

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(D) Indicator (pathfinder) elements and compounds in approximate order of efficacy

1. Au, Ag, As, Sb, Te: Applicable to all types of geochemical surveys for most types of gold (silver) deposits but especially useful in greenstone belts and propylitized terranes.

2. SiO_2, CO_2, B, F, S: Particularly applicable in primary halo surveys for epigenetic gold and silver deposits. Not useful for localizing auriferous quartz-pebble conglomerates and quartzites.

3. K, Na, Rb, Tl: Useful mainly in geochemical surveys based on primary halos associated with epigenetic gold and silver deposits.

4. Cu, Zn, Pb, Tl, Hg, W: Useful in most types of geochemical surveys for epigenetic gold and silver deposits, especially those with a polymetallic association.

5. U, Mo, Pt metals: U is a particularly good pathfinder for certain types of auriferous quartz-pebble conglomerates and quartzites and for certain types of epigenetic deposits ranging in age from Proterozoic to Tertiary. Mo is a useful indicator in many types of epigenetic deposits ranging in age from Archean to Tertiary. Pt metals are useful as indicators for certain types of auriferous deposits associated with ultrabasic and basic igneous rocks.

6. Rn and He: Useful in atmogeochemical surveys of auriferous and argentiferous deposits enriched in U and Th. See J below.

7. Au, Ag, Bi, Te, W, B, As, Sb, Sn, Zr, P, Pt metals: These elements are good indicators of placer deposits especially if employed in heavy mineral surveys.

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(E) Types of regional lithochemical surveys

1. Analyses of unselected rocks and/or mineral separates on a regional scale: Geochemical surveys of this type are not generally recommended except to obtain a reconnaissance overview of an area when samples are available from geological surveys or reconnaissance geochemical surveys.

2. Analyses of specific rock types and/or mineral separates on a regional scale (e.g., porphyry dykes; batholiths and small stocks of porphyry, syenite, and granite; specific beds or formations such as quartz-pebble conglomerates, tuffs, iron formations, jasperoid, etc.). Geochemical surveys of this type are best carried out on a grid or on a topographic or geological feature basis (e.g., ridge sampling; stratigraphic section sampling, etc.). Results should be carefully evaluated and detailed lithochemical surveys carried out as in (F).

3. Analyses of materials of all observed "leakage halos" on a regional or areal scale, including shear zones, fault breccia, fracture fillings, quartz veins, alteration zones, jasperoid, etc. Geochemical maps and sections derived from this type of survey should be carefully analyzed and favourable areas subjected to detailed lithochemical surveys mentioned in (F).

4. Reference: Boyle, R.W., 1982. Geochemical methods for the discovery of blind mineral deposits; Part 1, Bull. Can. Inst. Min. Metall., v. 75, no. 844, p. 123-142. Part 2, Bull. Can. Inst. Min. Metall., v. 75, no. 845, p. 113-132.

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(F) Types of detailed lithochemical surveys

1. Analyses of materials of all "leakage halos" as in (3) in Table E. Detailed overlay geochemical plans (maps) and sections should be constructed on data from these analyses, compared with geological, and geophysical data, and drill sites selected.

2. Analyses of rocks on profiles across shears zones, stockworks, etc. utilizing gold and its indicator elements in Table D. Such surveys are best utilized in searching for extensions of known gold-silver orebodies but may also be useful in virgin terranes. Use of chemical data overlays on geological plans (maps) and sections is recommended.

3. Analyses of rocks on profiles across shear zones, stockworks, etc. utilizing major elemental ratios, e.g., K/Na, SiO_2/CO_2, etc.: Such surveys are best utilized in searching for extensions of known gold-silver orebodies but may also be useful in virgin terranes. Use of chemical data overlays on geological plans (maps) and sections is recommended.

4. The three geochemical methods described above are particularly useful in searching for blind gold-silver orebodies.

5. Reference: Boyle, R.W., 1982. Geochemical methods for the discovery of blind mineral deposits; Part 1, Bull. Can. Inst. Min. Metall., v. 75, no. 844, p. 123-142. Part 2, Bull. Can. Inst. Min. Metall., v. 75, no. 845, p. 113-132.

WORKSHOP - PROSPECTING FOR GOLD AND SILVER DEPOSITS

(G) Types of pedochemical surveys

1. Near surface pedochemical surveys utilizing samples of soil, till, etc. and/or mineral separates (heavy minerals) from these materials: In some terranes the A (humic) horizon is the best for sampling; in others the B horizon. Panning (heavy mineral) surveys of the C horizon are recommended for most auriferous districts.

2. Deep overburden surveys utilizing near bedrock unconsolidated materials and/or mineral separates (heavy minerals) from these materials: In terranes heavily covered with till, gravel or glacial clay surveys of this type are recommended. Deeply lateritized terranes should be similarily surveyed. Heavy mineral (panning) surveys of near surface laterites may produce good results in some auriferous districts.

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(H) Types of hydrochemical surveys

1. Water (underground, spring, surface, snow): In general water surveys are not recommended using gold as an indicator unless very sophisticated analytical procedures are employed (e.g., resins, neutron irradiation, etc.). However, certain other indicators (e.g., Cu, Zn, As, Mo, U, etc.) may be useful in water surveys for localizing auriferous and argentiferous deposits. All springs should be sampled when found in an auriferous and/or argentiferous district. Similarily, spring precipitates (limonite, wad, carbonates, siliceous sinter, etc.) should be sampled. Regional and detailed spring survey maps may be useful in localizing auriferous (argentiferous) shear zones, zones of saddle reefs, etc.

2. Drainage sediments (stream, river, lake): Gold should be used as an indicator in these types of surveys, especially when 3 below is employed. Specific indicators (pathfinders) for both gold and silver are As, Sb, Te, Tl, B, F, Cu, Zn, Pb, Hg, W, U, and Mo.

3. Heavy minerals from drainage sediments (panning): These types of surveys are probably the best way to prospect for auriferous deposits. Use gold as the specific indicator. Other pathfinder elements may also be of use, especially As, Sb, Te, Tl, B, F, Cu, Zn, Pb, Hg, W, U, Mo.

4. Precipitates on stream sediments (limonite coatings, wad crusts, etc.): These are useful if properly employed. Use gold as an indicator as well as the other specific indicators (As, Sb, Te, Tl, B, F, Cu, Zn, Pb, Hg, W, U, Mo).

5. Precipitates at spring orifices (limonite, wad, silica-alumina gels, etc.): Maps of spring locations with data covering spring precipitate type and concentration of indicator elements (Au, Ag, As, Sb, Te, B, F, Cu, Zn, Pb, Hg, W, etc.) should be prepared as geochemical overlays on geological and geophysical maps.

WORKSHOP - PROSPECTING FOR GOLD AND SILVER DEPOSITS

(I) Types of biogeochemical surveys

1. Geobotanical: Requires specialized personnel in botany, although certain indicator plants can be easily recognized after brief training of field personnel. There are no specific indicator plants for gold or silver; certain ancillory indicator plants such as those for S, Se, Cu, Zn, etc. may be useful. Pilot surveys are strongly recommended before geobotanical surveys are utilized. Toxic (chlorotic) effects in plants due to superabundance of such elements as Ni, Cr, S(SO_4), etc. may be useful for indicating general mineralization.

2. Analyses of plants and animals: Surveys of this type have proven useful in desert and semi-desert terrains. They may also be useful in other types of terranes, although extensive data on their efficacy is not available. The best indicators of auriferous and argentiferous deposits are Au, Ag, As, Sb, Te, Tl, W, U, and Mo.

3. Analyses of fossil residues (coal, bitumen, thucholite, anthraxolite, etc.): It should be borne in mind that the largest gold deposits known (the Witwatersrand) have a fossil carbon (thucholite) signature. When bitumen, thucholite, antraxobite, etc. are found in a district they should be analyzed for Au and Ag and their pathfinder elements. Certain coal beds are slightly auriferous in some Mesozoic and Tertiary terranes.

4. Analyses of humic horizons of soil and till profiles: Surveys based on humus samples are more indicative of auriferous and argentiferous mineralization in some districts than those based on samples from other soil horizons. Pilot surveys are recommended before using the A (humic) horizon as a sampling horizon.

5. Analyses of bogs and other wet-site bodies: Certain bogs and marshes are greatly enriched in U, Cu, Zn, and other metals in metalliferous zones. Some bogs and other wet-site deposits may reflect the presence of argentiferous deposits as a result of their Ag, As, Sb, Cu, and U content. Auriferous bogs are uncommon, although some are known where the gold content exceeds 1 ppm and more. The gold in such bogs is apparently present as an uncharacterized gold-organic compound.

6. Analyses of termite and ant hills, gopher and groundhog mounds, etc.: The spoil thrown up by termites, gophers, etc. may contain higher than average contents of Au, Ag, and their pathfinder elements. Such hills and mounds should always be analyzed when found during pedochemical and other types of geochemical surveys.

7. References:

Brooks, R.R., 1972. Geobotany and Biogeochemistry in Mineral Exploration; Harper and Row, London, 290 p.

Brooks, R.R., 1983. Biological methods of Prospecting for Minerals; John Wiley & Sons, New York, 322 p.

WORKSHOP - PROSPECTING FOR GOLD AND SILVER DEPOSITS

(J) Types of atmochemical surveys

1. He and Rn associated with gold deposits containing U and Th: Various types of auriferous (argentiferous) deposits have associated uranium and thorium signatures. These include deposits ranging from Proterozoic to Tertiary in age (e.g., Witwatersrand; Jabiluka, N.T., Australia; certain Tertiary deposits). Some native-silver Ni-Co arsenide deposits have associated pitchblende. All such deposits are indicated by He and Rn. Long integrating detection systems (e.g., Track-Etch) are recommended for surveys utilizing He and Rn. Reference: Boyle, R.W., 1982. Geochemical prospecting for thorium and uranium deposits; Elsevier, Amsterdam, 498 p.

2. S, Se, H_2S, CH_4: Little data are available on methods employing these elements and compounds as indicators. All require further research as regards detection of auriferous (argentiferous) mineralization.

3. Particulate surveys (Airtrace, Surtrace, etc.): Further research is required as regards detection of auriferous (argentiferous) mineralization.

WORKSHOP - PROSPECTING FOR SILVER

ABSTRACT

SILVER DEPOSITS AND GEOCHEMICAL METHODS OF THEIR DISCOVERY

by

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

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

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

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

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

1. Copper-silver shale deposits (Kupferschiefer type).
2. Disseminations in sandstones ('red bed' type).
3. Silver-bearing skarn type deposits.
4. Lodes, veins, etc. dominantly in sedimentary rocks.

5. Silver-gold and gold-silver veins in or associated with volcanic flows, tuffs, etc.

6. Silver deposits in a complex geological environment comprising sedimentary rocks, volcanic rocks, etc.

7. Native silver-Ni-Co arsenide-sulphide deposits in a complex geological environment.

8. Miscellaneous sources: these include all gold deposits, Ni-Cu ores, massive sulphide bodies, polymetallic vein and lode deposits, kuroko ores, porphyry Cu-Mo deposits, and certain types of uranium (pitchblende) deposits.

Most of the world's production of silver is obtained as a byproduct of the deposits mentioned in 8 above; a small production (<5 percent) comes from the native silver-Ni-Co arsenide-sulphide deposits.

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

Practically all the geochemical methods of prospecting are applicable in the search for silver deposits. The most effective methods are those based on the sampling of drainage sediments and soils. Heavy mineral surveys based on drainage sediments and soils are useful in most terranes, and lithochemical, hydrochemical, and biogeochemical are applicable in certain terranes.

Silver is a good indicator of argentiferous deposits; other specific indicator (pathfinder) elements for silver are (Ba), (Co), (Ni), Cu, Zn, Cd, (Au), Pb, As, Sb, Bi, (U), (Se) and (Te). Those in parentheses are useful only for certain types of deposits.

Reference

Boyle, R.W.
1968: The geochemistry of silver and its deposits (with notes on geochemical prospecting for the element); Geol. Surv. Canada, Bull. 160, 264 p.

WORKSHOP - PROSPECTING FOR GOLD

ABSTRACT

GOLD DEPOSITS AND GEOCHEMICAL METHODS OF THEIR DISCOVERY

by

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Gold is a member of Group 1B of the Periodic Table, which includes copper, silver and gold. In its chemical reactions gold resembles silver in some respects, but its chemical character is markedly more noble. The principal oxidation states of gold are + 1 (aurous) and + 3 (auric). These states are unknown as aquo-ions in solutions, the element being present mainly in complexes of the type $[Au(CN)_2]^-$, $[AuCl_2]^-$, $[Au(OH)_4]^-$, $[AuCl_4]^-$, and $[AuS]^-$. There is only one naturally occurring isotope of gold: ^{197}Au.

In nature gold occurs predominantly in the native state or as a major constituent of various alloys containing mainly silver, copper or platinoid metals. Several gold and gold-silver tellurides are known of which the most common are sylvanite, calaverite, petzite, krennerite and nagyagite. The antimonide, aurostibite, $AuSb_2$, occurs as a hypogene mineral in some auriferous deposits, and there is also a selenide, fischesserite, Ag_3AuSe_2, a sulphide, uytenbogaardtite, Ag_3AuS_2, and a bismuthide, maldonite, Au_2Bi, which is fairly well differentiated. The principal ore minerals of gold are the native metal, aurostibite and various tellurides.

The abundance of gold in the upper lithosphere is approximately 0.005 ppm and the Au/Ag ratio is about 0.1. The average gold content of igneous-type rocks in parts per million is - ultrabasic (0.004), gabbro-basalt (0.007), diorite-andesite (0.005) and granite-rhyolite (0.003). The average gold content of sedimentary rocks in parts per million is - sandstone and conglomerate (0.03), normal shale (0.004) and limestone (0.003). Certain graphitic shales, sulphide schists, phosphorites and some types of sandstones and conglomerates may contain up to 2.1 ppm Au or more.

The average gold content of soils is 0.005 ppm, and the average for natural fresh waters is 0.00003 ppm. Sea and ocean waters contain an average of 0.000012 ppm Au. Gold is a trace constituent of many plants and animals. Some coals are slightly enriched in gold with 0.05 to 0.1 ppm Au in the ash.

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 deposits, exploited mainly for gold, can be distinguished:

1. Auriferous porphyry dykes, sills and stocks; coarse-grained granitic bodies, aplites and pegmatites.
2. Carbonatites and carbonatite-related bodies.

undergone radical chemical reworking during subsequent diagenetic and metamorphic events.

The oxidation processes in gold deposits are complex and depend essentially on the Eh and pH. Colloidal and coprecipitation phenomena also play a large part. Iron and manganese minerals and carbonates in the gangue and ore greatly influence the reactions that lead to the secondary enrichment of the element. Gold is not easily solubilized in nature, and its soluble forms are readily reduced to the metal by a great variety of natural materials. The result of this behaviour is that the only common gold mineral found in the oxidized zones of auriferous deposits is the native metal. In this form it ultimately collects in both eluvial and alluvial placers, which have been exploited throughout the world since time immemorial.

Practically all the geochemical methods of prospecting are applicable in the search for auriferous deposits. The most effective methods appear to be those based on the sampling of stream and lake sediments, glacial till and soils, analyzing these materials directly or analyzing heavy mineral separates obtained from them. Biogeochemical methods involving the analysis of plants should also prove useful in some terranes. The analysis of humus is effective where this material is well developed on soils and glacial materials. Lithochemical methods, utilizing gold and its indicator elements, and based on primary leakage halos, are useful where outcrops are plentiful in a mineralized belt. Gold is a good indicator of auriferous deposits; other specific indicator (pathfinder) elements for gold are Ag, As, Sb and Te.

Reference

Boyle, R.W.
1979: The geochemistry of gold and its deposits (together with a chapter on geochemical prospecting for the element); Geological Survey Canada, Bull. 280, 584 p.

3. Auriferous skarn-type deposits.
4. 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.
5. 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.
6. Gold-silver and silver-gold veins, lodes, stockworks, silicified zones, etc. in a complex geological environment, comprising sediments, volcanics and igneous or granitized rocks.
7. Disseminated stockwork gold-silver deposits in igneous, volcanic and sedimentary rocks.
    (a) Disseminated and stockwork gold-silver deposits in igneous bodies.
    (b) Disseminated gold-silver and silver-gold 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.
8. Gold deposits in quartz-pebble conglomerates and quartzites.
9. Eluvial and alluvial placers.
10. Miscellaneous sources: These include Ni-Cu ores, massive sulphide bodies, polymetallic vein and lode deposits, kuroko ores, porphyry Cu-Mo deposits, and certain types of uranium (pitchblende) deposits.

The quartz-pebble conglomerate deposits provide 50 percent or more of the world's production of gold. The other deposits, mainly the vein and disseminated types, eluvial and alluvial placers and the various polymetallic veins, lodes, massive sulphide bodies and stockworks (byproduct gold) provide the remaining 50 percent of the production.

The epigenetic vein, lode, stockwork and disseminated types of gold deposits appear to have originated mainly by metamorphic secretion processes, the source rocks of the gold and its associated elements being mainly in the enclosing volcanic and/or sedimentary piles. Modern gold placers are of sedimentary origin, the gold being winnowed into pay streaks as the result of both chemical (accretion) and physical (gravity) processes operating during weathering and subsequent sedimentation. The auriferous quartz-pebble conglomerate deposits appear to have originated as placers, the gold and many of its associated elements having

MINERAL EXPLORATION

Geochemical methods for the discovery of blind mineral deposits

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PREFACE

This paper comprises two parts. The first part discusses lithochemical surveys based on major, minor and trace elements in whole-rock samples from primary enveloping halos. The second part continues with discussions of surveys based on leakage halos, zonation of elements, stable and radioactive isotopic distributions, geothermometric, geobarometric, thermoluminescent, pedochemical, hydrochemical, atmochemical and biogeochemical methods. A selected bibliography follows the second part of the paper.

ABSTRACT

Areal (two-dimensional) geochemical surveys, based mainly on secondary dispersion halos and trains in media such as surface waters, soils and drainage sediments, have proven particularly successful in recent years and have greatly assisted in the discovery of a large number of varied mineral deposits. Three-dimensional surveys based on primary halos and leakage halos have received relatively little attention by research organizations and the mineral industry. Such surveys offer many novel approaches for discovering blind mineral deposits deeply buried below overburden or within their host bedrocks.

This paper reviews detailed methods for the discovery of blind mineral deposits based on sampling rocks (lithochemical methods), soils and other types of overburden (pedochemical methods), waters (hydrochemical methods), gases (atmochemical methods) and biological materials (biogeochemical methods). All are applicable to the discovery of blind deposits; the efficacy of each or in combination depends essentially on the type of mineralization, the extent of the development of the primary and secondary dispersion halos, and the finances available for sampling techniques employing overburden drilling, bedrock drilling, and sophisticated water, gas and vegetation collection.

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Dr. R.W. Boyle is a special projects officer with the Resource Geophysics and Geochemistry Division of the Geological Survey of Canada. A native of Wallaceburg, Ontario, he received his Ph.D. from the University of Toronto in 1953 and since then has been a member of the Geological Survey and former head of its Geochemistry Division.

Dr. Boyle's geochemical and geological work has taken him to many parts of Canada and has included research on the gold deposits at Yellowknife, the lead-zinc-silver deposits of Keno and Galena Hills, Yukon, the barite-sulphide deposits of Walton, Nova Scotia, and the sulphide deposits at Bathurst, New Brunswick, for all of which he has authored or co-authored significant monographs. In addition, he has carried out geochemical prospecting research in Yukon, Northwest Territories, Nova Scotia, New Brunswick and at Cobalt, Ontario. For his study on the geochemistry of gold, Dr. Boyle visited and worked in many part of the world, including Bulgaria, Eire, Fiji, Finland, Great Britain, Greece, Japan, New Zealand, Norway, Sweden, and the U.S.A. and U.S.S.R.

Dr. Boyle is a Fellow of the Royal Society of Canada, the Royal Canadian Geographical Society and the Geological Association of Canada, and a member of several national and international professional societies. In 1966, he received the Barlow Medal of The Canadian Institute of Mining and Metallurgy, and in 1971 the Willet G. Miller Medal of the Royal Society of Canada and the Public Service of Canada Merit Award. During the second world war, he served overseas as an artillery officer with the Royal Canadian Artillery.

Keywords: Exploration, Geochemical exploration, Mineral deposits, Blind mineral deposits, Metallogenic provinces, Lithochemical methods, Enveloping halos, Leakage halos, Carbonatites, Pegmatites, Skarn, Hornfels, Vein deposits, Massive sulphides, Carbonate-hosted deposits, Porphyry deposits.

PART 1

Introduction

Geochemical prospecting methods have gained acceptance by modern mineral explorationists principally because of their efficacy and economy in discovering mineral deposits. For instance, on a global basis in the last ten years some 20 major producing deposits and an equivalent or greater number of smaller deposits, ranging from porphyry and massive sulphide types to gold-silver veins and pegmatites, have been discovered by geochemical methods (Boyle, 1979b). This is a significant record considering the youth of the exploration method, one that only came into general use by industry some twenty years ago.

Nearly all of the deposits discovered to date by geochemical methods occur at or near the surface and were indicated and pin-pointed by secondary dispersion halos(1) or trains in drainage sediments, waters, soils and vegetation. In essence, the surveys that located these deposits were areal, that is, two-dimensional in nature. Three-dimensional surveys based on primary halos(1), especially leakage halos, as yet little utilized in exploration, offer many novel approaches for discovering blind deposits within the country rocks or deeply buried by overburden. The intention of this paper is to review and give some examples of detailed geochemical prospecting methods for discovering blind mineral deposits, particularly those based on rocks (lithochemical methods), soils and other types of

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(1) In this paper, primary dispersions and halos are considered to be coeval or nearly so with the mineralizing processes that produced the orebodies. Secondary dispersions and halos are those associated with supergene or other processes (e.g. radioactivity) following deposition of the orebodies.

MINERAL EXPLORATION

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PART 2

EDITOR'S NOTE

Part 1 of this paper, published in the August issue, covered lithochemical surveys based on major, minor and trace elements in whole-rock samples from primary enveloping halos.

Part 2, which follows, continues with discussions of surveys based on leakage halos, zonation of elements, stable and radioactive isotopic distributions, and geothermometric, geobarometric, thermoluminiscent, pedochemical, hydrochemical, atmochemical and biogeochemical methods. It concludes with a selected bibliography.

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Surveys Utilizing Leakage Halos

Leakage halos can be used as scalar or vector quantities in the search for deeply buried blind mineral deposits. In the first case, the occurrence of a leakage halo (e.g. a small pitchblende seam) may simply indicate the possible presence of pitchblende mineralization or orebodies; in the second case, the areal or three-dimensional distribution of leakage halos may, by their increasing frequency and/or increasing metallic or gangue element content, provide a means of vectoring in on loci of mineralization and orebodies. Examples of both cases are given in the following text.

Leakage halos are of many types, as shown in Figure 2 (Part 1), and are best discussed with respect to their associated mineral deposits. Furthermore, it should be noted that leakage halos are frequently offshoots or extensions of enveloping halos. Where this occurs, careful tracing of the leakage halo(s) downward or upward respectively will often lead to the apex or nadir (bottom) of the enveloping halo(s) and ultimately to mineralization or ore (Fig. 2).

Carbonatites

These bodies are marked by a number of indicators and leakage halos related to or associated with niobium, rare earth, copper and other types of mineralization in these complexes. General indicators include particularly the presence of a variety of silica-undersaturated rock types such as picrite porphyries, syenites, nepheline syenites, ijolites, damkjernites, feldspathoid lamprophyres and monchiquites in the form of ring dykes, radiating dykes, breccia pipes, sills and irregular bodies. Associated with these is usually a halo of fenitization in the country rocks (Fig. 3, Part 1) ranging from 2 m to 2 km or more in width and characterized by networks of veinlets of feldspars, feldspathoids, alkali amphiboles, alkali pyroxenes and biotite, seams and veinlets with higher than normal radioactivity, and disseminated molybdenite in places. In addition to these general indicators and leakage halos, more specific members of the latter, in both the complexes and their host rocks, include rare-earth-bearing carbonatite dykes and veins, siderite veins, rhodochrosite veins and disseminations, siderite-barite - rare earth carbonate veins, pyrrhotite veins, chalcopyrite-bornite-carbonate veins and seams, apatite-carbonate veins, barite-magnetite veins, and massive barite veins with or without strontianite. The more radioactive carbonatites may be marked by leakage halos comprising faults, fractures and shears characterized by anomalous dispersions of He, Rn and the daughter elements of thorium and uranium, particularly radium and radiogenic lead. Some carbonatite complexes are

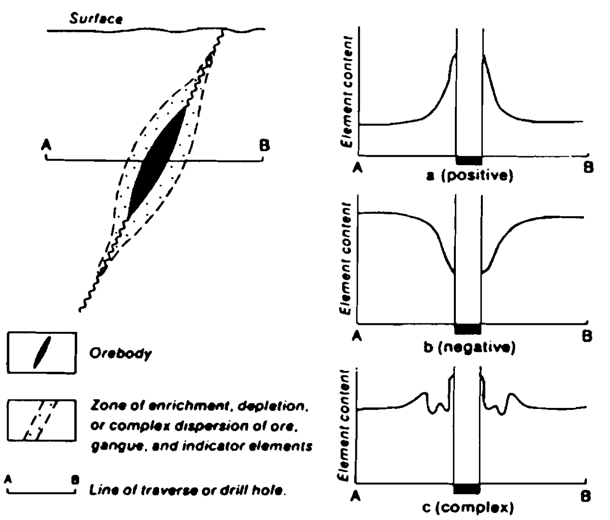


FIGURE 1. Diagram with profiles illustrating the nature of enveloping halos: (a) positive (additive) type; (b) negative (subtractive) type; and (c) complex type.

overburden (pedochemical methods), waters (hydrochemical methods), gases (atmochemical methods) and biological materials (biogeochemical methods). Before proceeding to these topics, however, short discussions are given in the following text on geochemical and metallogenic provinces and elemental indicators (pathfinders) for mineralization, subjects that are of importance in the planning of surveys based on primary halos and in the interpretation of results obtained from such surveys.

There is a large literature on the art and science of prospecting for blind mineral deposits that goes back a century or more. Most of the early work, based mainly on geological and mineralogical concepts, is summarized by Forrester (1946) and by McKinstry (1948) in his classic *Mining Geology*. Likewise, the literature on prospecting for blind mineral deposits utilizing geochemical methods and techniques is extensive; general reviews and papers of particular interest include those by Boyle and Garrett (1967), Sakrison (1971), Cameron *et al.* (1971), Shipulin *et al.* (1973), Smirnov (1976), Beus and Grigorian (1977), Sopuck *et al.* (1980), Rose *et al.* (1979), Govett and Nichol (1979), and Levinson (1980). The last three contain extensive bibliographies.

Geochemical and Metallogenic Provinces

A strict definition of the term 'geochemical province' is difficult to formulate. For the purpose of this paper, a geochemical province can be defined as a segment of the earth's crust within which some or all of the groups, sequences or specific types of rocks report anomalous abundances (clarkes of concentration) of one or more elements. Provinces that have higher than normal abundances or clarkes of elements, as compared with the average terrestrial elemental abundances, can be termed positive geochemical provinces; those with lower abundances can be described as negative provinces. Metallogenic provinces are characterized by the presence of an unusual number of mineral deposits, signifying that mineralization processes have been active over these segments of the earth's crust at one or more periods of the earth's history.

The dimensions of metallogenic provinces are usually measured in tens or hundreds of kilometres, but some are thousands of kilometres in length and breadth, an example being the tin and tungsten provinces of eastern Asia. The dimensions of geochemical provinces cannot be stated with assurance, as few have been outlined by appropriate surveys. Some are probably of the same dimensions as metallogenic provinces; others are possibly more extensive.

Positive geochemical and metallogenic provinces are commonly coincident, but there are examples of terranes where this is evidently not the case. At our present state of knowledge, the relationships of negative geochemical provinces and metallogenic provinces are largely unknown and hence conjectural. Geochemical provinces can be effectively outlined by lithochemical surveys utilizing fresh unmineralized samples of their constituent rocks and comparing the data obtained with the crustal abundances of the elements in the various rock types. Metallogenic provinces are self-evident from the distribution and number of their mineral deposits; extensions of such provinces or unknown provinces can usually be defined by surficial geochemical surveys utilizing drainage sediments, waters, vegetation, etc.

This paper does not deal further with lithochemical surveys designed to outline geochemical provinces or segments of these provinces. It should be pointed out, however, that such provinces or segments of provinces frequently constitute the primary mega-halos in many geological terranes within which are found the more restricted primary halos intimately associated with mineralization. The background values for particular elements in the mega-halos may exceed the regional or general elemental abundance by factors as high as 5. However, fluctuations in these factors over short distances may be present, features that should be taken into account during the interpretative phase of lithochemical surveys. It has been demonstrated that some of the fluctuations in abundance of the elements in mega-halos are due to variations in sedimentation, crystallization of magmas and metamorphic phenomena; others are the result of secondary (epigenetic) infiltration and precipitation of elements in primary structures (porous zones, etc.) and secondary discontinuities (mylonitized, fractured, faulted, brecciated and sheared zones). Supergene processes which leach near-surface rocks of their mineral constituents and precipitate them at varying depths or remove them completely from the system likewise have an effect on the abundance of elements in mega-halos.

Elemental Indicators

Concentrations of only a single element rarely occur in mineral deposits. More generally, a suite of elements is concentrated in a particular deposit because of certain intrinsic chemical properties that depend essentially on their electronic constitution and hence their position in the Periodic Table. Among these elements are some which, because of their relative high abundance or their ease and economy of analytical determination, serve as indicators of or pathfinders for specific ore elements; examples being arsenic or antimony, both good indicators of the presence of gold and silver, nickel, commonly a pathfinder for platinum metals, lithium for tin, and so on (Boyle, 1974a).

Of particular interest among the indicator elements or compounds of mineralization are a number known to economic geologists as mineralizers, including especially H_2O, B, CO_2, S, Se, F, Cl, Br and I, which provide the ligands for the facile transport of ore elements in both epigenetic and syngenetic processes. Most of these mineralizers, to which may also be added elements such as He, Rn, Hg, As and Sb, are volatile or form volatile compounds. These characteristics endow the mineralizers and analogous elements with high migration capacities, features that result in their broad dispersion, mainly by diffusion, but also in many cases by mass transport, from the sites of mineralization, particularly along fractures, faults and shear zones (leakage halos) that radiate from the main foci of mineralization, and also laterally and vertically through the rocks adjacent to the sites of deposition (enveloping halos).

One or more of the mineralizer and analogous elements are universal in practically all types of mineral deposits, yet we have not employed them to full advantage in geochemical prospecting surveys, especially those designed to locate blind deposits. Two of the mineralizer elements, boron and fluorine,

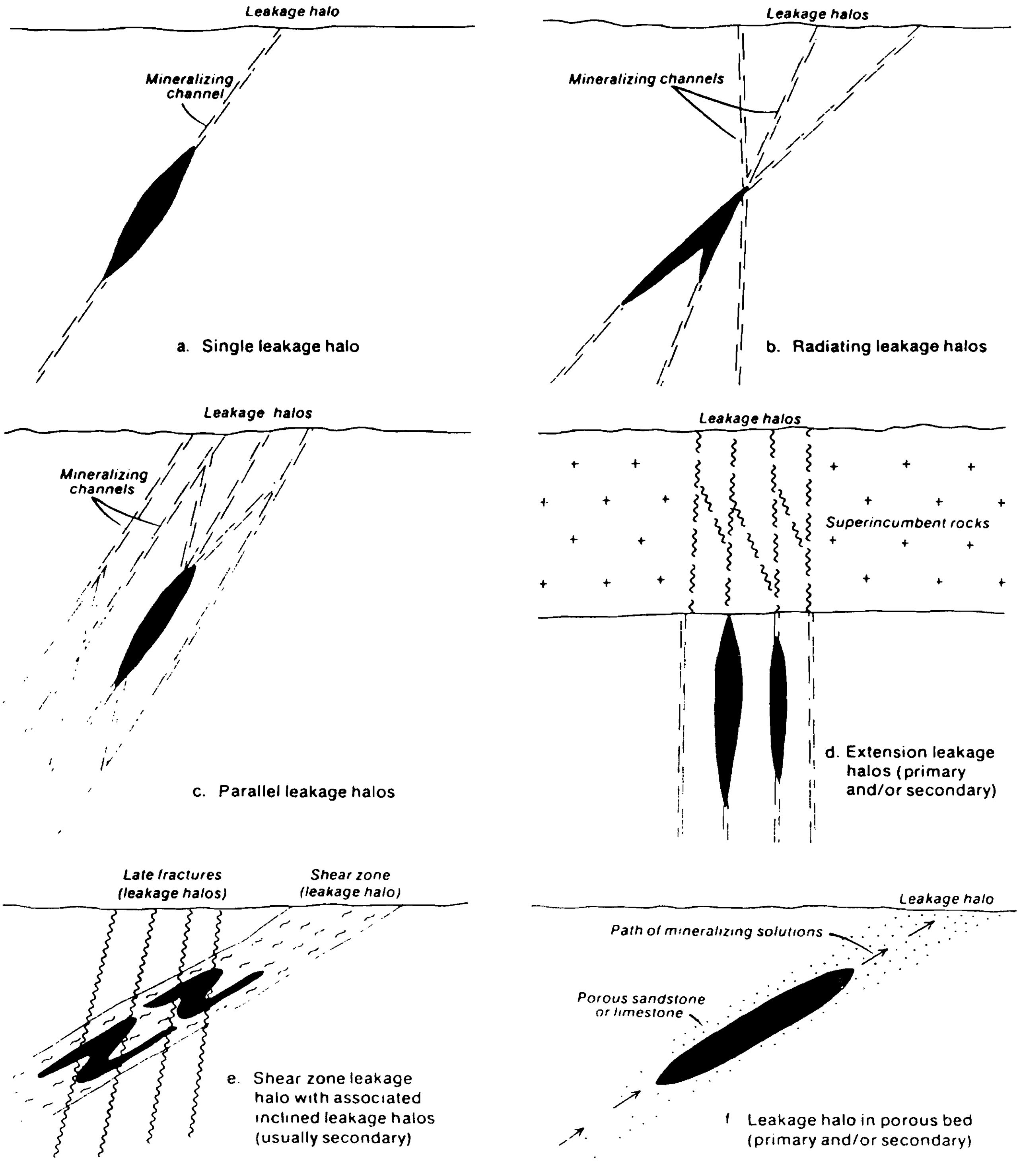


FIGURE 2. Diagrams illustrating the nature of some leakage halos. Orebodies are represented by solid black lenses.

are practically universal indicators of nearly all types of epigenetic deposits; where one is absent the other is usually present, and in many deposits (and/or their primary halos) both occur (Boyle, R.W., 1971; Boyle, D.R., 1976).

Lithochemical Methods

Lithochemical surveys designed to locate buried or blind mineral deposits are based essentially on primary halos. These are of two types—enveloping and leakage. Both serve a number of purposes in exploration, including (1) providing evidence of the presence of mineralization in an area, (2) marking the limits of mineralization, thus separating pregnant areas from those that are barren, (3) providing data for vectors that indicate progress toward or departure from the sites of mineralization and (4) most importantly, enlarging the target (orebody) sought.

Enveloping Halos

Enveloping halos mark a lithologic zone within which there is a primary dispersion of major, minor or trace amounts of ore or gangue elements (and/or indicator elements) adjacent to the deposits in question. Commonly these halos have a three-dimensional symmetrical outline about deposits, as shown in Figure 1; more generally, however, their morphology is irregular or discontinuous due mainly to the vagaries of the porous, fractured and brecciated patterns of the rocks contiguous to the sites of mineralization. The dispersive characteristics of elements and compounds within enveloping halos is usually complex, and zoning of elements both laterally and vertically is common in many types of deposits, as mentioned subsequently. Certain configurations of this zoning appear frequently and comprise positive (additive), negative (subtractive) and complex elemental distribution patterns best illustrated by the lateral profiles shown in Figure 1.

It should be noted that the terms additive and subtractive parenthesized above are generally used only in a descriptive sense. They are not intended to infer that the constituents were added to the wall rocks from mineralizing channels. Primary halos are usually complex and difficult to analyze with respect to the primary direction of flow of constituents. For example, in homogeneous, unfractured wall rocks an increase in a constituent toward a vein or lode site may indicate original movement of high concentrations of constituents from the mineralizing channels into the wall rocks; or alternatively it may indicate movement of constituents from the host rocks toward a dilatant zone (e.g. fracture, fault, breccia zone) and thus mark the frozen profile of a smooth buildup of diffusing ions at a precipitation front (i.e. the vein or lode site). Where the wall rocks are extensively fractured, an increase in constituents may indicate an increase in the number of small fractures as the vein or lode site (the main locus of fracturing) is approached. In this case again the constituents may have migrated from the main channel into all the subsidiary channels; or alternatively diffusion of constituents toward and into the vein or lode site from the host rocks may have resulted in the filling of the principal fractures as well as all of the small subsidiary ones. The subtractive halos may indicate that constituents moved toward and into the vein or lode sites; or alternatively that they were widely dispersed into the wall rock beyond the halo. The genesis of enveloping halos is really not the problem in geochemical prospecting, although it is advantageous to have an idea as to how each halo was produced. Empirically, it is known that some deposits have specific types of enveloping halos, whereas others have different types.

Leakage Halos

Leakage halos, marked by the presence of trace or minor amounts of ore and/or gangue elements (and indicator elements), record the passage of mineralizing media (gases, solutions, diffusion currents) along porous beds or structures such as faults, shears, breccia zones, mylonitized zones and fractures. Such primary mineralizing media may have deposited orebodies in certain places, in others only non-productive mineralization. Secondary processes may also produce leakage

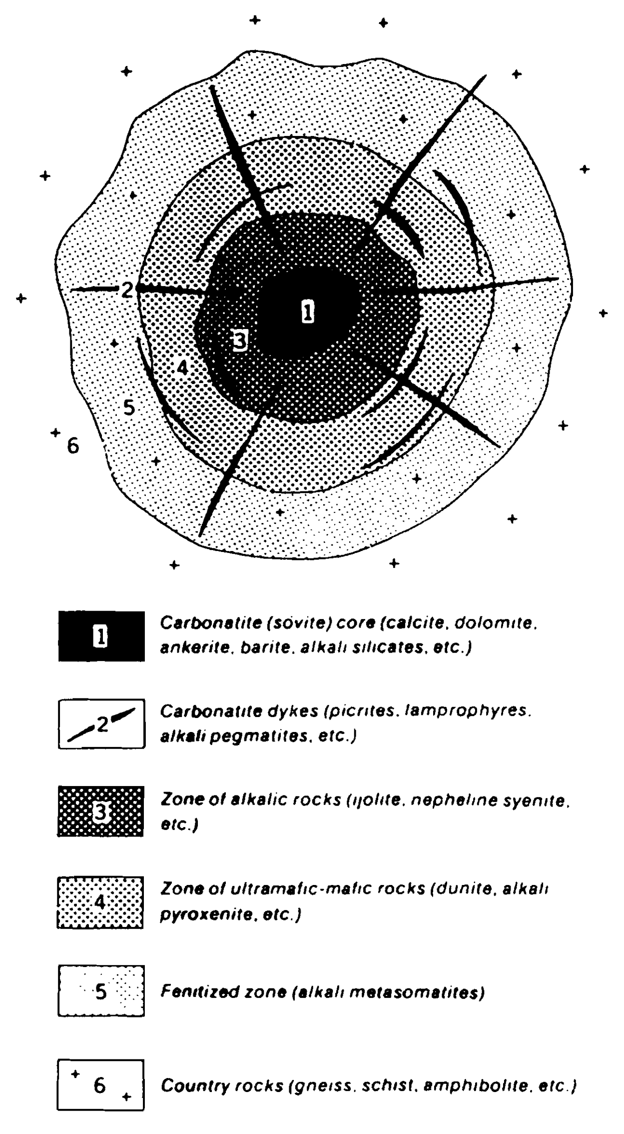


FIGURE 3. Diagram illustrating the idealized zonation of ring-type carbonatite complexes.

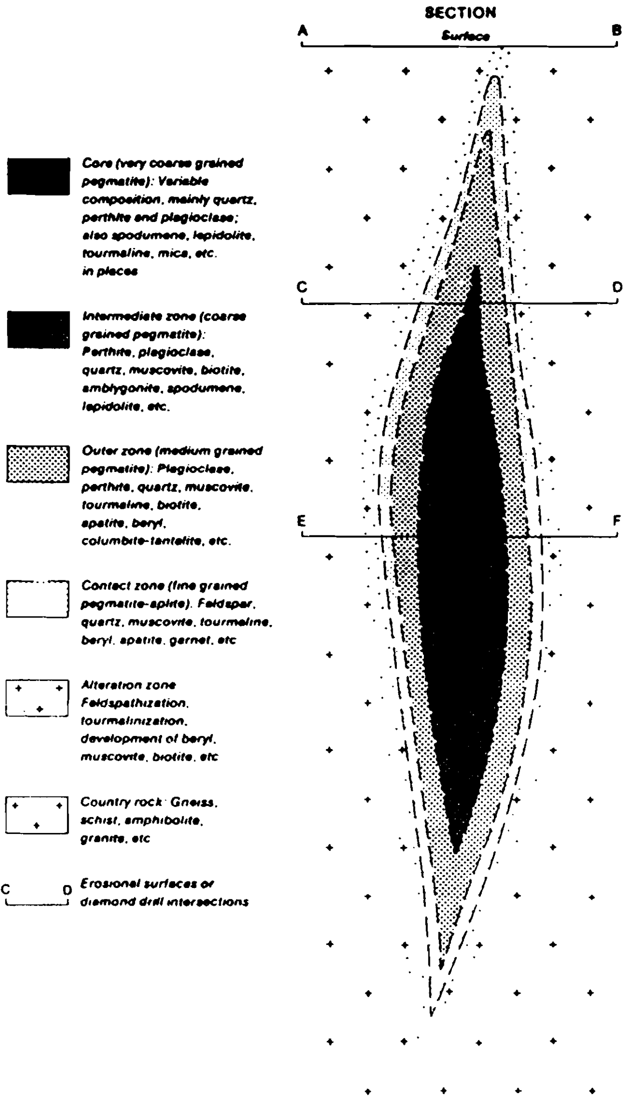


FIGURE 4. Diagrammatic section illustrating the idealized zonation of a complex pegmatite.

halos, an example being the escape upward or laterally along late faults and fractures of the daughter products, radon and helium, from the decay of their parents, uranium and thorium, in underlying primary (or secondary) deposits. The escape of radon, for instance, leaves a trail of radiogenic lead along the faults and fractures which can be readily traced by isotopic analyses. In addition, other elements and minerals may be precipitated from late-stage hydrothermal waters, metamorphic waters or ground waters traversing deposits and migrating vertically or laterally along the leakage structures. Leakage halos can, therefore, be classified broadly as primary and secondary. Among these, several common types can be recognized, as follows:

1. Single fracture channelways leading to or away from the foci of mineralization or orebodies (Fig. 2a).
2. Radiating fault, shear, breccia or fracture zone systems associated with the sites of mineralization orebodies (Fig. 2b).
3. Parallel fault, shear, breccia or fracture zone systems associated with sites of mineralization or orebodies (Fig. 2c).
4. Extension leakage halos (Fig. 2d).
5. Fault, shear, breccia or fracture zone systems inclined to or cutting the zones of mineralization or orebodies (Fig. 2e).
6. Porous beds or other conductive features and structures extending to or from the foci of mineralization (Figs. 2e and f).
7. Complex leakage halos comprising alteration zones, replacement zones, fractures, faults, dykes, etc. associated with carbonatites (Fig. 3) and pegmatites (Fig. 4); and alteration zones, brecciated zones, shear zones, and post-mineral faults and fractures associated with mineralized stockworks (Fig. 6).

Leakage halos may be laterally and vertically zoned in a

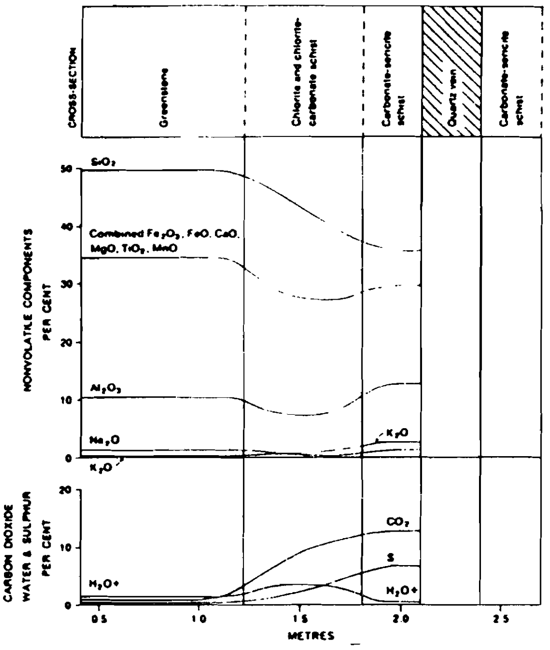
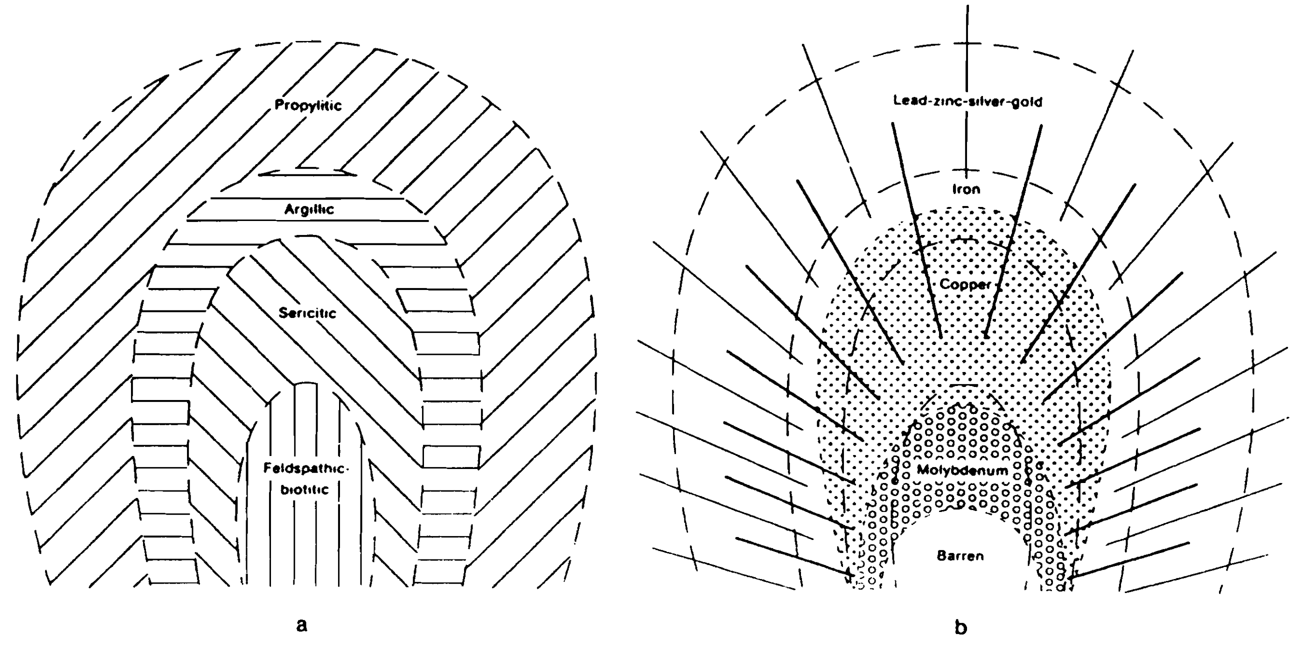


FIGURE 5. Typical profiles of the chemical changes resulting from alteration of greenstone, Negus-Rycon System, Yellowknife, Northwest Territories (after Boyle, 1961).



ALTERATION ZONE	INDEX MINERALS
Propylitic	*Chlorite, epidote group plagioclase quartz, carbonates (actinolite) (zeolites)*
Argillic	*Clay minerals quartz*
Sericitic	*Sericite quartz (anhydrite) (carbonates)*
Feldspathic-biotitic	*K-feldspar biotite quartz (anhydrite) (carbonates)*

SULPHIDE ZONE		INDEX MINERALS
Lead-zinc silver-gold	\ | /	*Sphalerite, galena, Ag-sulphosalts (gold)*
Iron (pyrite)	\ | /	*Pyrite, (magnetite) (pyrrhotite)*
Copper	∴	*Chalcopyrite, bornite chalcocite, (enargite)*
Molybdenum	○○	*Molybdenite, (wolframite)*
Barren (low grade)		*Magnetite, pyrite (molybdenite) (wolframite)*

GSC

FIGURE 6. Diagrams illustrating (a) the alteration zoning and (b) the sulphide zoning in disseminated and stockwork (porphyry) copper and molybdenum deposits. Modified in part from Guilbert and Lowell (1974), Bray and Wilson (1975), and others.

TABLE 1. Characteristic types of wall-rock alterations associated with epigenetic mineral deposits

Type of Deposit	Principal Wall-Rock Alterations	Characteristic Chemical Exchanges
Carbonatites	Fenitization (development of nepheline, Na-K-feldspars, Na-pyroxenes, Na-amphiboles, apatite, fluorite, fluocarbonates)	Removal of SiO_2 and additions of Na, K, Fe, Mg, Ca, Ba, Sr, Ti, Nb, Zr, P, F and CO_2
Pegmatites	Feldspathization, tourmalinization, silicification, development of mica (frequently Li-bearing), biotitization of mafic minerals	General introduction of Na and/or K, Li, B, Be, rare earths, P, F and H_2O
Skarn deposits	Skarnification (development of Ca-Mg-Fe-Mn silicates), silicification, tourmalinization, epidotization, chloritization; development of serpentine and talc in places	Skarnification may be essentially isochemical with removal of CO_2; more generally, however, skarnification involves major introductions of SiO_2, Mg, Fe, B, F, Cl, S and H_2O and consequently extensive removal of CO_2
Vein and replacement deposits (tin, tungsten, beryllium, molybdenum)	Feldspathization, greisenization, silicification, sericitization, tourmalinization, argillization	Introduction of Na and/or K, Li, F, B, S, P, SiO_2 and H_2O. Some deposits show losses of Na and SiO_2 from the wall rocks
Vein and replacement deposits (gold, silver, uranium, base metals)	Chloritization, sericitization, carbonatization, silicification, pyritization, argillization, alunitization; hematitization in uraniferous deposits (propylitization)[1]	Introduction of H_2O, CO_2, S, As, etc. Introduction of Mg, Fe, etc. in certain deposits. Shifts in SiO_2/CO_2, K_2O/Na_2O, F^{2+}/Fe^{3+} and other ratios
Replacement and open space filling deposits (carbonate-hosted Pb-Zn deposits)	Dolomitization, silicification, pyritization	Shifts (usually decreases) in Ca/Mg ratio; addition of SiO_2; addition of S
Replacement deposits (massive base metal sulphides)	Chloritization, sericitization, pyritization, silicification (propylitization)	Replacement of Ca by Mg and Fe; replacement of SiO_2 and other components by sulphides; decreases of Ca and CO_2; additions of S and base metals
Disseminated and stockwork deposits (copper, molybdenum, gold, silver, tungsten)	Propylitization, argillization, sericitization, silicification, pyritization, feldspathization and biotitization	Shifts in K_2O/Na_2O, SiO_2/total volatiles, Al_2O_3/CaO, Fe^{2+}/Fe^{3+} and other ratios; increases in S, F, B, H_2O and CO_2 in many zones (see text)

Note: 1. Propylitization is an all-embrasive alteration term combining the effects of chloritization, argillization, carbonatization, pyritization, etc.

manner similar to the enveloping halos of their associated deposits; in particular they are commonly zoned elementally, with the more mobile elements progressively removed in space from the principal foci of mineralization.

Surveys Based on Primary Enveloping Halos

Sampling procedures during surveys utilizing primary enveloping halos are generally based on drill core or on bedrock traverses across the halos. In the case of the latter, surface sampling may be done on exposed bedrock or on short drill holes into bedrock, care being taken that only fresh (unoxidized) samples are taken; or underground sampling along crosscuts, drifts or other available openings may be carried out, similar precautions being taken to obtain fresh sample material. When drill core is utilized, continuous split core lengths, properly cleaned and washed, should form the sampling medium for analyses, care being taken to ensure that only fresh (unoxidized) samples are collected. On surface and underground traverses, channel sampling is advisable; the sample should be washed and cleaned of extraneous coatings, dust and so on. The sample lengths of drill core or channel samples should be determined and controlled by the geological character of the host rock and extent of the enveloping halos. Metre lengths of core or channel samples are generally satisfactory; in porphyry copper and similar types of stockworks, however, 10-metre or longer core lengths will suffice, whereas in other deposits, such as narrow veins, half-metre or shorter lengths may be required to outline a meaningful primary dispersion pattern.

Two general types of sampling media can be utilized in surveys based on enveloping halos: (1) whole rock chips or split core samples of the halos and their enclosing host rocks; and (2) mineral separates (e.g. pyrite, arsenopyrite, magnetite, garnet) obtained from samples taken in (1). Chemical analyses of the samples may include total or in some cases partial determinations of the major constituents and/or the minor and trace constituents. Analogous analytical procedures include those based on radioactivity (drill-hole logging) for thorium, uranium and their daughter products and ultraviolet lamping of samples and core for minerals such as scheelite.

Detailed procedures for core and channel sampling of the type discussed above are contained in Forrester (1946), McKinstry (1948) and Peters (1978), and the preparation of samples for chemical analyses and the separation of heavy mineral concentrates (pyrite, arsenopyrite, etc.) from powdered rock samples are described in detail by Lavergne (1965).

The dispersion patterns of elements in primary enveloping halos are generally complex and varied and depend essentially on the nature of the ore and gangue-forming medium, specifically its state (gas, liquid or diffusion current), its chemical composition, and its temperature and pressure. In addition, the type and nature of the host rocks play a major role, including particularly their initial porosity and permeability and similar induced features resulting from brecciation, fracturing, shearing, mylonitization, etc. The interaction of these two factors yields a variety of epigenetic deposits commonly characterized by specific wall-rock alteration phenomena. Space precludes any detailed account of these deposits, but five general types can be recognized: carbonatites, pegmatites, skarn deposits, vein and replacement-type deposits, including carbonate-hosted and massive sulphide deposits, and large complex mineralized stockworks typified by the so-called porphyry copper and molybdenum deposits. Certain types of deposits that may have an epigenetic component according to some geologists are omitted in this paper principally because of their controversial origin and a general lack of knowledge with respect to their primary halos, if in fact they possess such features. These deposits include the Kupferschiefer and similar copper shales and schists and the great gold-uranium and uranium-thorium quartz-pebble conglomerates respectively of the Witwatersrand in South Africa and the Elliot Lake area in Ontario. The so-called magmatic deposits, including the kimberlites, the apatite deposits associated with alkaline complexes, and the layered chromite and platinum metal deposits associated with ultramafic-mafic complexes, are also omitted because of lack of data concerning their primary halos. All of these varied deposits are usually considered to be essentially syngenetic in origin, although in this writer's opinion some have marked epigenetic aspects.

A knowledge of the wall-rock alteration phenomena attending the five types of deposits mentioned above is a prerequisite for the pursuance and interpretation of primary halo surveys, especially when major elemental constituents or their ratios in wall rocks are utilized as indicators of mineralization. A simplified version of the principal types of wall-rock alteration associated with the five types of deposits, together with comments on the principal chemical exchanges involved, are shown in Table 1. Details should be sought in the papers by Boyle and others, *in* Pouba and Stemprok (1970), and by Meyer and Hemley and Rose and Burt respectively *in* Barnes (1967, 1979).

Wall-rock alteration generally has a marked zonal distribution which may be both lateral and vertical with respect to the vein systems, breccia zones or other dilatant sites. Most of the research carried out on wall-rock alteration has emphasized the lateral variations, but there are a few cases where studies of the vertical distributions have been done. Unfortunately, the latter are rarely extensive enough to draw any generalized conclusions.

The most pronounced visual regularity in the lateral zonation of wall-rock alteration is the presence near the deposit of the most intense phase of the alteration, which fades outward through less intense phases into unaltered rock. This phenomenon is normal in most types of deposits, and is manifest by intense mineralogical and chemical changes adjacent to the deposit and consistent decreases in these changes outward from the deposit. In this writer's experience, this applies also to most stratabound massive sulphide deposits, although the interpretation of the zoning relationships is conjectural.

The regular lateral zonation adjacent to veins and other types of epigenetic deposits has been interpreted in two ways. One school holds that the zonation is contemporaneous or nearly so with the deposition of the ore and gangue minerals, and that it is due to an attenuation of the altering medium (solutions, gas or diffusion current) as it migrated outward from the fracture or other dilatant feature. The other school holds that the lateral zones outward from deposits are of different ages and are due to successive waves or pulses of altering media. Thus, the farthest-out zones are the earliest, the intermediate zones next oldest and the intensely altered phases adjacent to the deposits the very latest or the final stages of the mineralizing process. The example of gold-quartz veins attended by an adjacent pyrite-sericite-carbonate zone that fades laterally through carbonate-chlorite and chlorite zones into unaltered andesite will serve to illustrate the two divergent views.

According to the first school, the sequence is due to an attenuation of the mineralizing and altering medium as it migrated laterally from the dilatant zone (the site of the quartz veins). As this medium diffused outward, it reacted with the wall-rock minerals, most actively with those near the vein and decreasingly so with those farther out as the concentration of its constituents, particularly K, CO_2, S and H_2O, declined through reaction. This school supports its argument mainly by the bilateral symmetry of the zonation with respect to the veins.

The other school interprets the zonation as due to successive waves or pulses of altering media. According to them, the chlorite zone formed first by extensive introduction of water. Then followed a wave containing some CO_2 which superimposed a weak carbonatization on a part of the chlorite zone, and finally a wave greatly enriched in CO_2, K and S superimposed an intense sericitized, carbonatized and pyritized zone on the earlier chlorite-carbonate phase adjacent to the vein. This school supports its argument by various paragenetic relationships and by the fact that patches, veinlets and protuberances of the more intense phases are frequently seen in an apparent cutting relationship with the less-intense phases.

Only a few descriptions of vertical zonation of wall-rock alteration are recorded in the literature, and these are rarely extensive, mainly mineralogical and, with a few exceptions, give no detailed chemical analyses. This is probably because most studies of wall-rock alteration are rarely continued throughout the history of a deposit. Further research is, therefore, desirable on the features of vertical zonation, particularly from the chemical aspect, which should be aimed at material balance calculations with respect to additions and subtractions within the vertical expanse of entire vein systems and other types of deposits.

Certain gold-quartz and polymetallic deposits of Tertiary age exhibit extensive near-surface argillization with increasing propylitization at depth, but these effects depend to a large extent on the type of host rocks. According to some investigators (e.g. Sher *in* Pouba and Stemprok, 1970), the intensity of biotitization and development of actinolite increases with depth in some gold-quartz deposits, a phenomenon that is often related to the presence of granitic intrusives at depth. This feature can be seen in the Madsen Mine at Red Lake, Ontario. Other gold-quartz deposits show an increase in carbonatization and sericitization with depth, as shown by the writer at Yellowknife (Boyle, 1961). This extensive carbonatization has released large quantities of silica that probably migrated upward to form the quartz lenses at higher elevations. There are also brief references in the literature to increases and differences in argillic types of alteration with depth in a variety of vein-type deposits. Most of the great stockwork copper and/or molybdenum deposits exhibit vertical zonations in their alteration patterns, with propylitization near the surface followed successively downward by zones of argillization, sericitization, and feldspathization and biotitization (Fig. 6).

Ontoev (*in* Pouba and Stemprok, 1970) remarks on the vertical zoning in altered granites containing Mo-W deposits in the Transbaikal district of the U.S.S.R. Near the apex of the granites there is a broad greisenized zone which passes downward into microclinized and muscovitized granite, and this in turn into albitized biotite and muscovite granite. Similar zonations have been described and examined chemically in detail in the tin-tungsten-lithium-bearing granite cupola of Cinovec in the Krusne hory Mountains of Czechoslovakia by Stemprok and Sulcek (1969). A general discussion of the zonations in altered rocks associated with tin, tungsten, beryllium and other rare elements in a granitic milieu is given by Beus (*in* Pouba and Stemprok, 1970). Other references to vertical zonations in altered rocks are given in the text below.

One of the features of wall-rock alteration that merits emphasis is the tendency of dissimilar rocks to converge to a uniform type of alteration. This feature has been noted by numerous investigators and is evidently due to prolonged attack by the mineralizing medium. There are, for instance, numerous references in the literature of interbedded slates, greywackes, amphibolites and other quite dissimilar rocks being all converted to carbonate-sericite schists, and of quartz porphyries, tuffs and shales intensely altered to an asemblage of quartz, sericite and clay minerals. Silicification of carbonate rocks, shales and sandstones, likewise, yields a convergent type of alteration in some deposits that is indistinguishable with respect to the host rock except by very detailed studies. Such regularities in convergent phenomena are particularly favourable when surveys based on major elements and major elemental ratios are employed in the search for hidden orebodies.

Surveys Based on Major Elements and Their Ratios in Whole Rock Samples

Primary enveloping halos associated with most epigenetic deposits exhibit definite dispersion patterns of major elements and major elemental ratios. Surveys based on these patterns have two objectives—firstly to guide exploration in the broadest sense and thus, mainly on a geological basis, to predict the possible location of orebodies and secondly, in a more detailed sense, to predict the location of orebodies ahead of the bit, adit or drift. The first objective utilizes scalar quantities in the language of mathematics, examples being the presence of excess quantities of pyrite (high S content) at some point which may suggest a sulphide body nearby, or the appearance of sericitization or carbonatization at some point which may indicate mineralization in the general vicinity. The second objective assumes that vector quantities can be measured, examples being consistent increases in sulphur content (pyrite) along a drill hole toward an orebody or a progressive increase in the K_2O/Na_2O ratio (usually marked by an increase in sericitization) as an orebody is approached.

Illustration of surveys based on these two objectives utilizing major elements is best shown by examples.

Carbonatites

These bodies are extremely complex magmatic and hydrothermal assemblages of rocks in which four stages can usually be recognized: (1) an ultramafic followed by an alkalic magmatic phase; (2) a magmatic dyke phase; (3) a (magmatic?) carbonatite phase; and (4) a late hydrothermal phase. The third and fourth phases are marked by extensive replacement processes in some complexes. Orebodies in these complexes comprise four general types: apatite-magnetite, rare metal - rare earth (Nb, Ta, U, Th, Zr, Y, Ce, etc.), phlogopite and base metal (mainly Cu). Some carbonatites yield nepheline syenite, aluminum (from nepheline), vermiculite (alteration (hydration) of phlogopite), calcite (lime), barite, baddeleyite (ZrO_2) and other minerals as economic products. Most carbonatites are zoned and have a ring pattern, but the zonation is usually complicated and intricate (von Eckerman, 1948; Pecora, 1956; Rowe, 1958; Heinrich, 1966; Tuttle and Gittins, 1966; Bloomfield *et al.*, 1971; Smirnov, 1976; Kapustin, 1980). Figure 3 depicts the ideal zonation of ring-type carbonatites, but it must be emphasized that some zones may be absent in certain carbonatites; in others, the zone may be incomplete, displaced, transposed, superimposed and otherwise irregular, depending essentially on the magmatic, structural and hydrothermal histories of the bodies. In addition, certain carbonatite-like bodies and massifs are large tabular to irregular sheets, sills, dyke swarms or stockworks. Such vagaries make predictions of the location of mineralization in carbonatites difficult and exploration costly, features that dictate the utilization of all available geological, geophysical and geochemical knowledge concerning these bodies.

Apatite-magnetite orebodies in carbonatites comprise disseminations, lenses and streaks in practically all rock types, but particularly in the carbonatite (sovite) core and apophyses and in the ultramafic, alkali mafic and mafic metasomatites. The rare metal - rare earth concentrations have a widespread distribution, but most of economic value occur within the carbonatite core, in the zone of alkalic rocks or in the fenitized zone(s). The phlogopite (vermiculite) bodies occur most frequently in dolomitic carbonatite cores, in mafic dykes and in the zone of ultramafic-mafic rocks. Base metal orebodies appear to lie mainly in late fractured and faulted parts of the rocks of all zones. In some carbonatites, sulphides, mainly pyrite, pyrrhotite, chalcopyrite and molybdenite, are widely distributed as (indigenous) disseminations in the fenites and rocks of all zones of the complexes; in the great Palabora deposit in South Africa the chalcopyrite and bornite occur in a disseminated (indigenous) form in a number of rock types, but the main concentrations are in the fractured transgressive carbonatite (sovite) complex and in transgressive carbonate veinlets that cut several rock types (Palabora Mine geological and mineralogical staff, 1976).

Detailed chemical surveys based on the primary dispersion of major elements as an aid in locating orebodies in carbonatites have not been published, and it is thus difficult to draw exact conclusions about the efficacy of the method. However, numerous analyses of the rocks of carbonatite complexes are recorded in the literature from which it is possible to suggest some chemical approaches that should aid in vectoring in on orebodies.

Mineralization in carbonatite complexes occurs principally in the carbonate (carbonatite) phases, in the zone of alkalic rocks and in the fenitized zones, although it should be pointed out that certain types of economic mineralization, especially copper sulphides, are associated with late-stage fracturing and brecciation and may be found in practically any rock in all parts of the complexes. The carbonatite phases, as well as the alkalic and fenitized phases, were formed by, or are the result of reactions of rocks with fluids rich in CO_2, K and Na. In most fenitized zones, a marked increase in Na and/or K content is evident from the outer to inner zones; concomitantly, a progressive increase in CO_2 and a marked decrease in SiO_2 is noticeable, although in some fenite zones the former feature is often erratic. In the complexes proper, alkali (Na,K) metasomatism, carbonatization, desilication, hydration, and the introduction of S, P, Fe and other major elemental constituents are notably erratic, although with approach to certain types of orebodies (e.g. Cu, Fe, Nb, rare earths, phosphate), there is often a general increase in CO_2 and alkali content. With approach to carbonate (carbonatite) cores in some complexes, a noticeable increase in radioactivity is observable, the phenomenon resulting mainly from increasing contents of thoriferous and uraniferous monazite, bastnaesite, zircon, sphene, pyrochlore, and other similar zirconium, titanium and niobium minerals. Similar increases may be observed where radioactive minerals and rare earths are concentrated in the alkalic and other rock zones. Changes in the Th/U ratio may also be significant in some complexes, the ratio decreasing or increasing, depending on whether the mineralization is essentially uraniferous or thoriferous, with proximity to orebodies associated with the carbonatite cores and alkalic and other rock zones. Increase in the magnetic susceptibility with proximity to carbonatite cores or other rocks mineralized with Fe-Ti and Fe oxides is also a characteristic of many carbonatite complexes.

These features suggest that chemical methods, if used judiciously with good geological control, can be a valuable aid in defining the loci of mineralized zones within carbonatite complexes. For example, an increasing Na or K content and a decreasing SiO_2 content in fenitized gneisses, amphibolites, schists and other wall rocks should signal approach to the carbonatite complex and in some cases to mineralization in the fenitized zone. Within the complex proper, a progressive increase in the CO_2 content of the rocks and similar increases in elements such as S, P and Fe should respectively indicate approach to the carbonate (carbonatite) core containing sulphides (copper), rare earths, niobium, etc., and to bodies enriched in phosphorus (apatite) and iron (magnetite). Similarly, a progressive increase in radioactivity in diamond drill holes should signify approach to various types of mineralization containing the radioactive elements, viz. carbonatite cores, apatite zones, and mineralized sections of the alkalic and other rock zones. Use of the K_2O/Na_2O ratio, as discussed subsequently in the section on vein and similar deposits, is not recommended without preliminary studies of the patterns assumed by this ratio because approach to mineralization in some complexes is signalled by a decrease in the ratio, in others by an increase and in still others by no systematic change.

In summary, it would appear that the use of major elemental indicators, combined with trace-element work and surveys based on leakage halos as outlined below should greatly assist in locating mineralization ahead of the bit in carbonatite complexes and their associated fenitized zones. However, considerable geological knowledge of the carbonatite complex being investigated is a prerequisite before commencing chemical work, and where possible pilot surveys should be carried out to ascertain the patterns of elemental dispersion before embarking on large-scale drilling programs utilizing major elements as indicators of mineralization.

Pegmatites

These bodies can be classified into two general categories—simple and complex (Fersman 1931a, 1931b; Ellsworth, 1932; Cameron *et al.*, 1949). Both types have salic and mafic members, but only the salic type is considered here, principally because few of the mafic types have been investigated in any detail. The simple salic pegmatites contain essentially quartz, feldspars and mica; the complex salic types carry these minerals in addition to numerous others containing a variety of rare elements (viz. Li, Rb, Cs, Be, Nb, Ta, U, Th, etc.) in minerals such as spodumene, lepidolite, beryl, tantalite-columbite and uraninite. The simple pegmatites may be zoned or unzoned; the complex types are commonly zoned in the manner depicted in Figure 4. It should be emphasized, however, that the zoning in this figure is idealized; in nature great variation is observed, some zones being absent, others highly irregular, diffuse or displaced. In addition, some pegmatites are characterized by various types of fracture fillings and irregular, tabular, sheetlike or podlike replacement bodies that are localized principally within the confines of the pegmatite bodies or in their adjacent wall rocks. The fracture fillings are generally small and economically unimportant. The replacement bodies are usually composed of medium- to coarse-grained quartz, albite (cleavelandite), muscovite and the various rare-element minerals, and are restricted to structurally prepared, commonly shattered and brecciated, sites where they replace pre-existing minerals comprising the various zones of the pegmatites. Many of these bodies are economic, especially for the rare elements.

Many pegmatites exhibit little or no wall-rock alteration effects, the bodies being frozen against the wall rocks; other pegmatites, both the simple and complex types, display varying degrees of wall-rock alteration, including principally feldspathization (introduction of Na and/or K), development of mica (introduction of K and Li where muscovitization is prevalent and K, Li and Mg where biotite predominates), development of holmquistite and other lithium amphiboles, chloritization (hydration), tourmalinization (introduction of B and Mg), formation of beryl (introduction of Be, Rb, Cs, etc.) and development of pyrite and/or arsenopyrite. These introductions and attendant alterations produce zones varying in width from centimetres to several metres or more marked in granite gneisses, quartz-mica schists, granodiorites and granitic rocks by quartz-feldspar (albite, microcline) granulites and lit-par-lit injection zones in which are developed muscovite, biotite, beryl, tourmaline and apatite, and in amphibolites by zones enriched in albite, biotite, chlorite, tourmaline, apatite, etc. Alterations associated with late fracture fillings and replacement bodies in pegmatites are generally diffuse, irregular and limited in width from centimetres to a metre or so and involve mainly silicification, albitization (cleavelandite), and the development of muscovite and various rare-element minerals. The wall rocks of thoriferous and uraniferous pegmatites commonly register increased contents of Th and/or U with approach to the pegmatite bodies proper, although in many such pegmatites (e.g. Bancroft area, Canada) the increase in radioactivity is often erratic. Similarly, the approach to thoriferous and uraniferous replacement bodies in pegmatites is usually signalled by an increase in radioactivity over distances of centimetres and metres. Such zones of increasing radioactivity are also commonly marked by a distinct reddening of the wall rocks or the pegmatite body due mainly to increasing contents of ferric iron (hematite), either introduced in solutions or exsolved from ferrous minerals as a result of radioactive bombardment. An increase in smoky quartz, a feature notable with approach to radioactive pegmatites or to radioactive zones in these bodies, is also due to the latter effect. The behaviour of the Th/U ratio in the vicinity of or within pegmatitic bodies depends essentially on the type of mineralization; that is, whether it is predominantly thoriferous or uraniferous. In the case of the former, an increase in the ratio can be expected; for the latter, a decrease.

The distribution of major elements in the wall rocks and within pegmatites shows great variation. Surveys utilizing primary major elemental halos should, therefore, always be preceded by pilot investigations to determine the existing patterns within the specific pegmatite field. Some pegmatites, principally those frozen against their walls, exhibit no or very restricted elemental halos; others, usually those of large size, have halos with widths of up to 10 metres or more. The most indicative major elements (compounds) for use in surveys of primary halos of pegmatites are Na, K and H_2O; SiO_2, S and P may be useful in some fields.

Numerous pegmatites, especially those enveloped by zones of feldspathization, biotitization and the development of muscovite, exhibit increases in K or Na, usually the former, but also the latter, as the pegmatites are approached, as shown in Table 2 and also illustrated in the paper by Kretz (1968). The distance over which this effect is manifest is variable and depends essentially on the size of the pegmatite and the initial and structurally induced porosity and permeability of the host rocks. Enrichment widths of up to 10 metres are not unusual in the vicinity of large pegmatites, a feature also shown by the alkali trace elements (Li, Rb, Cs), as mentioned subsequently. Use of the K_2O/Na_2O ratio as an indicator of approach to pegmatites in drilling is also useful in many fields. This ratio commonly increases with proximity to a pegmatite, although the reverse (Table 2) or no significant change may be registered, patterns that necessitate definition by pilot surveys before contemplating extensive drilling programs. Some pegmatites are characterized by chloritized and/or epidotized halos and others by those enriched in quartz, apatite and sulphides. Approach to these bodies is marked respectively by increasing contents of SiO_2, H_2O, P and S (Table 2).

TABLE 2. Analyses of alteration halo enclosing a lithium-bearing pegmatite, Prosperous Lake, Northwest Territories

Constituent (%)	P-1	P-2	P-3
SiO_2	65.8	66.8	70.6
Al_2O_3	16.2	16.2	16.2
Fe_2O_3	1.4	3.1	2.9
FeO	4.1	1.8	0.8
CaO	1.3	1.6	1.3
MgO	2.1	2.0	0.6
Na_2O	2.6	2.9	0.7
K_2O	3.1	1.9	2.7
H_2O (total)	1.8	1.7	1.8
TiO_2	0.65	0.62	0.36
P_2O_5	0.13	0.22	0.84
MnO	0.04	0.06	0.03
CO_2	<0.1	<0.1	<0.1
S	0.13	0.12	0.17
C	0.03	0.03	0.00
Total	99.38	99.05	99.00
S. Gravity	2.737	2.762	2.807
Li(ppm)	175	405	210
Rb(ppm)	92	640	700
Cs(ppm)	41.5	104	20
B(ppm)	15	>1000	>1000
F(ppm)	700	2300	3100
Sn(ppm)	7.6	45	100
As(ppm)	50	150	38
K_2O/Na_2O	1.19	0.65	3.85

P-1: Quartz-mica schist (10-1 metre from pegmatite)
P-2: Quartz-mica schist (1-0.1 metre from pegmatite)
P-3: Contact zone (0.1-0 metre from pegmatite)

Zoning in pegmatites is commonly erratic, as noted above, but some fields contain pegmatites with relatively regular zonations, such as those shown in Figure 4. In such pegmatites, increases in the K or Na contents or use of the K_2O/Na_2O ratio may indicate approach to the inner and core zones often enriched in many of the economic rare elements. Many pegmatite bodies record progressive increases in the K_2O/Na_2O ratio from their contact to core zones, a feature also paralleled by progressive increases of K in albite, alkalis in beryl, and general increases in perthite, microcline, muscovite and quartz from contact to core zones. Numerous zoned pegmatites also record increasing contents of the albite molecule in plagioclase from contact to core zones (see also Cameron *et al.*, 1949 for other zonations).

The location and delineation of replacement bodies and fracture fillings in pegmatites is difficult because of the erratic, diffuse and commonly unpredictable occurrence of these entites. Increasing amounts of Na, rare elements such as Li, Rb, Cs, Nb, U, Th and Zr, and marked gains in radioactivity are observable with approach to some replacement bodies; others exhibit increasing amounts of SiO_2, H_2O and K toward their diffuse boundaries. The behaviour of the K_2O/Na_2O ratio is varied with approach to replacement bodies; most register a decrease in this ratio, especially where albitization is pronounced.

Skarn and Hornfels Ores

Skarn and hornfels are notoriously complex rocks, and their orebodies are, likewise, complicated and difficult to locate and delineate. Two general types of skarn and hornfels orebodies are recognized—those in enclaves of country rocks within intrusives and those in various types of country rocks, commonly limestones and pelites, at or near the contacts of igneous intrusives, generally granites or granodiorites (pyrometasomatic or contact metamorphic deposits); and those developed remote from igneous contacts generally in metamophosed carbonate-bearing rocks. Both are characterized by the development of Ca-Mg-Fe-Mn silicates (e.g. pyroxenes, amphiboles, garnet, epidote, etc.), quartz and various oxides. The ores are those of Cu, Fe, Co, Zn, Pb, Mo, W, Sn, U, Th, Ag and Au in sulphide, arsenide, oxide, telluride or native form; some skarns and hornfels yield Be, rare earths, Zr, Hf, F and Pt-Pd ores. The ores of skarn and hornfels bodies are both of a massive and disseminated character. Their paragenesis and zonation is discussed below in the section on zoning.

The fundamental chemical feature in the formation of skarn and skarn orebodies is the marked replacement (or exchange) of CO_2 by SiO_2, the simplest reaction being:

$$CaCO_3 + SiO_2 - CaSiO_3 + CO_2.$$

The principal mineralizers involved in the formation of skarn and hornfels orebodies are B, P, As, S, F, Cl and H_2O.

Few studies of the nature of the chemical changes with approach to orebodies in skarns and hornfels along traverses, in drill holes or on grids appear to have been published, a serious gap in our knowledge in prospecting for skarn and hornfels ores. One study by the author (Boyle, 1974b) in the Whitehorse Copper Belt, Yukon, revealed a number of parameters that appear to be useful for vectoring in on skarn-type mineralization.

Briefly, the deposits in the Whitehorse Copper Belt consist of massive and disseminated bodies of magnetite and hematite with variable amounts of chalcopyrite, chalcocite, bornite, pyrite, molybdenite and gold, in a skarn composed of pyroxene, epidote, tremolite, wollastonite, garnet and other Ca-Mg silicates developed in limestone injected by granodiorite. Most of the copper orebodies occur at or near the skarn-limestone contact.

Approaching the Arctic Chief orebody from the granodiorite, the data from analyses of fresh rock on traverses across the granodiorite, skarn, copper orebody and limestone show that the K_2O/Na_2O ratio increases and the SiO_2/CO_2 and SiO_2/total volatiles⁽¹⁾ ratios exhibit a decrease, although the last two exhibit an erratic behaviour along parts of some traverses. As the orebody is approached from the limestone side the K_2O/Na_2O ratios show no change, whereas the SiO_2/CO_2 and SiO_2/total volatiles ratios register an increase.

This example illustrates the general chemical trend found in a number of ore-bearing (Cu, Mo, W, Au, etc.) skarn deposits examined by the writer. There is commonly a consistent increase in the SiO_2/CO_2 ratio as ore is approached from the limestone side and an increase in the K_2O/Na_2O ratio as ore is approached from the granitic rock side. The significance of changes in other ratios toward ore is uncertain.

The value of major elemental ratios as a vector guide in assessing proximity to ore during the exploration drilling of skarn zones and hornfels is difficult to judge precisely from the results obtained by the writer. Skarn deposits and those in hornfels are notoriously erratic, and ore may be found anywhere, apparently where the proper structural and replacement conditions prevailed either in the consolidated intrusive rock, in the skarn or hornfels proper, or in the carbonate rocks at or near the skarn-carbonate contact. The last site, the so-called "marble line", is a favoured zone in which to prospect for orebodies. In this geological situation, the K_2O/Na_2O ratios appear to be useful in signalling an approach to mineralization.

Relatively little work has been done on skarn-type deposits remote from igneous contacts. These deposits have a chemistry similar to those near igneous bodies and presumably the same geochemical techniques should prove useful in their exploration.

Vein-Type Deposits

Veins, lodes, and mineralized fault, fracture, shear and schist zones provide ores of practically all the elements of the Periodic Table. These deposits range from simple to complex and are found in rocks and structures of infinite variety. Investigations of the use of major elements in primary halos as an aid in prospecting for these types of deposits have been carried out by the writer in a number of mineral belts and are detailed in several publications (Boyle, 1961, 1965a, 1974b, 1979a; and Dass *et al.*, 1973). Brief summaries of these investigations as well as those of others dealing with similar work follow after a short discussion of the general behaviour of some major chemical constituents in primary halos associated with veins, lodes, etc.

The regularities of the wall-rock alterations associated with all types of veins, lodes, mineralized shear zones, etc. are well known and are discussed above and summarized in Table 1. It is not proposed to deal further with wall-rock alteration processes in any detail here, but a consideration of the behaviour of certain constituents during the processes of mineralization and a discussion of the nature of the characteristic elemental profiles which are induced in the wall rocks will serve to assist the reader in understanding the content of this section. The constituents studied extensively include K_2O, Na_2O, SiO_2 and the various volatiles, particularly, CO_2, H_2O, S and As. A number of clear-cut examples have been selected where the geological picture is accurately known and where the alteration sequences have been worked out in detail. The districts and types of deposits selected include: Yellowknife, Northwest Territories (gold); Cobalt, Ontario (native silver deposits); and Uranium City (uranium deposits).

Potash metasomatism is especially common in the vicinity of many types of veins, lodes, mineralized shear zones and massive sulphide deposits. The products are sericite, biotite, alunite, K-clay minerals, potash feldspar, etc. During the process, there is commonly an exchange reaction between potassium and sodium; the former generally increases uniformly toward mineralization and ore, whereas the latter shows a consistent decrease. The K_2O/Na_2O ratio, therefore, usually registers a consistent increase as mineralization and ore are approached. Reversals of this trend do occur, but they are rela-

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⁽¹⁾Total volatiles include $CO_2 + H_2O + S$

tively uncommon in this writer's experience. Among the many hundreds of wall-rock alteration sequences examined in the field and in the literature, only about 5% showed the reverse trend. Such sequences are usually present where albitization (and more rarely paragonitization) is notable and hence are readily recognizable from thin-section studies.

Studies of the distribution of SiO_2 in the primary alteration halos of ore deposits indicate four general trends. In one type of deposit, principally veins and lodes with a quartz gangue in mafic and intermediate rocks such as gabbro, andesite and chlorite schists, a marked loss of SiO_2 in the alteration halos is observed concomitant with an increase in CO_2 (carbonate). In other words, as CO_2 is introduced into the wall rocks as a result of mineralization processes there is a consistent loss of SiO_2. The SiO_2/CO_2 ratio, therefore, shows a consistent decrease as mineralization and ore are approached. The reason for this is usually obvious from thin-section studies—the silicates are attacked by CO_2, forming carbonates and releasing SiO_2 which evidently migrates into the vein and lode sites where it is precipitated as quartz. The reactions have been discussed in detail by the writer (Boyle, 1961; 1979). They can be illustrated by the following schematic equation:

$$\underset{\text{(amphibole, chlorite, etc.)}}{\text{(Ca,Fe,Mn,Mg)silicate}} + CO_2 \rightarrow \underset{\text{(ankerite)}}{\text{(Ca, Fe, Mn, Mg)}CO_3} + SiO_2$$

The behaviour of SiO_2 and CO_2 during the alteration of granitic rocks and siliceous sediments differs from that in mafic and intermediate igneous rocks. Commonly there is little change in both these constituents. In some deposits, however, SiO_2 is depleted in the more highly altered rocks; in others there is an addition of SiO_2. The SiO_2/CO_2 ratio is, therefore, variable and often erratic with respect to proximity to mineralization or ore. In many deposits, however, the $SiO_2/H_2O + CO_2 + S$ ratio exhibits a fairly consistent decrease as mineralization or orebodies are approached.

The third trend is found in the vicinity of massive sulphide bodies. Commonly a zone marked by silicification is present in the alteration envelope of massive sulphide bodies that are formed mainly by replacement of intensely sheared, brecciated and drag-folded rocks. In some places, this silicified zone is recognizable solely by an increase in silica, manifest mainly by the presence of fine-grained quartz or chert in the wall rocks; in other places, the zone is marked by the occurrence of a host of quartz stringers, boudins, and small lenses in fractures and contorted zones in the wall rocks or by diffuse layers or irregular pods of chert. In a number of deposits, analyses of the wall rocks commonly exhibit an increase in their silica content as the massive sulphide bodies are approached. The reason for this appears to be that as the sulphides, mainly pyrite, replace the silicates, SiO_2 is liberated and migrates from the sites of replacement (the present massive sulphide lenses) into the adjacent wall rocks. Schematically, the process can be illustrated as follows for the iron component of silicates:

$$\text{(Fe)silicate} + 2S \rightarrow FeS_2 + SiO_2$$

The fourth trend with respect to SiO_2 is noted in mineralized zones and orebodies associated with the low-temperature silicification of carbonate rocks. In this case, as SiO_2 is introduced into the rocks CO_2 (carbonate) shows a consistent decrease, and hence the SiO_2/CO_2 ratio registers a consistent increase with approach to mineralization. The reactions inherent in the low-temperature silicification of carbonate rocks are complex. Quartz (often chert), the stable mineral, is derived principally by the replacement of carbonates by silica, probably as follows:

$$CaCO_3 + SiO_2 \rightarrow \underset{\text{quartz}}{\underline{SiO_2}} + \underset{\text{removed in solution}}{\underline{CaCO_3}}$$

Other volatiles affect the final distribution of SiO_2 and other components in the wall-rock alteration zones enveloping orebodies, particularly those with a quartz and carbonate gangue. Thus, when the ratio of SiO_2/total volatiles is plotted in profile, marked variations and contrasts are noted. In this paper, the volatiles considered include the compounds and elements: H_2O, CO_2, S and As; B and F should also be included where tourmalinization, greisenization, or other types of boron and fluorine metasomatism are present.

Several other types of alteration result in significant changes in major elemental contents and ratios that signal approach to mineralization and ore. Particularly important are progressive increases in the magnesium content manifest by increasing chloritization of most rock types as pitchblende mineralization and orebodies are approached. Some types of copper and tin deposits are, likewise, marked by this phenomenon. Dolomitization, characteristic of carbonate-hosted Pb-Zn deposits, involves increasing addition of magnesium, replacement of calcite by dolomite, and hence a progressive decrease in the Ca/Mg ratio. Sideritization, such as occurs in carbonate and calcareous shale-hosted barite and other deposits, is a similar process involving the replacement of Ca by both Fe and Mg. (Caution is advised in using Ca/Mg ratios because certain limestone rocks, particularly reefs, are dolomitized by processes apparently unrelated to Pb-Zn mineralization.)

Increases in total iron with proximity to mineralization and ore are characteristic of many types of veins and lodes, especially those enriched in pyrite and arsenopyrite. Sulphur and arsenic follow a similar trend. Shifts in the Fe^{2+}/Fe^{3+} ratio are notable in certain types of deposits. Thus, with approach to pitchblende mineralization in various rock types a consistent decrease in the Fe^{2+}/Fe^{3+} ratio is observable due to hematitization. On the other hand, a consistent increase in the Fe^{2+}/Fe^{3+} ratio occurs as uraniferous mineralization is laterally and/or vertically approached in sandstone terranes, the result of sulphidization of ferrous/ferric minerals such as magnetite, etc. Similar features are noted in the host rocks of most vein-type deposits where sulphidization of their wall rocks is profound.

Aluminum commonly exhibits relatively little change across the wall-rock alteration zones of many vein-type deposits, but in some the variations are notable, especially where the mineralizing media have been either markedly acidic or alkalic. Use of aluminum as an indicator must, therefore, be preceded by pilot studies to determine the chemical trend. Where greisenization, alunitization and other similar types of alteration are prevalent, consistently increasing contents of aluminum are observable with approach to mineralization and orebodies.

Analyses of the various constituents discussed above can now be done rapidly and routinely in most laboratories combining X-ray fluorescence, flame photometric, atomic absorption, spectrographic and classical methods. A novel way of evaluating the SiO_2/CO_2 ratio in alteration zones of gold deposits by infrared absorption spectrophotometry has been described by Fakhry (1974). Hausen (1979) has described quantitative methods of estimating the degree of wall-rock alteration employing whole-rock sampling, quantitative XRD analyses of alteration minerals, computer processing of XRD alteration data, and methods of plotting and monomineralic contouring of alteration data. His methods offer an alternative guide to geochemical surveys and place mineralogical methods on a quantitative basis as compared with the somewhat subjective practise of estimating by eye the degree of propylitization, sericitization, argillization, etc. present in the vicinity of mineral deposits.

In the following tables and discussion, weight ratios are used for convenience because chemical analyses are usually expressed in terms of the weight percentages of the oxides. Atomic ratios are more meaningful in terms of geochemical processes; their use would not, however, change the trends observed in the alteration profiles.

The *gold deposits* in the Yellowknife district are of two types—gold-quartz veins and silicified bodies in shear zones in greenstones and associated quartz-feldspar porphyries; and

TABLE 3. Partial analyses and derived ratios for alteration halos enclosing gold-quartz bodies; composite samples of all shear zone systems in greenstones, Yellowknife, Northwest Territories

Constituent %	Greenstone[1]	Chlorite Schist[2]	Carbonate-Sericite Schist[3]
SiO_2	50.45	40.36	38.19
Na_2O	1.85	0.90	0.29
K_2O	0.39	0.41	2.82
H_2O+	2.36	5.20	1.16
CO_2	0.68	8.03	15.57
S	0.22	0.12	3.26
As	0.00	0.00	1.14
Ratios			
K_2O/Na_2O	0.21	0.46	9.72
SiO_2/CO_2	74.19	5.03	2.45
SiO_2/H_2O+CO_2+S+As	15.48	3.02	1.81

1. Composite chip and channel sample of greenstone country rock.
2. Composite chip and channel sample of chlorite and chlorite-carbonate schist. Widths vary from 0.3 to 21 m or more.
3. Composite chip and channel sample of carbonate-sericite schist. Widths vary from 0.15 to 3 m or more.

TABLE 4. Partial analyses and derived ratios for alteration halos enclosing gold-quartz veins in greywacke, slate and schist, Ptarmigan Mine, Yellowknife, Northwest Territories

Constituent %	Greywacke[1]	Greywacke[2]	Greywacke[3]	Greywacke[4]
SiO_2	62.9	62.4	53.1	51.3
Na_2O	3.3	2.0	2.8	3.1
K_2O	2.2	4.0	2.7	4.5
H_2O (total)	1.4	1.9	2.0	2.3
CO_2	<0.1	<0.1	0.1	0.1
S	0.06	0.42	0.96	1.56
As	0.00	0.00	0.35	0.00
Ratios				
K_2O/Na_2O	0.7	2.0	1.0	1.5
SiO_2/CO_2	>629	>624	531	513
SiO_2/H_2O+CO_2+S+As	41.7	26.3	15.6	13.0

1. Composite chip sample of greywacke (10.5 m - 0.6 m from vein)
2. Composite chip sample of greywacke (45 cm - 15 cm from vein)
3. Composite chip sample of greywacke (15 cm - 2.5 cm from vein)
4. Composite chip sample of greywacke (at vein contact)

TABLE 5. Partial analyses and derived ratios for alteration halos in quartz-feldspar porphyry enclosing massive lead-zinc-copper sulphide veins, Nigadoo Mine, Bathurst, New Brunswick

Constituent %	NIG-22	NIG-6	NIG-19	NIG-20
SiO_2	75.3	76.4	71.1	massive sulphides
Na_2O	2.4	<0.1	0.08	
K_2O	5.7	3.5	5.4	
H_2O (total)	0.89	1.8	1.9	
CO_2	0.50	1.4	3.2	
S	0.06	1.29	0.18	
Ratios				
K_2O/Na_2O	2.38	>35	67.5	
SiO_2/CO_2	150.6	54.57	22.2	
SiO_2/H_2O+CO_2+S	51.9	17.02	13.47	

NIG-22. Composite sample (25 kg) of drill core, quartz-feldspar porphyry
NIG-6. Composite sample (25 kg) of drill core sections through mildly altered quartz-feldspar porphyry (1 m - 0.3 m from vein)
NIG-19. Composite sample (25 kg) of drill core sections through quartz-sericite schist (0.3 m to vein contact)
NIG-20. Massive sulphides in vein

gold-quartz veins, pods and irregular bodies along bedding planes, in fractures and faults, and in drag folds in meta-sediments, mainly greywacke and slate. The former have extensive alteration zones; the latter are generally not attended by marked visible alteration effects, but some veins have a border zone in which black tourmaline is abundantly developed. Details of the deposits are given by Boyle (1961).

The data given in Table 3 and Figure 5 and discussed in detail elsewhere (Boyle, 1961, 1974b, 1979a) show a remarkable consistency with respect to changes in the various major constituents and their ratios as the gold-quartz orebodies in shear zones in greenstone rocks are approached. There is a marked increase in the K_2O/Na_2O ratios and consistent and marked decreases in the SiO_2/CO_2 and SiO_2/total volatiles ratios with proximity to ore.

Deposits in greywacke, slate and quartz-mica schist at Yellowknife (Table 4) exhibit changes in the various ratios similar to those in the greenstones. There is a general increase in the K_2O/Na_2O ratios and a general decrease in the SiO_2/CO_2 and SiO_2/total volatiles ratios as the gold-quartz veins are approached. The decrease in the SiO_2/total volatiles ratios is especially significant, not only in the Ptarmigan deposit, but also in the others tested in the meta-sediments. The SiO_2/CO_2 ratios are commonly erratic; in some deposits they show a decrease as the veins are approached, in others an increase is evident. These ratios also fluctuate widely in other deposits investigated in sedimentary terranes, principally because of the small amount of CO_2 (carbonization) present.

Similar trends in the three ratios discussed above have been noted in a great variety of gold deposits, including those in all types of igneous and sedimentary rocks as noted by the writer in a recent publication (Boyle, 1979). From these considerations, one can conclude that major element ratios should be useful in assessing proximity to gold-quartz mineralization during exploration and drilling in greenstone and meta-sedimentary rocks of all types. An increase in the K_2O/Na_2O ratio is particularly indicative of approach to mineralization in all types of rocks; a decrease in the SiO_2/CO_2 ratio is symptomatic of approach to mineralization in mafic and intermediate igneous rocks (greenstones); and a decrease in the SiO_2/total volatiles ratio as mineralization is approached holds for gold-quartz bodies in both igneous and sedimentary rocks. It should be noted, however, that the halos enveloping many gold-quartz deposits are relatively restricted and commonly narrow in their enclosing structures. The use of ratios in exploration, especially drilling, is therefore most effective in wide shear zone systems in mafic and intermediate volcanic and intrusive igneous rocks and in extensive structures such as breccia zones and drag-folds in meta-sediments.

An extended study of the wall-rock alteration features of the *native silver veins* at Cobalt, Ontario has been carried out by the writer and his colleagues (Dass, 1970; Jambor *in* Berry, 1971; Dass *et al.*, 1973; and Boyle, 1974b). The results with respect to the utilization of major elements and their ratios in primary halos are instructive in exploration for these types of deposits.

The native silver-Ni-Co arsenide deposits at Cobalt, Ontario are narrow veins (<0.5 metre) mainly in Archean greenstones, Proterozoic Huronian Cobalt Series sediments (mainly greywacke) and Nipissing diabase. Most veins are marked by faint to pronounced alteration halos generally only a few centimetres in width. The fresh host rocks grade transitionally veinward through a light grey bleached sericitized and carbonated zone to a characteristic, narrow dark chloritized, carbonated, albitic zone adjacent to the veins. These zones generally have bilateral symmetry with respect to the veins.

The data obtained during our surveys, and given in detail in the references cited above, show more or less the same trends in the various ratios as the native silver veins are approached. In the diabase, the K_2O/Na_2O ratio registers a small decrease due mainly to albitization; in the greywacke, this ratio is relatively uniform or shows only a slight increase due to the same phenomenon. In both rock types, the SiO_2/CO_2 and SiO_2/total volatiles ratios register general decreases, although there is an erratic behaviour of these ratios in some profiles.

The primary alteration halos in the native silver deposits at Cobalt are much too narrow for the effective utilization of major elemental indicators in exploratory drilling programs. The various derived ratios, however, are instructive, especially in showing that the K_2O/Na_2O ratio may register a reverse trend to that commonly found in alteration zones associated with epigenetic mineralization. This reversal in trend is related to albitization (introduction of sodium), which is a feature of certain types of gold, silver and base metal deposits.

Another example of the reverse trend in the K_2O/Na_2O ratio due to albitization (and rarely paragonitization) is found in many types of *pitchblende deposits*. A study of the alteration sequences at the Gunnar Mine, Crackingstone Peninsula, Northern Saskatchewan, and of certain pitchblende occurrences in the Uranium City district and in the Massif Central of France (Boyle, 1982) clearly shows that as the orebodies are approached a consistent decrease in the K_2O/Na_2O ratio takes place. This is accompanied particularly by gains in MgO, H_2O and CO_2 and significant decreases in the SiO_2/CO_2 ratio. Most of these orebodies occur in granite gneiss, granite and other salic rocks; some of those in amphibolites and mafic rocks exhibit increases in K with approach to ore and hence relatively consistent increases in the K_2O/Na_2O ratio.

Massive Sulphide Deposits

Massive sulphide deposits are of two general types—veinlike in discordant structures such as faults and breccia zones; and lenses or irregular tabular bodies conformable with the strata in which they occur or with the schistosity or foliation impressed upon their host rocks. The first type is obviously epigenetic; the second has given rise for more than a century to various hypotheses regarding their origin, ranging from magmatic, volcanic-sedimentary to hydrothermal epigenetic-replacement. The last is considered the most probable origin by the writer for reasons detailed in other publications (Boyle, 1965b, 1976).

Extensive wall-rock alterations accompany massive sulphide deposits of both types. These include principally chloritization, sericitization, pyritization and silicification. The changes in the major elements and major elemental ratios in the primary halos of massive sulphides are variable, yet relatively consistent, as shown by detailed studies in the Bathurst district of New Brunswick and in the Keno Hill - Galena Hill district of the Yukon.

TABLE 6. Partial analyses and derived ratios for alteration halos in argillites enclosing massive lead-zinc-copper sulphide veins, 185-m level, Nigadoo Mine, Bathurst, New Brunswick

Constituent %	NIG-1	NIG-2	NIG-3	NIG-4	NIG-5
SiO_2	58.6	50.2	61.2	63.0	massive
Na_2O	3.2	1.7	<0.1	0.8	sulphides
K_2O	1.7	2.4	2.6	3.9	
H_2O (total)	4.0	4.1	3.6	3.3	
CO_2	2.3	9.2	7.7	1.3	
S	0.06	0.29	0.41	0.15	
Ratios					
K_2O/Na_2O	0.53	1.41	>26	4.88	
SiO_2/CO_2	25.48	5.46	7.95	48.46	
SiO_2/H_2O+CO_2+S	9.21	3.69	5.23	13.56	

NIG-1. Composite chip sample of banded argillite (3 m - 0.6 m from vein)

NIG-2. Composite chip sample of mildly altered argillite (0.6 m - 0.3 m from vein)

NIG-3. Bleached fawn-coloured argillite (0.3 m to vein contact)

NIG-4. As above, but with spots (0.3 m to vein contact)

NIG-5. Massive sulphides in vein

TABLE 7. Partial analyses and derived ratios for alteration halos enclosing massive lead-zinc-copper sulphide bodies, Key Anacon deposit, Bathurst, New Brunswick

Constituent %	Chloritic Rock[1]	Sericitic Schist[2]
SiO_2	41.9	75.5
Na_2O	2.3	0.2
K_2O	1.1	2.8
H_2O (total)	4.7	2.2
CO_2	5.8	0.2
S	0.05	2.23
Ratios		
K_2O/Na_2O	0.48	14.0
SiO_2/CO_2	7.22	377.5
SiO_2/H_2O+CO_2+S	3.97	16.31

1. Composite sample of drill cores penetrating greenstone flow, chlorite-magnetite schist and chloritic iron formation; sample weight 25 kg
2. Composite sample of sericite schist and pyritic sericite schist enveloping massive pyrite-sphalerite-galena-chalcopyrite lenses; sample weight 25 kg

Two types of massive sulphide bodies occur in the Bathurst district of New Brunswick. One type comprises massive lenses and irregular bodies of pyrite, pyrrhotite, galena, sphalerite and chalcopyrite in sheared and contorted zones in Ordovician volcanics, sediments and iron formation. Examples are the Brunswick Mining and Smelting No. 6 deposits (Boyle and Davies, 1964) and the Key Anacon deposit (Boyle, 1965b; Saif *et al.*, 1978). Most of these sulphide deposits are enveloped by alteration zones marked by chloritization, sericitization and silicification. The Key Anacon deposit exhibits these phenomena most clearly and was chosen for careful study. The other type of massive sulphide deposit in the Bathurst district is veinlike, occurring as a series of elongated sulphide lenses in fractures and faults cutting Upper Silurian argillites and Devonian quartz-feldspar porphyry. The Nigadoo deposit, described in detail in the publication by Davies *et al.* (1969), is a typical example of this type of deposit. The principal minerals in the Nigadoo deposit are pyrite, pyrrhotite, arsenopyrite, sphalerite, galena, chalcopyrite and tetrahedrite. The gangue is minor, but where present includes carbonates and a little quartz. The sulphide lenses are enveloped by sericitized zones in the quartz-feldspar porphyry and by bleached (sericitized and carbonated) zones in the argillites.

The analytical data presented in Tables 5 and 6 for the Nigadoo deposit illustrate the alteration trends found for the vein-type massive sulphide deposits; of particular interest is the increase in the K_2O/Na_2O ratio and the general consistent decrease in the SiO_2/CO_2 and SiO_2/total volatiles ratios as the massive sulphide bodies are approached in both the porphyry

TABLE 8. Partial analyses and derived ratios for alteration halos enclosing massive lead-zinc-copper sulphide bodies, Key Anacon deposit, Bathurst, New Brunswick

Constituent %	KA-8	KA-9	KA-10	KA-11	KA-12	KA-13
SiO_2	42.5	38.2	47.3	massive	47.4	40.4
Na_2O	3.0	0.1	0.1	sulphides	0.2	3.1
K_2O	0.5	2.0	1.9		3.3	0.5
H_2O (total)	4.9	5.8	3.6		3.0	4.5
CO_2	6.2	6.3	2.7		4.6	7.3
S	0.06	0.82	8.4		6.4	0.22
Ratios						
K_2O/Na_2O	0.17	20.0	19.0		16.5	0.16
SiO_2/CO_2	6.86	6.06	17.5		10.3	5.53
$SiO_2/H_2O + CO_2 + S$	3.81	2.96	3.22		3.39	3.36

KA-8. D.D. Hole 5-36, 45.7 m - 51.8 m, chlorite and chlorite-magnetite schist
KA-9. D.D. Hole 5-36, 51.8 m - 52.7 m, sericite schist
KA-10. D.D. Hole 5-36, 52.7 m - 53.4 m, pyritic sericite schist
KA-11. D.D. Hole 5-36, 53.4 m - 54.2 m, massive sulphides
KA-12. D.D. Hole 5-36, 54.2 m - 55.5 m, sericite schist
KA-13. D.D. Hole 5-36, 55.5 M - 61.0 m, chlorite and chlorite-magnetite schist

and argillite host rocks. The trends are most consistent in the porphyry and less so in the argillite, especially in the latter where a peculiar type of spotted alteration is present and where there is a mild degree of silicification.

The data given in Tables 7 and 8 for the stratiform massive sulphide lenses at the Key Anacon deposit show trends similar to those recorded for the vein-type massive sulphide bodies at the Nigadoo deposit. A general and relatively consistent increase in the K_2O/Na_2O ratio that shows bilateral symmetry with respect to the massive sulphide bodies (Table 8) is characteristic. The SiO_2/CO_2 ratio registers a fairly consistent increase toward the massive sulphide lenses, reflected in general by increasing silicification toward the mineralization. The SiO_2/total volatiles ratios, likewise, exhibit an increase in some profiles, but in others the changes are somewhat erratic or remain relatively constant.

During exploration drilling for massive sulphide bodies of the Key Anacon type, one of the most useful ratios for assessing proximity to ore is the K_2O/Na_2O ratio, which usually registers a consistent increase. A similar behaviour has been noted in the alteration envelopes of the massive sulphide bodies at Boliden, Sweden (Nilsson, 1968), in those in the Abitibi District of Quebec (Descarreaux, 1973) and in the massive sulphide bodies at Bathurst, New Brunswick (Govett *et al.*, 1973). Where silicification is a feature, a plot of the SiO_2 content may indicate approach to ore, as this component frequently shows a consistent increase with proximity to massive sulphide bodies. The SiO_2/CO_2 and SiO_2/total volatiles ratios may also be useful because they may show consistent increases toward ore. Most primary halos associated with massive sulphide bodies are relatively extensive laterally, in places measuring tens of metres or more. This feature confers a considerable advantage if ratios are used during exploration drilling for these deposits.

The results obtained from primary halo studies utilizing drill cores and channel samples on traverses across greenstones, quartzites and argillites adjacent to the massive sulphide veins and lodes carrying Pb, Zn, Cd and Ag in the Keno Hill - Galena Hill district, Yukon, are similar to those obtained at Bathurst and need not be repeated in detail. Briefly, the analytical data show a general increase in the K_2O/Na_2O ratios and a general decrease in the SiO_2/CO_2 and SiO_2/total volatiles ratios as the lodes are approached. A knowledge of these trends should be useful in assessing proximity to mineralization during exploration drilling programs for these deposits, although it should be noted that the primary halos tend to be narrow, and the change in the ratios is manifest only over short distances, usually measured in centimetres or a few metres. Further details are given in Boyle (1965a, 1974b).

Porphyry Copper-Molybdenum Deposits

Alteration and chemical exchange phenomena in the great disseminated and stockwork porphyry copper and molybdenum deposits have been described in numerous publications, of which those by Schwartz (1955), Titley and Hicks (1966), Meyer and Hemley (1967), Lowell and Guilbert (1970), Guilbert and Lowell (1974), Bray and Wilson (1975), Chaffee (1975), Sutherland Brown (1976), Wallace *et al.*, (1978), Mutschler *et al.*, (1981), and Westra and Keith (1981) are representative and contain numerous references. It is evident from these publications and from my observations that most of these deposits are exceedingly complex, and general statements probably do not apply because of the diversity of host rocks in which the deposits occur, the great difficulty in interpreting the complicated geometry of alteration, the problem of defining clearly the mineralization and alteration sequences in the deposits, and the difficulty of separating hypogene (endogene) from supergene alteration effects in the oxidized and secondarily enriched deposits. Nevertheless, there are certain trends that appear to be significant and worthy of consideration in exploration using major elemental contents and ratios as guides.

Most of the disseminated and stockwork deposits are centered on or occur near granitic or syenitic bodies of various morphologies and usually intrusive into volcanic and sedimentary rocks. The alteration attending mineralization is variable, depending on the rock types, but considered broadly, there is a tendency to convergence of the alteration types regardless of rock type, particularly at depth in the deposits. The principal types of alteration are propylitization, argillization, sericitization, feldspathization and pyritization. Some investigators have presented models of alteration zonation which they claim are relatively distinct in the deposits. In my experience such zones are, however, complex, often diffuse and commonly overlap, interfinger or are telescoped. These features should be noted by those contemplating exploration of these deposits, and should certainly be borne in mind in viewing the schematic zoning shown in Figure 6.

The propylitic zones associated with stockwork and disseminated deposits constitute the fringes of the foci of mineralization and grade imperceptibly into the country rocks. In fact, in some terranes these zones cannot be clearly distinguished from the low-grade (greenschist) facies of metamorphism. Propylitic zones are characterized by developments of chlorite, talc, epidote group minerals, (actinolite), albite, (adularia), quartz, carbonates, pyrite, leucoxene (rutile/sphene), apatite, minor sericite, minor clay minerals and (zeolites). Those in brackets occur only in some deposits. The chemical changes involve mainly an introduction of H_2O, CO_2 and S and a minor extraction or redistribution of SiO_2.

Argillic zones feature the extensive development of clay minerals (essentially dickite, kaolinite, illite, halloysite and montmorillonite) accompanied by variable amounts of pyrophyllite, alunite, quartz, pyrite, leucoxene (rutile/sphene), tourmaline, dumortierite, small to minor amounts of sericite and chlorite, and usually minor amounts of residual K-feldspar and biotite. The chemical changes usually involve extensive removal of the bases (Ca, Mg, Mn) and some Na and SiO_2; additions include H_2O, CO_2, S and B. Argillic zones in some of the disseminated and stockwork deposits appear to be, at least in part, due to supergene processes.

The sericitic zones are characterized by the development of sericite, quartz, (topaz), (zunyite), pyrite, anhydrite, (gypsum) and tourmaline with residuals of K-feldspar and biotite. Chemical additions generally comprise K, H_2O, S, B, F, Cl and SiO_2, the last again depending on the original rock type; subtractions are Na, Ca, Mg and SiO_2, the last again depending on the original rock type.

Feldspathic zones are marked by the presence of authigenic (new) K-feldspar (orthoclase, microcline) and biotite, pyrite, magnetite, quartz, tourmaline, (topaz), anhydrite, (gypsum), and residual and (new?) plagioclase (albite). Chemical additions include K, S, F, B, (H_2O) and (CO_2); subtractions are principally Na, Ca and some SiO_2.

The age relationships of the various zones are uncertain. Judging from alteration sequences in a variety of other deposits, especially those in granitic and syenitic rocks, it seems probable that the feldspathic-biotitic zones were formed first. These were then modified and overprinted by mineralizing media giving rise to sericitization and argillization at the central focus of mineralization and to propylitization on the fringes as the elemental concentrations in the mineralizing media waned on their migration outward. Economic mineralization (Cu, Mo, W, Au, Ag, etc.) is invariably localized in the more highly sericitized and argillized zones, with lower-grade orebodies in the pyritic feldspathic-biotitic zones. Veins and lenses of pyrite, galena and sphalerite are common in the fringe (propylitic) zones of many disseminated and stockwork deposits, and skarn bodies with Cu, Pb, Zn, Mo, W, Sn, Ag and Au mineralization occur in carbonate sediments or calcareous pelites near the contacts of the intrusive granitic and syenitic bodies.

Studies of the available analyses of the host rocks and mineralized zones in the disseminated and stockwork deposits indicate a number of relatively consistent phenomena which should prove of considerable value during the exploration of these deposits and also in recognizing ore possibilities at depth from near-surface alteration patterns. These include: increasing K contents and decreasing Na contents and consequently increasing values of the K_2O/Na_2O ratio with approach to mineralization; a consistent decrease in the SiO_2/total volatiles ratio in many deposits as ore mineralization is approached; an increase in SiO_2 with approach to mineralization in many deposits, especially those enriched in Mo; decreases in the contents of the bases (Ca, Mg, Mn) and consequently increases in the Al_2O_3/CaO and other similar ratios with approach to mineralization; and only minor changes in the total iron content, but significant increases in the Fe^{2+}/Fe^{3+} ratio as mineralization is approached due to reduction of Fe^{3+} and the binding of most of the iron in the ferrous state in pyrite and/or chalcopyrite. The last relationship may be erratic in certain deposits, particularly in those where magnetite and hematite are prominent minerals; similarly, the K_2O/Na_2O ratio may show little change or may decrease with approach to mineralization in those deposits where albitization and/or paragonitization is marked.

Major element patterns and ratios have not been extensively used in the prospecting and exploration of disseminated and stockwork deposits. An investigation of two Highland Valley porphyry copper deposits in British Columbia by Olade (1977) showed that the K_2O and K_2O/Na_2O ratios consistently increase from the outer margins of the deposits to the inner zones of intense alteration (sericitization, K-feldspathization, biotitization) and mineralization; concomitantly, Na_2O, CaO, MgO and total Fe (as Fe_2O_3) exhibited a decrease inward. Olade concluded that the use of major elemental halos and the K_2O/Na_2O ratio is more advantageous and less time-consuming than quantitative mineralogical techniques in delineating epigenetic wall-rock anomalies and proximity to mineralization.

In another study of major element dispersion patterns around porphyry copper deposits in the Princeton area of British Columbia (Ingerbelle-Copper Mountain), Gunton and Nichol (1975) observed marked sodium enrichments in the rocks of the Ingerbelle deposit, whereas in the immediate vicinity of the Copper Mountain deposits the rocks are enriched in potassium relative to their host (Nicola) rocks.

Surveys Based on Trace and Minor Elements in Whole Rock Samples

Trace and minor element halos associated with mineralization are of the enveloping and/or leakage type; the former are discussed in this section and the latter in the following section. Enveloping trace and minor element halos have cross-sectional profiles of the types shown in Figure 1. In addition, the enveloping type may be laterally and vertically zoned with respect to the intensity of their trace and minor element content, a subject that is too complex to be discussed in any detail in the space available here. Briefly, the zonation of trace and minor element halos depends essentially on the initial and final concentrations of the elements in the mineralizing media, the chemical and physical nature of the host rocks, and the diffusion and/or infiltration rates of the specific elements horizontally and vertically through the rocks.

To be effective in exploration and in predicting mineralization ahead of the bit, the trace and minor element distributions in the vicinity of mineralized bodies or zones must exhibit vector quantities as discussed in the section on major elements; that is, their contents or ratios based on their contents, or other parameters (e.g. linear productivities), must exhibit a mathematical relationship (generally an increase or decrease) with approach to mineralization. Some examples and discussions of this feature in the various types of deposits follow.

Carbonatites

These bodies have received relatively little attention with respect to their detailed trace and minor element distribution patterns; consequently, it is difficult to make definitive statement regarding the efficacy of trace and minor element surveys in discovering and outlining blind orebodies in these complexes.

Studies of the distribution of niobium in published and private reports describing a number of carbonatite complexes indicate general increases in the content of this characteristic element as orebodies, generally in or near the sovite (carbonatite) zones, are approached; a similar, and commonly parallel, tendency is evident for barium, strontium, phosphorus, various rare earths, uranium, thorium and total radioactivity. Irregular distributions of these elements and erratic behaviour of the radioactive profiles are, however, evident in some complexes, features that require more detailed study to ascertain the causes of this behaviour. For further details on the dispersion of trace and minor elements in carbonatite complexes see especially the publications by Rowe (1958), Heinrich (1966), Tuttle and Gittins (1966), Bloomfield *et al.*, (1971), and Kapustin (1980).

The distribution of copper in carbonatite complexes appears to depend largely on the location and quantity of late-stage fracturing and brecciation. This feature is emphasized by the geological and mineralogical staff of the Palabora deposit (Palabora Mine geological and mineralogical staff, 1976). Their plans of the deposit show a marked concentration of copper (>0.9%Cu) in the late-stage transgressive carbonatite core; this concentration grades outward through an intermediate zone wherein banded carbonatite, foskorite and other rocks are fractured and mineralized by late-stage transgressive carbonates; the intermediate zone ranges from 0.9% to 0.3% in Cu content, and the outer zone is marked by low amounts generally less than 0.3% Cu.

Molybdenum is a common trace element in many carbonatite complexes and can probably be used as an indicator of

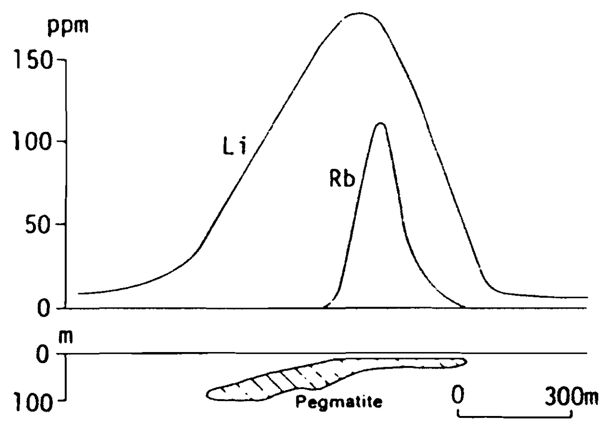


FIGURE 7. Profiles of lithium and rubidium contents over the Tanco pegmatite, Bernic Lake, Manitoba. Note the curtosis and skewed nature of the lithium profile due to the plunge of the pegmatite body (after Trueman, 1978).

position within the complexes. Thus, the feldspathized (fenitized) aureoles are commonly enriched in molybdenum as are also the iron-rich (siderite) late-stage transgressive phases of carbonatite represented usually by siderite-ankerite-barite-quartz veins in most complexes.

Pegmatites

Many pegmatites are characterized by enveloping halos that generally exhibit consistent increases in their trace and minor elemental contents as the bodies are approached. The trace elements exhibiting this behaviour include principally Li, Rb, Cs, Be, B, (Sc), (rare earths), (Th), (U), (Sn), (Ti), (Zr), P, As, (Bi), (Nb), (Ta), S, (Mo), (W), F and (radiogenic Pb). Those in brackets are generally only local in their efficacy as indicators.

Beus *et al.* (1968), Ovchinnikov (1976) and a number of other geochemists in the Soviet Union have extensively studied the nature of the primary halos associated with rare-element pegmatites. In general, their findings show that most pegmatites have associated aureoles enriched in the elements diagnostic of the type of pegmatite, viz. barren pegmatites - B; beryl-columbite pegmatites - B, Li, Sn, Be; and tantalite-bearing pegmatites - B, Li, Rb, Cs, Be, Sn. In addition, the Soviet geochemists have shown that the halos are commonly zoned elementally, with concentrations of Cs being nearest to the contacts followed outward by Rb and Li, the last element having a particularly broad (up to 200 m) primary dispersion outward from lithium-bearing and other rare-element pegmatites. This zonation, they claim, can also be effectively used to estimate the depth of burial of a pegmatite body, and under favourable circumstances to ascertain the direction of the dip or plunge components of the body (Fig. 7). The size of the trace-element halos is said to mirror the size of the pegmatites; in some examples, the halos about large pegmatites extend outward for distances of 150 metres or more, and some buried rare-element pegmatites can be detected at similar depths.

A study of a number of well-defined rare metal and simple pegmatites in the Yellowknife district carried out by the writer in 1952 and later in 1969 shows that most of these bodies are revealed by halos in which Li, Rb, Cs, U, B, Ga, Sn, As, Bi, F and Mo (locally) increase consistently in the wall rocks with approach to the pegmatites. The rare metal pegmatites are best indicated by Li, Rb, Cs, B, F, Sn and As, as shown in Table 2.

An investigation of the value of primary halos for rare metal pegmatites in the Bernic Lake area of Manitoba has been carried out by Trueman (1978) over the Tanco pegmatite. This large zoned pegmatite, renowned for its phenomenal concentrations of Li, Rb, Cs, Be, Ta and other rare elements, is a buried, relatively flat-lying bi-lobate doubly plunging body emplaced in amphibolite (metagabbro/metadiorite) near a granodiorite body in the Bird River greenstone belt. Crouse *et al.* (1979) have discussed the geology of the Tanco pegmatite in detail, and the mineralogy and geochemistry of this unique body have been extensively investigated by Cerna *et al.* and Cerny *et al.* in a large number of publications. (See the references in Crouse *et al.*, 1979 in the Selected Bibliography.)

The profiles (Fig. 7) found by Trueman (1978) show the broad extent of lithium dispersion and the more restricted migration of rubidium outward from the Tanco pegmatite, confirming the characteristic zoning pattern frequently encountered with pegmatites of the Tanco type. A gravity survey also carried out over the pegmatite established a unique gravity signature in which the extensive spodumene zone appears as a gravity high. These geochemical and geophysical features led Trueman to conclude that a combination of the two types of surveys can provide pre-drilling information as to the location, size, depth of burial, attitude, and degree of advancement of fractionation of a blind pegmatite body.

Gilani (1979) carried out a survey of the primary halos associated with the Etta, Peerless and Dan Patch pegmatites in the Keystone district, southern Black Hills, South Dakota. The Etta pegmatite is Li-rich (spodumene) and the Peerless has a moderate amount of lithium; the Dan Patch is essentially a feldspathic pegmatite with only minor amounts of Li minerals. The host rocks of these pegmatites are complexly deformed Precambrian sedimentary rocks (schists and gneisses). Gilani observed that lithium in whole rock samples forms a halo some 35 metres or more horizontally outward from the Etta and Peerless pegmatites, whereas the dispersion of rubidium and cesium is about half this width. The dispersion of Cu and Zn showed no systematic behaviour in the metasomatic halos. These facts led Gilani to conclude that grid sampling of schist, using Li, Rb and Cs as indicators, is a viable method of prospecting for large concealed zoned pegmatites in the pegmatitic terranes of the Black Hills.

Skarn and Hornfels Ores

Skarn and hornfels are notorious for the erratic distribution of their oreshoots and generally for the irregular distribution patterns of trace elements associated with mineralization. Judging from the surveys described in the literature and my experience with skarns and hornfels, it is apparent that the indicators of mineralization depend almost entirely on the elemental type of deposit; thus, Cu is best for copper deposits, W for tungsten deposits, and so on. Auxiliary indicators such as B, P, As, Sb, Se, Te, F and Cl are useful only under conditions where these elements occur in considerable concentrations in the deposits.

A survey of the trace-element distribution in the skarn bodies associated with the Whitehorse copper deposits, Yukon (Boyle, 1979a), revealed that Cu exhibited a marked, and relatively consistent, increase as the magnetite-bornite-chalcopyrite orebodies are approached, a feature also shown by Ag, Au, Hg and to a less extent As. Other elements such as Li, Zn, Te, Mo, W and F showed no distinct or consistent pattern in their distribution. In another survey, in this case of the scheelite-bearing skarns of the Dublin Gulch area, Yukon (Boyle, 1965a), the indicator that best showed proximity to tungsten mineralization was W, whereas other elements such as Cu, Ag, Mo, etc. were either erratic in their distribution or too low in their concentration to be useful as indicators.

Beus and Grigorian (1977) describe a number of primary halo surveys of mineralization in skarns including a bismuth deposit and a number of polymetallic deposits. They noted characteristic zoned halos for Bi, As, Ba, Ag, Pb, Zn, Co, Ni and Cu around the bismuth orebodies and found that some (e.g. Bi, Ag, Cu, etc.) extended 200 metres upward along their dip, in many cases to the surface. Similar features were noted for the polymetallic orebodies in skarns, orebodies at depths as great as 600 metres being indicated by zoned primary halos enriched in As, Pb, Zn, Cu, etc.

Vein-Type Deposits

The trace and minor element dispersion patterns in enveloping halos associated with vein-type deposits have been extensively investigated in many countries, and the literature is voluminous, quite beyond any systematic review in the space available here. Books in which the subject is discussed with extensive bibliographies include those by Beus and Grigorian (1977), Rose *et al.* (1979) and Levinson (1980).

As noted above in the discussion on pegmatites, trace and minor element distributions in the vicinity of vein-type deposits must exhibit vector quantities (increases or decreases in metal contents or metal ratios) or other parameters to be useful during exploration. This is commonly the case; in some deposits, the primary dispersion of the trace and minor elements is broad, relatively consistent and useful in estimating position with respect to mineralization; in other deposits, the lateral or vertical dispersion patterns are much too restricted to be of any value in exploration and drilling programs. Some trace and minor element halos exhibit relatively consistent zonation patterns of their elemental contents or of certain elemental ratios transverse to the sites of mineralization or along the strike and dip of mineralized structures. Such patterns, when quantitatively assessed, may indicate position with respect to the foci of mineralization and hence can provide a guide during drilling programs. It should be pointed out, however, that the zonation patterns of primary enveloping halos are complex, often fickle and erratic, and cannot be predicted *a priori* in most mineral belts. In my experience, the nature of the zoning patterns in primary halos should be ascertained by preliminary surveys in at least one ore-bearing structure in a belt before proceeding to detailed surveys utilizing primary halos in the search for other ore-bearing structures. As a guide in the work, the books by Beus and Grigorian (1977) and Rose *et al.* (1979) are recommended. They detail methods of treating the data obtained from primary halos including: various mathematical treatments (e.g. simple ratios, multiplicative ratios, linear productivity (metre % = average content of an element(s) in per cent multiplied by the distance in metres over the halo or ore zone or a part thereof enriched by the element(s)); zoning arrangements; and characteristics of supra-ore and sub-ore halos.

Surveys of the primary halos of tin, tungsten, and molybdenum, greisen-type and skarn deposits reported in the literature (Tischendorf, 1973; Pokorny, 1975; Taylor, 1979) show that the best indicators of mineralization are Li, Rb, Cu, Zn, B, As, Bi, Sn, Ga, W and Mo. To these I would add F and Mg from my experience with these deposits. Among these elemental indicators, Li, B, Sn, As, Bi and F generally have the broadest lateral dispersion, whereas Rb, Ga, W and Mo are more restricted; Mg is confined essentially to the zones of chloritization, particularly in tin deposits. The vertical zonality of the elemental halos is generally complex, but commonly complies with the following sequence from the surface downward (F, B), (Li, Rb), As, Pb, Zn, Cu, Bi, Mo, W, Sn, the first five elements being enriched in the extended supra-ore parts of the enveloping halos.

A number of surveys of primary halos of polymetallic (Cu, Pb, Zn, Ag, etc.) vein-type deposits are reported by Beus and Grigorian (1977) and Rose *et al.* (1979). Zoned halos were generally observed around all of the deposits tested. The dispersion in the enveloping halos ranged from metres to hundreds of metres, and similar dispersion characteristics were registered in the sub-ore and supra-ore (leakage) halos. The zoning of the enveloping halos is complex and depends essentially on the type of deposit and the nature of the wall rock (composition, degree of fracturing, etc.). Details should be sought in the original publications. In my experience, the best indicators in the primary halos of polymetallic deposits are the metals and semi-metallic elements in the ore and gangue elements within the oreshoots, although other elements of a camouflaged nature, such as Co, Ni, Ga, B and F, are also effective. Among these various indicator elements, Hg, As, Sb, S, Se, Te, B and F appear to have the most extensive dispersions in the halos of polymetallic deposits, although there are many exceptions to this generalization, and pilot surveys should be conducted on a known deposit before embarking on a major exploration program in a specific mineral belt. The host rock type appears to be a major controlling factor on the extent of dispersion of elements in primary halos associated with many polymetallic deposits. Thus, in the Keno Hill - Galena Hill area, Yukon (Boyle, 1965a), a suite of elements comprising Pb, Zn, Cd, Cu, Ag, In, Sn, As, Sb and Ga exhibits a consistent increase over distances as great as 15 metres as the lead-zinc-silver veins in quartzite, graphitic schist and phyllite are approached. In greenstones (meta-gabbro, meta-diabase), however, the lateral dispersion of these elements is greatly restricted, usually to a zone less than 1 metre. The difference in the extent of dispersion in the two types of host-rock suites is due entirely to the degree of lateral fracturing (dilation) in the wall rocks, being maximal in quartzites and minimal in meta-diabase.

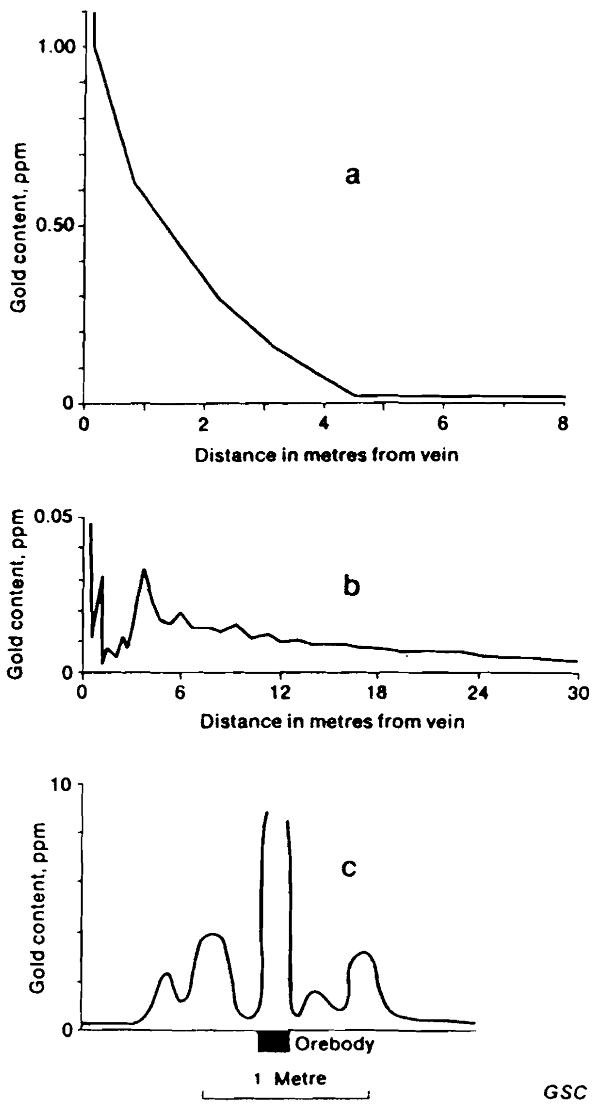


FIGURE 8. Lateral distribution of gold in primary halos of gold-quartz deposits: (a) positive type (Yellowknife, Northwest Territories); (b) negative type (Searchlight district, Nevada); and (c) complex type (Klyuchi orebodies, Transbaikal, U.S.S.R) (after Boyle, 1979a).

The behaviour of trace elements in enveloping halos associated with auriferous veins and replacement deposits is discussed in detail in the writer's monograph on gold (Boyle, 1979a). The conclusions drawn from a large number of investigations reported in the world literature and from my own experience with Canadian gold deposits can be summarized as follows:

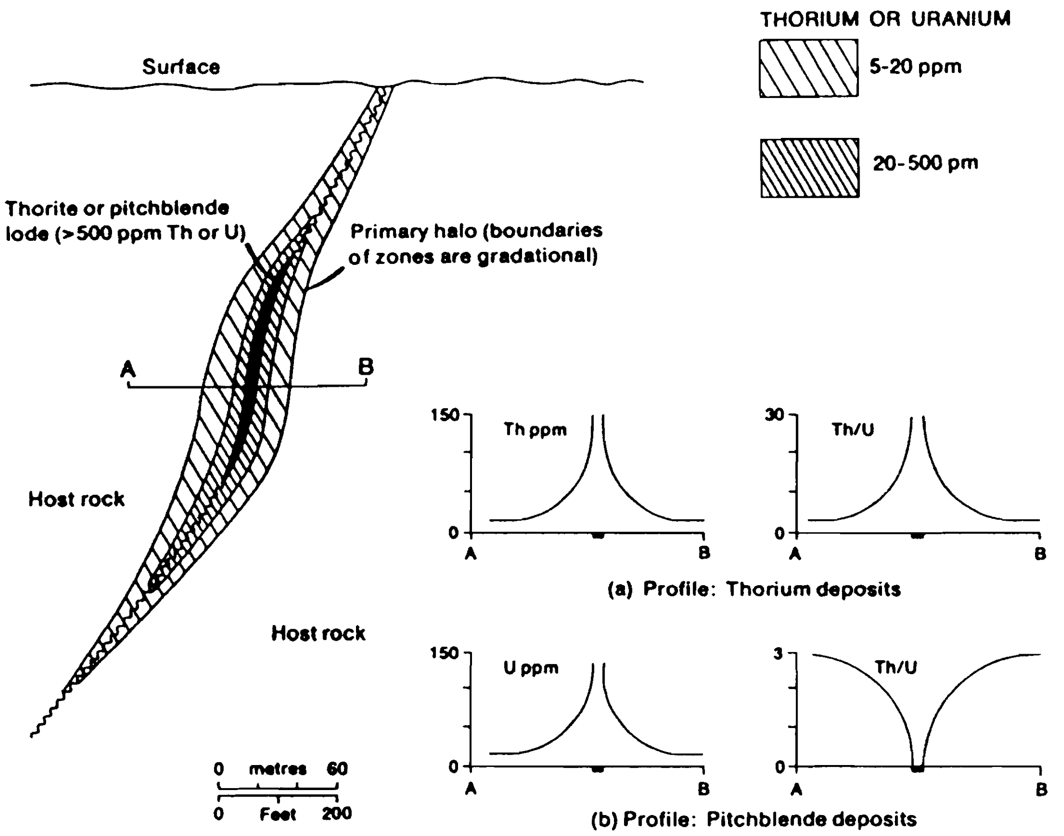


FIGURE 9. Idealized primary halos associated with thorium (thorite) and uranium (pitchblende) veins and lodes.

The primary trace-element halos associated with most types of gold veins, lodes and replacement bodies are marked. Widths, strike and up-dip projections vary widely depending on the type of host rocks, localizing structures, degree of wall-rock alteration, post-mineralization fracturing and other geological factors. Each gold belt and commonly each deposit has its individual characteristics. The most satisfactory indicators for use in primary halo surveys in the search for gold deposits are Au, Ag, As, Sb and Hg. Other elements such as Zn, Pb, Cu, B, Ba and W are applicable in certain belts. All investigators agree that As and Sb, particularly the former, are the best universal indicators. At Yellowknife, enrichments of these two elements in the shear zones can be noticed 100 m or more up-dip from underlying orebodies. Laterally, the schist and weakly mineralized material in shears and fractures are enriched in both elements up to distances of 100 m or more from known orebodies. At Norseman in central Western Australia, Mazzucchelli (1965) noted strong leakage halos of arsenic above lenticular gold-quartz reefs in inclined zones of reverse shearing. These persisted up the shear zones as much as 600 m up-dip from blind orebodies and could be detected in soils over the barren suboutcrops of the ore-bearing structures.

The details of the dispersion of various trace elements including gold in primary halos associated with auriferous mineralization are complex. Some observers find the lateral dispersion of most elements limited to a metre or less and even to a few centimetres in some gold districts; in others, the lateral dispersion may exceed 100 m. The lateral profiles of the distribution of gold in the primary halos may be positive, negative or complex, as shown in Figure 8. The vertical dispersion of most elements up-dip from orebodies in shear zones, fracture zones or replaced beds is commonly much greater than the lateral dispersion for reasons of permeability and porosity. In many auriferous districts, the leakage halos of many of the indicator elements can be detected at distances measured in hundreds of metres above blind orebodies.

Studies of the dispersion characteristics of Mn, Sb, As, Hg, Co, Ni, Ag, Zn, Pb, Cu and Mo in the primary halos associated with the native silver deposits at Cobalt, Ontario have been published by the writer and his colleagues (Boyle *et al.*, 1969; Dass *et al.*, 1973). The results show that this suite of elements has a broad dispersion, up to 30 metres or more, in the wall rocks of the native silver veins enclosed by Cobalt Series sediments (greywacke, quartzite, conglomerate) and up to 20 metres in Keewatin greenstones. Dispersion of this suite of elements is, however, greatly restricted in Nipissing diabase, being usually less than a metre or so. In most profiles studied, the best indicators are Ag, As, Sb, Ni and Co; these elements generally exhibit a consistent increase with approach to the native silver veins.

Relatively few detailed accounts are available on the utilization and efficacy of primary trace and minor element halos in the search for blind vein-type thorium and uranium deposits. My research (Boyle, 1982) indicates that the most suitable indicator elements for pitchblende and uraninite stockworks and veins in granitic and granitized rocks include U, Cu, Pb, Pb(rad) and Mo; others of limited use in deposits containing arsenides and selenides are As, Sb, V, Se, F, Ag, Bi, Co and Ni. In the halos associated with pitchblende, uraninite and thorium-bearing mineral veins and stockworks in metamorphic terranes, the best indicators are Th, U, Cu, (Ag), Pb, Pb(rad), (As), (Sb), (Bi), (V), (Se), Mo, F, (Ni) and (Co). Those in brackets apply mainly to the complex veins mineralized with Ni-Co arsenides, selenides, native silver, etc. The best indicators for thorium and thorium-uranium veins in or associated with alkaline and peralkaline intrusions include Th, U, Cu, (Ba), (Zn), B, (Sc), (Y), (La), (rare earths), (Zr), (Nb), (Pb), Pb(rad), P, (As), Bi, S, Mo, (W) and F. Those in brackets are only satisfactory for certain deposits or districts. The indicators most suited for primary halo surveys in sandstone-type deposits (disseminated, roll-front, veins, etc.) are U, Cu, (Ag), (Be), (Sr), (Ba), Zn, Pb, Pb(rad), (Zr), P, As, V, Se, (Cr), Mo and F; those in brackets are useful only in certain deposits. Further details are given in Boyle (1982). The use of mercury as an indicator in primary halo studies in uranium deposits has not been thoroughly studied. I have noted enrichments of this element in a number of types of deposits, mainly vein types, particularly in those with a complex sulphide-selenide paragenesis or with a Ni-Co arsenide - native silver paragenesis, but also in those hosted by quartz-pebble conglomerates. Others have noted the enrichment of mercury in certain sandstone-type deposits. Ryall (1981) has observed the enrichment of mercury in a number of Australian skarn-, vein-, stockwork- and calcrete-type uranium deposits; he advocates the use of the element in geochemical surveys designed to locate buried uranium deposits.

Various ratios can be helpful in assessing approach to ore when drilling for thorium and/or uranium deposits. Among these are the labile U/total U ratio and the Th/U ratio. The first, a measure of the easily extracted (by acids, acetate solutions, carbonate solutions, etc.) uranium in rocks compared with the total uranium, generally increases with approach to uranium mineralization. The second ratio, Th/U, depends on the type of deposit, as shown in Figure 9. Where thoriferous mineralization prevails, an increase in the ratio is generally evident; conversely, where uranium mineralization predominates, a consistent decrease in the ratio is commonly observed; and where the mineralization is both thoriferous and uraniferous, a relatively uniform or erratic ratio prevails.

An interesting aspect of trace-element halos in prospecting for thorium and uranium deposits is the use of radiogenic lead aureoles formed in their vicinity. These halos commonly envelop or radiate outward from the deposits along fractures and other discontinuities in the rocks (leakage halos). Such halos contain the lead, as ^{210}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb (referred to as Pb(rad) in the indicators above). The first of these isotopes is radioactive, with a half life of 22.26 y; the others are stable.

Radiogenic lead halos (enveloping and leakage types) are formed in one of two ways or by a combination of both. In one case, the thorium and uranium minerals precipitated in the enveloping and leakage halos ultimately yield the lead isotopes which remain essentially *in situ* in the halos; alternatively, the thorium and uranium minerals yield radium, radon and other daughters that migrate and ultimately leave a trail of lead along their migratory pathways.

To outline radiogenic lead halos, sampling of the enveloping and leakage types should be carried out in a manner similar to that employed in trace elemental halo work. Particular attention should be paid to obtaining samples of lead minerals such as galena, anglesite and cerussite where these minerals occur in the enveloping and leakage halos.

The interpretation of radiogenic lead halos is often difficult due to complex processes involving the migration and concentration of lead in nature, a subject discussed by the writer some years ago (Boyle, 1959). In general, where the halos are marked by a great excess of the radiogenic lead isotopes one can be reasonably certain that thorium and/or uranium concentrations occur in the vicinity; where the halos record only a moderate excess of radiogenic lead other interpretations are possible. The short-lived ^{210}Pb is specific for ^{238}U and may be useful in the interpretation of radiogenic lead halos.

Work on radiogenic halos associated with thorium and uranium deposits has not been extensive, yet the subject offers considerable scope both from research and practical viewpoints. Robinson (1955) examined the isotopic composition of lead in galena and clausthalite from the Goldfields (Uranium City) district of Saskatchewan. His results show clearly that one can differentiate radioactive (uranium-bearing) veins and structures from those that are non-radioactive, as shown below in two examples.

	^{206}Pb	^{207}Pb	^{208}Pb
Galena in pitchblende vein	58.1	21.90	37.05
Galena in non-radioactive vein	14.1	15.1	34.4

In the above examples, the ratios were calculated with ^{204}Pb = 1.00.

Rossman *et al.* (1971) examined the distribution of ^{206}Pb in the acidic volcanic host rocks and ores of uranium orebodies and observed that in the host rocks this isotope forms relatively broad halos that extend from the uranium orebodies up to the surface and are stable in the supergene zone. They concluded that the ^{206}Pb halo can be used for the evaluation of radioactive anomalies, including those weakly developed in the surface exposures of bedrock (leakage halos).

From work by the writer on halos, not yet complete, there is an indication that the U/Pb ratios decrease with distance from uraniferous orebodies. This would seem to indicate that the precursors of radiogenic lead (viz. Ra, Rn) migrate laterally (and probably vertically) much farther than uranium, resulting in more extensive radiogenic lead halos compared with those for uranium in rocks.

Few data are available on surveys utilizing primary halos associated with low-temperature vein deposits, including those of mercury, antimony (stibnite), antimony-arsenic (realgar-orpiment), fluorite and barite. Preliminary work on mercury, antimony and arsenic deposits by the writer suggests that the best indicators of these deposits are Hg, Sb and As; other ancillary indicators, such as Cu, Ag, Au, Sr, Ba, Zn, Cd, B, Tl, Ge, Pb, Bi, Se, Te, Mo, W and F, may be useful in some deposits, generally those formed at higher temperature. Mercury, arsenic and antimony appear to have a broad wall-rock dispersion from deposits enriched in the elements, but the exact nature and extent of their enveloping halos is unknown. Work done by the writer and his colleagues (Lalonde, 1974) (Boyle, unpublished) on the fluorite veins at Madoc, Ontario confirms that F is the best indicator of these deposits. In the limestones, the element is broadly dispersed, often as much as 10 metres or more from the veins, whereas in the granitic rocks the dispersion is restricted to a metre or less in most places. Work in other mineral belts containing fluorite deposits is reviewed by Shipulin *et al.* (1973) and Boyle (1976). They note that most fluorite deposits have well-developed, broad enveloping fluorine anomalies that usually extend well above and below the orebodies in most districts. In the Walton area, Nova Scotia, barium is the best indicator of the barite deposits (Boyle, 1972). In the vicinity of the massive barite pipe, barium is broadly dispersed into the adjacent wall rocks, but the halo is complex to say the least, being complicated by different rock types, superimposed Pb-Zn-Ag mineralization and supergene effects.

Massive Sulphide Deposits

Trace and minor element halos associated with conformable (stratabound) massive sulphide deposits in volcanic and sedimentary environments have been extensively investigated (Sakrison, 1971; Lambert and Sato, 1974; Cagatay and Boyle, 1977; Sinclair, 1977; Scott and Taylor, 1977; Boldy, 1979, 1981; Sopuck *et al.*, 1980; Govett and Nichol, 1979; Rose *et al.*, 1979; and Levinson, 1980). The last three references contain extensive bibliographies. The trace and minor element dispersion in the host rocks of these deposits is generally complex, some of the elements being concentrated in irregular zones in the footwalls, some in similar zones in the hanging walls and some in enveloping patterns. This variation in the dispersion characteristics of the trace and minor elements has evoked various interpretations ranging from syngenetic (related to original sedimentary and volcanic phenomena), modified syngenetic (due to the later actions of diagenesis and/or metamorphism) and epigenetic. The general morphology of the dispersion patterns, and their marked similarity to those associated with undoubted epigenetic massive sulphide bodies in faults and shear zones, suggests that the dispersion associated with conformable sulphide bodies is essentially epigenetic, perhaps modified in places by late metamorphic events.

The trace and minor elements most often encountered in anomalous amounts in the dispersion zones of conformable massive sulphide bodies are mainly chalcophile and include principally Cu, Ag, Au, Zn, Cd, Hg, Sn, Pb, As, Sb, Bi, Ni, Co, Fe, Se and Te; in addition, a number of other elements, particularly Mg, Ba, V, Mn, B, Tl and F, may occur in some of the dispersion zones in higher than normal amounts, especially where chloritization, tourmalinization, carbonatization, pyritization, sericitization, and the development of cordierite and feldspar are marked. The lateral and vertical extent of the dispersion of the trace and minor elements varies widely, depending essentially on the degree of porosity and permeability of the host rocks induced mainly by shearing, brecciation, etc. In some deposits, consistent increases in the various ore, gangue and indicator elements can be noted as much as several hundred metres above or below the orebodies, a feature that facilitates their detection and provides directional vectors for their precise location during drilling programs.

Carbonate-Hosted Lead-Zinc Deposits

The trace-element content of primary enveloping halos associated with carbonate-hosted lead-zinc deposits (Mississippi Valley type) does not appear to have elicited much interest as a prospecting guide judging from the paucity of published reports of surveys for these deposits. Limited investigations by the writer on these deposits suggest that the best indicators for use in primary halo surveys are Zn, Pb, Cd, Fe and S; in some deposits, Cu, Ag, As, Sb, Ge, Ga, Ni, Co, Ba and F may be of value. The dispersion of these elements in the wall rocks of the lead-zinc deposits is only poorly known, but in some deposits appears to be restricted mainly to halos more or less circumscribed by the lateral and vertical extent of silicification, dolomitization and development of marcasite (pyrite). Kennedy (1956) observed higher than normal amounts of zinc, lead and iron as much as 40 metres above some orebodies in the southwestern Wisconsin zinc-lead district. Lead gave rise to the smallest and least intensive halos, zinc was intermediate in its dispersion and iron produced the most widesprad halos. Kennedy concluded that such primary halos could be useful in detecting zinc-lead mineralization in carbonate-hosted deposits. Laverty and Barnes (1971) and Barnes and Laverty (1977) have studied the dispersion of zinc in the host rocks of Mississippi Valley type deposits (Wisconsin district) and its utilization in exploration. The extent of hydrothermal dispersion of the element was found to be directly related to the size of the mineralized zones, the maximum dispersion distance being 53 m from major orebodies. Details of the optimum sampling interval (9 m) and other statistical sampling parameters are given in the original papers.

Erickson *et al.* (1981) have conducted regional studies of the trace elements (Pb, Zn, Cu, Mo, Ni, As, Ag, etc.) in subsurface Cambrian rocks of southern Missouri, utilizing both whole rocks and insoluble residues. In the Rolla quadrangle, analyses of insoluble residues in apparently metal-barren carbonate rocks were found to be useful and informative in outlining the known mineralized trends in the ore-hosted Bonneterre Formation. A similar study of subsurface Cambrian carbonate rocks in the Rolla quadrangle and areas to the southwest, specifically in the atypical facies of the Eminence and Potosi Dolomites, revealed three geochemical parameters that appear favourable for the occurrence of underlying Bonneterre-type orebodies—high anomalous metal feet values in insoluble residues, a high Ag-Pb ratio and an offset zinc distribution. Details should be sought in the original papers. From the work done to date, Erickson *et al.* (1981) concluded that a spatial relationship between the atypical facies and the geochemical parameters noted above seems undeniable, whatever the cause.

Porphyry Copper and Molybdenum Deposits

Surveys based on the primary trace and minor element halos associated with porphyry copper and molybdenum deposits in Canada, the U.S.S.R. and the U.S.A. are discussed in considerable detail by Coope (1973), Jambor (1974), Sutherland Brown (1976), Chaffee (1976), Beus and Grigorian (1977), Hausen (1979), Rose *et al.* (1979) and Mutschler *et al.* (1981), and hence need only brief mention here. The principal indicator elements are Cu, Mo, Zn, Pb, Au, Ag, S and Se. Other indicators, such as Ni, Co, Hg and Te, are of limited value, often restricted to certain deposits. Boron seems to be more widespread in porphyry copper and molybdenum deposits than formerly thought and may be a good indicator in some districts in this writer's experience; the same applies to F, which is enriched in a number of deposits in the sericitic micas and also in topaz and zunyite.

The dispersion patterns of trace and minor elements in the halos associated with the mineralization in porphyry copper and molybdenum deposits are generally complex and appear to depend essentially on the degree of structural preparation of the host rocks and on the diffusion characteristics of the elements. The focus of mineralization (copper and molybdenum zones) (Fig. 6) in some deposits is marked by anomalously high concentrations of K, Cu, Mo, Au, Ag, Co, S, Se, Ba and B; in the iron and lead-zinc-silver zones the anomalously high indicators are Cu, Zn, Ag, Fe, S and Se. According to some investigators, elements such as Mn, Zn, Tl, Rb, Li and Na are anomalously low in the ore zones (Cu and Mo zones), as are also Tl, Li and Na in the halo zones (Fe zone). Hg appears to have an erratic behaviour in some deposits, but has been observed in anomalous amounts in the rocks peripheral to the ore zones; similar features seem to apply to Te, Au and Ag in some deposits.

Approach to ore zones in porphyry copper and molybdenum deposits is usually signalled by increases in Cu and Mo and also commonly by significant increases in K, Au and Ag. The most significant signal in most deposits is, however, usually increased contents of S (pyritization). Jambor (1974) emphasized this feature as an exploration clue in the Babine Lake area, B.C., when he concluded that: "Aside from copper itself, the element most obviously useful is sulphur. Nearly all the sulphur is attributable to pyrite, and hence anomalies are mappable by the field geologist. Not only does pyrite present a very broad target area, but field mapping alone should indicate the approximate location of the copper zone. The outer limits of hydrothermal pyritization (pyrite > background pyrite) form an enclosure within which the copper mineralization is, more or less, centrally located. Where significant copper mineralization is present, be it economic or sub-economic, pyrite percentages increase inwards and define an annulus that encloses the copper zone. Moreover, the size and intensity of pyritization in Babine area prospects is indicative of the size and grade of the copper zone; as was shown by Carson and Jambor (1974), large, strong pyrite haloes occur only in association with relatively strong copper mineralization".

(PART 2 of this paper will appear in the September issue)

marked by hematitized zones and/or swarms of hematitic ankerite-dolomite veins. Such zones and veins may be radioactive in places, although most have only a feeble radioactive response. A number of carbonatite complexes are haloed or marked by leakage halos (fractures, faults, slips) that are charged with alkalic saline waters containing NaCl, NaF, etc. Such phenomena are especially common in present-day rift zones (eastern Africa), but also mark carbonatites in or near ancient rifts in Canada, the U.S.S.R. and elsewhere.

Carbonatites and kimberlites often appear to be related (cogenetic) in some terranes and hence the presence of one may suggest or indicate the presence of the other. In this respect, see particularly the note by Dawson (1964).

Skarn and Hornfels Ores

The general indicator of deposits in skarn and hornfels is the presence of Ca-Mg-Mn-Fe silicates (e.g. garnet, pyroxene), commonly in massive bodies or disseminated in a carbonate matrix. Leakage halos indicating mineralization in skarn and hornfels comprise disseminations, pods and veinlets of quartz and carbonates containing sulphides, fluorite, scheelite and the other economic minerals of these bodies. Some skarn bodies are marked by flanking or overlying rocks characterized by broad halos composed of swarms of carbonate veins or by zones of carbonatization of various rock types. These halos are the result of silicification (skarnification) of carbonate rocks during which SiO_2 replaces CO_2 and some Ca, Fe, Mg, Mn, etc., all of which migrate laterally or vertically into dilatant zones (fractures) where they are precipitated as carbonates; in the case of carbon dioxide, carbonatization (e.g. of amphibolites) is the dominant process. All leakage halos associated with skarn and hornfels bodies, as well as the bodies themselves, should be lamped for minerals such as scheelite and tested for radioactive minerals. Skarns and hornfels harbouring radioactive minerals are commonly marked by leakage halos along faults, fractures, shears and slips characterized by anomalous dispersions of He, Rn and the daughter elements of thorium and uranium, especially radium and radiogenic lead.

Pegmatites

The principal types of leakage halos associated with pegmatites are small pegmatitic offshoots composed of quartz, feldspars and micas and small satellitic bodies containing quartz, micas, tourmaline, lepidolite and other rare-element minerals. In addition, some pegmatites are haloed by leakage halos consisting of zones of lit-par-lit injections of pegmatitic material and irregular seams, veinlets and pods of feldspars, quartz, tourmaline and other pegmatitic minerals. Many radioactive mineral pegmatites are marked by leakage halos comprising fractures, faults, shears and narrow breccia zones characterized by anomalous dispersions of He, Rn and the daughter elements of thorium and uranium, particularly radium and radiogenic lead.

Vein-Type Deposits

The leakage halos associated with veins, lodes, replacement orebodies and similar deposits are invariably restricted to faults, small shears, fractures, breccia zones, and porous and permeable beds that either intersect or lie on the extensions of the structures, favourable beds or flows hosting the deposits. Such leakage halos generally contain traces to minor amounts of the ore, gangue and indicator elements or may be marked by indicator minerals or mineral aggregates such as jasperoid, silicified or carbonated rock, limonite, wad, pyrite, arsenopyrite, tourmaline, carbonates, etc. Thorium and uranium veins, lodes and stockworks are generally characterized by leakage halos emitting He and Rn and containing a number of the daughter elements of the two radioactive parents, particularly radium and radiogenic lead.

Massive Sulphide Deposits

Massive sulphide bodies are marked by a variety of leakage halos, some not particularly evident without considerable detailed field and laboratory work. Silicification due to the mobilization of silica during replacement of silicates by massive sulphides is a feature of many of these deposits. This silicification takes several forms; in some terranes, as at the Britannia Mine, B.C., and Horne Mine, Quebec, it is manifest by irregular quartzose (cherty) zones somewhat removed from the orebodies, but generally restricted to the nearby enclosing sheared and contorted tuff beds, ignimbrites (quartz-feldspar porphyries) and rhyolites; in other terranes, the silicification is marked by the presence of broad halos of scattered quartz stringers, boudins, and veins and small lenses or nodules of chert in the host rocks. In the lower-grade metamorphic facies, another type of leakage halo associated with massive sulphide bodies marked by envelopes of chloritic alteration comprises seams, veinlets and irregular zones of chlorite and quartz that frequently extend vertically and laterally for distances of up to 500 metres along shears, fractures, small faults, slips, bedding planes and other surfaces of movement or discontinuity; in the higher-grade metamorphic facies, this type of magnesium (and iron) introduction or rearrangement during metamorphism is marked by the development of cordierite (pinite) which may give rise to irregular spotted (dalmatianite) zones or to seams, pods or irregular vein-like bodies containing the mineral. Pervasive zones of sericitization and pyritization, locally exhibiting some carbonatization, commonly envelope massive sulphide bodies; these, likewise, often extend vertically and laterally for considerable distances (hundreds of metres) along bedding planes, shears, fractures and other surfaces of discontinuity. Similar leakage halos, but with base metal sulphides and/or epidote, zoisite, clinozoisite and chlorite, also mark some massive sulphide bodies. Finally, a number of massive sulphide bodies are characterized by albitized and/or tourmalinized zones either on both their hanging wall or footwall or on one or other of these features. An example is the great Sullivan lode at Kimberley, B.C.; other examples occur in the Bathurst Camp in New Brunswick. In places, these zones project in an attenuated form along bedding planes, brecciated zones, faults and other surfaces of discontinuity for tens of metres in some places and a few hundred in others.

Carbonate-Hosted Lead-Zinc Deposits

Leakage halos associated with carbonate-hosted lead-zinc deposits (Mississippi Valley type) have not been studied in any detail, a gap in our knowledge that should be filled by suitable research. My limited observations suggest that the leakage halos most commonly associated with carbonate-hosted lead-zinc deposits comprise: weakly mineralized slips, fractures, faults and narrow breccia zones that intersect or lie on the extensions of mineralized zones; bedding-plane faults and brecciated and other permeable and porous beds up-dip, down-dip or otherwise extending from mineralized sites; gash veins; and mineralized reefal, brecciated or contorted beds (usually carbonates) above, below or on the extensions of the stratiform orebodies. Some carbonate-hosted lead-zinc deposits and other deposits of similar nature are marked by flanking and overlying rocks containing broad halos composed of swarms of carbonate veins or zones of carbonatization. These halos are the result of silicification and replacement of carbonate rocks by ore minerals, during which CO_2 and variable amounts of Ca, Fe, Mg, Mn, etc. are released to migrate laterally or vertically into dilatant zones (fractures) where they are precipitated as carbonates, or in the case of CO_2 which diffuses into reactive rocks where carbonatization takes place.

Porphyry Copper and Molybdenum Deposits

Leakage halos associated with the great stockwork and disseminated porphyry copper and molybdenum deposits are varied depending on their location in the specific zones (Fig. 6, Part 1) that characterize these bodies. Some are clearly visible in the field, whereas others require detailed chemical examination for identification. Within the barren zones, the principal indicator leakage halos are veinlets and seams of quartz-orthoclase-calcite or quartz-orthoclase-biotite; pyrite veinlets and disseminations may accompany these bodies, as may also veinlets and smears of copper sulphides, molybdenite and wolframite with or without topaz. The iron-rich zones in the stockwork and disseminated deposits are marked principally by disseminated pyrite and magnetite; in addition, copper sulphide veins and galena-sphalerite veins and seams may be present, particularly in the outer parts. In the lead-zinc-silver zones, the principal leakage halos are veins and lodes of galena, sphalerite and silver minerals with a gangue principally of quartz and carbonates. Late-stage veins and seams of pyrite, stibnite, realgar, orpiment and cinnabar occur in this zone in some terranes. Where carbonate rocks or calcareous shales form part of the sedimentary sequence invaded by mineralizing media, skarn bodies are developed near the intrusives and silicated bodies at a distance. In the skarn bodies, the stable minerals are principally copper sulphides, magnetite and scheelite; in the silicated bodies, the stable minerals are mainly galena and sphalerite. Alternatively, where visible sulphides, scheelite, etc. are lacking it is common to find that both the skarns and silicated carbonate beds are enriched in elements such as Pb, Zn, Cu, Ag, Au, W, As and Sb; this enrichment usually increases consistently with approach to the intrusive bodies and disseminated mineralized zones.

Summary

The use of analyses of the materials of the leakage halos mentioned above cannot be over-emphasized in prospecting for lightly covered and deeply buried, blind mineral deposits of all types. When carrying out a lithochemical survey based on leakage halos, and utilizing either rock samples or drill cores, the following points should be kept in mind. All shear zones, fractures, contorted zones and altered zones should be carefully sampled and analyzed for the element(s) sought in the blind deposits and for their indicator elements. A detailed geological map showing all these features as well as any small veins and other leakage halos, no matter what size, should be plotted and the contents of the element(s) sought as well as those of their indicator elements entered at the appropriate sites. Where drilling is done, sections with all of this detail should also be prepared. Only in this way is it possible to observe patterns in the primary dispersion in the rocks and from these patterns to predict the locus of large deposits. It should be constantly borne in mind that most large deposits have a halo of smaller satellites developed in subsidiary or parallel fractures or in favourable sites in porous, permeable and chemically replaceable rocks. Trace-element work on leakage halos, such as small shear zones, fractures, quartz and jasper segregations, pyrite seams, etc., increases the explorationist's ability to differentiate smaller and smaller satellites. It may well be that the data when plotted will show an increase in the element sought or in the indicator element content of various types of leakage halos in a certain direction, or that the number of leakage halos or their elemental concentrations increase toward a certain valley or draw beneath which lies a major shear or fault zone containing deposits. It is also advisable to contour the results in three dimensions, as this method often indicates zones that should be trenched or drilled.

Surveys Based on Selective Extraction of Elements or Minerals in Primary Halos

During epigenetic mineralization processes, the transporting media precipitate ore and gangue elements in the primary enveloping and leakage halos in excess of that constituting the normal abundance of such elements in the host rocks. A large proportion of these excess elemental constituents, commonly referred to as the labile component, is present in disseminated, finely divided ore or gangue minerals or occurs in a weakly bound, usually adsorbed form along grain boundaries, micro fractures and other discontinuities, and is thus readily removed by leaching powdered core or rock samples with weak acidic or alkalic solutions. Similarily, during mineralization processes minerals such as pyrite, arsenopyrite and magnetite are formed in the primary enveloping and leakage halos, and these minerals incorporate larger than normal amounts of ore elements (e.g. Ag, Au, Zn, Cu, etc.) compared with similar indigenous minerals in the host (country) rocks.

Surveys based on the labile elemental components of primary enveloping and leakage halos have several advantages over those based on total decomposition analyses: (1) the labile halos are commonly much more extensive, often by a factor of 2 or more, than those based on total decomposition analyses, a feature that greatly enlarges the target; (2) the labile halos usually register considerable enhancement and have stronger contrasts than those outlined by total analyses; (3) a general suppression of the background (syngenetic element content) is obtained, and variations in the background are eliminated when labile (epigenetic) constituents are used; (4) frequently, analytical detection limits for the indicator elements are much more readily attainable with labile constituents; and (5) increases or decreases in the ratio of labile element content/total element content in positive and negative halos may be much more indicative of approach to mineralization than increases or decreases in the total element content of rock and core samples.

Surveys based on labile elemental components in enveloping and leakage halos have been applied mostly in the search for blind uranium deposits, with only limited surveys on other types of deposits. Early work on labile uranium near mineralization on the Colorado Plateau and at Marysvale, Utah by Holland *et al.* (1957, 1958) showed promise; anomalies with considerable extent and contrast were outlined for some uranium orebodies. Similarly, in their textbook, Beus and Grigorian (1977) figure a number of primary uranium halos associated with blind orebodies and stress the advantages of using soluble uranium in a 2 per cent Na_2CO_3 extractant as compared with the total uranium content of samples. Plots of the linear productivity of soluble uranium indicate depth penetration at least 1.5 times greater than using total uranium. Other Soviet geochemists also stress the efficacy of labile uranium and claim considerable success in detailed exploration for uranium deposits using the method (Kablukov and Vertepov, 1965).

Only a few other studies on labile elemental components in enveloping and leakage halos have been published or are known to the writer. Whitehead and Govett (1974) observed a zinc-lead halo of considerable extent in the rocks above the Heath Steele massive Pb-Zn-Cu sulphide body, New Brunswick. The halos were distinguished by analyzing extracts of rocks (mainly quartz-feldspar porphyries) obtained by digestion in concentrated nitric acid. Goodfellow and Wahl (1976) utilized water-extractable analyses for Na, K, Ca, Mg, F and Cl in their investigation of the halos in the volcanic host rocks of the Brunswick No. 12 and Heath Steele B-zone massive sulphide deposits in New Brunswick. Single elements and combinations of elements successfully outlined halos with a radius of up to 800 m in the volcanic rocks overlying the Brunswick No. 12 and Heath Steele B-zone deposits. The halo zone in the mafic volcanic rocks overlying the Brunswick No. 12 deposit was outlined by high Cl and low K; the halo zone in the felsic volcanic rocks overlying the Heath Steele B zone was outlined by high Mg, Ca, pH and specific conductance. A hemispherical alteration zone with a radius of 600 m was characterized by high K, Ca, Mg and specific conductance, and low Na, Cl and pH in the felsic volcanic rocks stratigraphically below the Brunswick No. 12 deposit. A similar alteration zone was outlined in the felsic volcanic rocks below the A-C-D and B-zone massive sulphides at Heath Steele. The authors concluded that the size and intensity of the anomalous zones associated with both deposits, as well as the rapidity of water-extractable analysis, has much significance in the exploration for deeply buried massive sulphides in the Bathurst district.

Data in a number of other publications, and that from the writer's limited research on labile constituents in primary enveloping and leakage halos, suggest that Cu, Ag, Ba, Zn, U, Sn, Pb, Pb(rad), As, Sb, Bi, V, Cr, Mo, W and F are relatively good indicators of their respective types of blind deposits. The labile survey method for precious and base metals (excluding perhaps uranium) has not been sufficiently developed and offers a profitable field for thesis and other research work.

Analyses of selective mineral separates or insoluble residues from rocks such as carbonates confer certain advantages in surveys utilizing primary enveloping and leakage halos. These are essentially the same as those noted under labile constituents, but particular emphasis should be placed on the ease with which the analytical detection limits for the indicator elements can be more readily attained with mineral separates, especially for elements such as Au, Sn, Sb, Bi, Te and platinum metals. A disadvantage is the availability of certain mineral separates throughout the whole profile or extent respectively of the enveloping and leakage halos. Pyrite, for instance, is nearly universal throughout all types of halos, but minerals such as magnetite, arsenopyrite, gold, bismuthinite, barite, etc. usually have a more restricted occurrence. Another problem, long recognized by those who have used single mineral separates, is the difficulty of obtaining pure (uncontaminated by ore and gangue minerals) samples. This can be obviated in part by careful separation procedures, acid leaching and other techniques.

Surveys based on selective mineral separates or insoluble residues from powdered core and rock samples commonly use only the total heavy mineral or insoluble residue fractions as separated by acid leaching, heavy liquids, hand panning or mechanical (superpanner) panning. Such a procedure is usually permissable, but where enhancement of anomalies is a desired feature more specific mineral separations are advisable. Pilot studies should precede detailed surveys in order to decide which of the two procedures is most productive of results; in some cases, both procedures may have to be employed.

Descriptions of surveys based on selective mineral separates and/or insoluble residues in the halos of deposits are not common in the literature, suggesting that this field is a fertile one for further research. Beus and Grigorian (1977) discuss the general use of analysis of heavy fractions from samples of halos of uranium-sulphide deposits in the U.S.S.R. They note that the halos detected by the analysis of the heavy fractions have higher contrasts and are much more extensive than those detected by analyses of bulk samples. In addition, the detection limits for a variety of indicator elements are considerably elevated by using heavy concentrates as compared with bulk samples. Work by the writer (unpublished) at Keno Hill, Yukon, showed similar results. Utilizing separates of pyrite extracted from the wall rocks of the lead-zinc-silver deposits, anomalies in Pb, Zn, Ag, As and Sb increased the extent and contrast of the primary halos enveloping the lead-zinc-silver orebodies by a factor of 2 in some places and more in others. Similar work in the Nova Scotia goldfields, particularly in the vicinity of the Malaga (Molega) and Ovens veins in southwestern Nova Scotia, utilizing the gold content of separates of arsenopyrite obtained from the host wall-rock slates and greywackes, demonstrated that relatively wide (up to 10 metre) aureoles can be outlined in the vicinity of these gold-quartz veins.

Ryall (1977) observed a marked enrichment of a number of trace elements (Ag, As, Bi, Cd, Co, Cu, Mn, Ni, Pb, Sb, Sn, Zn) in pyrite separates in the vicinity of the Woodlawn massive sulphide deposit, New South Wales, Australia. The trace-element enrichment patterns in the pyrite are complex, but those in the chloritized and silicified alteration zones were considered by Ryall to have potential to indicate proximity to mineralization.

Other research papers dealing with pyrite separates as a guide to sulphide mineralization include those by Dawson and Sinclair (1974) (porphyry molybdenum deposits) and Tanimura *et al.* (1974) (Kuroko ores). Both papers emphasize the practical possibilities of the method in evaluating areas with ore potential and as a technique in detailed exploration to signal proximity to mineralization.

In the field of uranium exploration, Downs (1974) examined the trace-element content (Cu, Mn, Ni, Co) of pyrite associated with uranium roll-front and tabular (stratiform) bodies in the New Mexico and Wyoming sandstone terranes. The pyrite analyzed was that closely associated with the orebodies and present in smaller amounts in the altered rocks enveloping the orebodies. The trace elements in the pyrite were found to be concentrated under different conditions and are, therefore, distributed in different positions with respect to the orebodies. Concentrations of cobalt and nickel were found farthest from the redox interface and occur ahead of the roll fronts at distances of up to 60 metres and in an envelope surrounding the tabular orebodies. Cobalt and nickel maxima may or may not coincide, and the distance from the ore deposit of the maxima was found to depend on the size of the orebody with its surrounding reducing envelope. Copper is concentrated at the leading edge of the roll fronts and in the host rock surrounding the tabular orebodies. Manganese is concentrated adjacent to the redox interface, its maxima being within the confines of the orebodies. Details are given in the original thesis. Downs concluded that consistent changes in the trace concentrations of cobalt and nickel in pyrite can be used to determine the direction in which a sandstone-type uranium deposit may lie. An increase in the cobalt and nickel concentrations followed by an increase in the copper content indicates the proximity of a reducing environment which may contain uranium. Downs also remarked on the practicality of using pyrite as an exploration tool in sandstone terranes, pointing out that the limiting factors are the availability of pyrite and the complexity of the separation techniques. He felt that the use of a gold pan to concentrate the heavy minerals from core samples would improve the technique.

The trace-element content of minerals such as magnetite, biotite, muscovite, etc. has been utilized by a number of investigators in the search for methods of detailed prospecting for a variety of deposits. As an example, the work of Darling (1971) may be mentioned. He investigated the minor and trace elements in biotite from quartz monzonite associated with contact-metasomatic W-Mo-Cu ore in California, U.S.A., and noted that, of two plutons studied, the pluton directly associated with tungsten ore deposits contains biotite with higher amounts of F, Zn, Cu and Li, and smaller amounts of Na and Y. Within the ore-bearing pluton, biotite from traverses across mineralized contacts contains more Na, Yb and Sr than biotite from traverses across barren contacts. The biotite composition also changes as an ore-bearing contact is approached; its content of B, Bi, Cu, Sc, Ag, Sr, Y, Cr and V may increase and its content of F decreases as ore is approached.

The use of trace-element analyses of insoluble residues from carbonate rocks in the vicinity of carbonate-hosted lead-zinc deposits in southern Missouri is discussed by Erickson *et al.* (1981). See the section on trace elements in the halos of these deposits.

Surveys Based on Zonation of Elements in Mineral Deposits

Epigenetic (hypogene) zoning can be classified as regional (confined to a particular mineral belt) or local (confined to single deposits). In the first case, deposits exhibit progressive changes in elemental constitution (mineralization) laterally or vertically from some point or physical entity (e.g. a thermal source such as a granitic stock) or plane represented by a regional shear zone, fault system, etc. The precise causes of the relatively consistent primary zonations observed in mineral belts and individual deposits have long eluded the geologist because of the great multiplicity of complex interacting chemical and physical (mainly tectonic) factors; these are discussed in another publication by the writer (Boyle, 1979a, p. 417). In the present paper, the theoretical aspects do not concern us; the practical aspects of the factual data of zoning, on the other hand, can serve as valuable guides for prospecting for deeply buried or blind orebodies, as outlined in the discussion below.

For the practical utilization of primary zonation in mineral exploration, a number of conditions must prevail. Chief among these is the existence of significant recognizable and mappable changes in the mineral or elemental content of the ores or mineralized zones such that conditions ahead of exploration can be predicted from these changes. On a regional scale, this usually involves the presence of mappable systematic vertical or horizontal variations in the ages and types of mineralization or elemental distributions that permit forecasting the possible location of blind deposits prior to trenching or drilling. On the local mining scale, the zonation must have sufficient definition to allow recognition and mapping of vertical or horizontal patterns from which the conditions ahead of the adit, drift or bit can be predicted. To assist in both regional and local ore predictions, a careful record of the geological, diagnostic mineralogical and geochemical facts must be built up from detailed field and laboratory work on the host rocks, host structures, alteration zones, primary halos (enveloping and leakage), and the paragenesis and elemental constitution of orebodies. Finally, within mineral belts and the confines of mining properties, the features of zonation are often revealed by assay maps of adits, shafts, drifts, stopes and drill holes as well as detailed production records from mines. All these afford valuable data from which distributions of ore, gangue and indicator elements or of their ratios can be determined and correlated with geological features such as favourable host rocks and structures that limit mineralization to certain time periods, structures and rocks.

Supergene zoning is not considered in this paper, but it should be recognized that weathering effects commonly produce major changes in the vertical mineralogical and elemental zonation of orebodies, especially in those containing abundant sulphides such as the porphyry copper and molybdenum deposits, the auriferous and argentiferous polymetallic deposits, massive sulphide deposits, the pyritic gold deposits, and pitchblende deposits. Discussions with bibliographies of work done on the supergene alteration effects in deposits of these types are given in Boyle (1965a, 1968, 1972, 1979a, 1982), Boyle and Davies (1964), and Boyle and Dass (1971).

Carbonatites

Primary zoning in carbonatites is discussed in a section above and shown idealized in Figure 3 (Part 1). The lateral or plan zoning is commonly concentric about the carbonatite (carbonate) core, although there are many deviations from this idealized pattern. Relatively few carbonatites have been drilled or mined to depths greater than 1000 metres, and hence the precise details of the vertical zonation of these bodies is conjectural. The data available suggest that the concentric zones usually dip steeply and are more or less in the nature of annuli, some of which appear to taper downward in certain bodies. The lower levels of some carbonatite complexes are characterized by a prevalance of ultramafic rocks, whereas their upper levels are marked by an abundance of carbonatites and metasomatic (replacement) phenomena associated with the introduction of the carbonates and late-stage hydrothermal activity. The distribution and quantity of dykes may indicate the depth of erosion in some complexes; thus, an abundance of dykes widely distributed probably indicates a deep level of erosion. A knowledge of the zoning of carbonatites, especially lateral zoning, can be particularly useful in prospecting within these bodies, because if position can be established in the complexes it is often possible to predict the possible location of the carbonate cores, niobium mineralization, apatite bodies, magnetite concentrations and so on.

Pegmatites

Ideally, the zones in pegmatites tend to be bilateral about axes in both the horizontal and vertical planes, as shown in Figure 4 (Part 1). Deviations from this idealized pattern are, however, relatively common; in fact, in some pegmatite fields they predominate. Nevertheless, blind concentrations (shoots) of rare elements (minerals) can frequently be located during surface mapping, geological examination and drilling by a study of the zones encountered in surface traverses or drill holes such as are shown in Figure 4 (Traverses A-B, C-D, E-F). When position with respect to the zonation is thus established, prospecting or aiming the drill in the direction of suspected rare-element zones, as indicated from the idealized zonation pattern, is often successful in discovering ore shoots. In this respect, the use of various elemental ratios, as discussed in a previous section, may assist in the work.

Skarn and Hornfels Ores

Skarns host orebodies of two types—those formed contemporaneously or nearly so with skarnification and those formed during post-skarnification processes. Both categories of orebodies may exhibit a lateral and vertical zonation of silicate minerals, oxides and sulphides, although many of the zones are so erratic and discontinuous that they are often of little use as guides in prospecting. Optimum results using mineral and elemental zonation in skarns to predict location of orebodies can be expected where the mineralization is contemporaneous with the skarnification; where the orebodies are of post-skarnification age and are controlled by late tectonic dislocations (faults, shears, brecciated zones), prediction of the location of ore is generally of a low order. The primary exoskarn zones (outside the intrusives) are frequently zoned in accordance with a maximum abundance of certain Ca, Fe, Mg silicates, and comprise an outer zone typified by wollastonite, an intermediate zone typified by clinopyroxene and an inner zone nearest the intrusive typified by garnet. The endoskarns (within the borders of the intrusives) are usually characterized by garnet. The wollastonite zone is attenuated or absent in many skarn bodies. Zoning of the feldspars has been noted in some endoskarns, from oligoclase to bytownite as the contacts with the exoskarns are approached; similarly, the composition of garnet in exoskarns changes from grossularite to andradite (increase in Fe) with distance from the intrusive contacts. Zoning in skarns has been studied extensively in the field and laboratory by U.S.S.R. geologists. A good summary of their work is given in Smirnov (1976). Some of the field and theoretical aspects of zoning in skarns are discussed by Burt (1972, 1974), Dick (1980), and Newberry and Einaudi (1981).

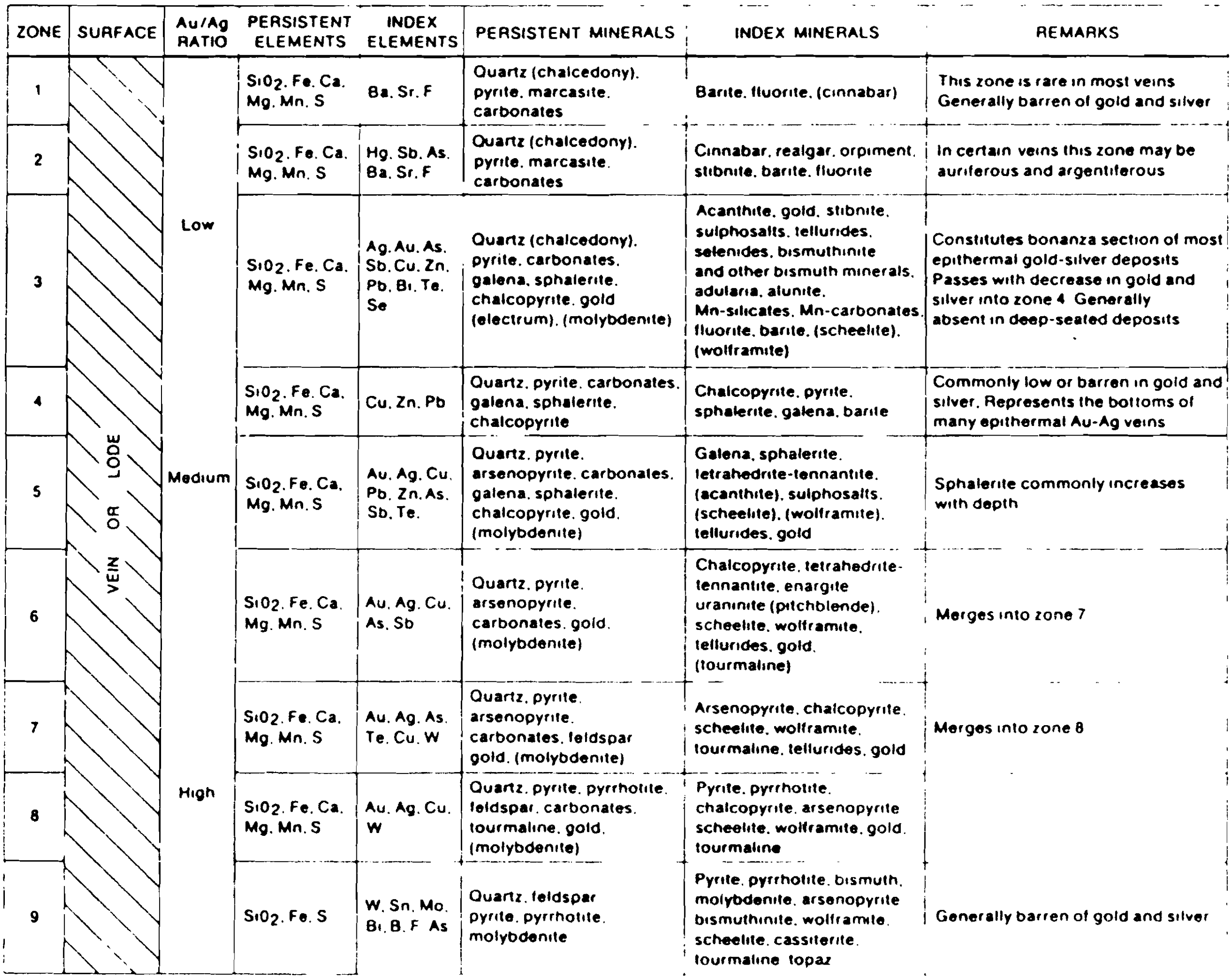
Some mineralized zones and orebodies formed contemporaneously or nearly so with skarnification tend to touch on the intrusive or lie in the exoskarn within a few hundred metres of the intrusive contact; others favour the "marble line", that is at or near the outer limit of the skarn (usually near the outer limit of the wollastonite or pyroxene zone) and the crystalline limestone or dolomite; in some terranes, orebodies may be found in the rocks on either side of this line. Skarnified carbonate or calcareous pelite enclaves within intrusives are favoured sites for skarn-type orebodies in a number of mineral belts. Deposits found in these various environments include magnetite, borate (ludwigite), graphite, certain scheelite lodes and certain copper sulphide bodies (e.g. Whitehorse copper deposits). Mineralization and orebodies formed by post-skarnification processes are largely controlled by tectonic elements such as faults, fractures, breccia zones, shear zones and structurally disrupted beds along all of which replacement is a major process. Such orebodies, which include many of those containing copper, cobalt, molybdenum, lead and zinc sulphides, uraninite, cassiterite, gold and scheelite, may occur practically anywhere within the endoskarns, exoskarns and border zones of the intrusives where favourable structural and replacement conditions prevail. Their location can be facilitated by studies of the alteration zones and leakage halos imposed on the intrusives and pre-existing skarns by the mineralizing media. The principal alterations include mainly silicification, hydration (formation of hornblende, talc, serpentine, chlorite and epidote), sericitization, argillization and carbonatization. The leakage halos along fractures, shears, replaced beds, etc., in both the endoskarns and exoskarns and also in places within their associated intrusives, are marked by these various alterations in addition to minerals or elemental traces of the various components of the mineralization and orebodies.

No well-defined zonation of the constituent elements of deposits within the limits of skarn bodies is apparent in most mineral belts. In some belts there is a crude zonation marked by the presence of one or more of Sn, Cu-Sn, Mo, W and graphite ores in the immediate vicinity of the intrusive, with Cu, Pb, Zn, Ag and Au ores at or near the "marble line" or on the carbonate rock side of the line. The position of iron is rarely well defined, as the element generally occurs in pyrite, arsenopyrite and pyrrhotite in most skarn-type sulphide deposits and seems unrelated to zonation phenomena. Some magnetite bodies occur at or near the intrusive contact, others at the "marble line". The position of gold in the sequence of zones in skarns is, likewise, variable; many auriferous bodies, commonly with abundant pyrite and arsenopyrite, occur in the endoskarns, in the invading intrusive or in the exoskarn near the contact with the intrusives; others are controlled by structures and may occur anywhere in the border zones of the intrusives, in the endoskarns, the exoskarns or on the limestone side of the "marble line".

Vein-Type Deposits

Vertical zonation of elements and minerals in vein-type deposits in fractures, faults and shear zones that cut deeply into the earth is manifest most clearly in Tertiary deposits; it is not marked in Precambrian deposits, some auriferous vein systems extending to depths of 3,500 metres (Kolar, India) or more without decrease in gold content and radical change in the mineralization, or with only a very gradual change from pyrite to pyrrhotite attended by diminution and finally disappearance of minerals such as stibnite and sulphosalts. The reason for this difference is not clear; one can speculate that the Tertiary deposits were precipitated under a steep thermal gradient, whereas the thermal gradient during the deposition of the Precambrian deposits would appear to have been gentle or practically nonexistent.

The vertical endogenic zonation of elements and minerals in vein-type precious and base metal deposits (exclusive of thorium and uranium) is shown in Figure 10. Details are given in Boyle (1979a). It should be understood that the figure is idealized and only rarely is the entire zonation sequence encountered in any one vein system. The more general situation is to find sections, in places extended, of the vertical zonation pattern within particular deposits. Nevertheless, it should be obvious to observant mining geologists, having due regard to the structural situation, that investigation of the characteristic chemical (mineralogical) composition of a vein system at the surface should facilitate judicious evaluation of the erosion level of the outcropping mineralization and thereby assist in predicting the possible presence and nature of blind ore at depth when reference is made to the idealized vertical zonation pattern. Similar observations made on mine levels under favourable conditions should, likewise, assist in the prediction of



ZONE	SURFACE	Au/Ag RATIO	PERSISTENT ELEMENTS	INDEX ELEMENTS	PERSISTENT MINERALS	INDEX MINERALS	REMARKS
1	VEIN OR LODE		SiO_2. Fe. Ca. Mg. Mn. S	Ba. Sr. F	Quartz (chalcedony). pyrite. marcasite. carbonates	Barite. fluorite. (cinnabar)	This zone is rare in most veins Generally barren of gold and silver
2			SiO_2. Fe. Ca. Mg. Mn. S	Hg. Sb. As. Ba. Sr. F	Quartz (chalcedony). pyrite. marcasite. carbonates	Cinnabar. realgar. orpiment. stibnite. barite. fluorite	In certain veins this zone may be auriferous and argentiferous
3		Low	SiO_2. Fe. Ca. Mg. Mn. S	Ag. Au. As. Sb. Cu. Zn. Pb. Bi. Te. Se	Quartz (chalcedony). pyrite. carbonates. galena. sphalerite. chalcopyrite. gold (electrum). (molybdenite)	Acanthite. gold. stibnite. sulphosalts. tellurides. selenides. bismuthinite and other bismuth minerals. adularia. alunite. Mn-silicates. Mn-carbonates. fluorite. barite. (scheelite). (wolframite)	Constitutes bonanza section of most epithermal gold-silver deposits Passes with decrease in gold and silver into zone 4 Generally absent in deep-seated deposits
4			SiO_2. Fe. Ca. Mg. Mn. S	Cu. Zn. Pb	Quartz. pyrite. carbonates. galena. sphalerite. chalcopyrite	Chalcopyrite. pyrite. sphalerite. galena. barite	Commonly low or barren in gold and silver. Represents the bottoms of many epithermal Au-Ag veins
5		Medium	SiO_2. Fe. Ca. Mg. Mn. S	Au. Ag. Cu. Pb. Zn. As. Sb. Te.	Quartz. pyrite. arsenopyrite. carbonates. galena. sphalerite. chalcopyrite. gold. (molybdenite)	Galena. sphalerite. tetrahedrite-tennantite. (acanthite). sulphosalts. (scheelite). (wolframite). tellurides. gold	Sphalerite commonly increases with depth
6			SiO_2. Fe. Ca. Mg. Mn. S	Au. Ag. Cu. As. Sb	Quartz. pyrite. arsenopyrite. carbonates. gold. (molybdenite)	Chalcopyrite. tetrahedrite-tennantite. enargite uraninite (pitchblende). scheelite. wolframite. tellurides. gold. (tourmaline)	Merges into zone 7
7			SiO_2. Fe. Ca. Mg. Mn. S	Au. Ag. As. Te. Cu. W	Quartz. pyrite. arsenopyrite. carbonates. feldspar gold. (molybdenite)	Arsenopyrite. chalcopyrite. scheelite. wolframite. tourmaline. tellurides. gold	Merges into zone 8
8		High	SiO_2. Fe. Ca. Mg. Mn. S	Au. Ag. Cu. W	Quartz. pyrite. pyrrhotite. feldspar. carbonates. tourmaline. gold. (molybdenite)	Pyrite. pyrrhotite. chalcopyrite. arsenopyrite scheelite. wolframite. gold. tourmaline	
9			SiO_2. Fe. S	W. Sn. Mo. Bi. B. F As	Quartz. feldspar pyrite. pyrrhotite. molybdenite	Pyrite. pyrrhotite. bismuth. molybdenite. arsenopyrite bismuthinite. wolframite. scheelite. cassiterite. tourmaline topaz	Generally barren of gold and silver

GSC

FIGURE 10. Idealized vertical endogenic zonation of elements and minerals in precious metal (mainly gold-quartz) and polymetallic vein-type deposits. Minerals and elements shown include only those in the deposits; minerals and elements in wall-rock alteration zones are excluded. (After Boyle, 1979a.)

the persistence or cut-off point of ore at depth. In this respect, models based on the ideal metal or mineral zonation patterns in ore shoots, as worked out by Sinclair and Tessari (1981) for some of the silver-rich veins at Keno Hill, offer promise in re-evaluating ends of old workings and vectoring in on undiscovered ore shoots during exploration.

Lateral zonations of vein-type deposits within mineral belts are discussed at the end of this section and shown in Figure 11 and Table 9.

Massive Sulphide Deposits

Vertical and lateral zoning within massive sulphide bodies is usually complex, each deposit having its own characteristics. Further complexity is introduced where massive sulphide bodies are deeply weathered and secondarily enriched. At the Brunswick No. 6 stratiform massive sulphide deposit, Bathurst, New Brunswick, Boyle and Davies (1964) found a most complicated zoning pattern of elements and their host gangue and base metal minerals, related to replacement phenomena of parts of an iron formation and to sheared zones in both the hanging wall and footwall. Copper is concentrated in the footwall shear zone, with lower amounts in the massive pyrite zones; lead and zinc favour the central parts of the massive pyritic body, particularly the zones of replaced iron formation. Similar complexities occur in most other stratiform massive sulphides examined by the writer; these are often ignored by those describing such deposits, apparently to focus a better light on synsedimentary and other similar models proposed as the origin of these bodies. Zonations of ratios in massive sulphide deposits are of interest. In some bodies, the Zn/Cu ratio traces out zinc cores and copper halos; similarly, the Zn/Pb ratio marks zinc cores and lead halos. Aberrations in these patterns are common.

Zoning in vein-type massive sulphides is common and tends

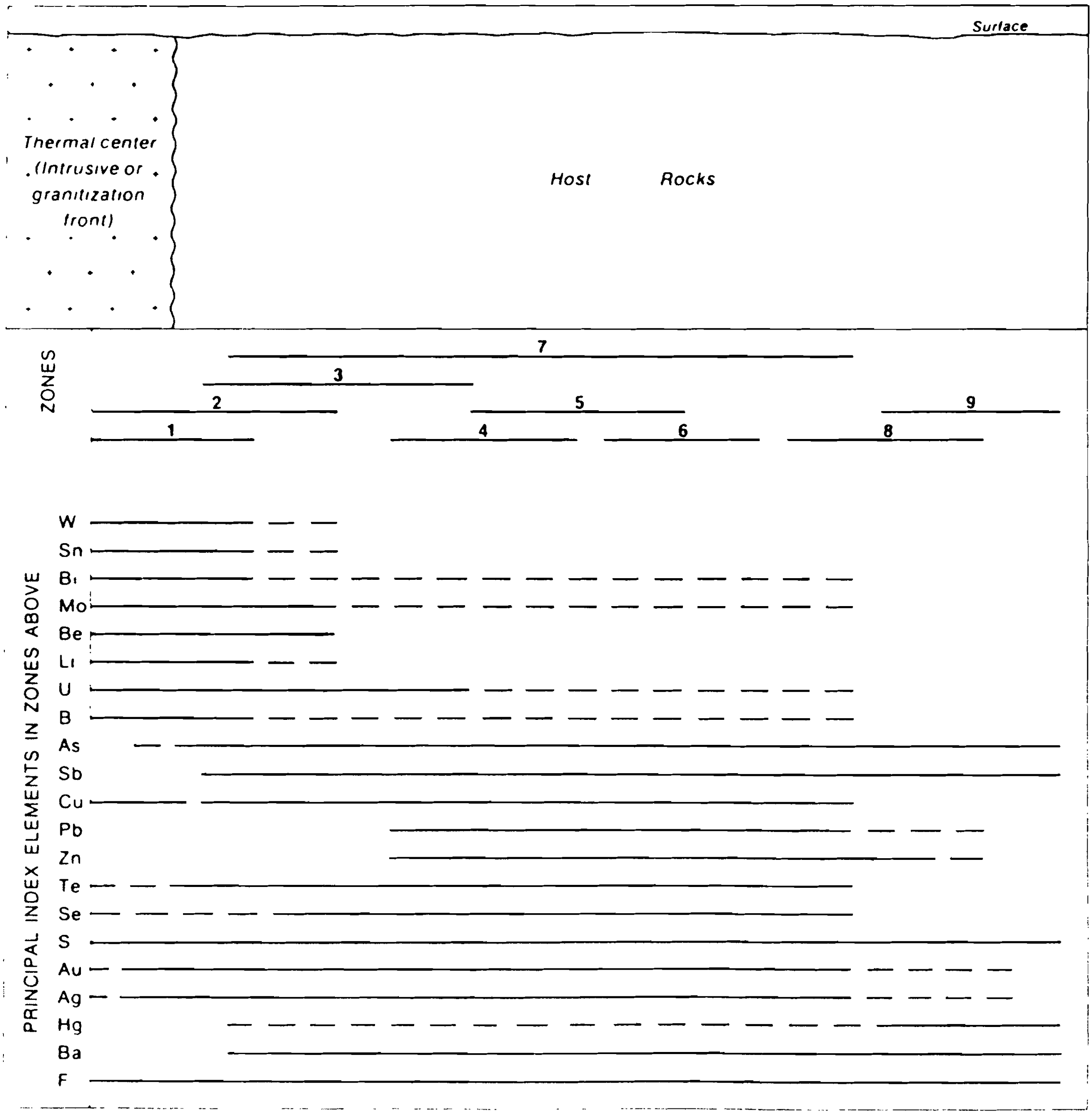


FIGURE 11. Generalized horizontal endogenic zonation of elements outward from a thermal centre. Elements shown include only those in skarn, stockworks, veins, lodes, massive sulphide bodies, etc.; elements in wall-rock alteration zones are excluded. Numbers on the bars in the upper part of the diagram refer to the zones shown in Table 9. (After Boyle, 1979a.)

to follow that described for other types of veins, although it should be remarked that major aberrations may occur in the idealized vertical sequence. At Keno Hill (Boyle, 1965a), the vein-type massive and disseminated Pb-Zn-Ag sulphide bodies (ore shoots) showed a characteristic lateral and vertical zoning in some deposits. The flanks, and particularly the ends, of many of the shoots are marked by numerous stringers of siderite containing pyrite and minor amounts of sphalerite and galena. These extend in places as far as 25 metres out from the main vein faults into the country rock. Inward, the amount of pyrite decreases and the main parts of the shoots contain essentially siderite, galena, sphalerite, freibergite, minor amounts of other sulphosalts, and quartz. The vertical sequence of vein minerals in many of the ore shoots is also marked. Galena predominates at the top of most shoots, giving a high lead content. Within a comparatively short distance down the dip (30 to 70 metres), the content of galena decreases and sphalerite is the principal mineral constituent. With increasing depth (150 metres), sphalerite decreases in turn, and siderite becomes the predominant mineral. Freibergite also decreases with depth, but its vertical range is much greater than that of galena, a feature which maintains a relatively uniform silver-to-lead ratio in the lower parts of many of the shoots. On their lower extensions, the shoots are composed mainly of siderite, with a considerable amount of freibergite and small quantities of galena and sphalerite. This assemblage gradually gives way to siderite containing only pyrite and small amounts of the ore minerals.

Porphyry Copper and Molybdenum Deposits

The great stockwork and disseminated porphyry copper and molybdenum deposits are marked by complicated lateral and vertical zonations involving alteration zones and metallic mineralization as idealized and shown in Figure 6a and 6b (Part 1). The alteration zonation in these deposits is described above in the section on surveys based on major elements; the sulphide zonation requires only brief comment.

Ideally, stockwork and disseminated deposits exhibit five vertical zones arranged in the form of inverted shells more or less centered on some form of granitic intrusive, mainly stocks or swarms of dykes. These zones comprise an outer lead-zinc-silver zone and inner iron, copper, molybdenum and barren zones. Few actual deposits, however, exhibit this ideal zoning; either one or more zones are absent or the pattern is obscured by events subsequent to the initial mineralization. In many deposits, an outer lead-zinc-silver zone partly in the argillitic and partly in the propylitic alteration zones is marked by the presence of fracture-controlled veins of galena, sphalerite and various silver minerals, commonly in a carbonate and/or quartz gangue; where carbonate rocks form part of the sedimentary sequence, skarn bodies with these minerals may appear near the intrusive bodies within the inner sericitic and feldspathic-biotitic alteration zones. The iron zone is characterized by abundant disseminated pyrite and in places by magnetite. This zone interfingers with the lead-zinc-silver zone and increases in intensity through the propylitic alteration

TABLE 9. Generalized horizontal endogenic zonation of elements and minerals outward from a thermal centre*

Zone	1	2	3	4	5	6	7	8	9
Persistent elements	SiO_2, Fe, S	SiO_2, Fe, Ca, Mg, Mn, S	SiO_2, Fe, Ca, Mg, Mn, S	SiO_2, Fe, Ca, Mg, Mn, S	SiO_2, Fe, Ca, Mg, Mn, S	SiO_2, Fe, Ca, Mg, Mn, S	SiO_2, Fe, Ca, Mg, Mn, S	SiO_2, Fe, Ca, Mg, Mn, S	SiO_2, Fe, Ca, Mg, Mn, S
Index elements	W, Sn, Mo, Bi, Cu, Be, Ta, Nb, Li, F, RE, Th, Zr, U, B, As, S	Fe, S, As, (Sb), (Te), Au, Ag, Cu, Mo	Cu, S, As, Sb, Au, Ag, Te, U	Zn, Cd, S, (Au), (Ag)	Pb, Ag, Au, S, Te	Ag, S, (Au)	Sb, As, S, Cu, Zn, Pb, Bi, Ag, Au, Fe, Te, Se	As, Sb, (Au), (Ag), (Hg)	Hg, (Sb), (As)
Au/Ag ratio (in auriferous deposits)	High	High		Intermediate	Intermediate		Low	Low	
Persistent minerals	Quartz, feldspar, micas, pyrite, chalcopyrite, pyrrhotite. (Magnetite and/or hematite may take the place of pyrite in some deposits)	Quartz, feldspar, pyrite, pyrrhotite, carbonates. (Magnetite and/or hematite may take the place of pyrite in some deposits)	Quartz, feldspar, pyrite, pyrrhotite, carbonates	Quartz, pyrite, pyrrhotite, carbonates	Quartz, pyrite, carbonates	Quartz, pyrite, marcasite, carbonates	Quartz, pyrite, marcasite, carbonates	Quartz, pyrite, marcasite, carbonates	Quartz, chalcedony, pyrite, marcasite, carbonates
Index minerals	Wolframite, scheelite, cassiterite, arsenopyrite, molybdenite, bismuth, bismuthinite, chalcopyrite, bornite, topaz, beryl, tantalite-columbite, uraninite and various other rare-metal minerals	Arsenopyrite, Ni-Co arsenides and antimonides, molybdenite, native gold, scheelite	Chalcopyrite, tennantite-tetrahedrite, enargite, barite, fluorrite, uraninite (pitchblende)	Sphalerite, barite, fluorite	Galena, tellurides, barite, fluorite	Acanthite	Stibnite, sulphosalts, barite, fluorite	Realgar, orpiment, stibnite, barite, fluorite	Cinnabar, realgar, orpiment, stibnite, barite, fluorite
Remarks	Mineralization commonly in the intrusives and their border zones. Deposits are generally not highly auriferous. Includes pegmatites and disseminated and stockwork ("porphyry") copper and molybdenum deposits	Contact metamorphic deposits may carry copper minerals such as bornite, chalcocite, molybdenite, etc. Some deposits may be in the intrusive thermal centre (porphyry Cu-Mo deposits)	May overlap zone 2	May coalesce with zone 5	May coalesce with zone 4	May coalesce with zones 4 and 5	May overlap zones 3-6	May overlap zone 7. Some veins and replacement deposits carry gold	May overlap zone 8. Rarely auriferous

*See also Figure 11
RE = rare earths

zone to its maximum in the sericitic alteration zone. Locally, structurally controlled copper sulphide, galena and sphalerite veins may occur throughout the iron zone, and siliceous or skarn-type galena-sphalerite bodies may occur in carbonate beds. The copper zone is essentially coincident with the sericitic alteration zone and is marked by disseminated and fracture-controlled chalcopyrite, bornite and chalcocite with pyrite, magnetite and pyrrhotite in varying amounts; some bodies feature enargite as one of the principal copper sulphides. The molybdenum zone is principally confined to the inner part of the sericitic alteration zone and the feldspathic-biotitic alteration zone and is characterized by the presence of fracture-controlled and disseminated molybdenite with more or less of various copper sulphides, pyrite, pyrrhotite and magnetite. The low-grade (barren) zone in most deposits is confined essentially to the feldspathic-biotitic alteration zone and contains indigenous magnetite, minor pyrite, minor copper sulphides and molybdenite, and in places wolframite. Few investigations of this zone are ever carried out; some could be economic for wolframite and perhaps in places for tin minerals.

Viewed in a lateral sense, the zones just described are usually relatively distinct concentric annuli that may extend over several hundred to a few thousand metres. In most deposits, the lateral alteration and metallic mineral zonations, as noted above, are more or less centered on granitic, often porphyritic, stocks, bosses, plugs or swarms of dykes. Much interfingering and/or overprinting of alteration types is evident on horizontal planes in all of the deposits seen by this writer, and there are, likewise, often aberrations in the ideal lateral zoning of the sulphides and oxides. In deeply weathered terranes, supergene processes also cause many anomalies in the lateral (and vertical) zoning arrangements, particularly in interpreting the extent of argillic alteration and in mapping the sulphide zones. Nevertheless, if these aberrant factors are taken into consideration it is usually possible to orient oneself within the zonation pattern and hence to predict the possible location of economic mineralization.

General Regional Zonations

A regional lateral (and vertical) zonation of elements and minerals outward (and upward) from intrusive granitic bodies or granitization centres has been observed in many mineral belts and commented on for almost a century. The details of this zonation vary from belt to belt and in some belts lack clear definition. A generalized view of the normal regional lateral (and vertical) zonation of deposits including mainly pegmatites, stockworks, skarns and veins in the vicinity of a thermal centre is shown in Figure 11 and elaborated in Table 9. Studies of the regional zonation can aid in a general way in predicting the possible location of mineralization and orebodies. Thus, if tin-tungsten mineralization is found in or near a granitic intrusive, lead-zinc-silver mineralization should be suspected and sought in the intermediate zone of the mineral belt. An example of this relationship can be seen in the Keno Hill district, Yukon (Boyle, 1965a). Similarly, outcropping lead-zinc mineralization in a mineral belt may signal the presence of tin-tungsten or (porphyry) copper mineralization in or near deeply buried intrusives. Other examples will be obvious to the perceptive geologist.

Regarding regional zonation of deposits within mineral belts, observations on the zone facies of metamorphism may also assist in predicting the possible occurrence and location of covered or deeply buried mineralization of various types. Thus, pegmatites are localized either in granitic intrusives or in their high-temperature metamorphic zones (pyroxene hornfels, granulite or amphibolite, and higher grade garnet-andalusite-sillimanite quartz-mica schist facies). Stockwork and disseminated copper and molybdenum deposits are similarly localized usually in or near high-level, often porphyritic, granite or dioritic intrusives. Tin, tungsten, molybdenum, beryllium and similar deposits characterized by the presence of greisen likewise frequent such an environment, as do most skarn deposits. The typical base and precious metal veins and lodes, including those particularly of copper, lead, zinc, silver and gold, tend to favour the lower-grade metamorphic facies (epidote-amphibolite, biotite and greenschist). Massive sulphide bodies, likewise, tend to occur in the lower-grade metamorphic facies, although because of their early epigenetic formation in the mineralization sequence, they may be overprinted by an advancing wave of both thermal and regional metamorphism (Boyle, 1976). Stratabound carbonate-hosted lead-zinc, barite, fluorite and similar deposits, and the typical cinnabar, realgar, orpiment, stibnite, barite and fluorite veins, are invariably localized in the greenschist or subgreenschist (diagenetic) metamorphic facies.

Surveys Based on Stable and Radioactive Isotopic Ratio Distributions

Stable isotopic ratios have been little used in surveys designed to locate deeply buried deposits or during exploration drilling for hidden orebodies, probably because of the relatively high cost of isotopic analyses and the general unfamiliarity with isotopic methods by exploration geologists. The most useful isotopes for these purposes would appear to be H, S, Pb, C and O, although Li, Cu, Ca, Zn, Cd, Hg, B, Tl, Si, Sb, Te, Cl, Ni, Mo and others may prove useful in future work. The field of stable isotopic ratio utilization in detailed exploration for blind mineral deposits and hydrocarbons is one that begs a sustained research effort. Some examples of results in the field to date, covering part of the spectrum of deposits discussed in this paper, follow.

Dontsova *et al.* (1977) examined the $\delta^{18}O$ composition of rare-element carbonatites related to alkalic rock suites and other carbonatite-like rocks, observing that the former had narrow ranges in $\delta^{18}O$ ($+3$ to $+9°/oo$ relative to the SMOW standard), close to those usually ascribed to carbonatites of igneous origin, whereas the latter ranged from $+14$ to $+18°/oo$. Such data should be useful in distinguishing rare-element carbonatites from those that are barren and should be particularly advantageous in assessing the importance of carbonate-bearing leakage halos associated with deep-seated rare-element carbonatite complexes.

Some of the results obtained from studies of the distribution of sulphur isotopes in the host rocks and ores of gold and base metal camps suggest their use in detailed prospecting. Wanless *et al.* (1960) observed a progressive increase in ^{34}S content of sulphides (mainly pyrite and arsenopyrite) across country rock and alteration zones as the auriferous ores are approached at Yellowknife, Northwest Territories; maximum enrichment in ^{34}S was found within the sulphidic gold-quartz lenses. Similar enrichments in the ^{34}S content of sulphides with approach to ore were noted by Shima and Thode (1971) in polymetallic deposits in Japan and Canada. Such phenomena are, however, not invariable, as Boyle *et al.* (1970, 1976) found in the Keno Hill - Galena Hill district, Yukon, and the Walton area, Nova Scotia. In the former district, the sulphides in the gold-quartz and Pb-Zn-Ag-Cd siderite lodes were lower in ^{34}S content compared with the host sedimentary rocks; in the latter area, similar conditions prevailed in the Pb-Zn-Ag lode associated with the massive barite body. From this it follows that the nature of the sulphur isotopic dispersion profiles about the deposits must be known before isotopic ratios can be used in estimating approach to mineralization. When this is clear, sulphur isotopic ratios in sulphides from drill cores may represent a useful ancillary procedure in conjunction with lithochemical ratios for estimating proximity to ore.

Jensen (1971) has remarked, in a summary of the use of stable isotopes in geochemical prospecting, that $\delta^{18}O$ surveys of rock and mineral samples may be of use in exploration, permitting the plotting of isopleths, i.e., lines of equal $\delta^{18}O$ values, indicating the increasing temperatures that existed as the source of the mineralizing solutions is approached. Figure 12 illustrates this approach in an idealized manner. Taylor (1974) reports that many epithermal (mainly Tertiary) precious

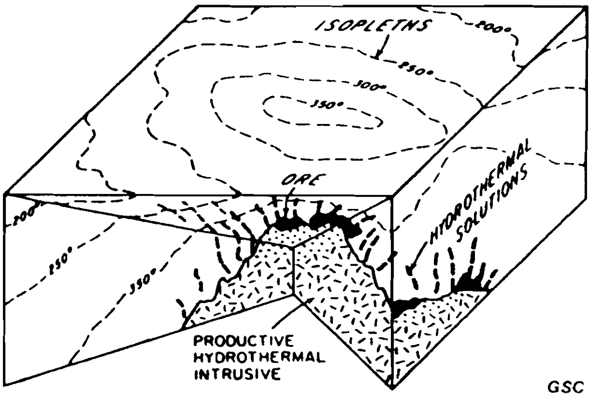


FIGURE 12. Idealized potential application of $\delta^{18}O$ studies to hydrothermally altered contact zones near a mineralizing fluid source (after Jensen, 1971).

metal and base metal deposits, as well as many porphyry copper deposits, all associated with various types of plutons, are surrounded by extensive zones or halos (in places extending over several kilometres) in which the isotopic ratios of $^{18}O/^{16}O$, ($\delta^{18}O$) and D/H (δD) are much lower than in their host rocks. This feature is interpreted as due to reaction of the invaded rocks with heated meteoric (surface) and/or "connate" waters during alteration and metal deposition. The $\delta^{18}O$ and δD values in such halos appear to provide vectors and should thus be a guide to mineralized centres; where isotopic data are available, they should also be useful for indicating blind deposits at depth.

Most mineral deposits containing lead tend to have a distinctive lead isotopic composition for all of the epigenetic lead minerals. For instance, lead minerals in uranium deposits usually have a high proportion of U-lead, that is they are enriched in ^{206}Pb and ^{207}Pb, the decay products of ^{238}U and ^{235}U; in thorium deposits, a high enrichment of Th-lead, ^{208}Pb, can be expected in the lead minerals. In ordinary lead-bearing deposits, the lead minerals have a component of original (primal) lead isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb), as well as varying amounts of radiogenic lead (^{206}Pb, ^{207}Pb, ^{208}Pb), depending, among other factors, on the age of the deposits. Finally, there are deposits in which the lead minerals have isotopic ratios that are unusual or anomalous (the J-lead of the Mississippi Valley deposits, but also of such deposits as Keno Hill, Yukon and elsewhere). The reasons for the variable isotopic composition of lead in deposits are extremely complex and certainly not yet understood. We need to understand the processes involved in the migration and concentration of lead isotopes before our theories can be placed on a firm basis (Boyle, 1959). These problems notwithstanding, it is possible to 'fingerprint' lead deposits and minerals derived from lead-bearing deposits by means of their isotopic ratios and in some cases to use the various lead isotopic ratios to vector in on buried deposits. This particular feature can be used in prospecting for gold, silver and base metal deposits containing lead, as Boyle (1968), Angino *et al.* (1971), Cannon *et al.*, (1971), and Doe and Stacey (1974) have suggested. The last two papers are particularly instructive in this matter. Cannon *et al.* (1971) observed evidence for a lead isotope gradient in the Leadville district, Colorado, that appeared to point toward the focus of mineralization and also found favourable prospecting indications from lead isotope gradients in the J-type lead in the Upper Mississippi Valley lead-zinc district. Doe and Stacey (1974) review the general application of lead isotopes in ore prospect evaluation and record a number of situations where lead isotopic analysis should prove useful in exploration for blind deposits. They also suggest that the lead isotopic composition may parallel the zoning of metals in a hydrothermal ore environment, a feature that would certainly be of use in vectoring in on concealed deposits in igneous and metamorphic terranes.

Finally, as noted above, certain types of lead reflect a uranogenic origin and others a thorogenic derivation. Thus, excess amounts of Th-lead and/or U-lead commonly characterize the lead minerals, native bismuth, native gold, the various primary and secondary sulphides, sulphosalts, arsenides, carbonates and sulphates (barite), and/or the secondary oxidation products (wad, limonite, anglesite, etc.) of thorium and/or uranium deposits and their alteration and 'leakage' halos. These minerals may also pass into the soil, eluvium and drainage sediments in regions containing thorium and uranium deposits. These particular features can be used in prospecting when isotopic analyses for lead are carried out as supplementary or complementary studies during lithochemical, gossan, soil and drainage sediment surveys of an area. The media for sampling during lithochemical surveys should include host rocks and alteration zones adjacent to faults, fissures and mylonitized zones (primary-secondary and 'leakage' halos), and mineralized material from fissures, faults, shear zones, 'leakage' structures and gossans, particularly lead minerals; for the other types of surveys, heavy minerals and chemical precipitates provide the best sampling material. When anomalous lead isotopic ratios involving ^{206}Pb, ^{207}Pb and ^{208}Pb relative to ^{204}Pb are encountered in primary/secondary contiguous and 'leakage' halos and in dispersion trains, thorium and/or uranium mineralization should be suspected. The use of isotopic analyses to detect excess stable radiogenic lead as a clue in the search for buried thorium and uranium deposits is discussed in some detail by Cannon *et al.* (1958, 1971), Adler (1958), Surazhskii and Tugarinov (1960), Angino *et al.* (1971), Rossman *et al.* (1971), Doe and Stacey (1974), Robbins and Gupta (1979), and Gulson and Mizon (1980). The latter investigators record that the ratios $^{206}Pb/^{207}Pb$, $^{206}Pb/^{208}Pb$ and $^{206}Pb/^{204}Pb$ in sulphides and whole rocks from the Jabiluka uranium deposit in the Pine Creek Geosyncline, Northern Australia, increase dramatically as U-mineralization is approached. Details should be sought in the original publication.

The $^{7}Li/^{6}Li$ isotope system commonly exhibits strong fractionation during a number of mineralization processes. This feature has been investigated by Divis and Clark (1979), who observed a marked enrichment of ^{6}Li in altered plutons with associated copper mineralization (porphyry copper deposits). They concluded that the low cost and ease of analysis of lithium isotopes by atomic absorption make the method particularly favourable in the exploration of "cryptic" alteration halos associated with blind molybdenum, copper and tin deposits.

The use of radioactive isotopes in exploration for deposits of thorium and uranium is well documented and requires little comment here. One of these isotopes, ^{222}Rn, is employed extensively in atmochemical methods to define secondary leakage halos marking the presence of buried uranium deposits. Similarly, the decay products of ^{238}U, particularly ^{226}Ra, and of ^{222}Rn, specifically ^{218}Po, ^{214}Bi, ^{214}Po, ^{210}Pb, ^{210}Bi and ^{210}Po, can be used to trace the migration of the various daughter elements along leakage halos associated with deeply buried uranium deposits. Finally, the uranium isotope ^{234}U has been found to have a relatively high mobility during endogenic and exogenic processes compared with its parent ^{238}U; consequently, the $^{234}U/^{238}U$ ratio exhibits considerable variation, a feature suggested by Cowart and Osmond (1977) as a method for signalling the presence of uranium orebodies in sandstone terranes. In some sandstone-type deposits in the Powder River and Shirley Basin areas, Wyoming, and in Karnes County, Texas, U.S.A., they noted marked decreases in the uranium concentration and dramatic increases in places in the $^{234}U/^{238}U$ ratio of the water regime down-dip from precipitation (reduction) barriers. They considered this to be due to the down-dip precipitation of the uranium at the reduction barriers coincident with an augmentation of ^{234}U to the downward-moving water from the initial concentrations of uranium at the barrier, and noted that accumulations of uranium in sandstone-type deposits generate an isotopic signal that is discernible for a number of kilometres in the direction of flow. They concluded that comparison of isotopic ratios of water samples in the areas of recharge with those down-dip at depth may prove to be a useful indicator for locating accumulations of uranium, including roll-front and other types of deposits in sandstones.

Surveys Based on Geothermometric, Geobarometric and Thermoluminescent Methods

Estimates of the temperature-pressure conditions of formation of epigenetic deposits have been made for many years utilizing mineral intergrowths and thermal stabilities, pyrite geothermometer, sphalerite geothermometer, isotopic data, decrepitation, liquid inclusion data and a number of other methods. In recent years, most of the emphasis has been placed on methods based on decrepitation of minerals and studies of liquid inclusions with the express purpose of identifying pressure and/or temperature gradients, directions of flow of mineralizing solutions, and other physico-chemical parameters involved in the deposition of ore shoots in vein systems and other epigenetic deposits. The literature on the subject is voluminous: that prior to 1953 is summarized by Smith (1953); later research is summarized by Roedder (1979). A specific example of the type of work done on gold deposits is that by Smith (1954), who determined the direction of flow of late-stage (auriferous) solutions in the Lamaque No. 6 vein, Bourlamaque, Quebec, a valuable guide that led to the location of concealed shoots. In the base metal field, an example is the work of Ermakov and Kuznetsov (1971), who outlined distinct enveloping decrepitation halos of considerable magnitude (up to 250 metres in lateral extent) in which the homogenization temperatures, maximum temperature of decrepitation, decrepitation intensity and other parameters increased toward the polymetallic veins of an area in the Ossetia Mountains of the Northern Caucasus, U.S.S.R.

It is difficult at present to evaluate the effectiveness of methods based on liquid inclusions in prospecting for epigenetic deposits. It would seem that up to now the methods have been of limited practical value in detailed prospecting, but have given considerable information on the temperature, pressure and nature of the solutions from which various elements have been deposited. Perhaps we cannot expect more at this stage of the research. Certainly more research should be focused on the nature of liquid inclusion (decrepitation) halos associated with epigenetic deposits and on detailed liquid inclusion techniques for determining the P-T conditions of deposition and pathways of solutions. Such data should provide vectors for homing in on blind orebodies.

Thermoluminescence of minerals has been proposed as a detailed prospecting tool, and some work has been done on minerals in alteration halos around various types of epigenetic mineral deposits. Thermoluminescence (thermostimulated phosphorescence) is the property of a mineral or rock to emit light (photons) when heated below red heat (below about 400°C), the emitted light usually being plotted as a glow curve. The phenomenon is due to unstable electronic conditions (trapped electrons) within crystal lattices. These conditions can be induced by radioactive bombardment, stress, heat absorption, and a variety of other causes not yet well understood. Details should be sought in the book edited by McDougall (1968).

MacDiarmid (1963) observed a general erratic distribution of thermoluminescence in the vicinity of hydrothermal deposits. On the other hand, McDougall (1964, 1966) considers that his investigations indicate that thermoluminescence should have at least limited application as an exploration tool. He observed a number of patterns adjacent to various orebodies, as follows: (1) no thermoluminescence is observed; (2) thermoluminescence is present, but no distinctive change is observed as the ore zone is approached; (3) thermoluminescence is low or nil immediately adjacent to the ore zone and rises to a higher background level at some distance away; (4) thermoluminescence is low or nil immediately adjacent to the ore zone and decreases away from it to a more or less uniform background (or to nil values). The thermoluminescent profiles figured by McDougall are remarkably similar to those obtained for numerous trace elements in the primary halos in rocks surrounding orebodies; they should, therefore, be of value in the search for blind orebodies. Further research on thermoluminescence methods seems desirable judging from favourable reports on more recent work in the U.S.S.R. and U.S.A. respectively on gold deposits (Grishin *et al.*, 1971) and uranium deposits (Spirakis *et al.*, 1979).

Pedochemical Methods

Pedochemical surveys based on sampling and direct analysis of soils, weathered residuum, calcrete, silcrete, ferricrete and glacial drift, including till, sand and gravel, and on analyses of light and heavy mineral concentrates from all these materials, have been utilized in the search for concealed mineral deposits for more than half a century. The results have far exceeded the expectations of those who initially suggested the method, so that today pedochemical surveys are one of the principal methods, if not the principal method, for discovering blind deposits of nearly all types of minerals (elements). The techniques employed in pedochemical methods are detailed in all of the standard textbooks on geochemical prospecting (see the Selected Bibliography) and certainly do not require amplification here.

In recent years, overburden drilling, an outgrowth of near-surface pedochemical methods, has been employed extensively in the search for deeply buried precious metal, base metal, uranium and many other types of mineral deposits. The techniques are discussed at length by Van Tassel (1969), Gleeson and Cormier (1971), and Wennervirta *et al.* (1971), and are particularly applicable to permafrost terrains, deeply covered glacial terranes, lateritic terranes, filled valleys, and buried eluvial and alluvial placer fields. Overburden surveys are conducted on grids or selected lines or traverses in a manner similar to that employed in pedochemical surveys. Samples for analyses may be collected from any level (horizon), but in general are usually obtained from the zone immediately above bedrock. It is advisable, particularly in gold placer fields, to sample the near-surface bedrock as well. The bedrock should also be sampled when lithochemical surveys based on sampling of bedrock, alteration zones and leakage halos are carried out.

Surveys based on the A (organic or biochemical) horizons of soils and on bogs to locate concealed deposits are discussed in the section on biogeochemical methods.

Hydrochemical (Water) Methods

Hydrochemical methods based on natural waters and their precipitates as sampling media have been used in reconnaissance geochemical prospecting surveys to outline mineralized belts in which concealed mineral deposits may occur. Despite many novel approaches, the methods have not been widely utilized in detailed surveys to pin-point deeply buried deposits or to prospect ground in the immediate vicinity of known orebodies.

For hydrochemical methods of detailed prospecting to be effective, the following conditions must be present:

1. Natural waters must come into contact with mineral deposits and remain in contact with them long enough to dissolve detectable amounts of either the ore, gangue or indicator elements.
2. Dispersion patterns must be present in the hydrologic systems in order to trace the elements back to their source. These patterns may take the form of halos, e.g. increasing amounts of elements in bodies of water toward the source(s), as shown in Figure 16, or they may be represented by dispersion trains, e.g. increasing amount of elements upstream in the hydrologic system (ground or stratal water) toward the source(s), as depicted in Figure 17.

These two conditions are met to varying degrees, depending on the geological situations and geomorphological settings as follows:

1. In many terranes, the host rocks and deposits are porous and permeable, permitting good circulation of ground waters; in others, the effects of diagenesis and/or metamorphism result in compact impermeable rocks and frequently the effective sealing of faults, fracture zones, joint systems and shear zones by minerals such as carbonates and quartz. In addition, mineral deposits in such terranes tend to be compact and impermeable. These features impose major restrictions on the circulation of ground waters and generally prevent them from coming into contact with sufficient surface areas of the ore and gangue minerals to permit solution of their constituent elements.

2. Hilly, mountainous and rugged topographic relief favour high hydrologic heads, relatively rapid movement of ground waters and abundant springs; rolling and flat topographic relief, such as characterizes much of the Canadian Shield, is marked by low hydrologic heads in the ground-water systems, restricted vertical percolation of ground waters, relatively few springs compared with mountainous areas and terrains, and generally stagnant low or non-oxidizing surface waters.

3. Glaciation: the effects of glaciation are manifold. In many areas covered by glacial clays, the mineral deposits are effectively isolated from circulating oxidizing ground waters. Similar conditions prevail in some terrains covered by thick till sheets.

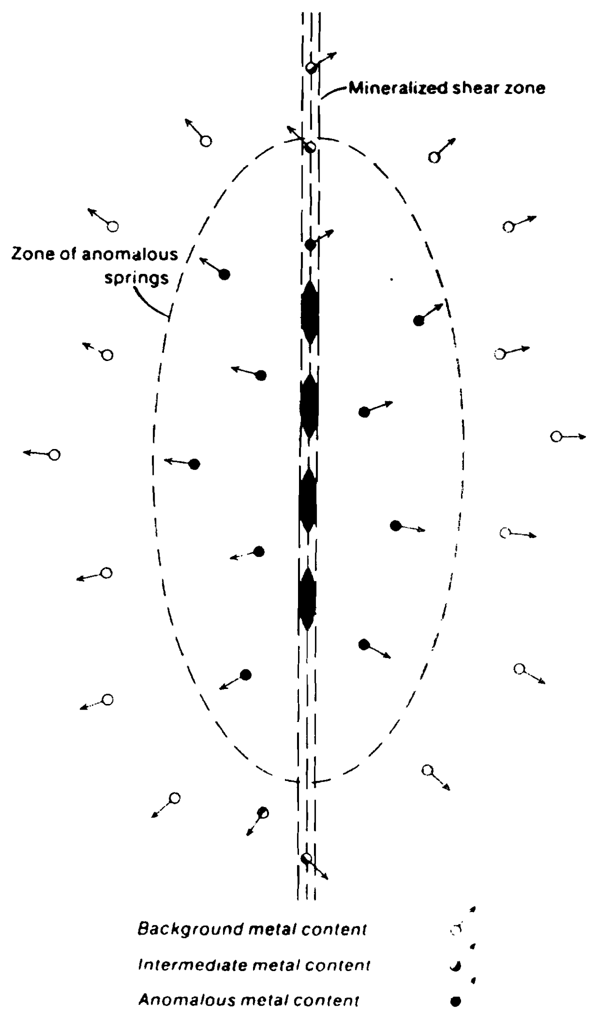


FIGURE 13. Idealized surface pattern of anomalous springs forming a halo around a mineralized zone.

4. The presence of permafrost effectively prevents circulation of ground waters. This is especially true where the permafrost extends to depths of 150 metres or more. Near-surface solution, leaching and transport of elements from deposits may, however, be notable in the active zone during summer months. In areas of high topographic relief, windows commonly occur in the permafrost, mainly in the vicinity of ground waters moving along faults and fracture zones. Similar conditions prevail near and under bodies of surface water (usually lakes) in some parts of the world underlain by permafrost.

Procedures for the sampling and analysis of waters and precipitates obtained from the orifices of springs, drill holes, etc. are covered in most standard text-books on geochemical prospecting and in the papers by Boyle *et al.* (1969, 1971) and Gleeson and Boyle (1976). Great care must be taken in sampling natural waters and their precipitates to prevent contamination of the samples and to ensure that the samples obtained are representative of the water and/or precipitate in the spring, well, drill hole, etc.

Hydrochemical methods of detailed prospecting for blind deposits can be based on analyses of the following:

(1) spring waters and their precipitates;

(2) ground waters and precipitates from drill holes, wells, faults, etc.;

(3) waters issuing from diamond drill holes, faults, shear zones, etc. into mine workings and open pits; also analyses of precipitates associated with these waters.

Each of these is briefly discussed below.

Spring Waters and Their Precipitates

The elemental constituents of springs and their precipitates are particularly useful as indicators to outline or locate mineralized zones in which deeply buried deposits may be present. Analyses of the water of springs are generally effective in this respect, although the precipitates frequently give better indications because they act more or less as resins, collecting the traces of metals and other elements present in the water. This

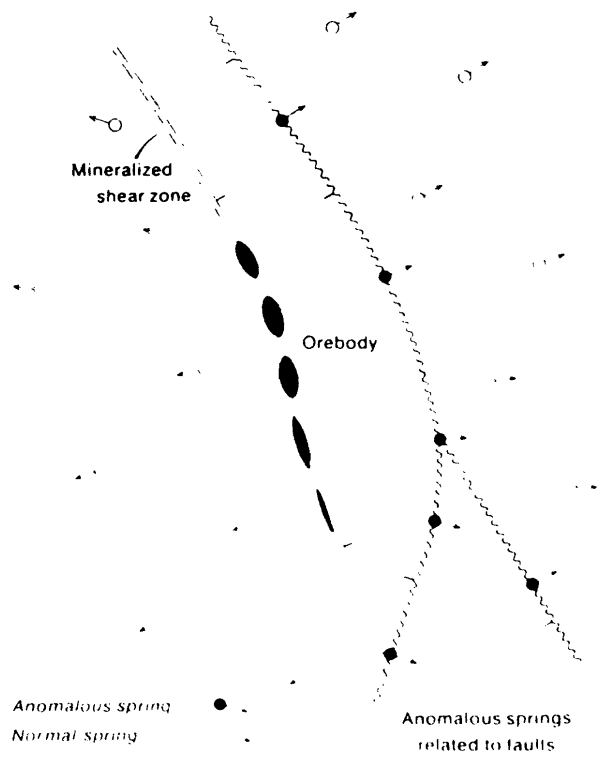


FIGURE 14. Idealized representation of anomalous springs forming a linear and sinuous pattern near a mineralized zone.

is especially so if the precipitates are high in hydrous manganese oxides, hydrous iron oxides and humic materials.

The use of springs in hydrogeochemical surveys is particularly effective in reconnaissance work where the springs are widespread and where the surface pattern of those that are anomalous assumes a halo about a concealed mineralized zone, as shown in Figure 13. More generally, however, the pattern of anomalous springs is non-symmetrical with respect to mineralized zones, being linear or sinuous in plan and related to the traces of mineralized faults and shear zones, bedding planes, beds of porous rocks, late faults, etc., as shown in Figure 14. In section, the relationships of springs to mineral deposits are complex, as shown by some examples in Figure 15. Other examples will suggest themselves to the imaginative exploration geologist.

Relatively little work has been done on the use of springs in hydrochemical surveys, and a proper assessment of the methods is, therefore, not possible. However, limited investigations suggest that the method is applicable in reconnaissance surveys and may also be useful in detailed work in conjunction with other types of geochemical surveys.

Extensive analytical work in the Cobalt area of Ontario (Boyle *et al.*, 1969) indicates that spring waters and their precipitates in the vicinity of the known native silver-Ni-Co arsenide deposits are greatly enriched in a number of metals compared with those in rocks that are essentially barren of deposits. This feature is especially marked for the contents of Zn, Cu, As, Sb, Ag, Ni and Co, which are an order to many orders of magnitude greater in the springs and their precipitates in the vicinity of mineralized zones as compared with those in barren areas. Details are given in the original publication.

Similar work by Gleeson and Boyle (1976) in the Keno Hill area of the Yukon shows that the lead-zinc-cadmium-silver deposits are marked, and in places haloed, by springs with waters that are highly anomalous in Zn, Fe, Mn and SO_4; the limonite-wad precipitates associated with these springs are, likewise, markedly anomalous, particularly in Zn, Cu, Pb, Ni, As, Sb, Mo and F (Gleeson and Boyle, 1980).

The writer has also determined the metal content of spring waters and precipitates in the vicinity of mineral deposits in a number of other mineral belts in Canada, especially at Yellowknife, N.W.T., Bathurst, New Brunswick, and Walton, Nova Scotia (Boyle, 1972). In these mineralized belts, seepages, springs and waters along faults, as well as the available precipitates, are enriched in Zn, Cu, Ag, As, Sb and other elements in the vicinity of the deposits, whereas other waters and precipitates at a distance have background values.

On limited data, therefore, one can conclude that mineralization and mineral deposits are generally reflected by the higher contents of the ore and gangue elements in nearby springs and particularly in their precipitates. This feature, when integrated with other geochemical patterns, provides another aid for explorationists in helping to delineate concealed mineralization.

Ground Waters and Precipitates From Drill Holes, Wells, Faults, etc.

This technique utilizes water samples obtained from drill holes put down in drift or bedrock, from domestic wells in drift, from rock wells and from old prospect shafts, adits, etc. The aim is to obtain samples of the ground water, and if possible to outline anomalies in the hydrologic system and trace the dispersion patterns up the hydrologic gradient to their source. Outlining anomalies in the ground-water system is relatively easy and depends entirely on the number of drill holes, wells, etc. from which samples can be obtained. Tracing dispersion patterns in ground-water systems is, however, difficult to say the least, as a knowledge of the direction of flow and the hydrologic gradient is imperative. To trace the direction of flow of underground waters one must have a thorough knowledge of the topography and the geologic structure. Certain

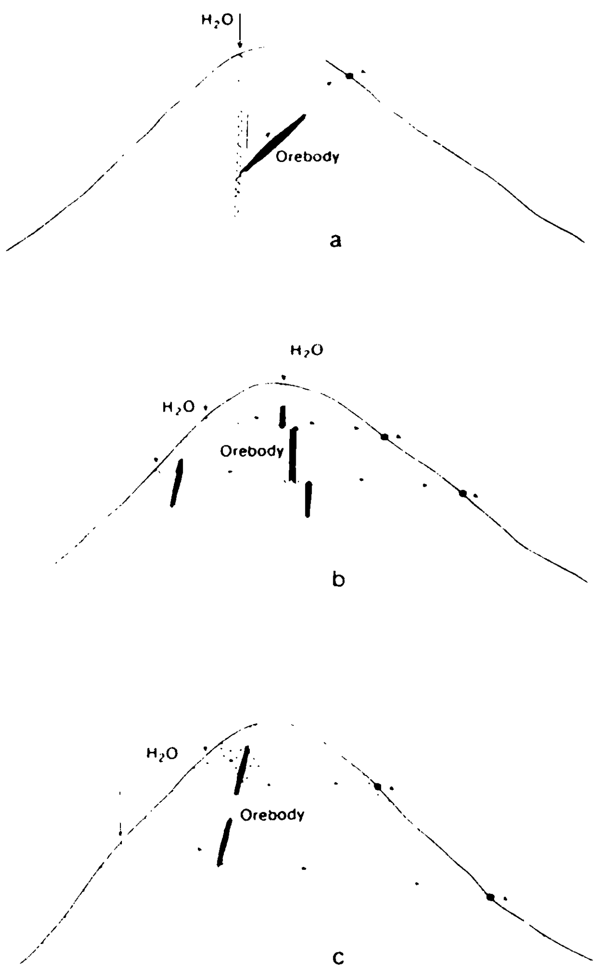


FIGURE 15. Diagrammatic sections illustrating: (a) spring at outcrop of mineralized fault; (b) springs along surface traces of cross faults; and (c) springs along surface traces of porous beds and bedding planes.

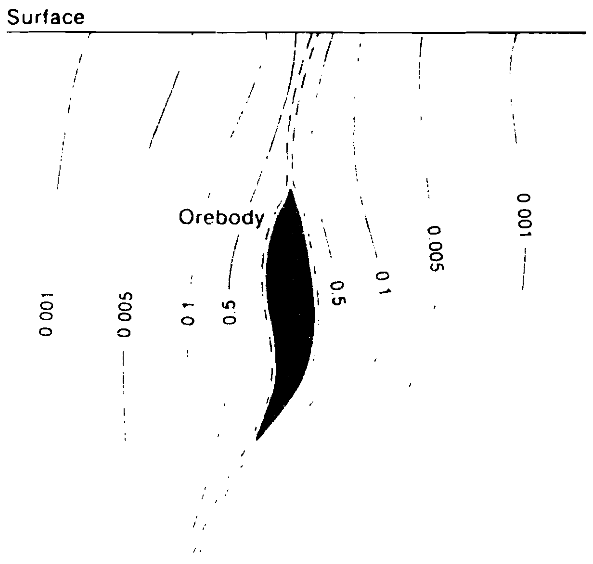


FIGURE 16. Idealized dispersion halo of elements in ground water in the vicinity of metalliferous deposits; values are in ppm Zn.

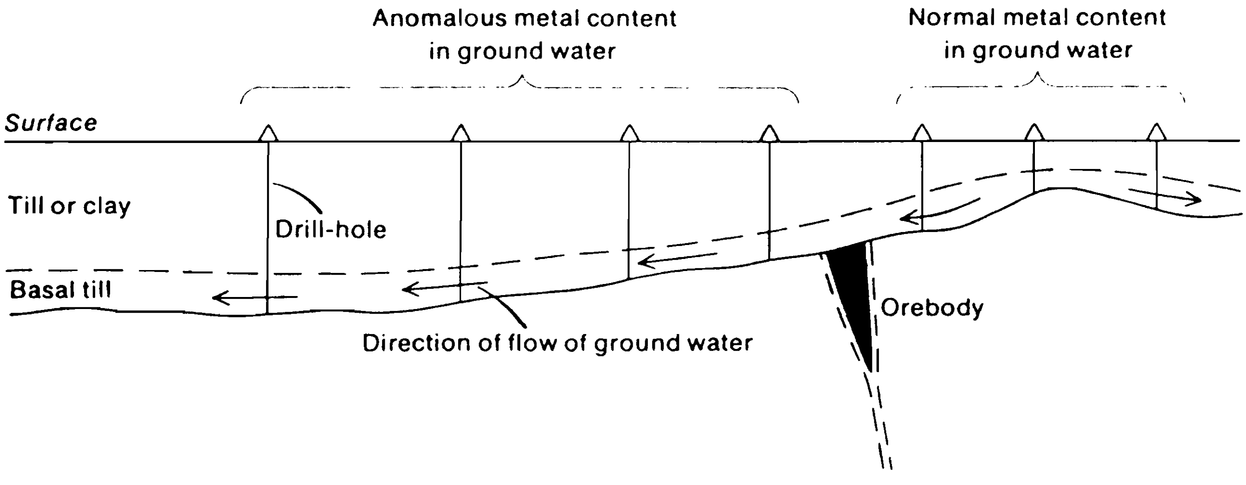


FIGURE 17. Idealized longitudinal section of a glacial valley showing distribution of normal and anomalous metal contents in ground water near a mineral deposit.

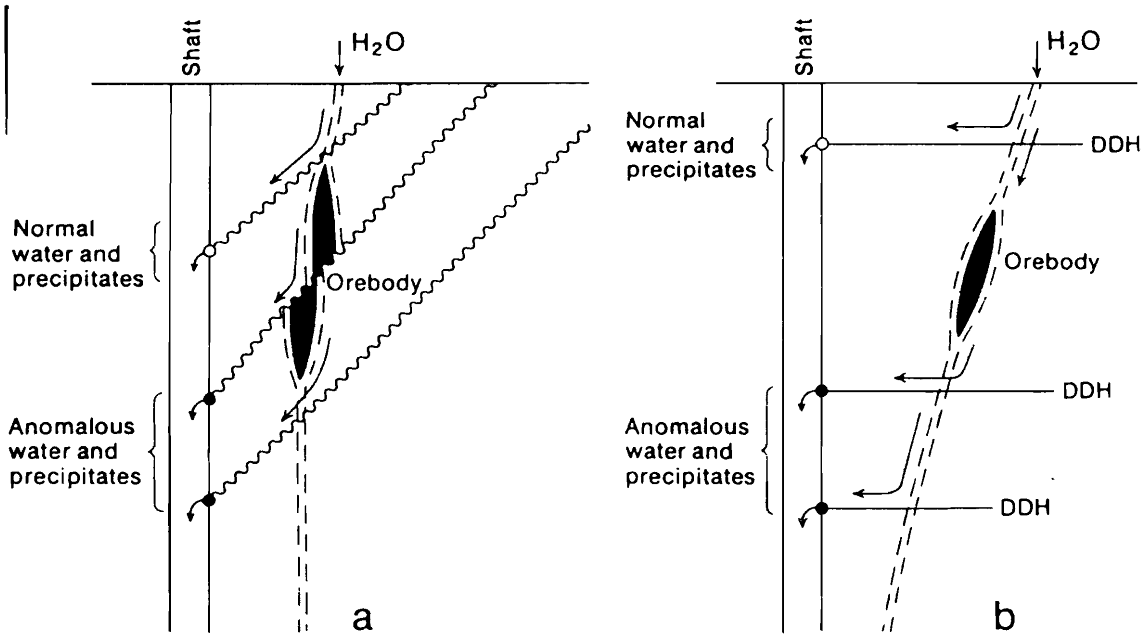


FIGURE 18. Sketches illustrating the use of water and precipitate analyses in mineral exploration: (a) analyses of water and precipitates along fault zones and other planar structures; (b) analyses of water and precipitates from diamond drill holes.

geophysical methods may be useful in some places, and radiotracers and dyes may assist where a sufficient number of drill holes are available.

The technique of sampling ground waters would seem to have a widespread application where the ground-water system is well developed in a mineralized belt. Limited data obtained in surveys conducted by the writer at Yellowknife, Northwest Territories, Bathurst, New Brunswick, Cobalt, Ontario, and Walton, Nova Scotia suggest that many types of mineral deposits have an anomalous water halo that pervades the country rocks, as shown in an idealized manner in Figure 16. The exact definition and nature of such halos, however, awaits concerted research. One can also model numerous applications of the technique of sampling ground waters in terrain covered by glacial deposits, particularly valleys of both glacial and preglacial age. One of these is shown in Figure 17; others will suggest themselves to the imaginative geologist.

A survey of all available drill-hole and well waters was carried out in the Cobalt and New Liskeard district of Ontario by the Geological Survey of Canada with a view to locating anomalous zones of ground water associated with as-yet undiscovered native silver deposits. The results are given in the paper by Boyle *et al.* (1969). A number of anomalies were discovered, but their significance requires further investigation.

The use of helium and radon in well waters, drill-hole waters and springs as an aid in locating radioactive deposits is described under Atmochemical Methods.

Analyses of Waters Issuing from Diamond Drill Holes, Faults, etc., in Mines and Open Pits

This technique is similar to that described above. Two applications suggest themselves, as shown in Figure 18; others will be apparent to the mining geologist. In addition to analyses of the water, one should pay particular attention to precipitates at the orifices of drill holes and have them analyzed for the elements sought in the deposits. Care should be taken to sample only the ground water and its precipitates, avoiding contamination due to mine waters, or those that have leached tailings, etc. The best results are obtained from long drill holes put out from mine workings to search for extensions of veins, lateral vein systems, etc. Drill holes frequently miss large orebodies, yet they may tap water that has access to such orebodies. By a simple analysis of drill-hole water, one may get a clue to hidden mineralization and may thus sometimes snatch fortune from adversity.

Hydrochemical methods, used in the various ways described above, provide a third dimension to prospecting in that waters search great volumes of the rocks and frequently carry to the surface or into underground workings clues of the presence of hidden mineral deposits. The methods are as yet only poorly developed for use in mineralized terranes. For this reason, concerted research is urgently required by the mineral industry, universities and government agencies on both a reconnaissance and detailed scale. I predict that the results will be well worth the effort and money spent.

Atmochemical Methods

Atmochemical surveys are based on the analysis of gases associated with mineral deposits. Water in its various forms is generally excluded. The gases form both mobile and static gaseous aureoles and leakage halos in the host rocks of deposits and in their overlying soils, glacial drift, etc. The mobile gases include those resulting mainly from oxidation, including bacterial oxidation, and degassing of various minerals in deposits (e.g. CO_2 SO_2, H_2S, COS, $(CH_3)_2S$, CS_2, I_2, Hg, $(Hg(CH_3)_2$, AsH_3, etc.), and from atomic disintegration of radioactive minerals, principally He, Rn and Ar. The gases in static aureoles and leakage halos are related to diagenetic, metamorphic and endogene mineralizing processes and include mainly CO_2, H_2S, N_2 and other volatiles trapped in various types of inclusions in minerals. Only the gases in mobile aureoles and leakage halos are considered here; those interested in the role of mineral inclusions in prospecting for blind deposits should refer to the works by Roedder (1979) for a variety of mineral deposits and Boyle (1979a) for auriferous deposits.

The sampling media employed in atmochemical surveys include: rocks; soils, glacial overburden, and their vapours; ground waters; and gases in the air of the atmosphere. Inorganic and organic particulates in the air can also be utilized (Weiss, 1971; Barringer, 1979). Techniques of sampling are given in the publications of Bristow and Jonasson (1972), McCarthy (1972), Smith *et al.* (1976) and Dyck (1976).

The literature is replete with references describing the application of vapour geochemistry in the search for concealed sulphide deposits. Most of the work has been of an experimental nature, and only a few detailed surveys seem to have been carried out with the express purpose of discovering blind deposits. Nevertheless, many of the experimental results are encouraging, especially for Hg (Bristow and Jonasson, 1972; McCarthy, 1972; Ovchinnikov *et al.*, 1973; Boldy, 1979, 1981), but much more research on the methods is required to place them on a routine survey basis and to provide adequate background data for the interpretation of the results obtained.

Atmochemical surveys based on the gaseous disintegration products of thorium and uranium have been widely applied in the search for deeply buried radioactive deposits. Radon (^{222}Rn) has been the most extensively utilized gas, although helium (^{4}He) has found some application. The literature is extensive on the use of radon surveys, a review of which is given by Boyle (1980, 1982). Two general procedures are commonly employed—direct extraction and measurement of radon in the geological sampling media, such as soils and waters (Smith *et al.*, 1976; Dyck, 1979, 1980); and photographic, alpha track etching, or instrumental methods for the detection and determination of the alpha active radon by implantation of the measuring apparatus or films in the overburden, stream sediments, lake sediments, etc. (Gingrich, 1974; Gingrich and Fisher, 1976; Gaucher, 1976; Hood, 1980, 1981). Helium surveys have found some application in prospecting for deeply buried uranium deposits (Dyck, 1976; Boyle, 1982) and also for oil and gas pools. The sampling media generally comprise soils and glacial overburden and natural waters. The samples are usually hermetically sealed in suitable containers in the field, after which the helium is extracted and analyzed isotopically in a well-established mobile or stationary laboratory (Reimer, 1976). An example of a helium survey carried out by Reimer (1977) over a roll-type uranium deposit in Weld County, Colorado is illustrated in Figure 19. The deposit lies some 10 metres below the surface.

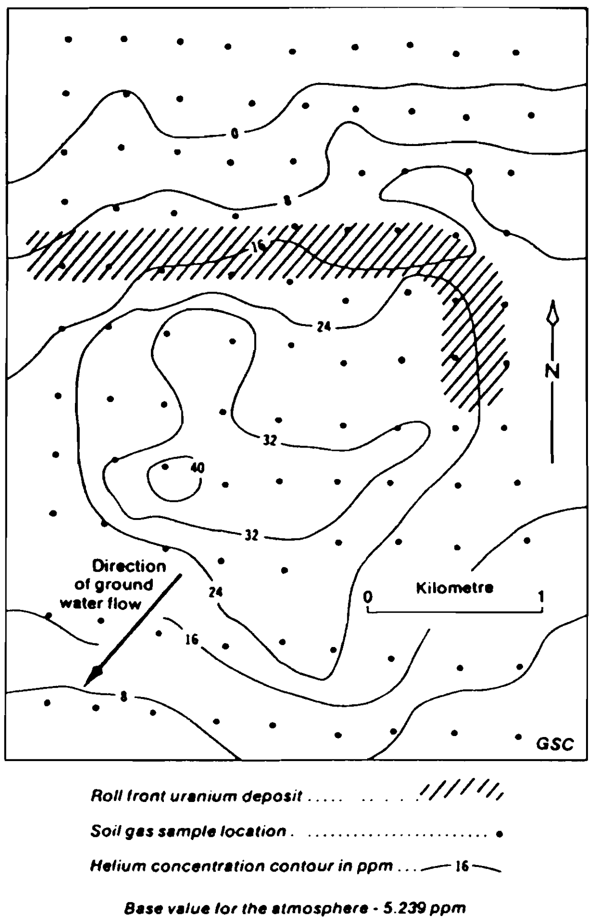


FIGURE 19. Contour map of helium in soil gas in the vicinity of the Weld County, Colorado, roll-type uranium deposit (after Reimer, 1977).

A review of the literature indicates that radon surveys have been successful in indicating the presence of deeply buried uranium deposits in a number of varied geological terranes. The depth of penetration is considerable, some investigators claiming that mineralized zones and orebodies can be detected up to 200 metres below the surface under favourable conditions. Similar claims have been made for helium surveys, although the number of examples are not as extensive as for radon.

Compared with other types of radiometric surveys, the great depth of penetration of helium and radon techniques is a considerable advantage because gamma-rays are completely shielded or severely attenuated by 0.5 to 1.0 metre of soil or water. Great care must be taken, however, in the interpretation of helium and radon surveys, especially those utilizing unconsolidated materials as sampling media, as displacement of anomalies with respect to the foci of mineralization is common, and spurious anomalies due to a variety of causes, mainly the channelling effects of faults, fractures, shear zones and conducting sedimentary beds and contacts, often confuse the unsuspecting geochemist.

Biogeochemical Methods

The techniques utilized in biogeochemical prospecting surveys are varied. One technique employs the indicator qualities of certain plants and animals (geobotany and geozoology); another utilizes chemical analyses of plants and animals for specific elements or their indicators in the search for deposits; and still other techniques employ chemical analyses of fossil residues or derivatives of plants and animals including the A horizon of soils, peat, lignite, coal and polymerized hydrocarbons. The methods and procedures employed in biogeochemical prospecting are discussed at length by Malyuga (1964), Cannon (1979) and Brooks (1972, 1979a, 1979b).

All the methods of biogeochemical surveys are probably effective in prospecting for blind mineral deposits, although some, such as the indicator qualities of plants and animals, require much more research to place them on a sound basis for the pin-point detection of deeply covered deposits. The other methods, specifically those based on the chemical analyses of plants and their fossil residues, especially the A horizons of soils and peat bogs, have a wide application in detecting and precisely locating deposits.

One of the great advantages of the use of plant analyses in searching for deeply buried deposits is the remarkably deep penetrating power of certain species (e.g. juniper), the root systems of which commonly tap the water table and/or mineralization as deep as 60 metres or more, especially in hot arid or semi-desert terrains. In temperate climates, the penetration is seldom as great, but the rootlets of alder, maple, juniper and willow have been noted by the writer as deep as 10 metres or more below the surface in till, gravel and clay overlying mineralization. It is obvious, therefore, that analyses of vegetation with deep penetrative root systems offer a potent method of prospecting for concealed deposits. In addition, the elements brought from mineralization at depth by plants and deposited on their death in the humic layers (A horizons) of the soil commonly lead to significant enrichment of many ore and indicator elements, a feature that provides a powerful method for detecting and localizing deeply buried deposits when humic horizons are analyzed, as indicated by numerous surveys mentioned by Boyle (1979a), Rose *et al.* (1979) and Levinson (1980). In fact, utilization of the A horizons of soils would appear to offer many advantages, particularly through ease of sampling, over other horizons of soils when prospecting for deposits in many types of overburdened terrain (Boyle and Dass, 1967).

Regional and detailed surveys utilizing the materials of bogs (muskegs) and marshes as sampling media offer a novel way of prospecting for concealed deposits, especially in northern terrains that have been glaciated. Many bogs (muskegs) in these terrains are ancient lakes infilled during a long period of time with gyttja and peat that have received enrichments of elements from flanking and underlying springs the waters of which have come into contact with deeply buried deposits. As most bogs and swamps are widely diverse in their origin and sedimentation history, it is not possible *a priori* to tell which horizon of the bog or swamp may be indicative of underlying or flanking mineralization, mainly because of the vagaries of the erosional processes and the hydrologic system that persisted during the development of the bog or swamp. In some places, surface samples may indicate the presence of mineralization; in others, intermediate or basal horizons, which in many cases are actually ancient lake sediments, may reflect the presence of deposits. In reconnaissance surveys, a single hole augured to bedrock (through underlying till if necessary) in the centre of the bog should be sufficient to ascertain the distribution of ore elements and their indicators in the profile of the bog (and underlying till); in detailed work, lines of holes spaced 20 to 100 metres apart on traverses perpendicular to the axis of the bogs and spaced at intervals of 100 to 500 metres will give a coverage that should not miss significant mineralization below the bogs or in the terrane on their flanks.

When bog and swamp surveys are carried out on a regional scale to locate concealed mineral deposits, it is advisable to analyze all bogs and swamps or at least a strategically high proportion of these organic deposits. The results should then be plotted and the geometric patterns of anomalous bogs and swamps assessed. In general, one or more of four idealized patterns will occur in a district: (1) no anomalous bogs or swamps are present, indicating a general lack of mineralization, or mineralization too deep or unaffected by oxidation processes, and hence not reflected by the bog or swamp materials; (2) a string or group of anomalous bogs or swamps overlies a mineralized belt usually in a topographically low-lying or basin environment; (3) strings or groups of bogs or swamps flank a mineralized belt usually on the down-drainage side; and (4) groups of bogs or swamps halo a mineralized belt.

Conclusions

It is axiomatic to say that in most mineralized belts of the world many undiscovered mineral deposits lie hidden below thick overburden or deep within the rocks in various favourable rocks and structures. To discover these hidden deposits is a major challenge to which neither geologists, geochemists nor geophysicists have really addressed themselves in earnest. Based on their knowlege of metallogenesis, field geologists can outline general areas in which specific types of deposits may occur, and they may even be able, by artful application of their acumen with respect to ore deposits, to pinpoint the fault system, shear zone, brecciated structure, or favourable bed or beds in which orebodies may occur. The geophysicists may assist by defining zones with specific magnetic, electrical and other properties, but they are commonly confounded by a great variety of stray fluxes that cost considerable money to discover their meaning. The geochemists are not much better off, as they must obtain samples before they can practise their art, and the proper samples are not readily obtained in most areas unless specific drilling programs are employed. It is obvious, therefore, that further progress in locating deeply buried mineral deposits will require extensive drilling of favourable structures and beds outlined by good geological field work and intuition. To assist in this effort, geochemistry has much to offer the explorationist in his search for blind mineral deposits.

This paper has reviewed techniques of using lithochemical methods based on leakage and enveloping halos. Such techniques offer deep penetration, and although few are foolproof, a number, especially those based on the vector properties of ratios, offer great promise. Pedochemical methods, likewise, have proven useful in discovering deeply overburdened deposits, expecially when overburden drilling has been employed. Hydrochemical, atmochemical and biogeochemical methods also offer techniques for assessing the mineral potential of ground to depths of several hundred metres or more under favourable conditions. The efficacy of each or of combinations of the various geochemical methods reviewed depends essentially on the type of mineralization, the extent of development of the primary and secondary dispersion halos, and the finances available for sampling techniques employing overburden drilling, bedrock drilling, and sophisticated water, gas and vegetation collection.

There is a woeful lack of fundamental research on geochemical methods designed to search for blind mineral deposits, a subject that must soon be addressed by the mineral industry, universities and government agencies if deeply buried blind mineral deposits are to be discovered in the future.

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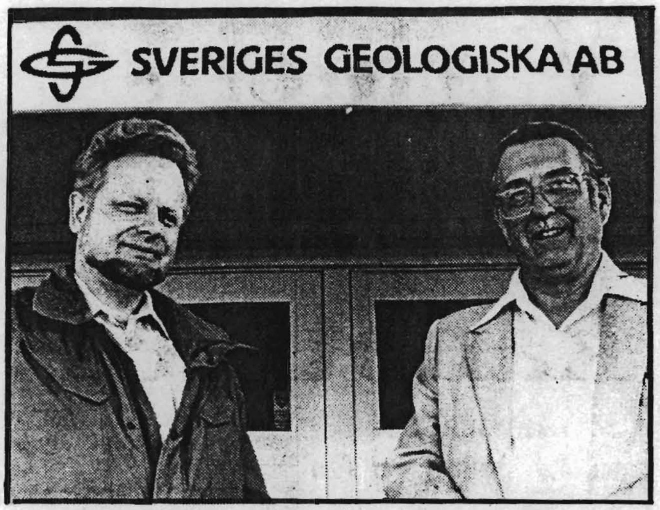
NSD FREDAGEN DEN 27 JULI 1984



Två experter reser just nu kors och tvärs i Norrbotten och letar efter guld. Det är SGAB:s Leif Carlson som hämtat förstärkning från Kanada via professor Robert Boyle.

Guldjakt i länet

Av HELENA NORDGREN

Luleå (NSD) Det finns goda möjligheter att hitta guld i Norrbotten. Så tror professorn och geologen Robert Boyle från Kanada. Han har under tio dagar rest runt i Norrbotten inbjuden av SGAB – Sveriges Geologiska AB – för att hjälpa till med att leta efter den dyrbara metallen.

Robert Boyle säger sig tidigare ha besökt alla guldländer i världen.

– Jag har arbetat över hela världen med guld. USA, Nigeria, Indien, Japan, Sovjet, Australien.

Till guldländerna tror han sig nu också kunna foga Sverige och Norrbotten.

Fast han understryker att sökandet efter guld är detsamma som att söka efter en nål i en höstack.

– Guld skiljer sig från andra metaller, det är mycket väl dolt, säger han.

Indikator

Och förklarar att guld därmed måste sökas via indikatorer.

– Den bästa indikatorn på guld är givetvis guldet självt. En andra indikator på att det finns guld kan vara förekomst av koppar. En tredje indikator kan vara förekomst av arsenik, fortsätter han.

Och konstaterar att Norrbotten både vad avser flora, fauna och geologi är mycket likt Kanada. Där utvinns årligen cirka 70 ton guld.

Och i Kanada har just en guldfyndighet i Hemlo vid Lake Superior börjat utvecklas.

Hur stor fyndigheten är säger han sig dock inte ha tillstånd att avslöja.

De första indikatorerna på guld i Hemlo hittades 1935. Efter fortsatt prospekterande glömdes området bort för att sedan åter tilldra sig intresse från privata undersökare 1980.

– Nu kommer troligen en ny stad att växa upp där ute i vildmarken. Troligen kommer tusentals människor att arbeta där, säger han.

Fil lic Leif Carlsson vid SGAB i Luleå har under de gångna tio dagarna släpat runt professorn till olika platser i länet.

Dels för att få hjälp till värderingar av redan anade indikatorer på guld dels för att få expertråd i största allmänhet.

– Vi har försökt få hit Robert Boyle sedan två år tillbaka och därför är det mycket värdefullt för oss att få tillgång till hans expertkunskap.

– Här i Sverige satsas det endast 200 miljoner per år eller tio procent på att söka guld, säger Leif Carlson.

– I Kanada är förhållandet motsatt. Där satsas cirka 80 – 90 procent av pengarna på att söka guld, säger Robert Boyle.

Än så länge har guldsökarna Leif Carlson och Robet Boyle alltså inte hittat något guld.

I går reste de upp till Kiruna för att fortsätta sina prospekteringar.

– Men vi har funnit indikatorer på vissa platser. Det finns goda geologiska, strukturella, kemiska och mineralogiska förutsättningar för att hitta guld i Norrbotten, säger Robert Boyle.

Och tar åter fram liknelsen om nålen i höstacken. SGAB:s projekt för prospektering av guld startade 1981 på uppdrag av NSG – Nämnden för Statens Gruvegendom.

– Men Hemlo är bara cirka 25 kvadratkilometer stort medan Norrbotten är cirka 100 000. Där är den bästa exemplifieringen av svårigheterna, säger Leif Carlson.

Robert Boyle arbetar bland annat på uppdrag av FN, liksom för statliga och privata bolag.

– Men jag söker inte guld för egen del. Och jag ställer mig helt utanför politiska överväganden. Jag är endast tekniker.

Han ska
leta guld

☐ **– Förutsättningarna för att hitta guld i Norrbotten är mycket stora.**

Orden kommer från Robert Boyle – en av världens främsta guldletare. Boyle, som är professor i Kanada, arbetar just nu som konsult åt SGAB i Luleå.

SGAB letar sedan fyra år efter guld i Norrbotten. Totalt har man 20 miljoner att använda varje år.

– Det tar lång tid att hitta guld – om det finns något.

Foto: STIG EIDEGREN

● *Det finns stora chanser att hitta guld här i Norrbotten, bland annat ur geologisk synpunkt, säger professor Robert Boyle.*

Världsauktoritet i guldjakt hjälper SGAB:

STORA CHANSER HITTA GULD HÄR

–Av Jackie Bortz–

LULEÅ. En av världens främsta guldletare är i Norrbotten. Han heter Robert Boyle och säger så här om eventuella fyndigheter i länet:

– Förutsättningarna för att hitta guld i Norrbotten är mycket stora.

● *– Det finns stora chanser att hitta guld här i Norrbotten bland annat ur geologisk synpunkt, säger professor Robert Boyle, en av världens främsta experter på guldletning.*

Foto: STIG EIDEGREN

Det är Sveriges Geologiska AB, SGAB, som plockat hit professor Robert Boyle från Ottawa i Kanada. Boyle fungerar som konsult åt SGAB.

Professor Boyle har besökt olika delar av länet där det finns förutsättningar att hitta guld. Just att leta guld är något speciellt.

☐ *Som en nål i en höstack*

– Koppar kan man hitta genom att se det. Uran kan man hitta genom att använda olika mätinstrument. Men så kan man inte göra när man letar efter guld. Letandet efter guld påminner om att leta efter en nål i en höstack, framhåller Robert Boyle.

Hur bär man sig åt för att hitta guld?

– Först måste man studera geologin. Därefter använder man geofysik och geokemi. Man bearbetar alltså olika fyndigheter och ser om det finns guld.

Att SGAB anlitar en världsauktoritet på guldjakt är naturligt: Sedan fyra år letar SGAB guld i länet. Totalt har man 20 miljoner kronor att använda varje år.

Projektledaren för guldletningen i Norrbotten heter Leif Carlsson.

☐ *"Vänta inget Klondyke"*

– Det tar lång tid att hitta guld – om det finns något. Sedan tar det lång tid innan brytning kan komma igång. Något Klondyke tror jag dock ingen ska gå att vänta på, säger han.

Men just ett Klondyke är vad professor Robert Boyle berättar om. Det gäller en fyndighet i norra Onatorio i Kanada.

– Den här guldfyndigheten ligger vid en plats som heter Hemlo. Fyndigheten är en av världens största. Just nu förbereder man brytning och den beräknas komma igång nästa år.

Nu tog det lång tid innan man hittade Hemlo.

– Redan 1935 var det några amatörgeologer som hittade tecken på att det fanns guld just här. Men de kunskaperna glömdes bort. Så på 70-talet var det åter några som letade men inte heller då hittade man något av värde.

Först 1980 gjordes upptäckten, berättar professor Boyle.

☐ *Brytning nästa år*

– Det var några geologer som färdades med bil på den Transkanadensiska vägen som hittade guld. De tog prover längs vägen. Det var för fyra år sedan. Nästa år kan brytningen börja.

Den lilla järnvägsstationen Hemlo ligger mitt i ödemarken i norra Onatorio. Snabbt förvandlas ödemarken till något annat: Här ska tusentals människor bo – en hel stad håller på att byggas upp.

Exakt hur stor fyndigheten är vill inte professor Robert Boyle säga – det enda han berättar är att fyndigheten är en av världens största.

Så här säger Leif Carlson om att ha professor Boyle som konsult:

☐ *"Oerhört glädjande"*

– Det är oerhört glädjande för oss att få en sådan auktoritet till hjälp. Professor Boyle har en oerhörd kunskap och erfarenhet av guldletning – han började som geolog när jag föddes!

Och nu hoppas alltså SGAB att Robert Boyles kunskaper ska hjälpa till att hitta de guldfyndigheter som troligen gömmer sig lite här och var i länet.

Norrbottens-Kuriren fredag 27 juli 1984