THE BEHAVIOUR OF THE ELEMENTS Ni, Co, Cu, Pb, Zn, Au, Ag, Mo, SN, W AND U IN THE MAGMATIC, HYDROTHERMAL, SEDIMENTARY AND WEATHERING ENVIRONMENTS

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CONTENTS

INTRODUCTION

In the last two decades much has been published on the behaviour of certain elements in the magmatic, hydrothermal, sedimentary and weathering environments, but the information is scattered throughout the literature. This situation prompted the present study on the elements Ni, Co, Cu, Pb, ZN, Au, Ag, Mo, Sn, W and U.

The behaviour of the elements Ni, Cu, Pb, ZN, Au, Sn, W and U has been studied experimentally in some depth. Ag has been moderately studied, but there is very little information about Co and Mo. Studies on the complexes formed by the elements within the hydrothermal and aqueous environment are often inconclusive and controversial, but conclusions are drawn as to the more likely complexes formed.

A genetic classification of ore deposits is used as a framework for the discussion. The source of the elements is regarded as being the mantle, and therefore discussion on other possible sources is beyond the scope of this dissertation. The crystal chemistry and geochemistry of the elements are presented and the essay concludes with a discussion on the elements within their depositional environments.

Appendices 1 and 2 are Periodic Tables of the Elements illustrating atomic number and weight, atomic and ionic radii, crystal structures, electronegativity values etc. Appendix 3 is a tabulation of the concentration of all elements within various rock-types and Appendix 4 is a table which illustrates common compounds of the elements.

I GENETIC CLASSIFICATION OF ORE DEPOSITS

The following genetic classification of ore deposits (Figure 1) provides a framework for a discussion on the behaviour of selected elements.

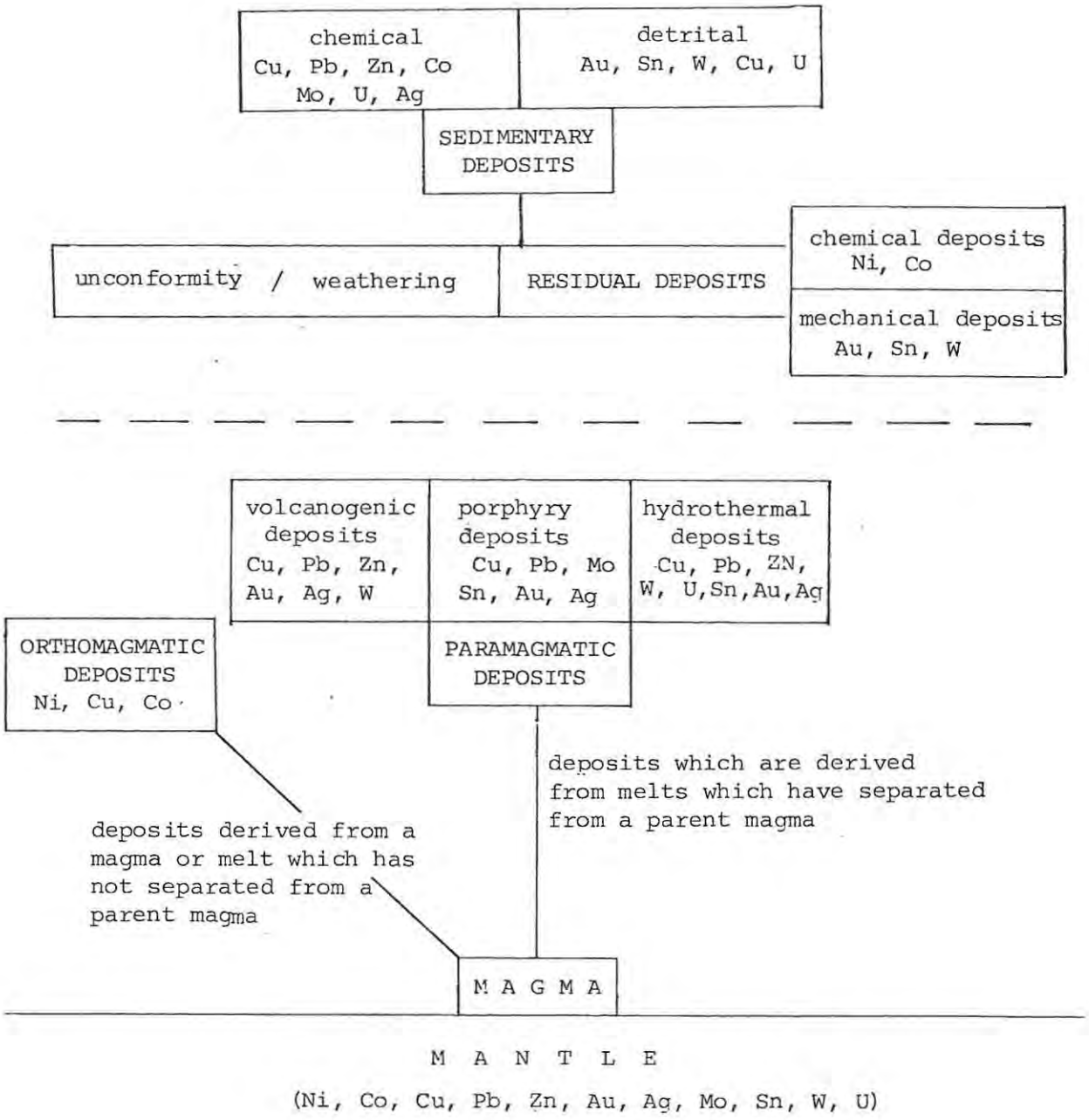


Figure 1. Genetic Classification of Ore Deposits.

ORTHOMAGMATIC DEPOSITS[*]

A) Nickel/Copper Deposits

Nickel, copper and cobalt are the only elements of the group under consideration which have orthomagmatic affiliations and nickel is the only one of these which is exclusively orthomagmatic in origin. Corbett (1978) in a review of orthomagmatic deposits suggested that nickel/copper sulphide deposits could be classified into three major groups :

1. Deposits with a Ni/Cu ratio of 10:1 to 20:1, associated with the high magnesium basalt suite (komatiites).

(a) Volcanogenic extrusive deposits of massive sulphides. Examples are Kambalda, Scotia (Western Australia), Shangani, Damba (Rhodesia), Alexo, Langmuir (Abitibi Belt - Canada), and part of the Thompson nickel-belt (Canada).

(b) Subvolcanic intrusive deposits of disseminated sulphides. Examples are Agnew, Mt. Keith, Mt. Clifford (Western Australia), Trojan (Rhodesia) and part of the Thompson nickel-belt (Canada).

2. Deposits with a Ni/Cu ratio of $\pm$ 3:1, associated with injected suites, dykes and plugs of gabbro/hartz burgite, include Sudbury (Canada, the Carr Boyd Pipes (Australia), the Vlakfontein Pipes (South Africa) and Pechenga (Kola Peninsula, Russia).

3. Deposits with a Ni/Cu ratio of 1:1 or less, associated with tholeiitic sills and complexes differentiated *in situ*.

(a) Deposits intruded into mobile belts and greenstone belts. Examples are Lynn Lake, the Dundonald sill (Canada), Pikwe Selibe (Botswana), and Empress (Rhodesia).

(b) Deposits intruded into stable cratonic areas. Examples are Insizwa, and Merensky Reef of the Bushveld Igneous Complex (South Africa), Palisade Sill (New Jersey, U.S.A.), and Noril'sk (Western Siberia, Russia).

B) Diamond Deposits . Kimberlite pipes.

[*] See Figure 1 for definition of Orthomagmatic and Paramagmatic.

PARAMAGMATIC DEPOSITS

A) Volcanogenic Deposits

1. Central vent-type

Deposits included in this class are :

(a) The Canadian Archaean copper/zinc orebodies at Noranda, Kidd Creek, Mattagami Lake, Flin Flon and Snow Lake.

(b) The Kuroko-type polymetallic (Cu, Pb, Zn) deposits of Japan, Fuji.

(c) The Prieska copper/zinc deposit.

2. Rift-type

(a) Cupreous-pyrite deposits.

(i) Incipient rifting of oceanic crusts. Cyprus-type deposits;

(ii) Incipient rifting of stable continental crust. Besshi-type deposits and those deposits associated with the Matchless Amphibolite belt-Otjihase, Gorob, Hope etc.

(b) Polymetallic (Cu, Pb, Zn) deposits. Incipient rifting of stable continental crust. Iberian/Scandanavian/New Brunswick deposits.

3. Exhalative-type

Deposition of metals from hydrothermal fluids of magmatic origin issuing forth from the floor of broad, fairly shallow, rift controlled basins.

(a) Associated with bolcaniclastic rocks. The Rosh Pinah lead/zinc deposit. The Sullivan deposit is possibly one of the most important in this class.

(b) Not associated with rocks of a distinctive volcanic origin. Examples include Mt. Isa, McArthur River.

B) High-level intrusive deposits

1. Porphyry Copper/Molybdenum deposits. Examples include Chuquicamata, Bingham, El Salvador, El Teniente, Sar Cheshmah, Bougainville etc.

2. Porphyry Molybdenite deposits. Examples include Urad-Henderson, Climax, Questa.

3. Porphyry Tin deposits. Examples include Llallgua, Chorolque (Bolivian tin-belt).

C) Hydrothermal deposits
(not obviously related to a cupola or stock of porphyry affiliations)

1. Elevated temperature of deposition

(a) Veins. Examples include Rooiberg (tin), El Dorado (uranium).

(b) Disseminations. Examples include Zaaiplaats (tin), and endogranitic deposits of tin, tungsten, molybdenum etc.

(c) Stockworks and breccias. Examples include Messina (copper), Rössing (uranium) and Krantzberg (tungsten), Palabora (copper).

(d) Pegmatites. Examples include Uis (tin), and Brandberg West (tin and tungsten).

2. Low temperature of deposition (waters not necessarily originating from an igneous source)

(a) Stratabound/stratiform uranium/vanadium deposits. Uranium/vanadium in sandstone. Colorado, Wyoming, Karoo, etc.

(b) Calcrete deposits. The Yeelirrie uranium deposits.

(c) Karst-type deposits. Mississippi Valley-type lead/zinc deposits.

RESIDUAL DEPOSITS

(deposits related to weathered unconformities)

A) Chemical deposits. Nickel laterites and bauxites.

B) Detrital deposits. Concentrations of minerals which are resistant to weathering - diamond, gold, cassiterite, wolframite, scheelite.

A) Chemical Deposits

1. Stratabound/stratiform copper, lead and zinc deposits. Includes certain deposits of the Zambian Copper Belt, the Kupferschiefer and Red Beds copper deposits.

2. Stratiform Iron and Manganese deposits. The Transvaal and Hammersley basins.

B) Detrital Deposits

1. Stratabound/stratiform gold/uranium placer deposits.* Examples include the Witwatersrand (gold, uranium) and Elliot Lake (uranium) deposits.

2. Alluvial deposits. Examples include the Malayasian tin deposits, Oamites and Roan Antelope (copper).

3. Beach Sand deposits. Examples include Richards Bay heavy mineral deposit, and the diamond deposits at Oranjemund.

* A distinction is made between placer and alluvial deposits on the basis that the word "placer" as used here implies deposition from braided streams, and subsequent reworking of the sediments.

II CRYSTAL CHEMISTRY

The distribution of elements within different minerals and rocks of the earth's crust are governed by certain laws and rules and the following summary of these rules, and the chemical aspects of the selected elements, is drawn from the following texts : Bell and Lott (1963), Companion (1964), Cotton and Wilkinson (1972), Krauskopf (1967), Mackay and Mackay (1969), Mason (1952), Sisler et al. (1967), amongst others.

(a) Goldschmidt's Rules

In 1937 Goldschmidt classified the elements according to the stability of the compounds they formed with other elements. Elements which are generally inert (relative to iron) and which have a tendency to form metallic phases, were called siderophile. Elements which tend to concentrate in sulphides were called chalcophile, those which concentrate in silicates, were called lithophile, and those which are gaseous and/or present in the atmosphere were called atmophile. Table I is a list of the elements grouped according to their tendencies. The geochemical character of an element is considered to be governed mainly by its electron configuration. Lithophile elements have ions with an outer *8e* shell, chalcophile elements have ions with an outer *18e* shell, and siderophile elements have ions with incompletely filled outer electron shells.

TABLE 1. GOLDSCHMIDT'S GEOCHEMICAL CLASSIFICATION OF THE ELEMENTS

Siderophile	Chalcophile	Lithophile	Atmophile
Fe Co Ni	Cu Ag (Au)*	Li Na K Rb Cs	H N (C) (O)
Ru Rh Pd	Zn Cd Hg	Be Mg Ca Sr Ba	(F) (Cl) (Br) (I)
Re Os Ir Pt Au	Ga In Tl	B Al Sc Y Rare earths	Inert gases
Mo Ge Sn C P	(Ge) (Sn) Pb	(C) Si Ti Zr Hf Th	
(Pb) (As) (W)	As Sb Bi	(P) V Nb Ta	
	S Se Te	O Cr W U	
	(Fe) (Mo) (Re)	(Fe) Mn	
		F Cl Br I	
		(H) (Tl) (Ga) (Ge) (N)	

* Parentheses around a symbol indicate that the element belongs primarily in another group, but has some characteristics that relate it to this group.

(from Joyce, 1976, p. 21).

Goldschmidt believed that the principal factors controlling the distribution of the elements within crystal lattices were the atomic and ionic radii of the elements. The rules which Goldschmidt proposed as being important in governing the behaviour of elements are :

(i) If two ions have the same radius and charge, they will enter into solid solution in a given mineral in amounts proportional to their abundances. The trace element is "camouflaged" by the major elements.

(ii) If two ions have similar radii and the same charges, the smaller ion will be preferentially concentrated in the solid phases.

(iii) If two ions have similar radii but different charges, the ion with the higher charge will enter a crystal structure preferentially.

If the trace element has a higher charge it is "captured" by the major element and enters early fractions. If the trace element has a lower charge it is "admitted" by the major element and enters late fractions.

(b) Exceptions to Goldschmidt's Rules

The above rules appear to satisfy the demands made upon them, with a few notable exceptions. For example, the Zn^{2+} ion (0,74Å) is intermediate in size between the Mg^{2+} ion (0,65Å) and the Fe^{2+} ion (0,76Å), thus it is expected that zinc would enter ferromagnesian silicates as does the Ni^{2+} ion (0,72Å) and the Co^{2+} ion (0,74Å). However zinc discriminates against octahedral sites (prevalent in ferromagnesian minerals) and prefers tetrahedral co-ordination. Thus Ringwood (1955), using the electronegativity concept, added a further rule which states that, for two ions of similar valencies and ionic radii the one with the lower electronegativity will be preferentially incorporated because it forms a stronger and more ionic bond than the other. [(In explanation, the concept of electronegativity is a measure of the attraction that an ion has for electrons, thus should the electronegativity of an ion be low, it will ionize

relatively easily, thereby being able to form strong ionic bonds. Generally, electronegativity values decrease across the periodic table from right to left and down the table within a Group)].

(c) Crystal Field Theory

The rules so far presented do not adequately explain the behaviour of the transition elements, whereas the crystal field theory, developed by Bethe (1929) and Van Vleck (1932), does. The crystal field theory is based upon the fact that the transition elements have an incomplete *d* electron shell and thus their behaviour is different from "normal" ions. Curtis (1964, p. 390) writes, "The wave-mechanical single electron wave functions for atoms can be written as the product of a radial function and a function dependent only upon the angular co-ordinates of the electron. In the case of a complete electron shell, the summation over all the electrons is that the shell shows no net angular component. Thus the total wave function has only radial components, being spherically symmetrical. This is the theoretical basis for the concept of a spherical ion. In the case of the transition elements, however, the ions may not be symmetrical within a given field".

The *d* electron shell, which when completely filled will contain 10 electrons, has five atomic orbitals as illustrated in Figure 2.

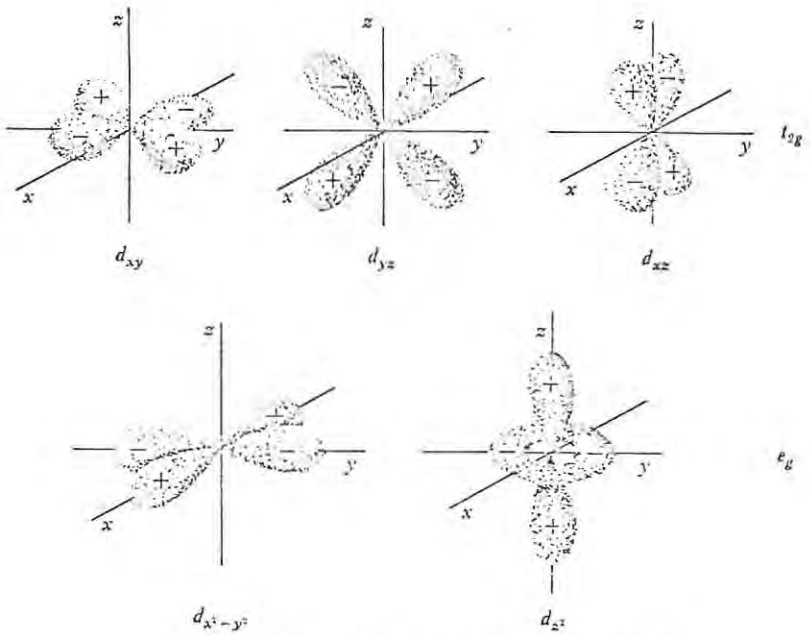


FIGURE 2. Boundary surfaces of atomic orbitals.

The boundaries represent angular distribution probabilities for electrons in each orbital. The sign of each wave function is shown. The *d* orbitals have been classified into two groups, t_{2g} and e_g, on the basis of spatial configuration with respect to the cartesian axes.

(from Burns, 1970, p. 7).

TABLE 2. *Electronic configurations of the elements of the first transition series*

	Atomic number	Element	Electronic configuration: Atom	*M* (II)	*M* (III)	*M* (IV)
	19	K	$(Ar)4s^1$	—	—	—
	20	Ca	$(Ar)4s^2$	(Ar)	—	—
† First transition series ↓	21	Sc	$(Ar)3d^14s^2$	$(Ar)3d^1$	(Ar)	—
	22	Ti	$(Ar)3d^24s^2$	$(Ar)3d^2$	$(Ar)3d^1$	(Ar)
	23	V	$(Ar)3d^34s^2$	$(Ar)3d^3$	$(Ar)3d^2$	$(Ar)3d^1$
	24	Cr	$(Ar)3d^54s^1$	$(Ar)3d^4$	$(Ar)3d^3$	$(Ar)3d^2$
	25	Mn	$(Ar)3d^54s^2$	$(Ar)3d^5$	$(Ar)3d^4$	$(Ar)3d^3$
	26	Fe	$(Ar)3d^64s^2$	$(Ar)3d^6$	$(Ar)3d^5$	—
	27	Co	$(Ar)3d^74s^2$	$(Ar)3d^7$	$(Ar)3d^6$	—
	28	Ni	$(Ar)3d^84s^2$	$(Ar)3d^8$	$(Ar)3d^7$	$(Ar)3d^6$
	29	Cu	$(Ar)3d^{10}4s^1$	$(Ar)3d^9$	$(Ar)3d^8$	—
	30	Zn	$(Ar)3d^{10}4s^2$	$(Ar)3d^{10}$	$(Ar)3d^9$	—
	31	Ga	$(Ar)3d^{10}4s^24p^1$	$(Ar)3d^{10}4p^1$	$(Ar)3d^{10}$	—
	32	Ge	$(Ar)3d^{10}4s^24p^2$	$(Ar)3d^{10}4p^2$	—	$(Ar)3d^{10}$

(Ar) = Argon core, $1s^22s^22p^63s^23p^6$.

(from Burns, 1970, p. 9).

Within the transition elements (Table 2) it will be seen that the Sc^{2+} *d* electron orbitals can accommodate nine further electrons, whereas Cu^{2+} only one more. In an isolated transition metal ion an electron can enter any one of the unaccommodated *d* orbitals available. In the ground state the electrostatic field associated with a transition element can be considered to be spherical, but when the ion enters a crystal structure the electrostatic field becomes distorted (not uniform in all directions) and the five *d* orbitals "split" into different energy levels, or subgroups. The manner in which the splitting occurs depends upon the position of the other ligands within the structure, relative to the orientation of the *d* electron orbitals in space. In octahedral co-ordination, with 6 identical ligands (Figure 3, Burns), the electrons in the five *d* electron orbitals are repelled by the ligands (not all equally), with the result that the energy within the centre of the ion is raised.

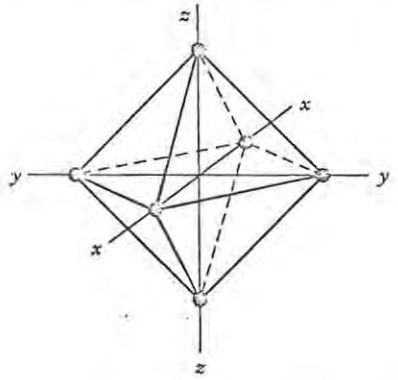


Figure 3. Orientation of ligands and *d* orbitals of a transition metal ion in octahedral co-ordination, also illustrating the orientation with respect to the axes (from Burns, 1970, p. 11).

To accommodate this "extra" energy the d orbitals split into two different levels of energy (Figure 4). With reference to Figures 2 and 3 it is seen that the e_g orbitals extend along the axes *towards* the ligands, thus the electrons of these orbitals are repelled with a force greater than the t_{2g} orbitals which project *between* the ligands. The energy level within the e_g orbitals is raised and conversely the energy within the t_{2g} orbitals is lowered. In Figure 4 the energy separating the t_{2g} and e_g electron group is designated Δo.

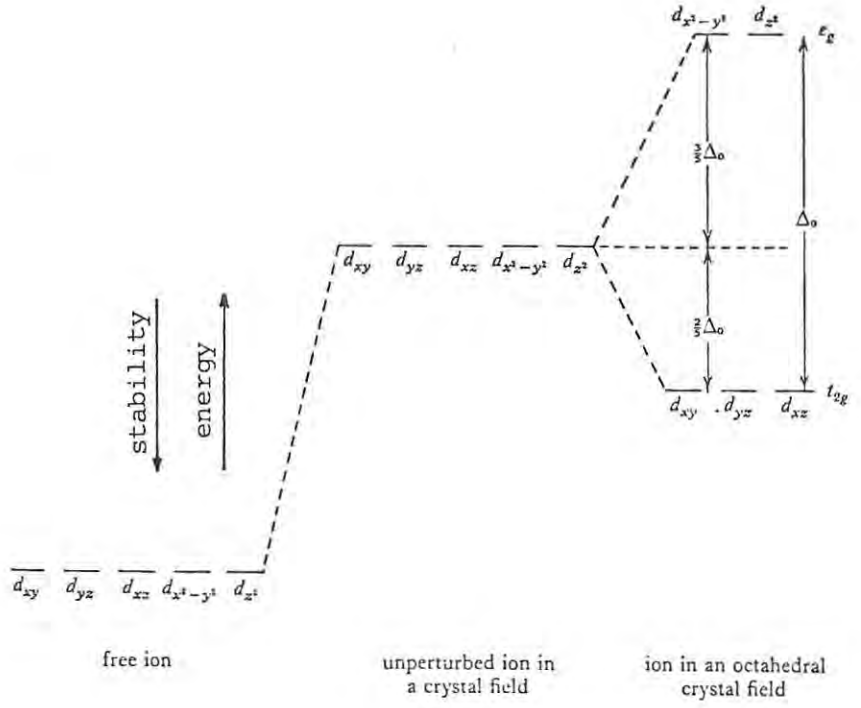


Figure 4. Relative energy levels of d orbitals of a transition metal ion in octahedral co-ordination (from Burns, 1970, p. 11).

The e_g orbitals will be the less stable group since electrons within these orbitals are closer to the negatively charged ligands of the crystal lattice. The energy of the three t_{2g} orbitals is lowered by $2/5\Delta o$ and the energy of the e_g orbitals is raised by $3/5\Delta o$. Therefore an electron in the t_{2g} orbital stabilizes a transition ion by $2/5\Delta o$, and conversely every electron in an e_g orbital diminishes stability by $3/5\Delta o$. The resultant nett stabilization energy is termed the crystal field stabilization energy.

In accordance with Hund's rule any electrons entering the d orbitals will distribute themselves within the orbitals in such a manner as to avoid pairing within any one orbital, and furthermore, due to the effect of crystal field splitting the electrons will favour the lower energy group (the t_{2g} orbitals) due to the increased stability. Thus the first three electrons added will enter the t_{2g} orbitals, the fourth electron added will be able to pair within one of the lower t_{2g} orbitals, or it will enter into one of the "empty" e_g orbitals. Thus high-spin and low-spin electron configurations result. Ions with one, two or three electrons (Ti^{3+}, V^{3+} and Cr^{3+} respectively) have electrons within the t_{2g} group, but an element with four electrons such as Mn^{3+} can have its fourth electron entering either one of the high-spin e_g orbitals or one of the low-spin t_{2g} orbitals. The crystal field stabilization energy is reduced by the electron entering the high-spin e_g group of orbitals, and vice versa should the electron enter and pair in one of the t_{2g} orbitals. Similarly high-spin and low-spin states are possible for the d^5, d^6 and d^7 configurations. Ions having d^8, d^9 and d^{10} $3d$ electrons (Ni^{2+}, Cu^{2+} and Zn^{2+}) can only possess one electron configuration as the t_{2g} group of orbitals is completely filled.

Table 3 demonstrates the algebraic calculation of the stabilities achieved as electrons fill the different electron orbitals.

Table 3

Number of d-electrons	Orbitals	Stabilization Δ	Total stabilization
1	(d_{xy})	$+\frac{2}{5}$	$+\frac{2}{5}\Delta$
2	$(d_{xy})(d_{xz})$	$+\frac{2}{5}+\frac{2}{5}$	$+\frac{4}{5}\Delta$
3	$(d_{xy})(d_{xz})(d_{yz})$	$+\frac{2}{5}+\frac{2}{5}+\frac{2}{5}$	$+\frac{6}{5}\Delta$
4	$(d_{xy})(d_{xz})(d_{yz})(d_{x^2-y^2})$	$+\frac{2}{5}+\frac{2}{5}+\frac{2}{5}-\frac{3}{5}$	$+\frac{3}{5}\Delta$
5	$(d_{xy})(d_{xz})(d_{yz})(d_{x^2-y^2})(d_{z^2})$	$+\frac{2}{5}+\frac{2}{5}+\frac{2}{5}-\frac{3}{5}-\frac{3}{5}$	Zero

(from Curtis, 1964, p. 391).

Table 4 gives the crystal field stabilization energies of the transition metals ions in octahedral co-ordination. From Table 4 it can be seen that the ions with d^3, d^8 and low-spin d^6 configurations acquire large crystal field stabilization energies. Therefore Cr^{3+}, Ni^{2+} and Co^{3+} are expected to show a strong preference for octahedral co-ordination sites and conversely for Ca^{2+}, Zn^{2+}, Mn^{2+} and Fe^{3+} (Burns, 1970).

TABLE 4 *Electronic configurations and crystal field stabilization energies of transition metal ions in octahedral co-ordination*

		High-spin state			Low-spin state		
Number of $3d$ electrons	Ion	Electronic configuration t_{2g} e_g	Unpaired electrons	CFSE	Electronic configuration t_{2g} e_g	Unpaired electrons	CFSE
0	Ca^{2+}, Sc^{3+}, Ti^{4+}		0	0		0	0
1	Ti^{3+}	↑	1	$\frac{2}{5}\Delta_o$	↑	1	$\frac{2}{5}\Delta_o$
2	Ti^{2+}, V^{3+}	↑ ↑	2	$\frac{4}{5}\Delta_o$	↑ ↑	2	$\frac{4}{5}\Delta_o$
3	V^{2+}, Cr^{3+}, Mn^{4+}	↑ ↑ ↑	3	$\frac{6}{5}\Delta_o$	↑ ↑ ↑	3	$\frac{6}{5}\Delta_o$
4	Cr^{2+}, Mn^{3+}	↑ ↑ ↑ ↑	4	$\frac{3}{5}\Delta_o$	↑↓ ↑ ↑	2	$\frac{8}{5}\Delta_o$
5	Mn^{2+}, Fe^{3+}	↑ ↑ ↑ ↑ ↑	5	0	↑↓ ↑↓ ↑	1	$\frac{10}{5}\Delta_o$
6	Fe^{2+}, Co^{3+}, Ni^{4+}	↑↓ ↑ ↑ ↑ ↑	4	$\frac{2}{5}\Delta_o$	↑↓ ↑↓ ↑↓	0	$\frac{12}{5}\Delta_o$
7	Co^{2+}, Ni^{3+}	↑↓ ↑↓ ↑ ↑ ↑	3	$\frac{4}{5}\Delta_o$	↑↓ ↑↓ ↑↓ ↑	1	$\frac{9}{5}\Delta_o$
8	Ni^{2+}	↑↓ ↑↓ ↑↓ ↑ ↑	2	$\frac{6}{5}\Delta_o$	↑↓ ↑↓ ↑↓ ↑ ↑	2	$\frac{6}{5}\Delta_o$
9	Cu^{2+}	↑↓ ↑↓ ↑↓ ↑↓ ↑	1	$\frac{3}{5}\Delta_o$	↑↓ ↑↓ ↑↓ ↑↓ ↑	1	$\frac{3}{5}\Delta_o$
10	Zn^{2+}, Ga^{3+}, Ge^{4+}	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	0	0	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	0	0

(from Burns, 1970, p. 13).

In tetrahedral co-ordination (Figure 5) where four negatively charged ligands surround the transition ion, the situation is reversed (Figure 6).

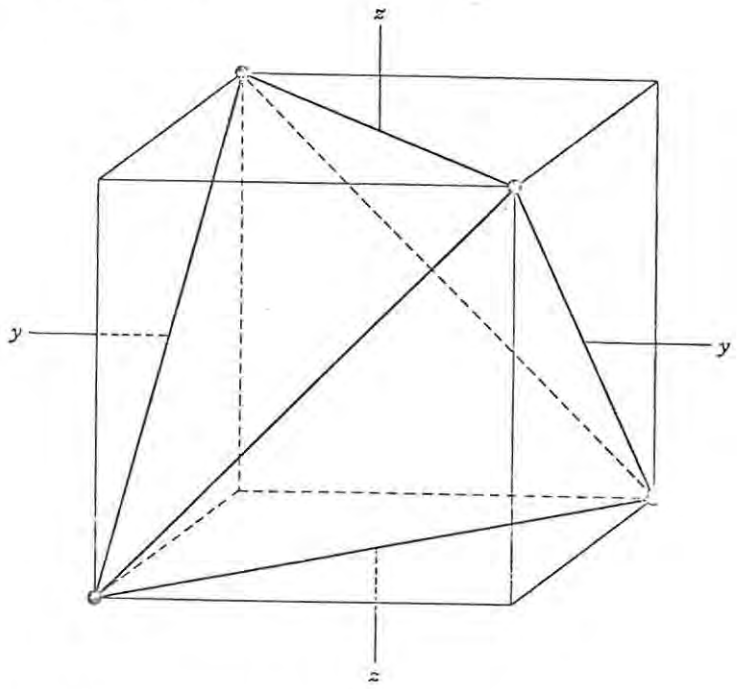


Figure 5. Arrangement of ligands in tetrahedral co-ordination about a transition metal ion (from Burns, 1970, p. 14).

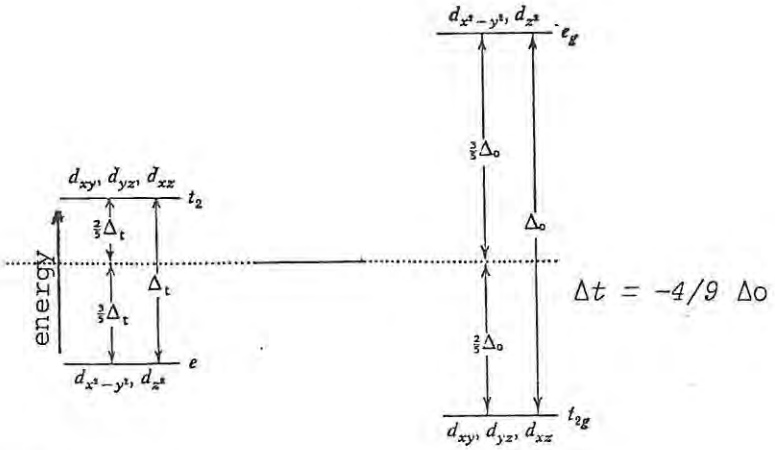


Figure 6. Relative energy levels of the d orbitals of a transition metal ion in tetrahedral and octahedral co-ordination (from Burns, 1970, p. 15).

The reasoning applied to octahedral co-ordination is still applicable, the difference being that different orbitals experience an apparent increase in energy which results in the e group (or e_g group in octahedral co-ordination) orbitals becoming more stable relative to the t_2 group orbitals (or t_{2g} group in octahedral co-ordination). Table 5 gives the stabilization energies acquired by the transition elements in tetrahedral co-ordination.

TABLE 5 *Electronic configurations and crystal field stabilization energies of transition metal ions in tetrahedral co-ordination*

Number of $3d$ electrons	Ion	High-spin state				Low-spin state			
		Electronic configuration e	t_2	Unpaired electrons	CFSE	Electronic configuration e	t_2	Unpaired electrons	CFSE
0	Ca^{2+}, Sc^{3+}, Ti^{4+}			0	0			0	0
1	Ti^{3+}	↑		1	$\frac{3}{5}\Delta_t$	↑		1	$\frac{3}{5}\Delta_t$
2	Ti^{2+}, V^{3+}	↑ ↑		2	$\frac{6}{5}\Delta_t$	↑ ↑		2	$\frac{6}{5}\Delta_t$
3	V^{2+}, Cr^{3+}, Mn^{4+}	↑ ↑	↑	3	$\frac{4}{5}\Delta_t$	↑↓	↑	1	$\frac{9}{5}\Delta_t$
4	Cr^{2+}, Mn^{3+}	↑ ↑	↑ ↑	4	$\frac{2}{5}\Delta_t$	↑↓ ↑↓		0	$\frac{12}{5}\Delta_t$
5	Mn^{2+}, Fe^{3+}	↑ ↑	↑ ↑ ↑	5	0	↑↓ ↑↓	↑	1	$\frac{10}{5}\Delta_t$
6	Fe^{2+}, Co^{3+}, Ni^{4+}	↑↓ ↑	↑ ↑ ↑	4	$\frac{3}{5}\Delta_t$	↑↓ ↑↓	↑ ↑	2	$\frac{8}{5}\Delta_t$
7	Co^{2+}, Ni^{3+}	↑↓ ↑↓	↑ ↑ ↑	3	$\frac{6}{5}\Delta_t$	↑↓ ↑↓	↑ ↑ ↑	3	$\frac{6}{5}\Delta_t$
8	Ni^{2+}	↑↓ ↑↓	↑↓ ↑ ↑	2	$\frac{4}{5}\Delta_t$	↑↓ ↑↓	↑↓ ↑ ↑	2	$\frac{4}{5}\Delta_t$
9	Cu^{2+}	↑↓ ↑↓	↑↓ ↑↓ ↑	1	$\frac{2}{5}\Delta_t$	↑↓ ↑↓	↑↓ ↑↓ ↑	1	$\frac{2}{5}\Delta_t$
10	Zn^{2+}, Ga^{3+}, Ge^{4+}	↑↓ ↑↓	↑↓ ↑↓ ↑↓	0	0	↑↓ ↑↓	↑↓ ↑↓ ↑↓	0	0

(from Burns, 1970, p. 16).

(d) The Jahn-Teller (or Distortion) Effect

Transition ions, with unfilled *d* electron shells, such as Cu^{2+} (d^9) in octahedral co-ordination may have electrons in one or two orbital configurations. For example Cu^{2+} can have the following orbital arrangements, $(d_z2)^1$ $(d_x2 - _y2)^2$ or $(d_z2)^2$ $(d_x2 - _y2)^1$. In the latter case the electrons in the *xy* plane tend to screen the nucleus from the anions less effectively than those electrons in the *z* axial plane. Therefore the anions in the *xy* plane will be attracted by the apparent extra energy of the nucleus of the transition ion more than the anions in the *z* axial plane. Consequently electron "rearrangement" occurs which results in the shortening of the inter-atomic distances in the *xy* plane, and in increasing separation along the *z* axis (Curtis, 1964). Figure 7 diagrammatically represents the above situation. This explains why certain ions with unfilled *d* electron shells such as Mn^{3+} (d^4) and Cu^{2+} (d^9) will be destabilized in octahedral field and Cr^{3+} (d^3) Mn^{3+} (d^4), Ni^{2+} (d^8) and Cu^{2+} (d^9) in tetrahedral field.

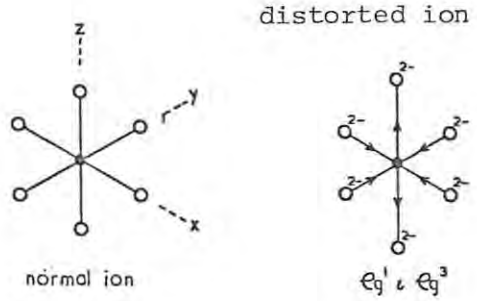


Figure 7. Diagrammatically illustrates the distortion undergone by certain ions when accommodated within ordered crystal structures (from Curtis, 1964, p. 393).

Crystal field stabilization energies for the different dipositive elements has been experimentally determined to be $Ni^{2+} > Cu^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$ but available data indicate that Cu^{2+} ions are very seldom found in regular octahedral co-ordination as would be present in silicate lattices. It appears that the distortion is great enough to overcome the effect of crystal field stability and Cu^{2+} will, once concentrations are high enough, enter into phases that can accommodate the distortion. Thus a copper-rich phase (immiscible sulphide globules) would begin to accumulate or copper could bond with other elements as stable complexes.

(e) The partitioning of elements between melts and crystallizing phases

In silicate melts of granitic and basaltic composition, tetrahedral and octahedral sites predominate and the transition metal ions can enter both (Burns and Fyfe, 1964). Transition metal ions are rarely found within tetrahedral sites, preferring octahedral sites due to the high crystal field stabilization energy. Therefore during magmatic crystallization a partitioning of ions takes place between octahedral sites and tetrahedral sites within the magma, and octahedral sites within a crystal. (Magmas have been demonstrated to be quasi-crystalline in character, Burns, 1970.) This can be written as follows :

$$(M^{n+}_{tetr.})_{magma} + (M^{n+}_{oct.})_{magma} \longrightarrow (M^{n+}_{oct.})_{crystal}$$

During the crystallization of a basaltic melt the uptake of transition metals into the octahedral sites of a forming crystal is :

$$Ni > (Cr) > (Cu) > Co > Fe > Mn \geqslant Ca, Zn \text{ for } M^{2+} \text{ ions}$$

$$Cr > (Mn) > Co > V > Ti > Fe \geqslant Sc, Ga \text{ for } M^{3+} \text{ ions}$$

Figure 8 represents the uptake of the transition metal ions into silicate minerals crystallizing from a magma. Note that copper becomes enriched in the residual melt, not entering the silicate structure because of distortion effects.

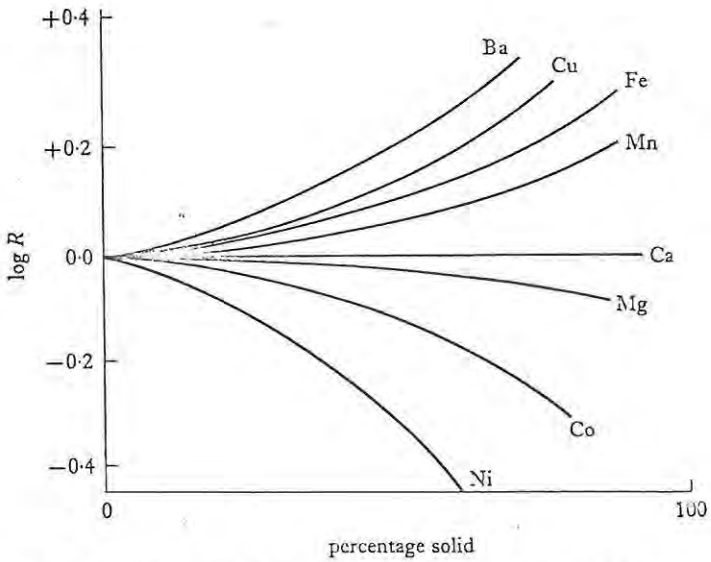


Figure 8. The uptake of divalent transition metal ions into silicate minerals crystallizing from a magma. R is the ratio of the concentration of the element in the magma after x percent solidification to the concentration of the element in the initial liquid (from Burns, 1970, p. 156).

(f) Certain aspects of bonding

Ionic and covalent bonds are important in determining whether an ion will enter into a crystal, or perhaps form complexes and remain stable within melts and solutions. The ability of chemical elements to form ionic or covalent bonds depends upon the attraction an atom has for its orbital electrons (electronegativity). Alkali metals have the weakest attraction for their outer electrons, and those atoms which strongly attract their outer electrons appear on the right-hand side of the peiodic table.

Should an atom "capture" the valence electron of another atom the type of bond formed will be ionic. Should reacting atoms share their valence electrons (pairing with opposite spins in a molecular orbit) the bond is considered to be covalent (the electrons belong similtaneously to both atoms). The specific type of bond is determined to a large extent by the difference in electronegativity values between two interacting atoms. The greater the difference, the easier it is for the element of high electronegativity to "capture" a valence electron of another less electronegative atom. Thus alkali metals (having low electronegativity values) when reacting with halogens, oxygen, or sulphur readily loose their outer electrons. The bonding is thus largely ionic. As the difference in the electronegativities of the reacting atoms becomes smaller, the atom with the higher electronegativity does not have enough energy to remove the valence electrons from the other reacting atom thus covalent bonds are formed. The molecules of the gases H_2, O_2, Cl_2 and F_2 exhibit covalent bonding as their electronegative values are the same. But normally the electronegativity values between two reacting atoms is different thus pure covalent bonding rare, and bonding is usually a mixture of ionic and covalent bonds.

The covalent bond is important with regard to the transport of ore elements within magmatic melts, hydrothermal and aqueous solutions. Compounds which are ionically bonded tend to dissociate, but may be transported in the ionic state. For example:

$$\underset{\text{SOLID}}{KCl} \rightleftharpoons \underset{\text{SOLUTION}}{K^+ + Cl^-}$$

Compounds with predominantly covalent bonding do not dissociate in solutions and migrate in combined form as complex ions. Examples of such complexes are $(CO_3)^{2-}$, $(SO_4)^{2-}$ and $(NO_3)^{-}$. Dissociation of a compound in solution can be written :

$$Na_2\ (CO_3)_{solid} \rightleftharpoons 2Na^{+} + (CO_3)^{2-}_{solution}$$

Certain elements such as Sn, W, Mo, Pb, Zn, and U form strong covalent bonds with oxygen and thus remain stable within solutions and melts and do not show a great tendency (due to the large molecule formed) to enter into silicate lattices. They become concentrated in late-stage paramagmatic deposits (Beus and Grigorian, 1977).

III ASPECTS OF THE CHEMISTRY AND GEOCHEMISTRY OF THE SELECTED ELEMENTS

Although zinc (Group IIb) is closely related to the first series of transition elements, iron, copper, nickel and cobalt, it has a completely filled *d* shell, and is thus not a transition element. Copper (Group Ib) is a true transition element in the Cu^{2+} oxidation state, but not in the Cu^{+} state. The Group VIb elements, molybdenum and tungsten, have similar geochemical behaviours, as do the elements of Group Ib, gold and silver. Molybdenum and silver belong to the second series of transition elements, while tungsten and gold belong to the third. The second and third transition elements are characterized by partially filled *f* shells. Tin and lead belong to the Group IVa elements, while uranium belongs to Group VIIb and is one of the actinide series. The filling of the *4f* orbitals through the lanthanide series causes a steady contraction in atomic and ionic sizes. This is referred to as the *Lanthanide contraction.* Thus the expected increase in the size of the elements of the third series relative to those of the second transition series does not occur as might be expected from the increased numbers of electrons and higher principal quantum numbers of the third series. There is in general little difference in atomic and ionic sizes between the two heavy atoms of a Group, whereas the corresponding atoms and ions of the first transition series are significantly smaller.

NICKEL

Ni^{2+} is the only oxidation state of importance in the aqueous chemistry of nickel, and with the exception of a few special complexes in other oxidation states, Ni^{2+} is also the only important oxidation level in nonaqueous chemistry. Figure 9 illustrates certain stability relationships of nickel sulphide compounds at $25^{\circ}C$ and at one atmosphere pressure.

Nickel is a chalcophile element with two features dominating its crystal chemistry. The first is the readiness with which it forms strong metallic bonds, and the second is the strong preference of Ni^{2+} for octahedral co-ordination in crystal structures. High-spin Ni^{3+} ions, although relatively unstable, should favour tetrahedral co-ordination, while low-spin Ni^{3+} and Ni^{4+} may occur in minerals formed in strong oxidizing environments. The majority of the ionic minerals of nickel are oxygen-bearing and most occur as weathered products of nickel ores. Nickel oxides tend to be insoluble in water but dissolve in certain acids. Hydroxides of nickel are also

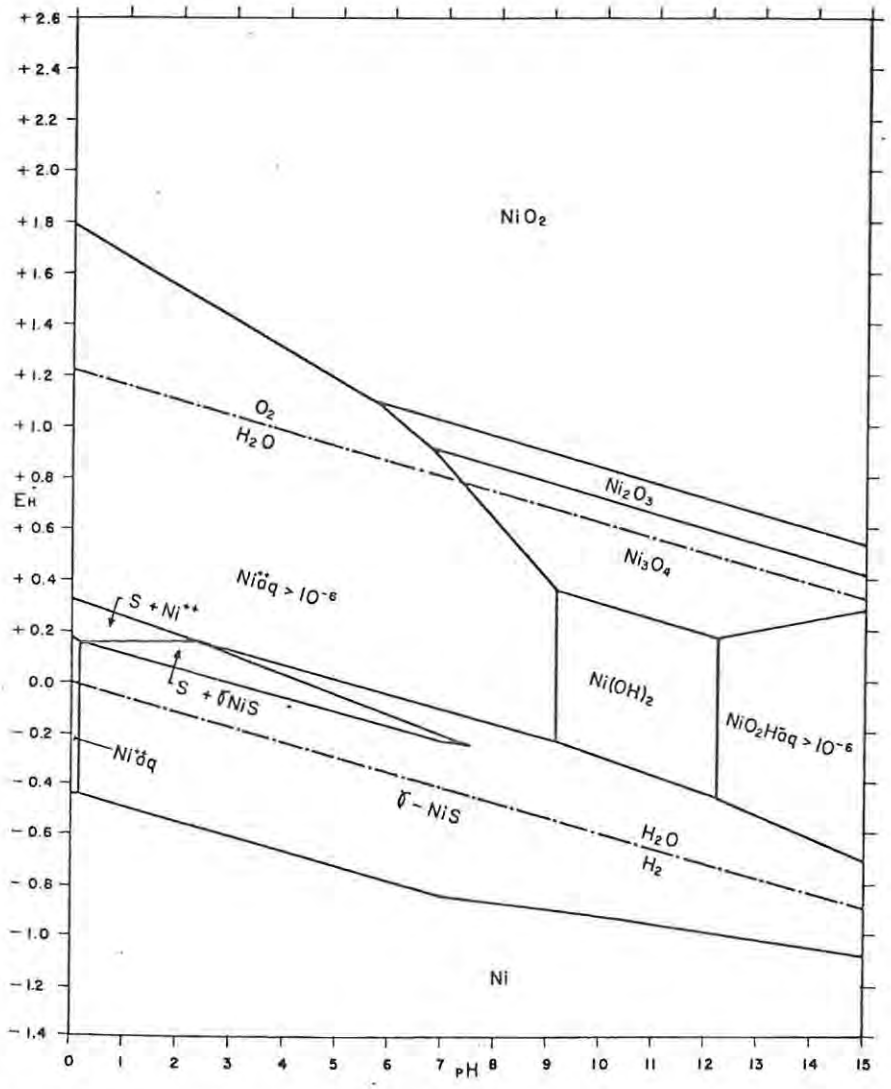


Figure 9 illustrates that nickel sulphides are stable over a large pH range under reducing conditions while the oxides and hydroxides of nickel should be soluble, as indicated by the large field of Ni^{2+} under acidic conditions, and NiO_2H^- under alkaline conditions (Garrels and Christ, 1965). Despite the large aqueous field of nickel it seldom occurs within sedimentary environments. This is possibly due to its strong sulphophile and oxyphile tendencies, and its high stability in octahedral co-ordination. These facts indicate that the removal of a nickel ion from its crystal environment would require relatively high levels of oxidation (from Garrels and Christ, 1965, p. 245).

soluble in certain acids and alkalies and the halides of nickel are soluble in water. Nickel generally occurs bonded with arsenic, antimony, sulphur and iron, and native nickel is rare. Nickel occurs in minerals such as millerite (NiS), pentlandite $(Fe, Ni)_9 S_8$, mackinawite $(Fe, Ni)_{1+x}S$, violarite (Fe, Ni_2S_4), heazlewoodite (Ni_3S_2). The hydrous silicates of the garnierite group consists of a variety of phyllosilicates. Garnierite is the general name for nickel-bearing phyllosilicates and includes the serpentine minerals nepouite (chrysotile), pecorite (clinochrysotile) $[(Ni_6Si_4O_{10}(OH)_8]$, and willemsite [talc, $Ni_6Si_8O_{20}(OH)_4$].

COBALT

Cobalt is a chalcophile element and closely resembles nickel in many of its physical and chemical properties. Although it is less abundant than nickel, it frequently occurs with nickel in a variety of minerals, for example langisite (CO, Ni) As, moorhouseite (Co, Ni, Mn) $SO_4 \cdot 6\ H_2O$, siegenite $(Ni, Co)_3S_4$.

The electronic configuration is such that in ionic compounds it is stabilised by octahedral and tetrahedral co-ordination (Burns, 1970). Its ionic radius in octahedral co-ordination is 0,74Å which is intermediate between Mg^{2+} (0,72Å) and Fe^{2+} (0,77Å) so that it can substitute for these cations in several silicates. The Co^{3+} ion has a low spin configuration in oxygen compounds and in this oxidation state, cobalt acquires a high crystal field stabilization energy in octahedral co-ordination.

Figure 10 illustrates the stability of some cobalt compounds in an aqueous system containing carbonate species. The stability fields are remarkably similar to that of nickel.

COPPER

Natural copper consists of two isotopes, Cu^{63} and Cu^{65} with the relative abundances being 69 and 31 percent respectively. Copper is a chalcophile element and is widely distributed as native metal and in sulphides, arsenides and chlorides. It occurs in three valence states Cu, Cu^{1+} and Cu^{2+}. Within environments of low oxygen fugacities and high temperatures Cu^{+} might be the prevailing state. (It should be noted that should an ion tend to be stable in a certain valence state the extent to which the oxygen fugacity can determine a change in that valency is uncertain.) Natural waters are usually equilibrated with atmospheric oxygen at low temperatures, and under these conditions copper most likely occurs as the Cu^{2+} ion. The relative stabilities of Cu^{1+} and Cu^{2+} in aqueous solution depends strongly on the nature of the anions or other ligands present, upon the solvent and the nature of the atoms within the crystal. In aqueous solution only low concentrations of Cu^{1+} can exist and the only cuprous compounds that are stable in water are the insoluble CuCl and CuCn compounds, but cuprous chloride solubility is enhanced by an excess of halide ions (owing to the formation of

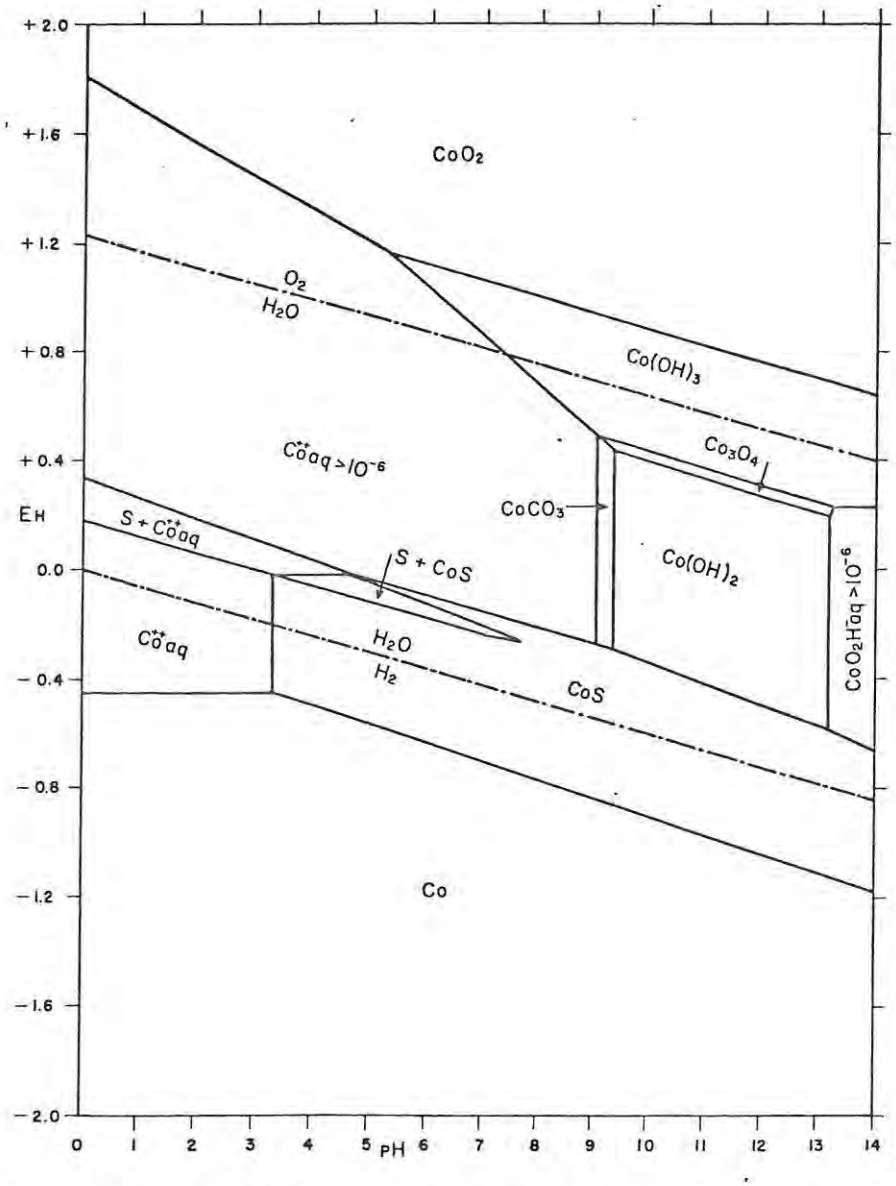


Figure 10. Stability relations among some cobalt compounds in water at 25°C and 1 atmosphere total pressure. Total dissolved sulphur species = 10^{-1}, total dissolved carbonate species = $10^{-4.9}$ (from Garrels and Christ, 1965, p. 250).

complexes such as $CuCl_2^-$, $CuCl_3^{2-}$) and other complexing species such as CN^-, NH_3, $S_2O_3^{2-}$. With simple ligands such as the halides, the co-ordination is invariably tetrahedral. Copper sulphides are insoluble in water but soluble in bisulphide solutions.

The dipositive state is the most important for copper. Most cuprous compounds are readily oxidized to cupric compounds, but further oxidation to Cu^{3+} is difficult. For the Cu^{2+} ion there are a large number of salts of various anions, many of which are water-soluble. Most salts dissolve to give the cupric ion $[Cu(H_2O)_6]^{2+}$.

The following phase equilibrium diagrams (Figures 11, 12, 13) illustrate the variety of compounds within which copper can occur. Phases in the Cu - S system are characterised by rapid reaction rates of components and the existence of unquenchable species with cation-disordered structures. Figure 11 illustrates the isothermal condensed phase relations in the Cu-Fe-S system at 600°, 400° and 200°C.

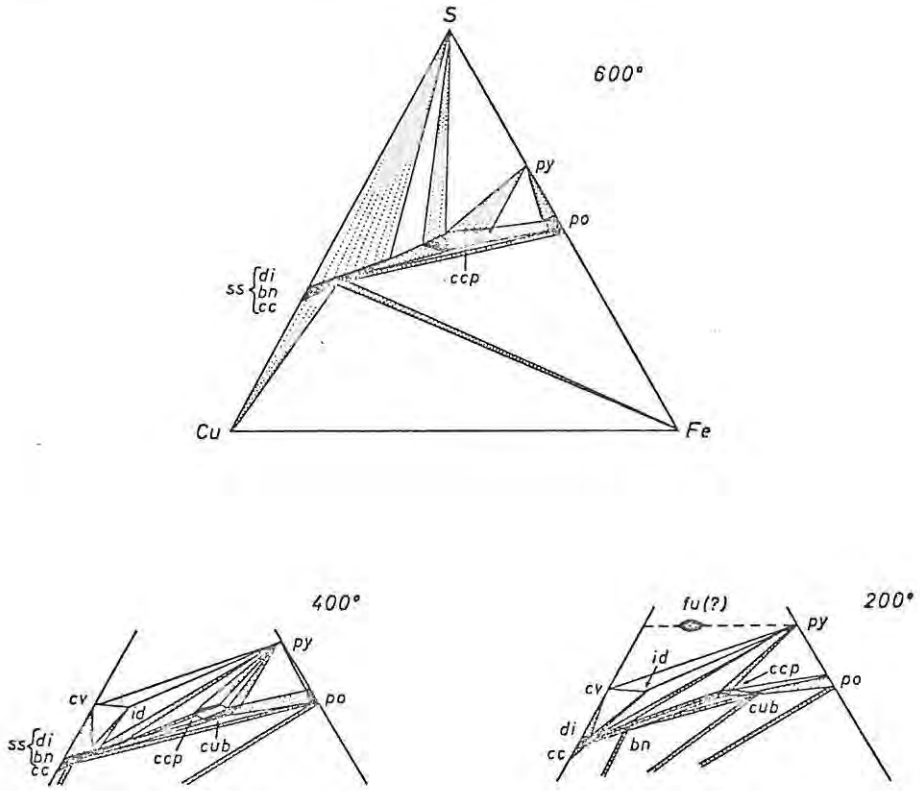


Figure 11. Isothermal condensed phase relations in the system Cu-Fe-S at 600°, 400° and 200°C (according to Barton and Skinner, 1967, and references in their Table 7.1). Solid areas are single solid phase, dotted two solid phases, blank three solid phases. All assemblages coexist with vapour (bn : bornite; cc : chalcocite; ccp : chalcopyrite; cb : cubanite; cv : covellite; di : idaite; fu : fukuchilite, according to Shimazaki and Clark, 1970; po : pyrrhotite; py : pyrite) (from Wedepohl, 1974, p. 29-0-0).

Stable phases in the Cu-Fe-S system are :

(i) at 600 - 700°C : a bornite-digenite-chalcocite solid solution, a chalcopyrite-cubanite solid solution, pyrrhotite and pyrite.

(ii) at 400°C : covellite, a bornite-digenite solid solution, chalcocite, idaite, chalcopyrite, cubanite, pyrrhotite and pyrite.

(iii) at 200°C : covellite digenite, chalcocite, fukuchilite $(Cu, Fe)_4S_3$ idaite, bornite, chalcopyrite, cubanite, pyrrhotite and pyrite.

Natarajan and Garrels (Garrels and Christ, 1965) have computed the relations of stable phases in the Cu-Fe-S-O-H system at 25°C and at 1 atmosphere pressure (Figure 12), and Figure 13 illustrates the stability fields of copper compounds within the $Cu-H_2O-O_2-S-CO_2$ system.

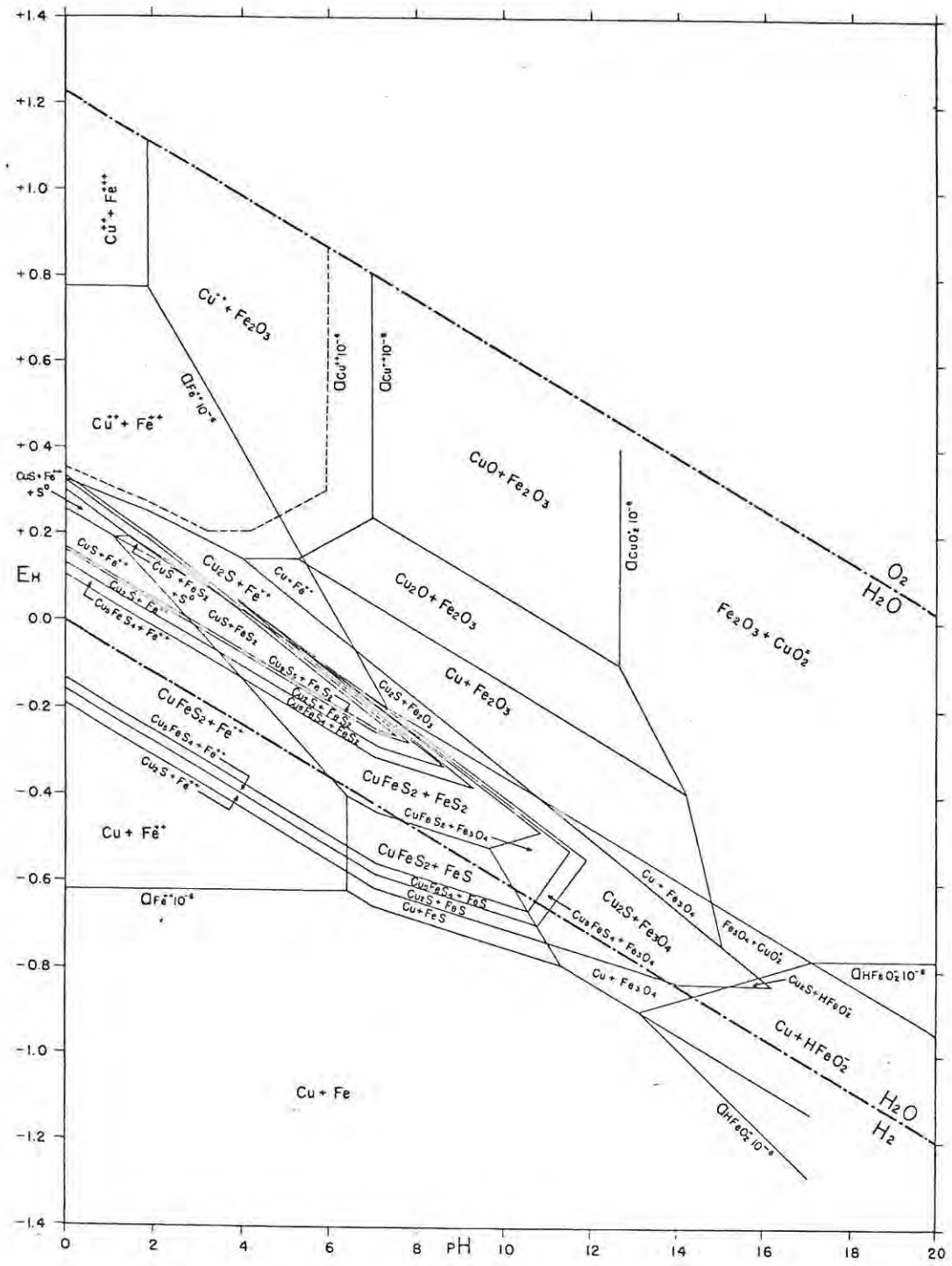


Figure 12. The system Cu-Fe-S-O-H (in part) at 25°C and 1 atmosphere total pressure. Total dissolved sulphur = 10^{-4} m (from Garrels and Christ, 1965, p. 232).

Figure 12 can be used in understanding the zones of oxidation and secondary enrichment of ore deposits. The only copper sulphide to project appreciably above a line drawn from approximately Eh + 0,35 (pHO) to approximately Eh - 1,0 (pH20) is chalcocite (Cu_2S). Iron and copper oxides predominate above this line. This accounts for the chalcocite "blankets" formed as a result of secondary enrichment. Oxidation under acidic conditions would probably produce Cu^{2+} and Fe^{2+} ions, or at a slightly lower acidity, Cu^{2+} and solid Fe_2O_3 (or $Fe_2O_3.H_2O$). Native copper could occur as a secondary product should the descending solutions be neutralized.

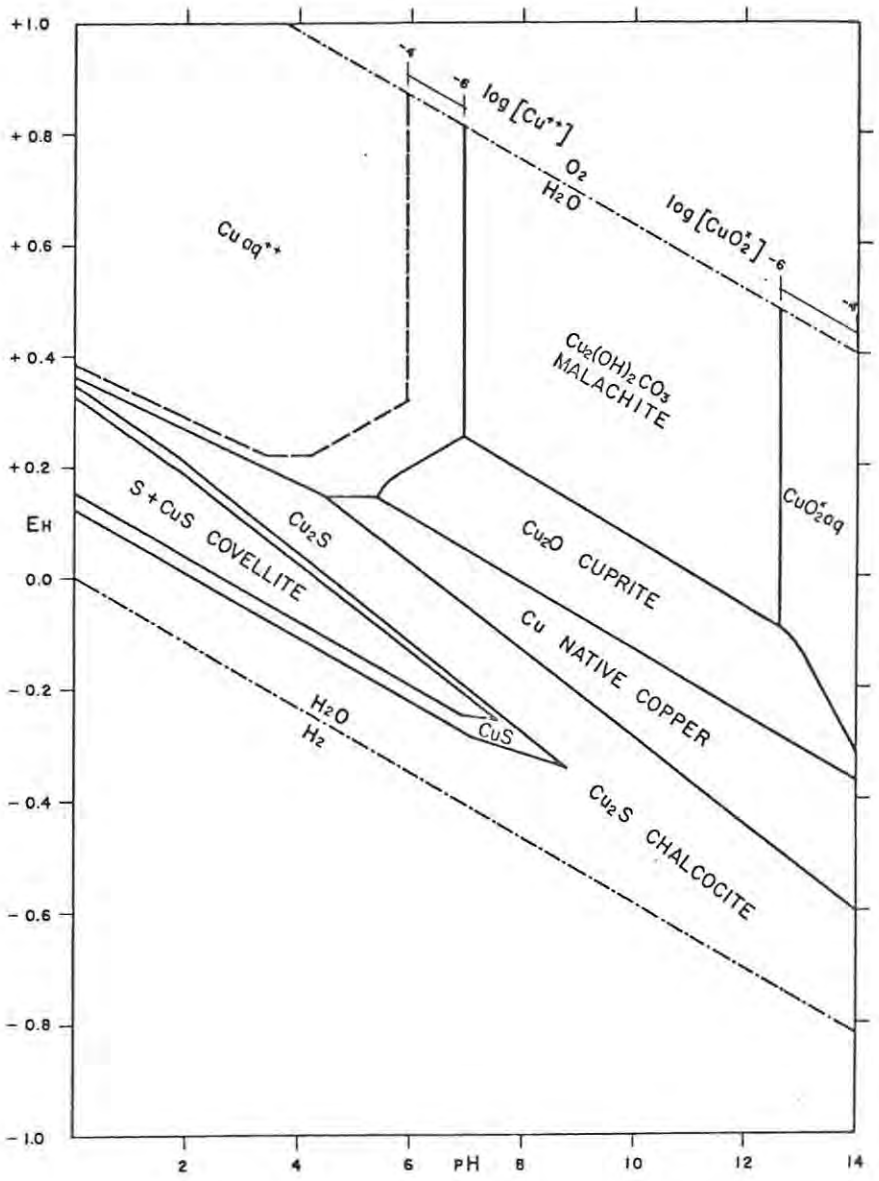


Figure 13. Stability relations among some copper compounds in the system $Cu-H_2O-O_2-S-CO_2$ at 25°C and 1 atmosphere total pressure. $P_{CO_2} = 10^{-3.5}$, total dissolved sulphure species = 10^{-1} (from Garrels and Christ, 1965, p. 240).

Figure 13 illustrates the field occupied by certain secondary minerals during the weathering of an orebody. Even in the presence of sulphur, native copper has a relatively large stability field. The sulphide field projects deeply into the acid range under reducing conditions thus explaining the precipitation of chalcocite when copper-bearing solutions encounter sulphide at depth. This also illustrates that chalcocite should be deposited within the sedimentary environment under reducing conditions.

LEAD

Divalent lead is more common than tetravalent lead, and except for the nitrate, most Pb^{2+} salts are insoluble in water and all Pb^{2+} salts, except PbS can be dissolved in excess OH^-. Pb^{2+} forms complexes in aqueous solution, particularly in the presence of halide ions (e.g. members of the series PbX^+ —— PbX_3^-, where X = F, Cl, Br, I).

Goldschmidt (1954) describes the chemistry of lead as being dominated by its chalcophile and lithophile properties. The first assertion is evident from the dominance of galena (PbS) as the major lead ore mineral and the extensive sulphosalt mineralogy of lead. The lithophile properties result from the large ionic radius which enables Pb^{2+} to replace K^+, Sr^{2+}, Ba^{2+}, Ca^{2+} and Na^+ in certain minerals such as feldspar, augite and apatite. The sulphates and carbonates are common oxidation products from the weathering of galena, but oxides are less common.

One of the most important phase equilibrium systems, because of the natural abundance of galena containing appreciable concentrations of silver and bismuth, is the Ag-Bi-Pb-S system studies by Van Hook (1960). Isothermal sections at 180°, 400° and 600°C in the Ag_2S, Bi_2S_3, PbS part of the system is illustrated in Figure 14.

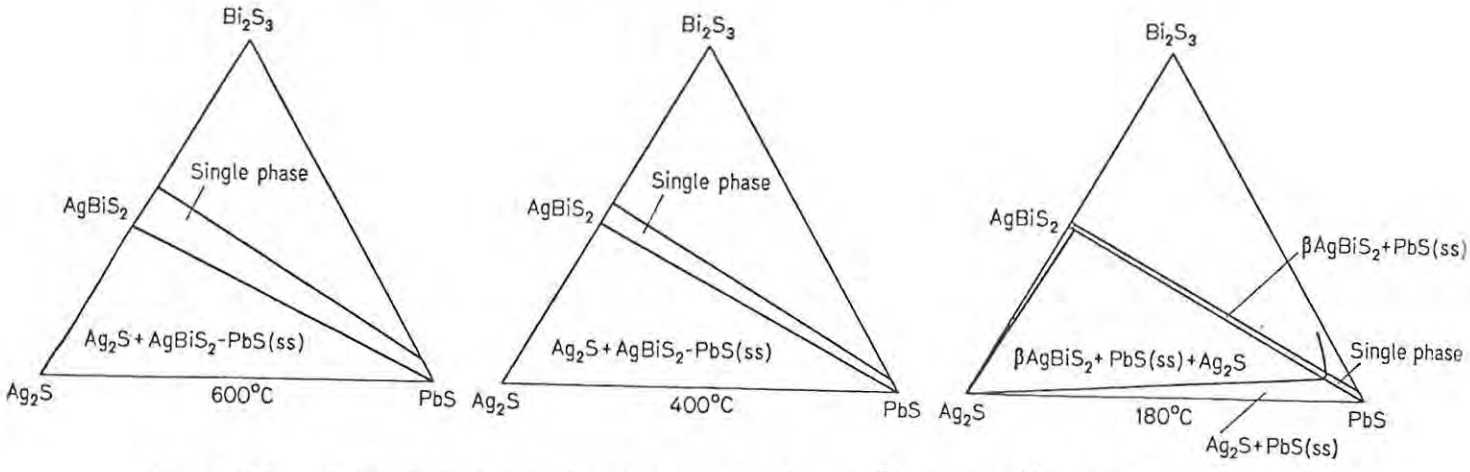


Figure 14. Subsolidus equilibria at 600°, 400° and 180°C in the system Ag_2S-Bi_2S_3-PbS (from van Hook, 1960, p. 783).

There is complete solid solution between $AgBiS_2$ and PbS above 210°C. The solubilities of FeS in galena and PbS in pyrite and pyrrhotite at 700°C are very slight. Ternary compounds do not occur in the Fe-Pb-S system (Brett and Kullerud, 1967). Figure 15 illustrates the stability relationships of lead compounds within a system containing sulphur and carbonate species.

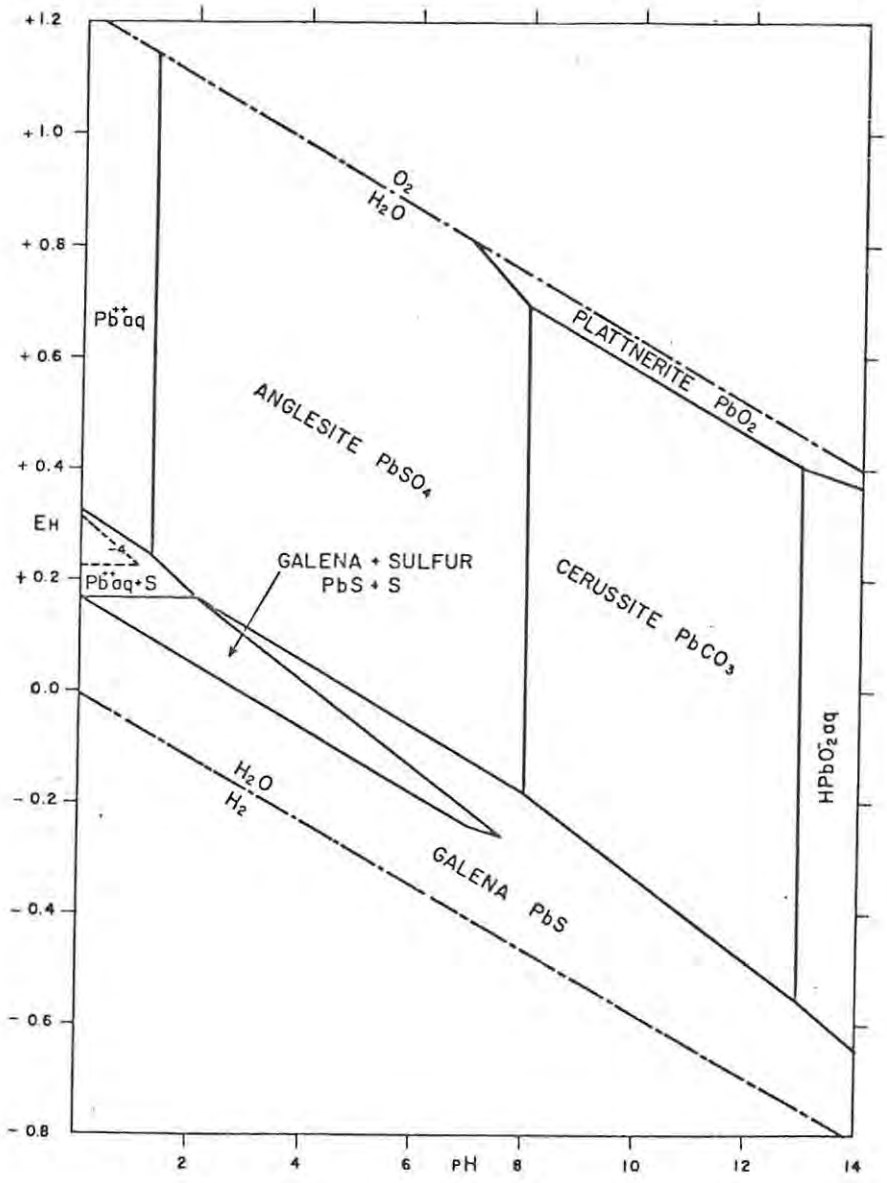


Figure 15. Stability relations among lead compounds in water at 25°C and 1 atmosphere total pressure. Total dissolved sulphur = 10^{-1}, $P_{CO_2} = 10^{-4}$. Boundaries of solids at total ionic activity of 10^{-6}. Dashed line is contour at activity of dissolved lead species of 10^{-4} (from Garrels and Christ, 1965, p. 237).

Figure 15 illustrates the system which probably represents the surface environment during the oxidation of an orebody. The total sulphur content (10^{-1}) is high, whereas that of CO_2 is approximately that of the surface environment (10^{-4}). Galena has a large field within which it is insoluble, only releasing aqueous ions under conditions of extreme acidity and alkalinity (conditions generally not found in the geological environment). The large fields of the insoluble secondary products Anglesite ($PbSO_4$) and cerussite ($PbCO_3$) indicate that the mobility of lead in the aqueous and secondary environment would be substantially reduced, and that mechanical dispersion over short distances is possible.

ZINC

Five isotopes of zinc occur in nature; Zn^{64} (49%), Zn^{66} (27%), Zn^{67} (4%), Zn^{68} (18%), Zn^{70} (0,6%). Zinc occurs extensively combined with other elements, and in all known compounds it occurs in the divalent state. In a few cases metallic zinc has been found. Zinc forms halide complexes in aqueous solution and with oxides and sulphides favours tetrahedral co-ordination. Although dominantly chalcophile, and frequently occurring as ZnS (sphalerite or wurtzite), some lithophilic characteristics result from the similarity of radii between Zn^{2+} and ions of similar ionic radii (Mg^{2+}, Fe^{2+}, Co^{2+}, Mn^{2+}). Thus Zn^{2+} can enter oxide and silicate structures. Simple oxides and silicates of zinc are rare and the common oxidation products of zinc sulphide are sulphates and carbonates.

The stable silicate at normal temperature and pressures of the ZnO - SiO_2 system is Zn_2SiO_4 (willemite). In the sulphide system, at normal pressures, the transition from sphalerite to wurtzite occurs at $1025 \pm 5^{o}C$. The sulphur-bearing part of the Fe-Zn-S system is simple and contains only sphalerite (wurtzite), pyrrhotite, pyrite and sulphur in the range 200 - $700^{o}C$ (Barton and Skinner, 1967). The range of substitution of iron for zinc is wide on the nearly binary FeS - ZnS join (Figure 16).

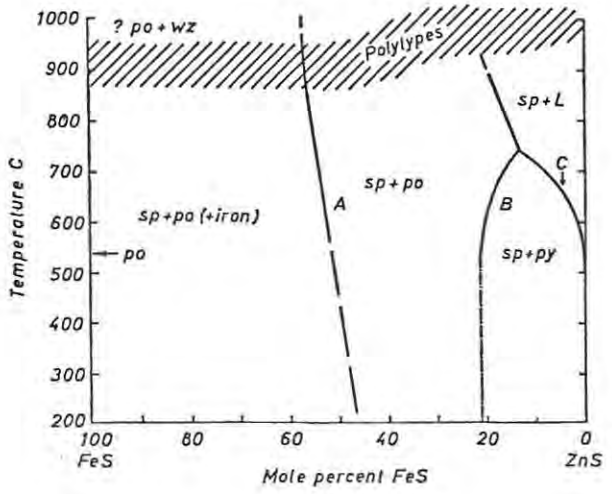


Figure 16. Compositions of sphalerites in the system Fe-Zn-S in the temperature range 200 to 1000°C after Barton and Skinner (1967) (with additions after Scott and Barnes, 1971). Vapour is present in all assemblages. Symbols : po = pyrrhotite, py = pyrite, sp = sphalerite, wz = wurtzite, L = liquid sulphur. Curves A, B and C give compositions of sphalerites in equilibrium with pyrrhotite of FeS composition, with pyrite+pyrrhotite and with pyrite+liquid sulphur respectively (from Wedepohl, 1972, p. 30-D-9).

SILVER AND GOLD

Silver and gold (Group Ib) have a single *s* electron outside a completed *d* shell, as does copper, but in spite of the similarities in electronic structures and ionization potentials, there are few resemblances between Ag, Au and Cu, and there is no simple explanation for the many differences (Cotton and Wilkinson, 1972). Gold is mono-isotopic in nature consisting of the single nuclide, Au^{197}. Silver has two stable isotopes, Ag^{107} (51,4%) and Ag^{109} (48,6%). While both the silver isotopes may be largely primordial in origin, they are also both stable fission products of U^{235}, Ag^{107} being derived from Pd^{107} (half-life 7,5 x 10^6 years) and Ag^{109} being derived from Pd^{109} (half-life 13,6 hours). Boyle (1968) points out that it is unlikely, bearing in mind the fission yields and the observed isotopic ratio, that silver of ore deposits has been formed directly by natural fission of uranium. The two stable isotopes could possibly be the products of U^{235} fission deep within the earth over long periods of geological time, and have become well-mixed and homogenized in the materials of the upper crust. This is possible but the occurrence of silver in Archaean volcanogenic deposits casts doubt on the possibility that substantial concentrations of silver would be the result of U^{235} fission. It would also be expected

that Ag^{109} would be more abundant than Ag^{107} because of the far shorter half-life of Pd^{109}, but the situation could be accounted for by the possibility that the concentration of Pd^{109} produced by U^{235} fission is far less than Pb^{107}. Gold and silver are widely distributed in nature, in the metallic state, in sulphides and arsenides; silver also occurs as AgCl. Silver is chemically less reactive than copper, except toward sulphur and hydrogen sulphide. The metal dissolves in oxidizing acids in the presence of oxygen, and Ag^{+} is soluble in water; the halides, AgCl and AgBr are insoluble in water. The only stable cationic species, apart from complex ions, is Ag^{+}. Gold is chemically unreactive and is not attacked by oxygen or sulphur, but reacts readily with halogens or with solutions containing chlorine. Au^{+} is unstable while Au^{3+} is invariably complexed in all solutions, usually as anionic species such as $(AuCl_3OH)^{-}$. The oxidation states Ag^{2+}, Ag^{3+} and Au^{+} are either unstable in water, or exist only as insoluble compounds and complexes.

There is little correlation between silver content and the overall chemical composition of the rock, and silver and gold occur throughout the deposit-types presented in the classification.

Gottfried et al. (1972) suggest that for rock suites of the calc-alkaline affinity, gold becomes depleted in the residual melt as magmatic differentiation procedes, and in both volcanic and plutonic rock-types the gold content generally decreases from mafic to felsic rocks.

In compounds of univalent silver, with the exception of sulphides, the element forms bonds which are of moderately ionic character, but covalent bonding characterizes compounds in which the elements occur in the higher valence states. Variable, and often high concentrations of silver have been recorded in sulphides, as for example in galena. In copper the silver concentration varies from 0,1 - 4,0% and in gold from 0,1 - 20%. Pyrite and sphalerite invariably contain traces of silver. Pyrrhotite shows much lower concentrations and in chalcopyrite there may be appreciably substitution of silver for copper in the structure. Sulphides such as pyrite exhibit bonding which, although dominantly covalent in character, take on a considerable metallic character, so that silver may be expected to substitute for iron. Silver, being a chalcophile element, will form covalent bonds with sulphur. Silver may also replace zinc in sphalerite. Both gold and silver occur in combination with tellurium, forming mineral compounds known as tellurides.

Van Hook's (1960) diagram for $AgBiS_2$ - PbS join in Figure 14, indicates that solid solution persists over most of the compositional range down to temperatures of $\pm$ 200°C, with unmixing of $AgBiS_2$ occurring at 195°C. At room temperature galena can contain several percent silver. Van Hook's (1960) experiments indicate that the presence of bismuth greatly increases the solubility of silver in galena. Figure 17 illustrates the stability relationship of gold compounds in a system containing sulphur and chloride species.

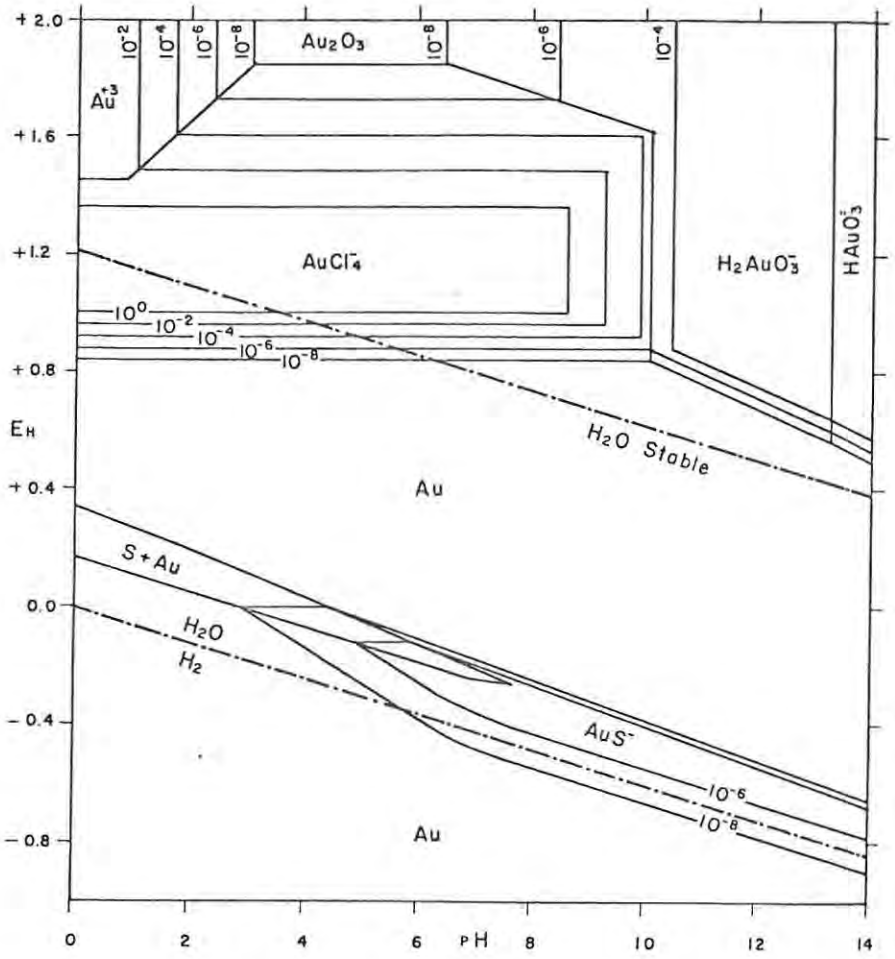


Figure 17. Stability relations among some gold compounds in water at 25°C and 1 atmosphere total pressure. Total dissolved chloride species = 10^0; total dissolved sulphur species = 10^{-1} (from Garrels and Christ, 1965, p. 258).

Figure 17 illustrates the complexes formed by gold with chlorine and sulphur. Ionic activities of gold are demonstrably low while the stability fields of gold (Au) are large. Eh values above those of water stability are included in the diagram to illustrate overall reactions, but these are not geologically applicable. In the presence of a high chloride concentration gold is slightly soluble in acidic oxidizing solutions as $AuCl_4^-$. At high sulphur concentrations a minor amount of gold is dissolved as the AuS^- complex over a wide range of strongly

reducing conditions. Thus the diagram illustrates that gold can be transported as a chloride or sulphide complex during oxidation of sulphide orebodies, and during the formation of low temperature sedimentary and vein deposits.

MOLYBDENUM & TUNGSTEN

Mafic rocks contain less tungsten than felsic rocks and it is possible that volcanic rocks might have slightly more tungsten than plutonic rocks of similar composition. The reserve is possibly true for molybdenum. The chemistry of molybdenum and tungsten is complex and encompasses a wide range of oxidation states. In nature they tend to bond hexavalently with oxygen, and occur only in two sulphide species, molybdenite and tungstenite. The chemical behaviour of the two elements is very similar, and isomorphism between corresponding compounds is common, sometimes leading to solid solution systems. The common sulphide ore mineral of molybdenum, molybdenite (MoS_2), has physical properties very similar to graphite. Under strong oxidizing and weathering conditions various oxymolybdates are formed, the principal one being wulfenite ($PbMO_4$).

The only natural sulphide of tungsten is tungstenite (WS_2). This mineral is rare and is isostructural with molybdenite. Two principal groups of oxy-compounds are known, wolframite $(Fe,Mn)WO_4$ and scheelite ($CaWO_4$). The latter is tetrahedrally co-ordinated, whilst the former is octahedrally co-ordinated. Elements which can enter the wolframite structure are Fe^{2+} (ferberite, $FeWO_4$), Mn^{2+} (hübnerite, $MnWO_4$), and Zn^{2+} (sanmartinite $(Zn, Mn)WO_4$). Stolzite ($PbWO_4$), powellite ($CaMoO_4$), and wulfenite (Pb,MoO_4) are isomorphous within the scheelite group of oxytungstates.

The solid solution series hübnerite-wolframite-feberite exhibits complete mixing only at temperatures greater than $\pm$ 400°C. Solid solution between scheelite and wolframite is limited to a fraction of a percent at ordinary temperatures, but becomes extensive at temperatures above 600°C. Some tungstates show extensive solid solution with corresponding molybdates. Only trace amounts of molybdenum are found within the wolframite group, but in scheelite molybdenum may be present up to 24% as MoO_3. A complete solid solution series may exist between scheelite and powellite.

Molybdates are more soluble than corresponding tungstates, a fact correlated with the slightly greater electronegativity of molybdenum and hence with the greater covalent character of its bond with oxygen. The separation of the two elements in nature depends on the tendency of molybdenum to form sulphides (MoS_2) in hypogene deposits. Molybdates are stable only where oxygen is abundant, such as in the zone of weathering. Molybdenum and tungsten resemble one another in the weathering environment and both form insoluble compounds with lead, copper and iron. The greater solubility of most of the compounds of molybdenum, gives it greater mobility and wider dispersion in the surface environment.

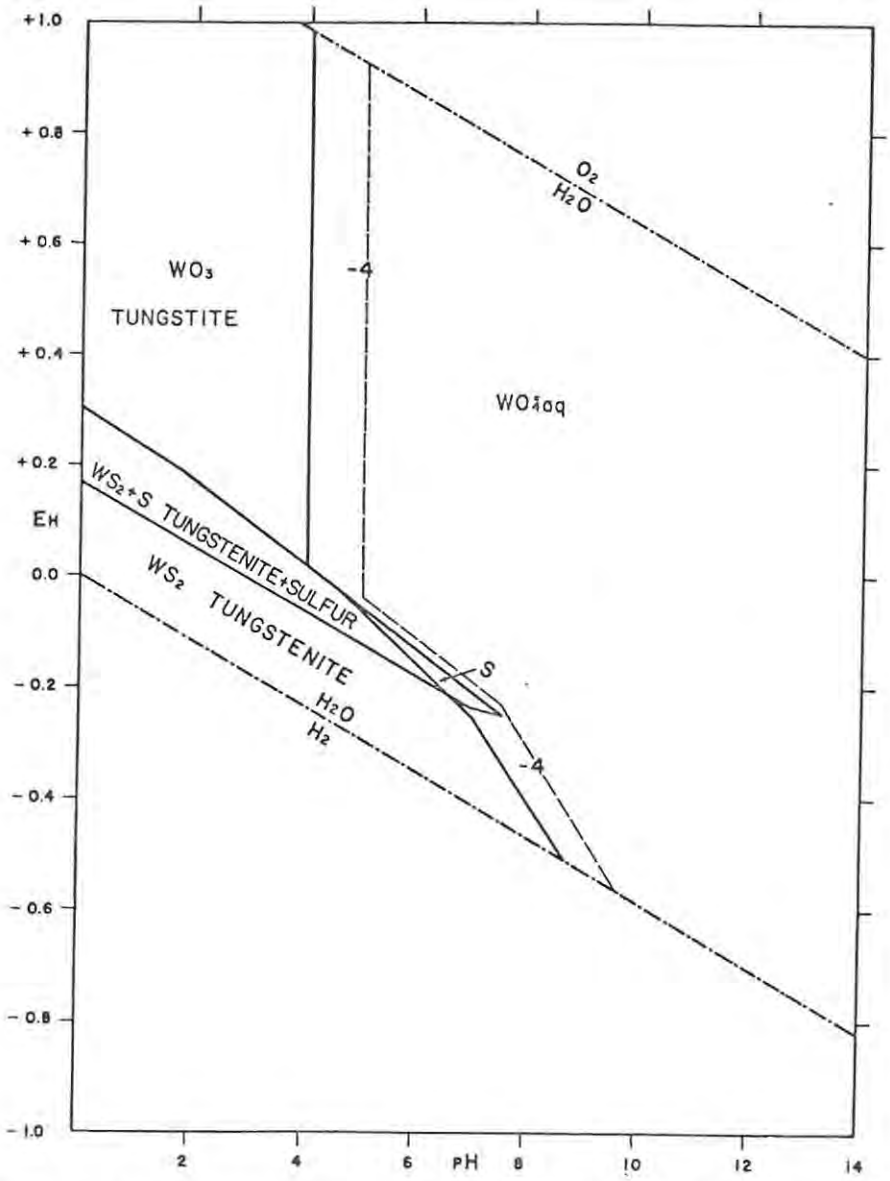


Figure 18. Stability relations among some tungsten compounds in water at 25°C and 1 atmosphere total pressure. Total dissolved sulphur species = 10^{-1}. Boundaries of solids at activity of dissolved species at 10^{-6}; dashed line at activity = 10^{-4} (from Garrels and Christ, 1965, p. 252).

Figure 18 illustrates the stability relationships of some tungsten oxides and sulphides. Tungsten is an amphoteric element as is illustrated by the large field of WO_4^{2-}, and by the stability of WO_3 in acidic solutions. This suggests the possibility that tungsten might exist as does uranium within sandstone, but in nature the WO_4^{2-} ion tends to bond strongly with calcium ($CaWO_4$), iron ($FeWO_4$) and other cations. Tungstenite is stable in reducing acidic to slight alkaline solutions, thus on oxidation and weathering WO_4^{2-} ions and WO_3 complexes will be released.

TIN

Tin has ten stable isotopes between mass numbers 112 and 124 (Table 6).

Table 6. Tin isotopes

Mass number	Relative abundance (%)	Mass number	Relative abundance (%)
112	0.95	118	24.01
114	0.65	119	8.58
115	0.34	120	32.97
116	14.24	122	4.71
117	7.57	124	5.98

(from Wedepohl, 1969, p. 50-B-1).

This is the largest number of isotopes for any element. Shima (1964) suggests that tin can be expected to be siderophile at high temperatures and lithophile at low temperatures. It has been shown that at low temperatures the affinity of tin for sulphur increase whereas at intermediate to high temperatures it occurs almost exclusively in oxygen-bearing compounds - often cassiterite. There are relatively few tin minerals and cassiterite (SnO_2) is the most important. It occurs in 'pneumatolytic' and high temperature hydrothermal veins or metasomatic deposits that are genetically associated with highly siliceous igneous rocks such as granite or rhyolite. Tin occurs in many sulphide ores in the form of tin sulphides or incorporated with a number of other metals, in more complex sulphides. Stannite (Cu_2FeSnS_4) occurs in tin-bearing veins associated principally with chalcopyrite, sphalerite, tetrahedrite, pyrite, cassiterite, wolframite and quartz. Teallite, a lead tin sulphide ($PbSnS_2$) is sometimes found in large amounts in the silver veins of Bolivia. Wurtzite, cassiterite, sphalerite, pyrite and sometimes stannite and franckeite are associated with teallite.

Franckeite is a common mineral in the silver tin-vein deposits of Bolivia, sometimes found in large quantities.

The phase relations in the binary tin-sulphur system were studied by Albers et al. (1961), Albers and Schol (1961), Moh (1962/63). The results obtained by Moh are illustrated in Figure 19.

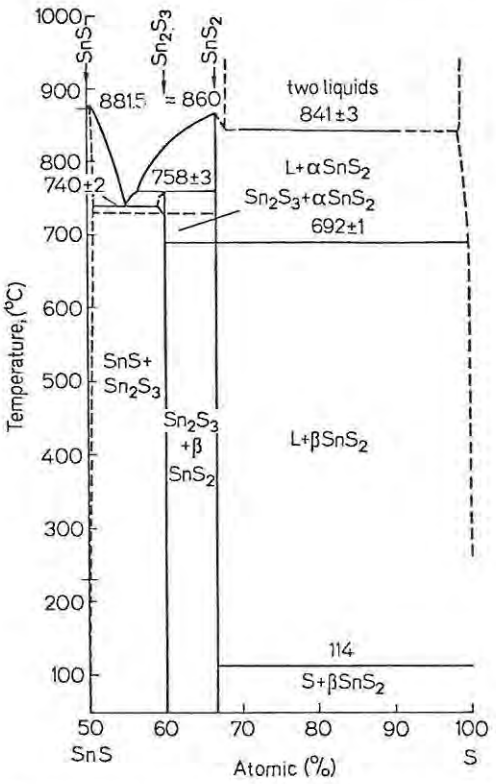


Figure 19. Phase relations in the SnS-S portion of the system Sn-S (from Wedepohl, 1969, p. 50-D-6).

URANIUM

Uranium belongs to the group of elements with atomic numbers 89 and above, of which only thorium and uranium occur in appreciable quantities in nature. Uranium occurs within a number of valencies, U^{4+} and U^{6+} being the most important. Naturally-occurring uranium consists of three different isotopes U^{238} (99%), U^{235} (0,7%), U^{234} (0,005%). The U^{238} and U^{235} are parent isotopes of two separate decay series which ultimately yield Pb^{206} and Pb^{207} respectively. The third isotope, U^{234} is intermediate in the decay series of U^{238} and is formed by the emission of an alpha particle, followed by two beta particles.

The most abundant uranium mineral is uraninite, with a formula varying from UO_2 to U_3O_8. The variability of chemical composition apparently results largely from oxidation of UO_2 to U_3O_8 after deposition, and a number of compositions between the end members is possible.

An important feature or uranium is its ability to become oxidized to the highly soluble uranyl ion (UO_2^{2+}). This ion is easily mobilized in surface and near-surface waters, consequently, regardless of their origin, most uranium deposits contain an assemblage of secondary minerals. The various secondary minerals consist of carbonates, phosphates, vanadates, silicates and sulphates.

Uranium is found in both high and low temperature veins. In high temperature veins it occurs associated with titanium minerals, betafite $(U,Ca)(Nb,Ta,Ti)_3O_9.nH_2O$ and brannerite (UTi_2O_6) and in low temperature veins is found as pitchblende (amorphous uraninite), and coffinite $[U(SiO_4)_{1-x}(OH)_{4x}]$. In pegmatites uranium occurs as uraninite and is found in minerals in combination with niobium, thorium and other rare earths. The lower temperature veins are characterized by the presence of sulphides and may contain disseminated iron oxide. Thorium is associated with uranium in igneous rocks and pegmatites, and sandstone deposits but it is rare in the vein deposits.

Figure 20 illustrates the effect of CO_2 on uranium solubility. Hexavalent uranium is strongly complexed as the uranyl dicarbonate and tricarbonate species so that at relatively high carbon dioxide concentrations they project into the stability field occupied by uraninite in the absence of carbon dioxide. This diagram illustrates that carbonate-bearing solutions are possible transporting agents for uranium.

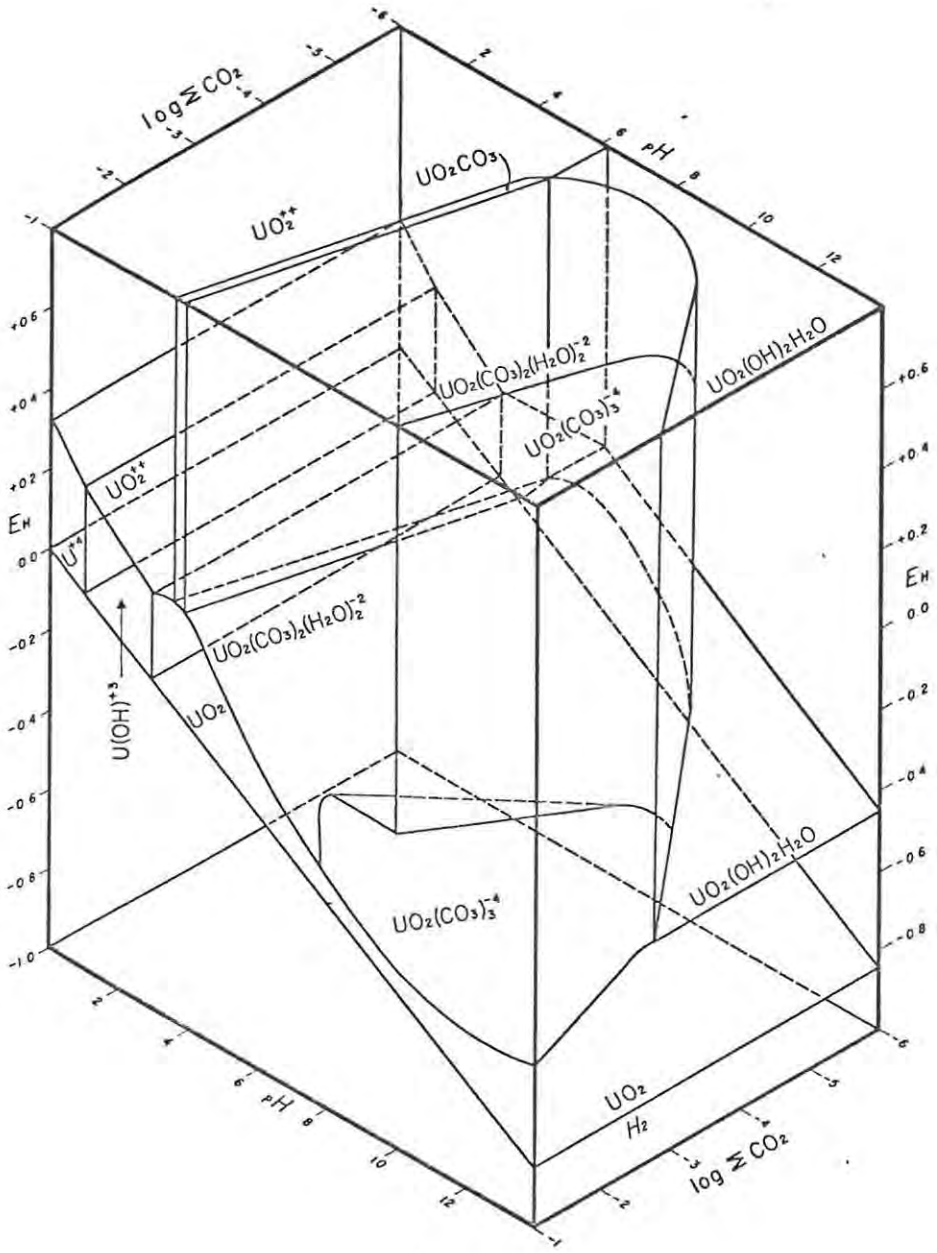


Figure 20. Stability relations among some uranium compounds in water at 25°C and 1 atmosphere total pressure as a function of pH, Eh, and total dissolved carbonate species. Boundaries of solids at activity of total dissolved uranium-bearing species of 10^{-6} (from Garrels and Christ, 1965, p. 255).

The potassium uranyl vanadate (carnotite) is often present in the zone of oxidation and is often an important mineral in deposits of calcrete. Figure 21 is a section of the multicomponent system $U\text{-}O_2\text{-}H_2O\text{-}K\text{-}V\text{-}CO_2$ drawn at fixed activities of K, V, and CO_2. The concentrations of the latter 3 components are at geologically feasible levels. The large field of Eh and pH conditions under which carnotite is precipitated is well illustrated.

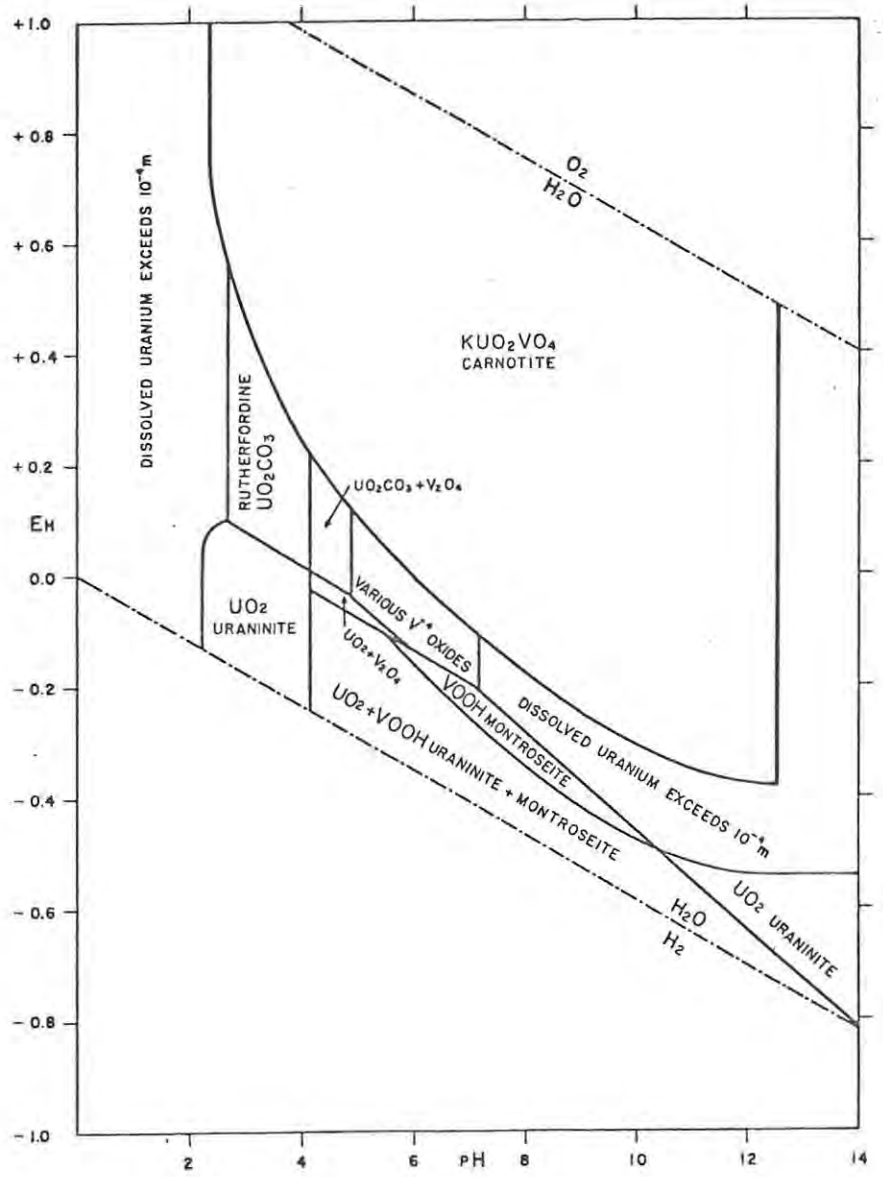


Figure 21. Stability relations among some uranium and vanadium compounds in water at 25°C and 1 atmosphere total pressure. Total dissolved vanadium species = 10^{-3}; total dissolved carbonate species = 10^{-1}; total dissolved potassium species = 10^{-3} (from Garrels and Christ, 1965, p. 256).

IV BEHAVIOUR OF THE ELEMENTS WITHIN THE MAGMATIC ENVIRONMENT

During crystallization and differentiation of a magma the elements are distributed between various phases of the magma such as crystallizing silicates, crystallizing sulphides, immiscible liquid phases, and aqueous volatile phases within the melt. The extent of the partitioning of the elements is controlled by the activities of oxygen and sulphur, temperature, pressure and the composition of the melt.

The possibility that immiscible sulphide phases existed at some stage during the crystallization of a magma was first suggested by Vogt (1921). Field evidence and the recognition of immiscible phases within the melts of blast furnaces strongly supported his proposal. Four decades later Skinner and Peck (1969), following routine sampling of the Alae lava lake (a tholeiitic basaltic lava) in Hawaii, discovered the presence of immiscible sulphide-rich globules in association with crystalline silicates. The melt had obviously become saturated with respect to sulphur and a sulphide-rich liquid had separated from the magma. Table 7 lists the compositions of the phases present.

Table 7. Chemical analyses of basalts from Alae lava lake, Hawaii (in weight percent).

Component	1 (Weight percent)	2 (Weight percent)	3 (Weight percent)
SiO_2	50.44	50.25	51.4
Al_2O_3	13.66	12.76	13.0
Fe_2O_3	1.54	1.24	1.5
FeO	9.55	12.56	12.3
MgO	7.55	5.66	3.0
CaO	11.11	9.66	9.6
Na_2O	2.38	2.62	3.1
K_2O	0.54	0.80	1.0
H_2O+	0.05	0.06	0.13
H_2O-	0.02	0.01	<0.05
TiO_2	2.74	3.77	4.0
P_2O_5	0.27	0.43	0.45
MnO	0.17	0.20	0.17
CO_2	0.02	0.02	N.D.
Cl	0.02	0.03	N.D.
F	0.04	0.06	N.D.
Total	100.10	100.13	99.70

1. Average of 18 samples of pumice and quenched partly molten lava.
2. Quenched ooze of interstitial melt containing immiscible sulphide liquid.
3. Glass fraction separated from 2.

(from Skinner and Peck, 1969, p. 311).

Experimental work by Fincham and Richardson (1954) showed that the distribution of sulphur within a melt could be demonstrated by the following equation :

$$\tfrac{1}{2}S_{2(gas)} + O^{-2}_{(melt)} = \tfrac{1}{2}O_{2(gas)} \quad (S^{-2})_{melt}$$

This expression, due to the very low oxygen fugacities within a melt, can be rewritten as :

$$C_s = Sm \frac{fO_2^{\frac{1}{2}}}{fS_2^{\frac{1}{2}}}$$

where C_s is the sulphur dissolving capacity of an anhydrous silicate melt at varying temperatures, partial pressures of O_2 and S_2 and composition, and Sm is the weight percent sulphur dissolved in the melt.

The effects of composition on sulphide capacity (C_s) of a silicate melt are illustrated in Figure 22.

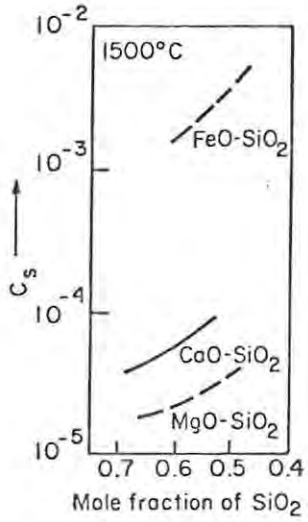


Figure 22. The effect of composition on the sulphide capacity (C_s) of a silicate melt. The relative importance of species such as MgO and CaO are greatly overshadowed by that of FeO, and the principal compositional effect controlling the solubility of sulphur in magmas is the FeO content. Variations in the SiO_2 content of magmas have a minor effect on sulphur solubility (from Skinner and Barton, 1973, p. 203).

Maclean (1969) suggested that immiscible sulphide liquids could be generated by two mechanisms :

(i) by the crystallization of other phases with the subsequent enrichment of sulphide, and

(ii) the intersection at the interface between the crystallizing silicate liquid and the immiscibility gap (Figure 23).

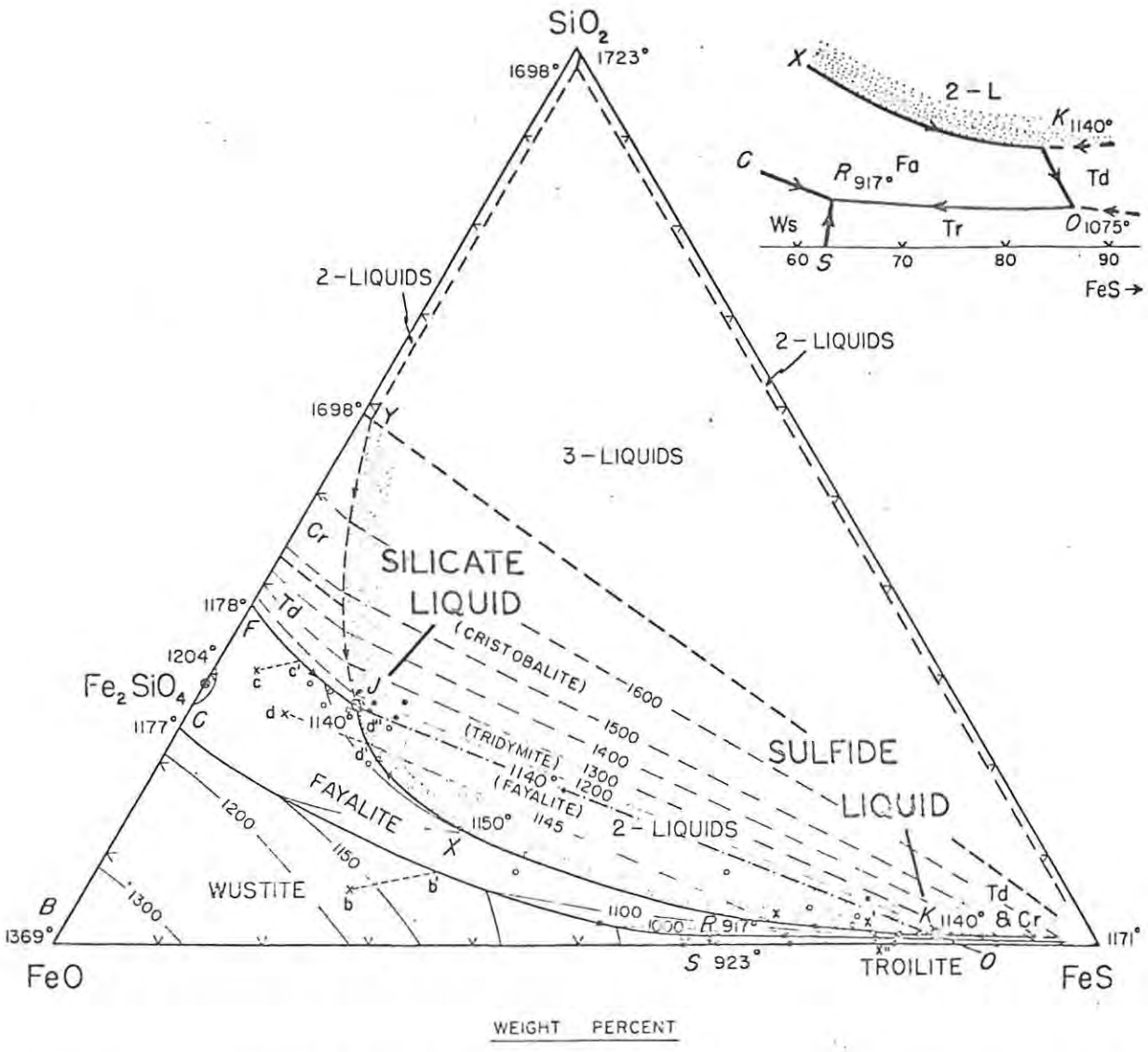


Figure 23. Liquidus phase relations in the FeS-FeO-SiO_2 illustrating the system used to generate immiscible sulphide liquids (from Maclean, 1969, p. 874).

In a series of models, Maclean (1969) demonstrated that by varying the composition and oxygen fugacities of melts within the FeS-FeO-Fe_3O_4-SiO_2 system, sulphide immiscible liquids with varying concentrations and compositions could be generated at various temperatures.

The factors which control the solubility of sulphur in mafic magmas are temperature, composition and the fugacities of oxygen and sulphur. Haughton et al. (1974) demonstrated that an increase of 100°C was sufficient to increase the sulphur-dissolving capacity of a magma by 5 - 7 x's, and that increasing the oxygen fugacity caused a decrease in the sulphur-dissolving capacity. An increase in sulphur concentration tends to increase sulphur solubility.

Iron in the ferrous state is important in controlling sulphur solubility in a magma and a lowering of the ferrous iron content was found to induce immiscibility. A decrease in the ferrous iron content can be produced by the oxidation of ferrous to ferric iron and also by the precipitation of oxides such as chromite, magnetite and ilmenite. This will change the oxygen fugacity of a magma so that the sulphur content will increase and finally form an immiscible sulphide phase. The precipitation of Mg-rich olivines and pyroxenes will enrich the melt relatively in iron and thus cause a reversal of the process.

At high temperatures, within a magma, pyrite is unstable and pyrrhotite is probably the more important phase (Skinner and Barton, 1973). Magnetite depresses the pyrrhotite melting point and whether the precipitating phase is crystalline or liquid depends on the temperature at which saturation occurs and on the partial pressures of sulphur and oxygen. The range of PS_2 and PO_2 in mafic magmas is limited and this confines the Fe-S-O liquid composition to the primary field of pyrrhotite. Once the system is saturated with sulphur it is possible to have simultaneous precipitation of crystalline pyrrhotite and a Fe-S-O liquid (Skinner and Barton, 1973). Figure 24 illustrates that the compositions of the immiscible droplets from the Alae lava lake and the ore from Strathona and Alexo mines all plot in the pyrrhotite field.

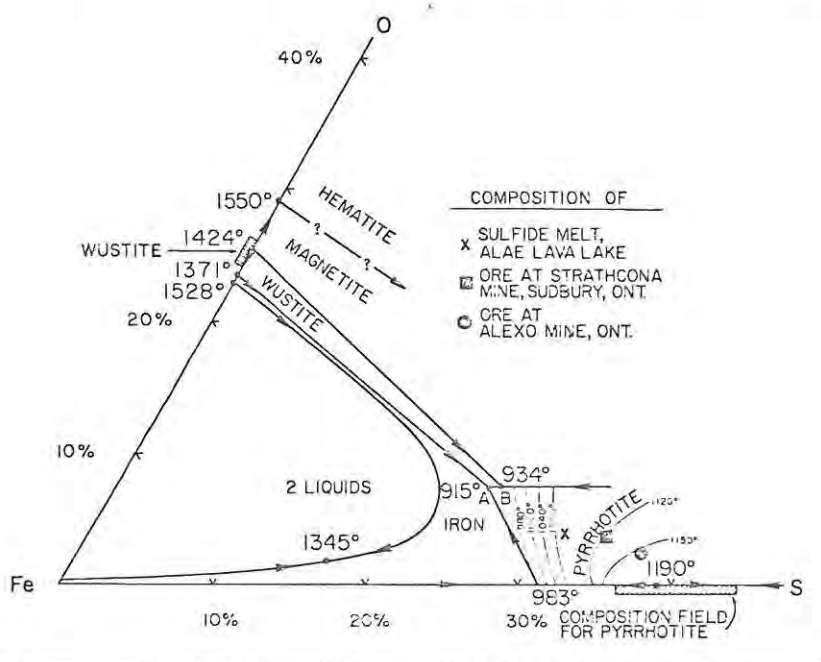


Figure 24. Phase diagram for the system Fe-S-O. Natural immiscible sulphide liquids fall in the region of the pyrrhotite phase field, the liquidus surface of which is contoured. When such a liquid cools and reaches the liquidus surface, pyrrhotite will separate and push the residual liquid towards the cotectic along which magnetite and pyrrhotite crystallize. The composition of the Alae lava lake sulphide liquid, collected at 1065°C, is plotted together with two average ore compositions from deposits widely accepted as being formed by immiscible sulphide liquid segregation (from Skinner and Barton, 1973, p. 204).

The partitioning of metals other than iron between coexisting silicate and sulphide liquids has been studied by, among other, Maclean and Shimazaki (1976), Rajamani and Naldrett (1978), and Feiss (1978). Most of this work has been based upon the observations of Burns and Fyfe (1964) of, and the subsequent clarification of the crystal field theory by Burns (1970). Magmatic melts were demonstrated to be quasi-crystalline, and it was shown that in silicate melts of granitic and basaltic compositions both tetrahedral and octahedral sites are present. Burns (1970) demonstrated that the transition elements of the first series are able to enter both these sites, but that within silicates the elements are rarely present in tetrahedral co-ordination, but occur within the octahedral sites. Therefore, during crystallization a partitioning of ions takes place between the octahedral and tetrahedral sites of the magma and the octahedral sites within a crystal (see Section II).

Maclean and Shimazaki (1976) measured the partitioning of Fe, Ni, Co, Cu and Zn between sulphides and silicate liquids in the FeS-FeO-SiO_2 system. They measured the relative preferences of the different transition elements for octahedral sites in magmatic melts and calculated the distribution coefficients by the following formula :

$$Km = \frac{\text{wt. \% of metal in sulphide liquid}}{\text{wt. \% of metal in silicate liquid}}$$

and they found the order of partitioning between sulphide and silicate melts to be Ni > Cu > Co > Fe > Zn. This order can be explained by the crystal field theory and distortion effects. It can also explain the observed concentration or depletion of certain elements forming orthomagmatic ore deposits. Figure 25 illustrates the relative preference of the transition metals for octahedral sites within the sulphide liquid.

Thus nickel and copper are greatly enriched in those sulphide liquids which can separate from a magma and form massive sulphide deposits such as Kambalda, or if complete crystallization takes place before extrusion, disseminated sulphide deposits such as Mt. Keith. Zinc has a very low preference for octahedral co-ordination within mafic melts and is thus relatively enriched within the residual melt and possibly becomes strongly complexed to sulphur with increasing differentiation and decreasing temperature. Zinc occurs in volcanic and exhalative deposits with a more felsic character than nickel.

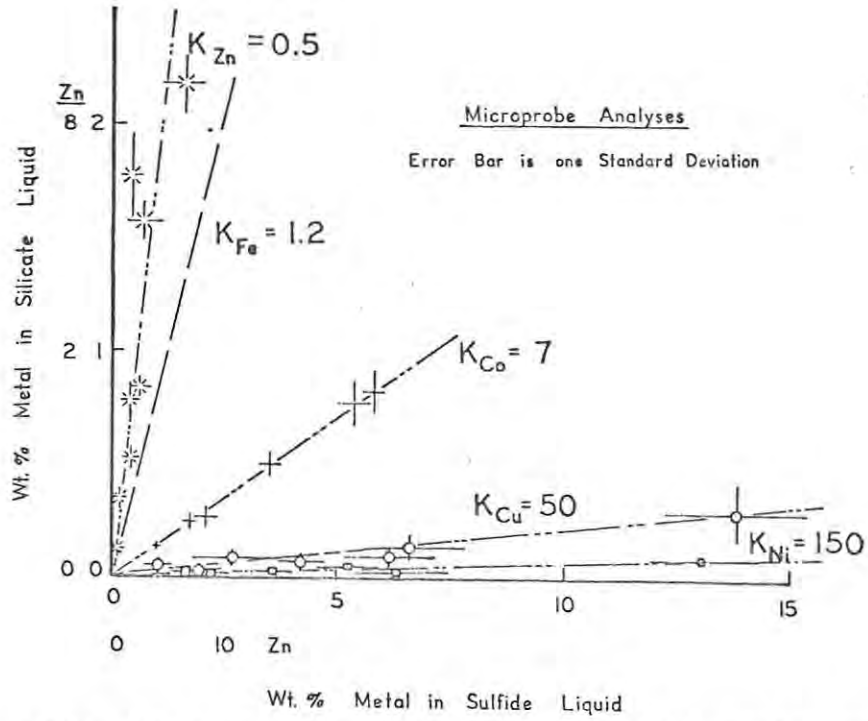


Figure 25. Plot of the experimental data on the partitioning coefficients. The error bars are one standard deviation of X-ray counting statistics (from Maclean and Shimazaki, 1976, p. 1052).

Mafic and ultramafic melts are enriched in copper and depleted in nickel through the crystallization of olivine (Figure 26).

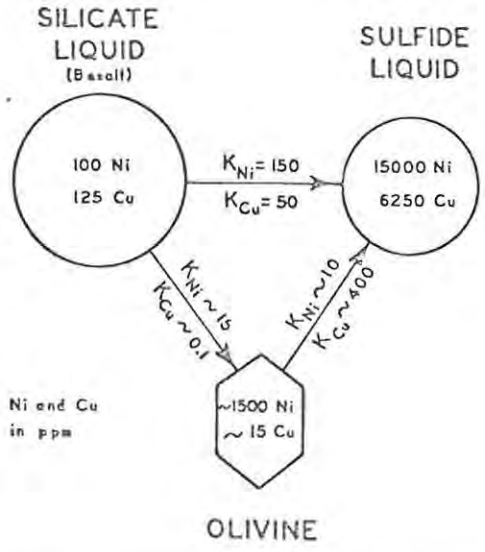


Figure 26. Diagram showing the partitioning of elements between phases under equilibrium conditions. The presence of olivine does not affect partitioning between the liquids, but the precipitation of olivine may rapidly deplete the liquids in Ni and slowly enrich them in Cu (from Maclean and Shimazaki, 1976, p. 1055).

Thus should crystallization and the subsequent removal of olivine occur prior to the formation of immiscible sulphide globules, the "residual" liquid will become enriched in Cu, Zn, Pb and Co, and a nickel-silicate deposit will be formed. This explains why layered igneous complexes are not regarded as prime exploration targets for nickel-sulphide.

Rajamani and Naldrett (1978) observed that the composition of the silicate liquid must have a significant effect on the partitioning of nickel and copper. They indicate that in andesitic melts with 4, 5 wt. % MgO, nickel tends to be more sulphophile than copper. Whereas in more basic melts (13,5 wt. % MgO), nickel tends to behave as if it were less sulphophile. This can be explained by the fact that it has a high octahedral site preference energy regardless of the phase within which the site occurs, but once the liquid becomes slightly more felsic there is a relative decrease in the number of octahedral sites within the silicate phases and the tendency for nickel to enter the octahedral sites within sulphide phases increases.

Mafic rocks show an enrichment in nickel and a low Cu/Cu + Ni ratio. Naldrett and Cabri (1976) and Rajamani and Naldrett (1978) worked on the compositions of rocks in relation to their nickel and copper content. Figure 27 illustrates the relationship between MgO content and the variation in the nickel and copper contents of a segregated sulphide liquid. Figure 28 illustrates the calculated relationships between the MgO content of a magma and the Cu/(Cu+Ni) ratio of sulphide liquids and superimposed are the MgO vs. Cu/(Cu+Ni) contents of certain deposits.

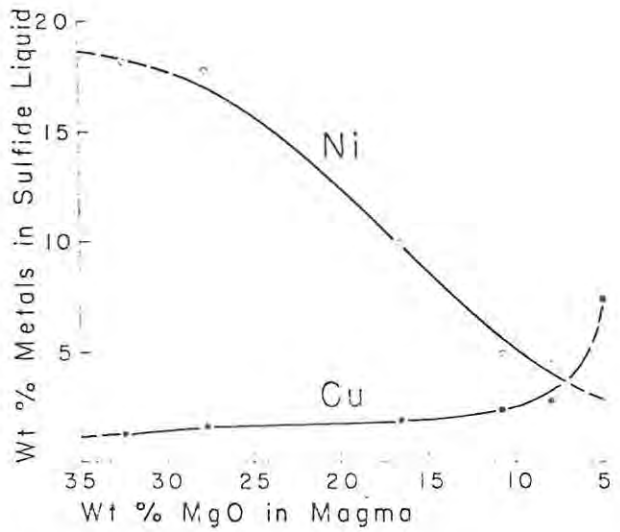


Figure 27. Variation in the Ni and Cu contents in the sulphide liquid segregating from successive liquids of a fractionally crystallizing komatiitic magma with weight percent MgO of these liquids.(from Rajamani and Naldrett, 1978, p. 90).

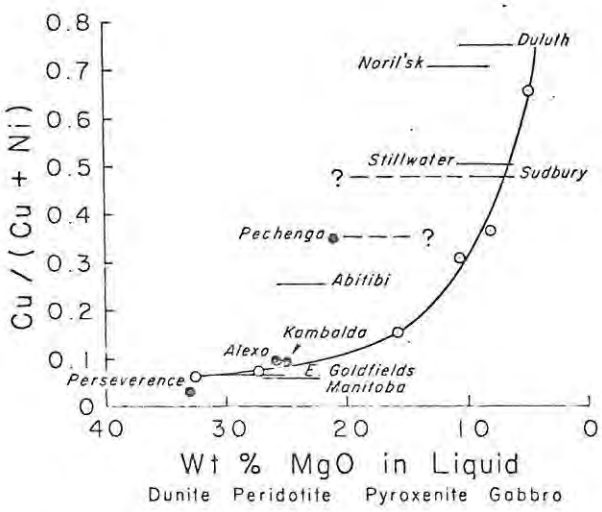


Figure 28. Calculated relationship between the Cu/(Cu+Ni) ratios of sulphide liquids and weight percent MgO of komatiitic magma. The open circles represent the calculated ratios (from Rajamani and Naldrett, 1978, p. 91).

The concentration of cobalt does not seem to be associated with any particular rock-type, but there appears to be a slight preference for olivine relative to a basaltic melt. The strong preference of nickel for the sulphide liquid is probably due to the combined effect of the π bonds formed with sulphur ligands and the high stability in octahedral sites. High spin Co^{2+} and Fe^{2+} form two π bonds with sulphur ligands while nickel forms three.

Lead and zinc within the FeS-FeO-SiO_2(Fe_3O_4)(Na_2O) systems are not partitioned strongly to the sulphide liquid, and although their values are affected by change in Na_2O content and fO_2 the concentrations are too small to form deposits with economic considerations (Maclean and Shimazaki, 1976). Pb^{2+} is intermediate in size between Ca^{2+} and K^{+} and may be expected to enter in K-feldspar and K-mica structures, but because of the double charge and smaller ion, the more covalent character of the Pb-O bond offsets such effects. Pb^{2+} should enter late Ca^{2+} positions but because of the more covalent character of the Pb-O bond of the large Pb^{2+} ionic radius, lead will be partitioned into the melt. Within the melt it will possibly begin to complex with chlorine but because of the predominance of galena (PbS) with increasing differentiation lead will probably start competing for sulphur with zinc and copper. Thus lead and zinc tend to increase in the residual magma during differentiation of melts

until the composition of the melt is andesitic in character, and this is possibly the time when removal of these elements occurs.

Burns (1970) illustrated that the $Al_2O_3/K_2O + Na_2O + CaO$ ratio of a magma is proportional to the number of octahedral sites available in the melt. Thus with the preference that Cu^{2+} exhibits for octahedral sites within sulphide phases it follows that during crystallization Cu^{2+} will tend to become depleted in the magma. Feiss (1978) illustrated that the high alkalic content within a granitic magma would drive Cu^{2+} into early formed crystals but in contrast, a high Al_2O_3 concentration would decrease the number of tetrahedral sites in the silicate liquid. This, plus the Jahn-Teller effect, ensures that Cu^{2+} stays within a melt until it complexes within solution and becomes available for deposition within porphyry and hydrothermal deposits.

Silver enters sulphide phases and the extremely covalent nature of the Ag-O bond in comparison with Fe-O or K-O bonds will lead to the virtual exclusion of silver from silicate lattices, and its subsequent concentration in the sulphide phase. This will cause a depletion of silver in the melt and an enrichment in galena, chalcopyrite and pyrite. The behaviour of silver tends to be comparable with copper, but occurs in much smaller concentrations, and forms a more covalent bond with oxygen, and during fractionation of a melt the Ag/Cu ratio is expected to increase in silicates (Taylor, 1965).

The geochemical behaviour of silver is complex and four separate factors must be considered (Taylor, 1965) :

(i) Entry of Ag^{2+} into Fe^{2+} positions, accompanying Cu^{2+}. The more covalent character of the Ag-O bond compared with the Fe-O and Cu-O bond will lead to the rise in the Ag/Fe, Ag/Cu ratios.

(ii) Entry of Ag^{2+} in to Cu^{2+} and Na^{2+} positions. This will be slight because of the very ionic character of the Ca-O, Na-O bonds and will lead to the rise in silver content during fractionation.

(iii) A similar substitution for K^{+} in mica and K-feldspars.

(iv) Removal of the accumulated silver by separation of a sulphide phase. This will deplete a magma in silver in the same manner as copper.

The geochemistry of gold is dominated by its occurrence in the metallic state. Gold is considered to be more siderophile than silver, and because of this non-sulphides carry more gold than silver. Gold is commonly associated with iron, bismuth and antimony, and Goldschmidt (1954,p. 202). writes that the cause "is to be sought in the ability of these elements to form packings of such large ions that gold can be collected in the interstices". Anders et al. (1971) argue that in a strongly reducing environment, as possibly exists within a mafic magma, the siderophile elements (such as gold and silver) could possibly be concentrated in the metallic state.

Molybdenum and tungsten, due to the high valence states and subsequent high ionic potential form $(MoO_4)^{2-}$ and $(WO_4)^{2-}$ complexes which will be concentrated in residual magma. There will thus be a concentration of these elements in residual or volatile-rich magmas. The complexes which the metals form with oxides and halides etc. disallow entry into silicate minerals. For the quadrivalent ions, relative bond strength will be important, and the more covalent character of the Mo-O and W-O bonds will lead to the concentration of molybdenum and tungsten in later fractions. With regard to the hexavalent states concentration in residual magmas is facilitated by a charge discordancy relative to $(SiO_4)^{4-}$. Electronegativity values do not indicate any difference in bond type for the two elements, but the ionic potentials indicate that the Mo-O bond should be more ionic than the W-O bond.

Uranium can enter the lattices of minerals such as monazite, allanite and sphene, but uranium tends to become enriched in the residual magma during differentiation. Uranium is normally present as U^{4+} in igneous rocks and the high ionic potential of U^{4+} will lead to complex formation and subsequent concentration in residual magmas. The hexavalent ion (UO_2^{2+}) occurs under oxidizing conditions. The high ionic potential of Sn^{4+} will favour the formation of $(SnO_4)^{4-}$ in silicate melts. This complex ion, due to its size, (and due to complexes formed as halides, fluorides, sulphides, etc.), will not be incorporated into silicate lattices and so becomes enriched in the residual melt.

V BEHAVIOUR OF THE ELEMENTS IN HYDROTHERMAL AND AQUEOUS SOLUTIONS

(a) Characteristics of Hydrothermal Solutions and Certain Transporting Agents

The exact mechanism of ore metal transport in nature is unknown and can only be inferred from field observations and laboratory studies. Subsequently rather diverse ideas have been presented, however, there remains a number of geochemical and chemical limits which restrict the number of possible mechanisms.

In all cases the mechanism of migration of elements depends on the stability of the migrating ion or compound within a specific physico-chemical environment. Thus the mobility of an element depends on the stability and solubility of chemical compounds which it can form in solution. Reaction between the ore elements and other compounds within the solution can cause precipitation of the ore element, thus the complex must be soluble, stable and relatively unreactive in order that transport over appreciable distances may be achieved. Individual dissociated ions of certain elements may be transported, provided they do not react with other components of the transporting medium (Beus and Grigorian, 1977). Barnes and Czamanske (1967,p.337) describe a complex as "Complex ions or molecules are species in solution formed by strong interaction of ions and/or molecules which then respond as a single aqueous species in many chemical reactions".

Ore solutions must contain alkalies, chlorides, carbon species, sulphur, hydrogen, oxygen and flourides. This is obvious from the study of fluid inclusions, emanations of fluids and gases from volcanoes, and hydrothermal springs, and the composition of the minerals within ore deposits. Korzhisnkii (1963) and others, have shown that during crystallization of a magma, the residual melt becomes enriched in acidic components (CO_2, HCl, Hf, H_2S, etc.) that do not form part of the mineral assemblage. Condensation of volatile acidic components, as well as increasing density due to decreasing temperature of solutions approaching "boiling point", produces an increase in acidity. Berzina and Sotnikov (1977) conclude that ore deposition can occur from solutions enriched in CO_2 at 400° - $200^{\circ}C$ and that phases which separated earlier from the magma would probably be enriched in flouride and later stages in flouride-carbonate, or chloride and carbon dioxide. Itsikson (1963) suggests that the main components of ore-bearing solutions are water, flouride and iron in conjunction with tin, lead, copper, zinc, arsenic and sulphur,

and states that while studying the process of ore transport an account is made only of those compounds which occur in minerals as it is not clear what roles such compounds as Cl and CO_2 played during transport and deposition.

Argillic alteration suggests that the pH must have been less than 2,5 units below neutrality because of the presence of K-mica. If strongly alkaline conditions prevailed, K-mica would be converted to K-feldspar. Data from hydrothermal fluids, and calculations indicate that the pH of the ore solutions must have been within one pH unit below and within two pH units above neutrality.

The lack of native sulphur in ore deposition also suggests a limit to the pH of deposition. Figure 29 illustrates the stability field of certain minerals and sulphur. It indicates that the lowest pH of the ore solutions must have been above 4.

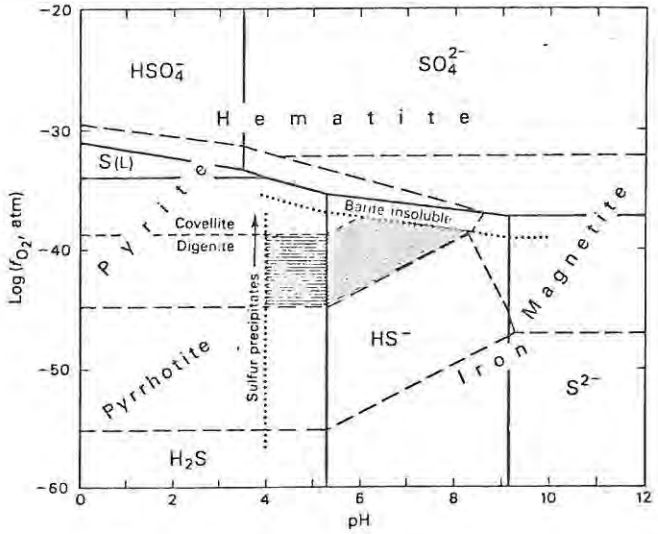


Figure 29. Stability fields for the Fe-S-O system plus other selected minerals and aqueous species at 250°C, $\Sigma S = 0.1$ based on data at 25°C which were adjusted to 250°C by the van't Hoff equation. Dashed lines represent boundaries between stability fields of minerals and heavy, solid lines between aqueous species (from Barnes and Czamanske, 1967, p. 351).

Barnes and Czamanske (1967) emphasize the importance of textures, paragenesis and the zonation of metals found in hydrothermal deposits (see Ch. 8, Barnes and Czamanske, 1967). Reversals in the zoning, or paragenetic sequence can occur between metals which are situated paragenetically close to one another. For example sphalerite is usually found

deposited earlier than chalcopyrite, but should the ore-forming fluids contain a greater concentration of copper than zinc, chalcopyrite will be deposited before shpalerite. The aqueous complex of copper is slightly more stable than that of zinc, but the mass-action effect causes a reversal in the depositional sequence.

The textures of deposited minerals and the zonal relationships place certain restrictions upon what mechanisms can be used for transporting ore elements. Deposition from volatiles cannot produce the observed sequence of minerals formed, and furthermore, the vapours of the majority of metals, at geologically feasible temperatures, are insufficient to be of importance in ore transport. Colloidal transport of ore metals is not considered as a viable mechanism, as colloids are unstable in brine solutions. Furthermore, colloidal transport could not produce the observed zoning, and colloidal textures would be generally expected to be preserved in massive sulphide deposits - and they are not. Elements are transported either by appreciable solubility in the aqueous phase or by a variety of possible complexes.

Taylor (1963) suggested that the relative abundances of the chalcophile elements in a given ore-bearing solution will be determined primarily by the concentration of these elements in the source material and by the partition co-efficients between the source and the ore-fluids. Thus elements can be transported a long way because they are not concentrated enough to be deposited, and there is evidence of hydrothermal deposition of oxides and/or silicates in considerable amounts before sulphides. The metallic sulphides were possibly undersaturated in the ore-fluid during the earlier stages of migration and deposition. Ore-fluids will change composition with time and distance from their source, and therefore solubilities ought to have little effect on the relative abundances of the heavy metals in most ore-forming fluids until these heavy metals begin to precipitate (Taylor, 1963).

Of the stable complexes of sulphur only H_2S, SO_4^{2-}, and HS^- are likely to be important. $H_2SO_4^-$ would require too great an acidity, and S^{2-} too great an alkalinity. It is possible that polysulphide and thiosulphide ions are metastable above 200°C and decompose. The aqueous stability fields of 25°C and 250°C are probably similar (Barnes and Czamanske, 1967). At above 250°C - 300°C the bisulphide solution reacts as follows : $2HS^- \longrightarrow H_2S + S^{2-}$ thus becoming unstable. Metal complexing could then be H_2S or S^{2-}.

The stability of sulphur complexes tends to be unaffected by the addition of carbon species (CO_2, CH_4) because no aqueous ion or molecule is formed between carbon and sulphur. Barnes and Czamanske (1967) state that if stable complexes are formed with HS^-, and the addition of Cl^-, NH_3, HCO_3 does not increase the solubility of the complex, these additional species cannot be part of the chemical mechanisms of ore transport.

Herr and Helz (1978) suggest that bisulphide ion-pairs could be important at high temperatures but note that the effect of HS^- on ion-pairing need not be one of enhancing mineral solubility but instead it could have the opposite effect. Barnes and Czamanske (1967) have pointed out that for a fixed high chloride ion concentration the character of the dominant base metal complex depends on reduced sulphur concentration and pH. If the concentration of total reduced sulphur is very low then metals are possibly transported in the form of chloride complexes. However, if total reduced sulphur is high, then the concentration of base metal chloride complexes in equilibrium with sulphide minerals is strongly depressed, and bisulphide complexes predominate. In the latter case where bisulphide complexes predominate, alkaline earths could compete with the base metal for the solubilizing ligand, and this would tend to depress the capacity of acid solutions to carry base metals. With increasing migration an ore solution undergoes oxidation, thus sulphur present will be in the sulphate form. Evidence from Roedder (1967) indicates that brines are low in sulphur and that the sulphur present is predominantly sulphate. The presence of barium, as baryte ($BaSO_4$) in volcanogenic deposits can thus be explained.

Above 575°C H_2S decomposes entirely and it is possible that from temperatures above 500°C the dominant sulphur phase would be SO_2. Barnes and Czamanske (1967) suggest that at temperatures above 374°C HCl is as weak as acetic acid at normal temperatures. They state that this is the same with regard to alkali chlorides and that complexes formed at these high temperatures would be very unstable. Ganeev (1963) states that the main difficulty in proposing possible ore transporting mechanisms lies in the limited knowledge of complex stability under high temperatures and pressures. Certain complexes retain their chemical stability on heating up to 300° - 350°C because the increase in pressure under high temperature conditions would generally support the complex and maintain stability.

In table 8 those elements with electronegativity values between 190 and 270 K.cal/g-atom are referred to as the amphoteric elements (i.e. they exhibit both alkaline and acidic properties depending on the composition of the solution in which they occur).

Table 8. Electronegativity values of certain element (from Beus and Grigorian, 1977, p. 30).

EN	Element	EN	Element	EN	Element
90	Cs^{+}	180—190	Pb^{2+}, Ag^{+}, Cu^{+}, Fe^{2+}	250	Ti^{4+}, Cr^{3+}
97—100	Rb^{+}, K			260—270	Si^{4+}, Sn^{4+}
115—120	Ba^{2+}, Na^{+}	190—200	Sb^{3+}, Bi^{3+}, Co^{2+}	270—280	S^{4+}
120—130	Li^{+}, Sr^{2+}, Ca^{2+}, La^{3+}	200—205	Zn^{2+}	280—290	B^{3+}
140—150	Ce^{3+}	205—210	Be^{2+}, W^{4+}, Ta^{5+}, U^{6+}, Ni^{2+}	290—300	As^{5+}
160—170	Th^{4+}	210—220	Hg^{2+}, Al^{3+}, As^{3+}	300—310	P^{5+}
170—180	Mg^{2+}, U^{4+}	220—230	V^{3+}, Nb^{5+}, Mo^{4+}	310—315	H^{+}
		230—240	Fe^{3+}, Cu^{2+}, Hg^{+}, Pb^{4+}	370—380	C^{4+}, S^{6+}
				460	Cl^{7+}
				530	O^{8}
				605	F^{7+}

The amphoteric property of these elements determines their ability to form soluble, stable complexes within ore-metal transporting solutions. These complex compounds are referred to by, amongst others, Beus and Grigorian (1977), as acidocomplexes. These complexes are characterized by strong covalent bonding with subsequently diminishes the activity of the element in solution. Generally an acidocomplex is an amphoteric element covalently bonded to an acid atom or radical (addend). The formula can be written as $B_m[MA_n]$, where B is an alkaline element (K,Na,Li,Rb,Cs,Ca); M an amphoteric element (W^{4+}, Zn^{2+}, U^{6+}, Mo^{4+}, Zn^{2}, Cu^{2+}, Ni^{2+}, Sn^{4+}); and A is an addend (Cl,F,S). These acidocomplexes dissociate in aqueous solution as follows $B_m[MA_n] \quad {}_mB^{+} + [MA_n]^{m-}$ (Beus and Grigorian, 1977).

Complexes with mixed addends (Ganeev, 1963) could be important in ore-metal transport. Change in the addends would depend on their concentration in solution and an important factor in changing the addends could possibly be the reaction of the fluids with the wall-rock during migration.

Investigations indicate that heteropoly acids (egs. $[(HW_6O_{21})^{-5} \times H_2O]$ $H_8[Si(WO_7)_6].3H_2O$; $H_3[P(W_3O_{10})_6] .xH_2O$; $H_3[Sb(W_3O_{10})_6].xH_2O$)

in aqueous solution readily form anions and aggregate with the simultaneous formations of highly polymeric compounds. (A high degree of polymerization was found in acidic solutions of sodium wolframite). The degree of polymerization is a function of the concentration of the substances in solution. Polymeric compounds are stable in both acidic and neutral environments, but in alkaline solutions they tend to decompose. Examples of the complexes studies by Ganeev (1963) are $[SN(OH,F)_6]^{2-}$, flouroaqueous complexes $[AlF_3(H_2O)_4]^{+}$ and $[UO_2(CO_3)_2(M_2O)_2]^{2-}$.

The process of aggregation (polymerization) of hydroxy compounds could be of importance in ore transport. The following is a list of ce.tain elements and the extent to which they polymerize :

(i) Ag^{+}, Fe^{2+} hydrolyse to form mononuclear complexes,

(ii) Cu^{2+}, Fe^{3+}, Sn^{4+} polymerize to a limited degree, and

(iii) $(UO_2)^{2+}$ can occur as a continuous series of multinuclear complexes.

The stability of polymers is frequently determined by the concentration of other complex-forming elements in solutions which can decompose polymeric compounds of a given element, and by the presence of addends able to substitute for oxygen and to form more stable compounds.

As supercritical solutions develop in to hydrothermal solutions, due to a decrease in temperature, the internal structure of the solution experiences major rearrangements, and its chemical properties change. This conversion from a supercritical to a hydrothermal solution is accompanied by an abrupt increase in the solubility of bases, which causes a decrease in their activity. The solubility of acids in a hydrothermal solution on the other hand decreases markedly and their activity increases. In addition a decrease in temperature and the appearance of the liquid H_2O phase lowers the stability of high-temperature complexes. Therefore, decomposition of some acid-ocomplexes which are stable in supercritical high-pressure solutions occurs and this dissociation releases anions of strong acids. Consequently, as

the temperature of the system decreases the supercritical nature of the solution changes to hydrothermal, the acidity increases, reaching a maximum at the beginning of the hydrothermal stage of the postmagmatic process. Greisenization therefore occurs due to the increased acidity of the solutions.

Certain types of mineralization are associated with a particular host rock, for example tin within granite, but other elements such as copper, lead and zinc appear to be deposited over a wide range of temperature and pressure conditions, and within no particular host-rock-type. Volcanogenic exhalative deposits are predominantly associated with sedimentary rocks, the porphyry deposits are related to a cupola or stock and the hydrothermal deposits (per sé) are found in areas of low pressure-tension gashes, veins, fractures and faults, not always related to an obvious igneous source. These three types of hydrothermal ore deposits may be distinguished according to the hydrological and tectonic conditions during mineralization as follows :

(i) Deposits formed from solutions that ascend to the surface.

(ii) Deposits formed from solutions that did not reach the surface. Thus the solutions ascended some distance from the parent magma before mineralization crystallized under closed conditions.

(iii) Deposits formed from solutions which did not separate from the parent magma; the ore forming fluids being supplied by convection of solutions within the magma.

The first group of deposits would include the exhalative-type copper, lead, zinc silver deposits.

The second group of deposits would include the hydrothermal deposits of porphyry affiliation and hydrothermal deposits situated in areas of low pressure.

The third group of deposits would include endogranitic (and possible skarn-type) mineralization - deposits of tin, tungsten, uranium, minor copper, lead and zinc.

The level to which the solutions would rise would depend upon the pressure of the solutions within the magma relative to confining pressure, thus greatly dependant on the permeability of the fracture system, and porosity of the rock. The formation of large deposits, within closed systems may occur without the supply of geological unfeasible amounts of solutions, and that solubilities are not required for ore transport (Berzina and Sotnikov, 1977).

Acidic hydrothermal solutions interact with enclosing rocks. This tends to cause the removal of alkali and alkali-earth metals from surrounding rocks which leads to the neutralization of the solutions and to the progressive increase in the activity of the strong bases in solution. The country rocks thus become altered. High-silicon rocks (quartzite, sandstone) tend not to affect the composition of hydrothermal fluids, and therefore do not cause the decomposition of acidocomplexes. Feldspathization can result when these rocks interact with alkaline solutions. If the acidity of the mineral-forming solution is high, this may cause the silicification of rocks such as granite, syenite, gneisses, schists. These rocks provide strong bases to the fluids and interaction therefore leads to a gradual increase in the alkalinity of the solution, which tends to decompose the complexes thereby causing precipitation. Basic and ultrabasic igneous rocks as well as their metamorphic equivalents are low in alkalies, but rich in calcium which is a precipitant for some acidic anions (F^-, CO_3^{2-}) and some trace elements such as tungsten. Carbonate rocks cause the neutralization of the acidic mineral-forming fluids especially if these solutions contain flourine.

(b) Possible Transporting Complexes and Solubilities of the Selected Elements

COPPER

The solubility of copper sulphides in pure water is extremely low and is only slightly increased by the addition of H_2S. In contrast, the solubility of copper sulphides in bisulphide solutions is high. The concentration is temperature dependant and increases 4 to 5 times from 25° - $200^\circ C$. The complex formed is, $CuS + H_2S_{(g)} + HS^- \longrightarrow CU(HS)_3^-$.

The presence of NH_4Cl depresses the solubility to approximately half that in pure bisulphide solution, and there does not appear to be a polyanion complex formed with copper sulphide involving both HS^- and NH_4^+ or Cl^- in sulphide solutions. Simple chloride complexing of Cu^{2+} is apparently ineffectual, but the ion, Cu^+ does form a trichloride complex (Barnes and Czamanske, 1967). These authors believe that it is only within environments containing very low sulphide concentrations, and at low temperatures, that chloride complexing can account for the transport of copper.

Romberger and Barnes (1970) determined that covellite solubility is possibly proportional to the concentration of HS^- in solution and that this is in turn dependent upon the activity of H_2S and temperature. At 25°C, at pH's less than 7,3, the important complex was determined to be $Cu(HS)_3^-$, and at pH's greater than 7,3 the complex $CuS(HS)_3^{3-}$ is possibly important. At 200°C, at pH's less than 6,6 the important complex is probably $Cu(HS)_4^{2-}$ and at pH's greater than 6,6 the important complex was shown to be $CuS(HS)_3^{3-}$. They conclude that in neutral to weakly alkaline conditions bisulphide complexes are important in ore transport.

Crerar and Barnes (1976) measured the solubilities of chalcopyrite bornite and chalcocite at temperatures ranging from 200° to 350°. They conclude that, because the work by Roedder (1971) indicates that ore fluids typically contain above 10^{-2} to 10^{-1} *m* chloride, sufficient copper, and iron, may be transported as the species Fe^{2+}, $FeCl^+$ and CuCl in the presence of sufficiently reduced sulphur to account for copper sulphide deposition. They add that the cuprous-bisulphide complexes become significant in weakly basic solutions, at high concentrations of sulphur, and at lower temperatures, and that the bisulphide complexes are more important at 250° than at 350°C.

Cu^+ complexes with chlorides more effectively than Cu^{2+} in sulphide-free concentrated NaCl solutions. At temperatures from 20° to 90°C the complex $CuCl_4^{2-}$ was found to be responsible for copper solubility (Helgeson, 1964). Helgeson (1969) calculated the solubility of Cu_2S and $CuFeS_2$ in NaCl solutions and found that the solubility of Cu_2S increases from 0,05 ppm at 100°C to 950 ppm at 300°C. Under the same conditions the solubility of $CuFeS_2$ was found to increase from 0,034 ppm to 12,7 ppm.

According to Rickard (1972) the most probable dissolved phase of copper in seawater is undissociated cupric carbonate. Experimental work

using cupric salts in an aqueous sulphide solution indicate that covellite and blaubleibender covellite were the two most common copper minerals formed. Rickard (1972) suggests that for chalcocite formation, cuprous copper (Cu^{+}) needs to be present, and he has demonstrated that unusual conditions are needed for the preservation of cuprous copper in the aqueous environment, but Rose (1974) prefers the concept of copper transport as the cuprous chloride complexes $CuCl_2^-$ and $CuCl_3^{2-}$ because of the insolubility of copper under the normal oxidising conditions of the surface environment. He regards the Cu^{2+} complexes with OH^-, SO_4^{2-}, SO_3^{2-} and Cl^- as having little effect on copper solubility in natural waters. Thus he is in direct conflict with Vaughan (1976) and Rickard (1972). Vaughan (1976) states that the most important state of copper in the aqueous environment is Cu^{2+}. This is due to the greater lattice and solvation energies of the Cu^{2+} ion compared with Cu^{+}, which is only stable in very low concentrations. Vaughan (1976) believes that the cupric ion $[Cu(H_2O)_6]^{2+}$ is important in the aqueous environment and that complexes can be formed by the displacement of water molecules from the cupric ion, for example $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

LEAD

Galena in pure water has a solubility, at temperatures up to 250°C, of 0,1 mg/litre and experimental studies have shown that lead does not readily complex with sulphur. Anderson (1962) suggested that the complex $Pb(HS)_3^-$ might be responsible for a certain amount of lead solubility and in 1973 he demonstrated that PbS could be precipitated from a slightly acidic chloride-rich brine containing low sulphur concentrations at $\pm$ 100°C. Barnes and Czamanske (1967) suggest that in alkaline solutions lead solubility can be increased 10 times (relative to that in pure water) due to the formation of the $Pb(HS)_3^-$ complex.

Abundant work on fluid inclusions seems to indicate that chloride complexes are possibly important in lead transport. Should this be so, then sulphur either as H_2S, or SO_4, must be transported within the fluids, via a different mechanism, and with the change in Eh, pH, temperature and pressure in the surface environment the chloride complex would have to decompose, and due to the sulphophile tendencies of lead, deposition of galena could then occur.

Helgeson (1964) suggests that chloride complexes can develop with Cl^- in high concentrations of NaCl, HCl, KCl. He demonstrated that at pH 5, and at 125°C, significant concentrations of lead could be carried as the chloride complexes $PbCl^+$, $PbCl_4^{2-}$. At lower temperatures the $PbCl_4^{2-}$ complex ion tends to dominate in concentrated solutions and in dilute solutions $PbCl^+$ is possibly dominant. At high temperatures $PbCl^+$ is dominant in both concentrated and diluted solutions. This was confirmed by Nriagu and Anderson (1971). Nriagu and Anderson (1970) calculated that the solubility of PbS, CuS and other sulphides in concentrated brine solutions containing Cl^-, S^2, HS^- and H_2S was due to complexing with chloride and that the brine could transport enough reduced sulphur to precipitate considerable concentrations of metal. At low temperatures, for the transport of lead as chloride complexes, a high chloride content, the absence of sulphur and a low pH appears necessary. In high concentrations of NaCl the presence of H_2 increases the solubility of lead, reaching possible ore-solution concentrations below a pH of 4,5.

Nriagu (1971) experimentally determined the solubilities of galena in sodium chloride solutions saturated with H_2S. He concludes that at pH's greater than 6 the solubility increases due to the increase in the formation of $Pb(HS)_3^-$ complex ion, but Hamann (1973) and Hamann and Anderson (1978) have suggested that the lead bisulphide complex is not sufficiently stable to provide ore quantities of lead in brines at $\pm$ 100°C and Barnes and Czamanske (1967) concede that lead might be one of the few metals for which chloride complexes may be important as transporting agents.

ZINC

Complexing of zinc sulphide by H_2S, or by other minor species containing sulphur is weak in weakly acidic solutions. The HS^- complex, $ZnS_{(5)} + H_2S_{(9)} + HS^- \longrightarrow Zn(HS)_3^-$ which appears to be stable, could possibly be important in the transport of zinc. Up to 200°C this complex appears to be unaffected by temperature. The presence of NH_4^+ and Cl^- appears to depress the solubility of zinc as a bisulphide complex.

The solubility of sphalerite in NaCl is 5 times greater than in NH_4Cl. Experimental work indicates that no important complex exists which contains both HS^- and NH_4^+ or Cl^-. Sawkins (1964) in a study of the distribution of sphalerite in the Provedencia District, Mexico, found no correlation between the sulphide distribution and salinity of the hydrothermal fluids as indicated by fluid inclusions, but Lebedev et al. (1971)

as a result of work done on the Cheleken brines, emphasises the importance of the $ZnCl_3^-$ complex.

Helgeson (1964) contends that when the sulphur content is low, chloride complexing is possibly important in contributing to the solubility of sphalerite and that sulphide complexes are only important when sulphur concentrations are high. Anderson (1973) concludes that it is possible to transport enough zinc and sulphur within a slightly acidic chloride-rich brine to precipitate ZnS, but Barnes and Czamanske (1967, p. 355) conclude, "At least to 250°C, there appears at present to be no alternative, among the species H_2S, Cl^-, and NH_4^+, to transport of sphalerite by the bisulphide complex".

GOLD

The behaviour of gold is dominated by its occurrence in the metallic state, thus it tends to be chemically inert and it can occur distributed throughout a deposit in a number of phases, or within minerals as isolated occurrences. It tends to concentrate in sulphide phases, but is possibly associated more strongly with silver than with copper (Taylor, 1965).

In acidic solutions, at moderate temperatures, gold is appreciably soluble in the form of chloride complexes, but only in the presence of strong reducing agents such as MnO_2, but it is soluble in alkaline and neutral solutions containing bisulphide or sulphide ions. Barnes and Czamanske (1967) suggest that gold can be transported as a sulphide complex possibly AuS^-, which would form in bisulphide solutions as follows :

$$2\ Au_{(s)} + 2HS^- + \tfrac{1}{2}O_{2\,(g)} \rightleftharpoons 2\ AuS^- + H_2O(l)$$

For such a complex to be stable and to obtain sufficient concentrations of HS^-, the ore solutions would have to be nearly neutral.

According to Helgeson and Garrels (1968) the transportation of gold has been attributed to a number of possibilities, such as the dispersion of gold in stable "colloidal form", as an alkali thioaurate, as gold sulphide complexes in alkaline sulphide solutions, or as $AuCl_4^-$ under highly oxidizing conditions. Helgeson and Garrels (1968) suggest that gold is possibly carried in the aurous state and they have thermodynamically illustrated that at low pH's (2,7 to 3,0) a chloride-rich solution could possibly transport gold

as the complex $AuCl_2^-$, and that deposition would occur at temperatures above 175°C. Sodium chloride acidic solutions in equilibrium with pyrite and quartz could possibly be an important transporting mechanism. Goleva et al. (1970) suggest, as a result of field studies and calculations, that the transport of gold as $AuCl_2^-$ or $AuCl_4^-$ is only possible in extremely acidic waters (pH less than 1). But in weakly acidic and alkaline environments the presence of thiosulphates supports the complex $[Au(S_2O_3)_2]^{3-}$.

Weissberg (1970) noted an increase in the solubility of gold with an increase in the concentration of NaHS in solution. The solutions were near neutral and he attributed the solubility to the complex AuS^-.

Henley (1972, cited in Wedepohl, 1974) attributed gold solubility to the formation of $Au_2Cl_6 \cdot (HCl)_n$ in solutions which were rich in KCl and HCl. They found that gold solubility increased from 20 ppm at 300°C to 900 ppm at 500°C in 2 *m* KCl, possibly due to the formation of complexes such as $Au_2Cl_6 \cdot (HCl)_n$.

Ewars and Keays (1977) propose that thio-complexes of gold and silver, will become stable due to the loss of H_2S, CO_2 and/or NH_3 during ascent to the surface and subsequent boiling.

SILVER

Anderson (1962) showed that acanthite (Ag_2S) was soluble in weakly acidic solutions saturated with H_2S at 25°C. The presence of NaCl was found to depress the solubility of silver, whereas HS^-, in alkaline conditions (pH7), increases the solubility by a factor of twenty. Anderson suggests that the solubility is due to the complex $Ag_2S \cdot 2H_2S$, but Cloke (1963) attributed silver solubility to the complex $Ag(HS)S_4^{2-}$. Barnes and Czamanske (1967) state that a complex of Ag_2S containing HS^- exists, and that it is possibly more stable than complexes involving H_2S.

Some complexing compounds such as SO_4^{2-}, NO_3^- and HCO_3^- increase silver solubility whereas Cl^-, Br^-, I^- cause precipitation of silver compounds and inhibit mobility. The presence of H_2S or S^- will precipitate silver sulphide, but the thiosulphate ion $(S_2O_3)^-$ leads to the soluble complex $[Ag(S_2O_3)_2]^{3-}$. This complex ion may be locally important but it tends to decompose in acidic solutions. Excess Cl^- in solution may similarly lead to the formation of soluble and mobile ionic complexes $AgCl_2^-$, $AgCl_3^{2-}$.

Other possibly important complexes are $Na(AgCl_2)$, complex sulphides and polysulphide ions such as AgS^-, $Ag(S_4)_2^{3-}$, and $Ag_2S \cdot nH_2S$.

TIN

Nekrasov and Bortnikov (1974) suggest that an increase in the sulphur concentration of a melt leads to the formation of tin sulphides and sulphostannates. The same effect is achieved with a decrease in temperature. At high pH's a stable complex, SnS_2, forms. At 300°C, even at low fS_2, teallite and frankeite, rather than cassiterite will form. At higher temperatures cassiterite will precipitate more readily from solutions with a high fO_2. Nekrasov and Bortnikov (1974) consider that the Eh negligibly influences the order of precipitation on sulphostannates, and that the order of cassiterite and sulphostannate deposition is determined by temperature, pH and the concentration of the various components.

Ryabchikov et al. (1974) propose that the prominant role of flourine in the transportation of tin is possibly proved by the close association of tin and flourine mineralization in many deposits. Experimental studies indicate that flourohyroxy compounds can transport tin, and that the partitioning of tin between fluids and the melt is enhanced by the addition of topaz (a common mineral in hydrothermal tin deposits).

The association of tin and boron is common, and experiments indicate that boron encourages the extraction of tin from magmatic melts. Charoy and Weisbrod (1974) suggest that the transport of tin could possibly have occurred as a tin-boron complex. Taylor and Hosking (1970) suggest that flourine may transport tin in a gaseous state, or as an alkaline complex such as $K_2Sn(OH)_6 \rightleftharpoons 2K(OH) + SnO_2 + 2H_2O$, but many workers, as Itsikson (1963) indicates, assume that tin is transported in the form of the thiosulphate complex Na_2SnS_3. Smith (1946) proved the crystallization of cassiterite from aqueous solutions as stannates of sodium or potassium. Aquo-complexes are more easily soluble than anhydrous forms of that compound, and the Soviet geochemists seem to prefer the transport of tin in the form of the easily soluble complex $Na_2[Sn(OH,F)_6]$, or complex ion $[Sn(OH,F)_6]^{2-}$ (Ganeev, 1963). Experimental studies on the flourohydroxy complex $[Sn(OH)_xF_{6-x}]^{2-}$, indicate that the complex can form in chloride solutions containing fluorine, sodium and potassium at 300°C, at a pH of 8 - 10.

Hydrolysis of this hydroxyflourostannite complex, and precipitation of tin to form cassiterite can occur at pH's 7,5 - 8,0. However available evidence suggests that late-stage magmatic fluids tend to be acidic, thus the extent to which the aforementioned complexes are important is uncertain.

TUNGSTEN

Chemical analyses indicate that significant amounts of lithium and flourine occur within tungsten deposits and experimental studies indicate that tungsten can be transported in the form of hydroxy and oxyflouride complexes (WF_6, WOF_6, WO_2F_4), but Studenikova et al. (1970) have shown that the volatile flouride complexes hydrolize relatively easily, $WF_6^{(g)} + 3H_2O \rightleftharpoons WO_3^{(s)} + 6HF^{(aq)}$. They suggest therefore that the volatile flourite hypothesis in untenable, as is the situation with alkaline solutions:

$$WF_6^{(g)} + 8OH^- \rightleftharpoons WO_4^{+} + 6F + 4H_2O^{(aq)}$$

Experimental studies with H_2WO_4 in concentrated potassium-flouride solutions were carried out, and it was found that $K_2(WO_2F_4)$ in KHF solutions and $K_2(WO_3F_2)$ in KF solutions are characterized by low solubility in cold water. In the presence of excess flouride the oxyflourotungstates were found to be reasonably stable at high temperatures in aqueous solutions, and were not subject to hydrolysis. But the existance of complex potassium oxyflourotungstates in nature is limited by the fact that the complex ion $(WO_2F_4)^{2-}$ is destroyed in acidic conditions, forming Ca^{2+}, CaF_2, and H_2WO_4 salts. Thus the existance of the oxyflourotungstate anion in acidic potassium-flouride hydrothermal solutions is only possible in the presence of excess flouride which can remove any calcium from the system as CaF_2. The ratio of oxyflourotungstates in relation to the cations Fe^{2+} and Mn^{2++} on one hand and Ca^{2+} on the other will possibly determine whether wolframite or scheelite will be deposited. It is possibly for the above reasons that wolframite (and not scheelite) plus flourite are found associated in skarn deposits.

Foster (1973) experimentally determined the possibility of tungsten being deposited from flouride-free solutions because of his observations of flouride-free tungsten deposits in the Archaean. He maintains that volatile flourine should escape into fractures ahead of the main ore-bearing solutions,

and Foster et al. (1978) believe that tungsten can exist as a stable aqueous species in the molecular and ionic state with the stability of the ionic state being maintained by the high density of the fluid. Foster (1973) showed that partitioning of tungsten into a granitic melt was possibly a function of the activity of the water in the melt, as illustrated by the reaction, $WO_{x(scheelite)} + nH_2O_{(magma)} \rightleftharpoons WO_x \cdot nH_2O_{(magma)}$. He demonstrated that tungsten existed within chloride-rich fluids in a silicate melt with a composition close to the ternary minimum in the system Ab - Qr - Qtz. He emphasizes that the activities of Ca^{2+}, Fe^{2+}, Mn^{2+} and the oxidation state of sulphur will determine the depositional sequence of scheelite, wolframite and sulphides. He states that WO_4^{2+} will dominate at subcritical temperatures, and that the molecular hexahalide will probably be important at higher temperatures. Tungsten would be partitioned into the fluid derived from a crystallizing magma as an aqueous hexahalide molecule.

MOLYBDENUM

Molybdenum and tungsten have very similar chemical properties in the 6^+ state, thus it is expected that the transport mechanism of the two elements will be very similar, but molybdenum has a greater affinity for iron than tungsten, therefore during deposition and differentiation separation of the two elements occurs. The transition of tungsten, tin and molybdenum oxides to sulphides were thermodynamically evaluated by Krauskopf (1967) who found that the WS_2/WO_3 equilibrium is established at much higher sulphur fugacities that the same equilibrium for MoS_2 and MoO_3. Flourine-bearing and lithophile elements are present in molybdenite deposits and it is possible that the stability of the Mo^{6+} is not as great as the stability of the Mo^{4+} ion. Thus during differentiation, Mo^{4+} could form compounds and precipitate while tungsten could, with the increase in oxygen fugacity, become the 6^+ ion, a stable state, and thus be transported further.

URANIUM

The concentration of uranium in aqueous solution is affected by the presence of (SO_4^{2-}) and (F^-). Sulphate complexes formed are $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$ with the uranyl ion. The uranous ion forms complexes USO_4^{2+}, $U(SO_4)_3^{2-}$ and $U(SO_4)_4^{4-}$. The uranyl ion forms several complexes with F^- such as ($UO_2F_6^{4-}$) which is stable up to a pH of 6,7 at 25°C and uranous ions form a soluble flouride complex, possibly UF_2^{2+},

which is only stable below a pH of 4. With increasing temperature these complexes tend to become unstable. In solutions with pH 4,4 U^{6+} is largely present as $UO_2(OH)^+$ and UO_2^{2+}, in solutions with pH between 5,6 and 7,2 largely as $UO_2(CO_3)_2^{2-}$ and in solutions with pH in excess of 7,2 largely as $UO_2(CO_3)_3^{4-}$. The importance of these carbonate complexes for the transport of uranium in oxidizing solutions is considerable at low temperature as well as at high temperatures. The sulphate and flouride complexes of uranium may be of importance in uranium transport, but their effect is probably less pronounced than that of the O^{2-}, OH^- and CO_3^{2-} complexes (Rich et al., 1977).

Hydrothermal veins are notable in that there is a lack of thorium. This is possibly the result of the oxidation of U^{4+} to $(U^{6+}O_2)^{2+}$ without a parallel oxidation of Th^{4+}. Thus the uranyl ion is transported into vein and other areas of low pressure.

There is a wide spread association of uranium with haematite and this may be explained by the following reaction :

$$3H_2O + 2Fe^{2+} + (U^{6+}O_2)^{2+} \longrightarrow F_2O_3 + U^{4+}O^2 + 6H^+$$

The U^{4+} ion in aqueous solutions can be oxidized relatively easily to the uranyl ion $(U^{6+}O_2)^{2+}$, $U^{4+} + 2H_2O \longrightarrow (U^{6+}O_2)^{2+} + 4H^+ + 2e$. U^{4+} tends to be stable under the same conditions as H_2S, HS^- and S^{2-}. The $(U^{6+}O_2)^{2+}$ ion is stable and it is likely that during differentiation of a magma, uranium becomes enriched in the residual melt as the uranyl ion.

(c) Chloride or Sulphide Complexes

Transport of certain metals is thought to be either by complexes of sulphur (amongst others, Barnes and Czamanske, 1967), or of chlorine (amongst others, Helgeson, 1964), and due to the low solubility of sulphides in water and in certain sulphur containing solutions, there is strong support for the suggested transport of metal ions as chlorides. During an experimental study, Skinner and Barton (1973) chose a concentration of 0,7 ppm zinc within solutions as being geologically sufficient to form an ore deposit. Figure 30 illustrates the problem which confronts the geochemists.

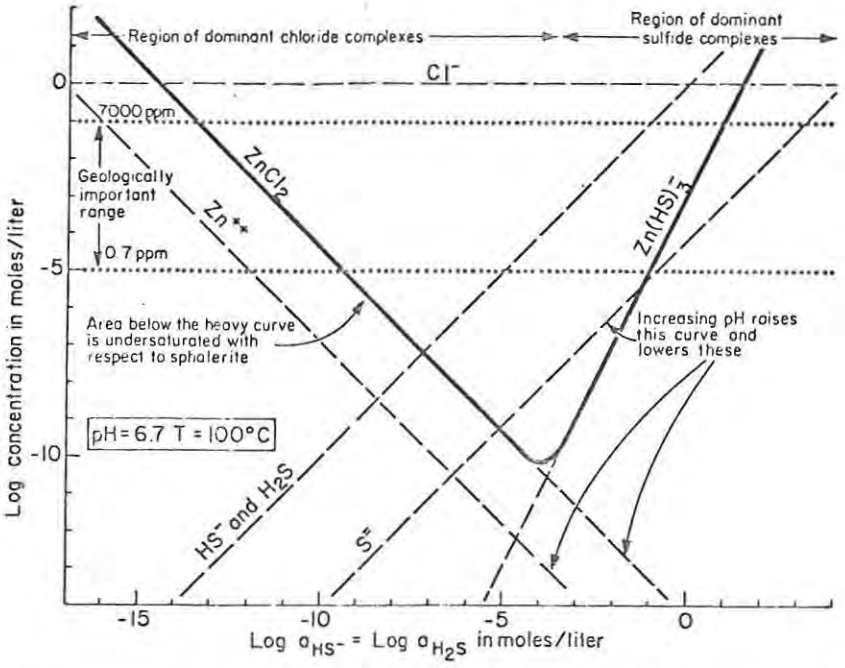


Figure 30. Comparison of chloride and bisulphide complexes for zinc. Conditions are : chloride activity 10^{0}; temperature $100^{\circ}C$; pH 6.7, which is the acidity given by the HS^{-}-H_2S buffer (from Skinner and Barton, 1973, p. 195).

Under the specified conditions the $ZnCl_2$ complex reached sufficient concentrations in solutions containing only minor amounts of HS^{-}. Skinner and Barton (1973) suggest that transport by chloride complexing could be possible should sulphur be carried as sulphate and reduced to sulphide in order to precipitate ZnS. They add that the bisulphide complex $Zn(HS)_3^{-}$ is stable only in high concentrations of HS^{-} but at these high concentrations H_2S would be present and as such any iron or silicate oxides present would be converted to iron sulphide. Skinner and Barton (1973, p. 194) state that "because iron oxides and silicates are common associates of sphalerite we must conclude that the solutions were not sulfide-rich and that the sulfide complexes are not important for zinc transport". But Barnes and Czamanske (1967) have proved that chloride complexes are unstable in the presence of sulphur. This is important in view of the fact that sulphur is one of the most abundant gases emanating from volcanic vents. Therefore at temperatures below $400^{\circ}C$, experiments with fluids not containing sulphur are very possibly invalid and geologically inapplicable. Furthermore, numerous elements occur in nature as sulphides. Table 9 presents data for sulphide-poor solutions, and Barnes and Czamanske (1967) suggest that the low solubilities of NaCl, LiCl and $ZnCl_2$ in solution provides evidence against chloride complexing.

Table 9. Solubilities (in gm/kg) of sphalerite in various solutions at 550 bars.

Solution	360°C	450°C
6 N $ZnCl_2$	0.4	0.8
6 N KF	2.0	1.0
6 N K_2CO_3	2.0	6.4
4.65 N LiOH	4.0	5.9
6.24 *m* NaOH	11	23
6.47 *m* KOH	11.9	26
8.0 *m* CsOH	7.1	15
Solutions saturated at 25°C		
NaCl	0.5	0.8
$NaBO_2$	1.75	3.75
LiCl	1.1	2.8
NH_4Cl	11	56

(from Barnes and Czamanske, 1967, p. 356).

Substances containing HCl and KCl become highly concentrated in aqueous solutions at high temperatures and thus chloride complexes may become more stable and therefore could become important in ore transport with increasing temperature. Ridge (1973) suggests that solutions containing high concentrations of NaCl will probably not reach the sea floor should temperatures be greater than 200° - 230°C. Boiling and the subsequent deposition of halite would occur at some depth below the surface. Thus ore-fluids emanating into shallow seas must have temperatures below 230°C. Alternatively, ore-fluids at temperatures greater than 230°C could have reached the sea floor if the depth of the water was slightly greater than 915 metres. Solutions such as these might therefore be the parent fluids of the deposits within the Red and Salton Sea brines.

Much support for the theory of chloride complexes being important as ore-transporting mechanisms has resulted from studies of fluid inclusions within ore and gangue minerals, but inclusion fluids, particularly from gangue minerals, may not be representative of the ore-bearing solutions as they are commonly poor in reduced sulphur and have a total sulphur concentration less than that of total metal content. It is possible that the fluids within the inclusions represent the spent ore-solution — solutions from which the metals and sulphide have already been removed. Arguments proposing the transport of metal sulphides by chloride complexes from studies of minute inclusions of fluid situated within millions of tons of sulphide ore are considered by the writer to be suspect.

Barnes and Czamanske (1967) conclude that high concentrations of Zn^{2+} in natural solutions, such as the Salton Sea brines, are not sufficient for ore formation in that the solution does not contain enough sulphur to precipitate the heavy metal content. High concentrations of silver have been recorded in the wells of the Salton Sea geothermal area, and it appears that the element forms complexes with alkali chloride (Wedepohl, 1974). Two factors are of interest, (1) the silver occurs abundantly in solutions — not precipitated, and (2) Skinner et al. (1967) report 0,8 ppm and 2 ppm silver in two brines, and up to 6 *weight percent* silver in the copper sulphide-rich scale deposited in the pipes discharging the hot brines. It would appear therefore that the Salton Sea brines might not be representative of true ore-bearing solutions, and that Barnes and Czamanske's argument that sulphur is necessary to precipitate metals is correct.

The argument is often used that because a certain compound is found to be soluble in some or other solution, that solution must be important as the transporting mechanism of that compound. This might not always be logical.

The proponents of chloride-complexing argue that the metals could be transported via one system, and the sulphur via another, or introduced from "outside". In certain ore deposits this would appear to be a strong possibility. For example, Mt. Isa, MacArthur River and other volcanogenic sulphide deposits are associated with pyritic carbonaceous shales, and it could be argued that the presence of these shales is indicative of the fact that the environment into which the metal-bearing chloride complexes were extruded was euxinic and sulphur-rich. But there are numerous sulphide ore deposits that are not associated with pyritic carbonaceous shale, therefore within these environments the sulphur must have come from the same system as the metals. The possibility of chloride complexes transporting the metal, then, at or near the surface, the complex decomposing and the metals then forming sulphides is unattractive, as this would possibly lead to a "dumping" effect of the metals, and secondly, halite or sylvite occurrences should be present in the massive ore.

Skinner and Barton (1973) proposed that sulphur could be carried as a sulphate in chloride-rich solution, then converted to sulphide with the subsequent precipitation of ZnS. It is probably more feasible that sulphur

as a sulphide exists at depth within hydrothermal and magmatic solutions and that with migration, and on entry into an oxidizing environment the sulphide might then convert to sulphate. Further, iron sulphides, in the form of pyrrhotite and pyrite tend to be more prevalent in lead/zinc deposits than iron oxides. Thus despite the present trend towards hypothesizing the transport of metals as chlorides, possibly no one mechanism should be applied to ore-transport in general. Individual and/or groups of deposits should be judged within their own merits, i.e. should the metal in a deposit occur as a sulphide, the ore-transporting mechanism was more than likely of a sulphide-type, should the deposit consist of oxides, then the transporting mechanism was probably some type of oxy-complex. Thus, in a deposit containing wolframite and flouride, the transporting mechanism was possibly an oxyflourotungstate.

VI THE WEATHERING ENVIRONMENT

(a) Weathering of Rocks and Minerals

Weathering, the chemical and mechanical decomposition of rocks and minerals leads to the dispersion of the broken-down products. These products subsequently accumulate as sediments. For efficient chemical weathering to occur abundant water, carbon dioxide and oxygen are normally essential. In cold (polar regions) and arid regions, weathering is essentially mechanical, but for efficient mechanical weathering to occur a rugged topography is essential.

Certain mineral species are more resistant to chemical weathering than others, the general sequence of resistance being oxides > silicates > carbonates and sulphides. Krauskopf (1967) has observed that chemical weathering consists essentially of four facets - ionization, addition of water and carbon dioxide, hydrolysis and oxidation. The weathering of silicates and carbonates is primarily a process of hydrolysis where H^+ and OH^- ions become incorporated into the structure of the mineral. Essentially it is a reaction between water and the ion of a weak acid or a weak base. In most igneous and metamorphic rocks, iron is present in the ferrous (Fe^{2+}) state in a reducing environment, but on contact with air oxidation to the ferric (Fe^{3+}) state occurs, as is found in minerals such as haematite (Fe_2O_3), goethite or lepidocrocite (FeO(OH)). Oxidation produces gossans and secondary dispersion patterns of metals around ore-bodies.

During hydrolysis, released elements become ionized, and become mobile (in some form) in water. Carbonic acid may be of prime importance during the oxidation of sulphide minerals as illustrated in the following reaction :

$$PbS + H_2CO_3 + 2O_2 \longrightarrow PbCO_3 + H_2SO_4$$

Krauskopf (1967) has summed up the net result of chemical weathering of sulphides by the observation that it gets ions into solution or into stable insoluble compounds under surface conditions; it converts sulphides to sulphates, and produces relatively acidic solutions. The solubilities of different compounds of the same metal differ substantially. The following is a list of compounds of the elements and their relative solubilities :

(i) Carbonates : none of the metals under consideration has appreciable solubility in water.

(ii) Chlorides : Co, Cu, Fe^{2+}, Fe^{3+}, Pb, Ni, Sn^{2+}, Zn are all soluble in water, but Au^{+} and Ag are insoluble.

(iii) Sulphates : Co, Cu, Fe^{2+}, Ni, Sn^{2+}, Zn are soluble, the remainder tend to be insoluble.

The above list is not necessarily geologically applicable as the solvent is water and during weathering a number of relatively strong hydrolyzing, reducing and oxidizing agents are present.

(b) Crystal Field Theory Applied to the Weathering of Minerals containing Transition Elements

The following is a summary of Burns (Chap. 8, 1970). During the weathering of a mineral an ion is removed from the crystal lattice and goes into solution. Most transition metal ions occur in six co-ordinated sites in silicate minerals, and as hexahydrated ions $M(H_2O)_6^{n+}$ in solution. Removal of an ion from a crystal lattice will be more easily carried out along crystal faces and fractures due to the greater accessibility of water into the environment surrounding that ion.

Substitution reactions involving transition metal ions in silicate minerals probably bear resemblances to bimolecular substitution reactions of octahedral complex ions in solution. The process is beleived to pass through a 7 - co-ordinated transition state which is formed by the substituting group entering the octahedral transition ion environment along the plane in which one of the low energy e_{2g} orbitals is "empty". This is represented in Figure 31. A water molecule enters the environment of the transition ion (M) along a t_{2g} orbital plane and forms a 7 - co-ordinated transition state. The water molecule forms the seventh group and is bonded through the lone-pair electrons to the oxygen atom. There is a spontaneous reaction to form a metal hydroxy silicate and a hydroxysilicate residue. The process is repeated until the mineral completely decomposes.

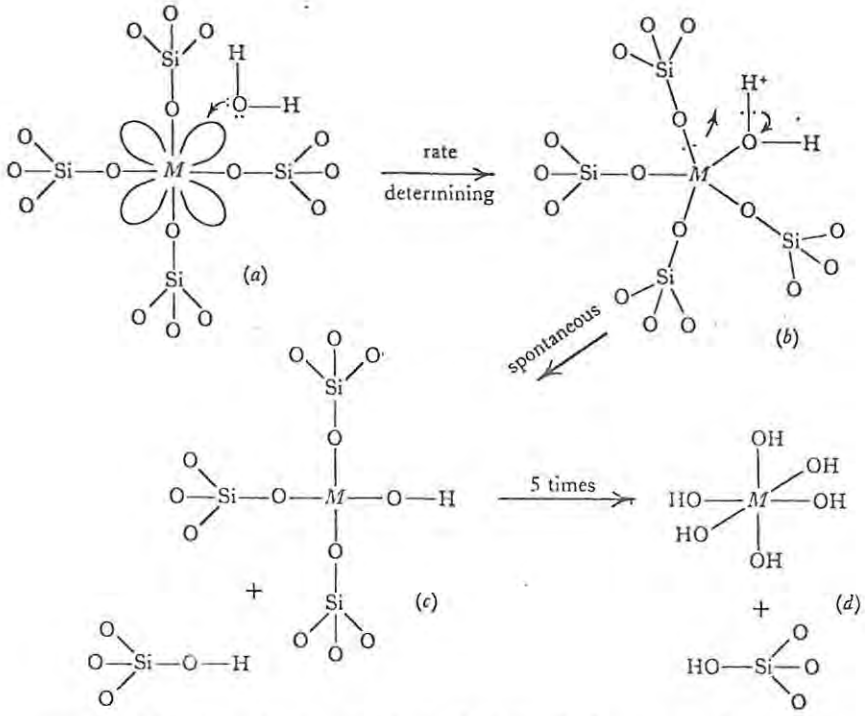


FIGURE 31 A mechanism for the hydrolysis of a ferromagnesian silicate.

The figure is a two-dimensional representation of the reaction. Two additional silicate groups lie above and below the plane.

(*a*) a water molecule approaches the central transition metal ion (*M*) along a vacant t_{2g} orbital, forming

(*b*) an activated complex possessing pentagonal bipyramidal symmetry. The H_2O molecule forms the seventh group, and is bound through the lone-pair electrons of the oxygen atom. Formation of the activated complex is the rate-determining step. The activated complex disproportionates spontaneously forming

(*c*) a metal hydroxysilicate and a hydroxysilicate residue. Formation of these products involves an inductive electron transfer in the activated complex. This process is depicted by arrows.

(*d*) repetition of the process (five times) yields a metal hydroxide or hydrated oxide plus a hydroxysilicate residue.

(from Burns, 1970, p. 164).

The transition metal ions with d and d^2 configurations, thereby possessing at least one empty t_{2g} orbital, might be expected to react more rapidly than an ion possessing a d^3 configuration, in which all the t_{2g} orbitals are singly occupied. In order that substitution reactions can occur with ions having more than three d electrons, energy is required to pair electrons in the t_{2g} orbital so as to leave one t_{2g} orbital vacant in order that substitution can occur. Therefore ions with high-spin d^4, d^5, and d^6 configurations might show intermediate reaction rates, and those with d^7, d^8 and d^9 configurations might display very slow reaction rates since no t_{2g} orbital can be vacated entirely in these ions. Ions with d^6 low spin configurations would be expected to show very low rates of substitution. Metal ions with d^3, d^8 and low-spin d^6 configurations are the most affected as far as crystal field stabilization is concerned. The energy required to remove ions such as Cr^{3+}, Ni^{2+}, Co^{3+} is predicted to be

high because rates of the substitution reactions will be low. The enrichment of these ions in laterite deposits and weathered ultrabasic rocks may depend upon the resistance of these ions to substitution reactions and subsequent leaching, and partly due to their high stability in oxide structures. These are the elements which acquire a high crystal field stabilization energy in octahedral co-ordination.

(c) Mobility of Elements

The migration of elements within the supergene environment is primarily determined by the pH and Eh conditions at the weathering surface. Further factors affecting migration are :

(i) the nature of the medium - mobility in groundwater will differ from that in streams;

(ii) the mechanism of transport - carried in solution, as colloids or mechanical transported;

(iii) the rock-types - host-rock and rock-types through, or over which the solutions move;

(iv) the presence of organic material - algae, other micro-organism or carbonaceous matter;

(v) the solubility of salt compounds which a metal may form with anions in the same solution. For example, the mobility of lead is severely restricted by the formation of cerussite;

(vi) the formation of complex ions. For example, the mobility of molybdenum is enhanced by the formation of the complex MoO_4^{2-} and decreased by the formation of $HMoO_4^-$;

(vii) the presence of dissolved gases;

(viii) factors such as permeability and porosity.

Table 10 is a classification of the mobility of elements based on Eh and pH. Andrews-Jones (1968) considers oxidizing, acidic, neutral to alkaline and reducing conditions as the four main environmental factors controlling the mobility of ions in the aqueous environment. Under oxidizing conditions Cu, Co, Ni, Ag and Au have a medium mobility, a high mobility under acidic conditions have become immobile under neutral to alkaline conditions. Mo and Cu have either medium or high mobilities in oxidizing and acid environments, but in neutral to alkaline environments molybdenum remains mobile whereas copper mobility is decreased. In exploration for porphyry-type copper-molybdenum mineralization, molybdenum may be used as a path-finder element, but in the presence of iron, the mobility of molybdenum is reduced either because it is adsorbed by hydrous ferric oxide or precipitated as ferrimolybdate, $Fe_2(MoO_4)_2 8H_2O$. Another example of restricted mobility, due to the presence of other ligands, is silver, which becomes insoluble in the presence of chlorine (AgCl).

Table 10. Relative mobilities of the elements in the secondary environment.

RELATIVE MOBILITIES	ENVIRONMENTAL CONDITIONS			
	Oxidizing	Acid	Neutral to Alkaline	Reducing
VERY HIGH	Cl, I, Br S, B	Cl, I, Br S, B	Cl, I, Br S, B Mo, V, U, Se, Re	Cl, I, Br
HIGH	Mo, V, U, Se, Re Ca, Na, Mg, F, Sr, Ra Zn	Mo, V, U, Se, Re Ca, Na, Mg, F, Sr, Ra Zn Cu, Co, Ni, Hg, Ag, Au	Ca, Na, Mg, F, Sr, Ra	Ca, Na, Mg, F, Sr, Ra
MEDIUM	Cu, Co, Ni, Hg, Ag, Au As, Cd	As, Cd	As, Cd	
LOW	Si, P, K Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl	Si, P, K Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl Fe, Mn	Si, P, K Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl Fe, Mn	Si, P, K Fe, Mn
VERY LOW TO IMMOBILE	Fe, Mn Al, Ti, Sn, Te, W Nb, Ta, Pt, Cr, Zr Th, Rare Earths	Al, Ti, Sn, Te, W Nb, Ta, Pt, Cr, Zr Th, Rare Earths	Al, Ti, Sn, Te, W Nb, Ta, Pt, Cr, Zr Th, Rare Earths Zn Cu, Co, Ni, Hg, Ag, Au	Al, Ti, Sn, Te, W Nb, Ta, Pt, Cr, Zr Th, Rare Earths S, B Mo, V, U, Se, Re Zn Co, Cu, Ni, Hg, Ag, Au As, Cd Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl

(from Levinson, 1974, p. 143).

Figure 32 illustrates the usual limits of Eh and pH found in the near-surface environment.

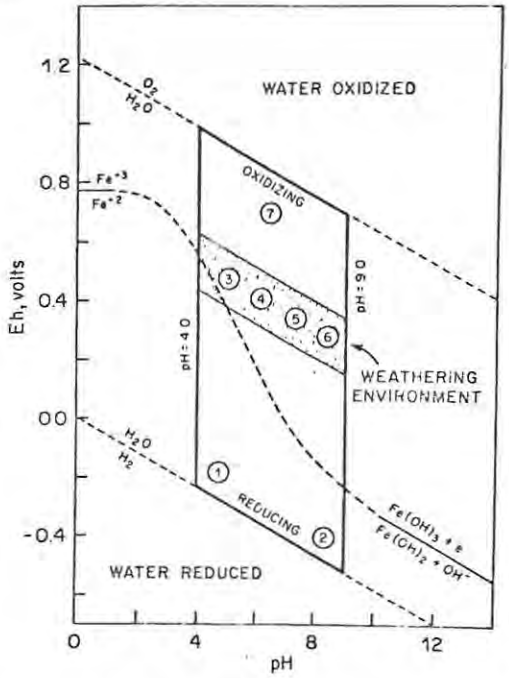


Figure 32 Framework for Eh-pH diagram in which the most usual limits of Eh and pH in the near-surface environments are outlined. The upper limit of the weathering environment is in direct contact with air, whereas the lower limit is considered to be the water table. Numbers indicate other environments: (1) bogs and waterlogged soils; (2) reducing marine sediments; (3) acid mine waters; (4) rain; (5) river water; (6) ocean water; (7) oxidizing lead sulfide deposits. The oxidation-reduction potential for the simple ions and hydroxides of iron are indicated (at 25°C and 1M). The horizontal dashed portion of the line (top) represents the reaction of $Fe^{+2} = Fe^{+3} + e$, and the solid portion (bottom) $Fe(OH)_2 + OH = Fe(OH)_3 + e$, and the high slope dashed portion $Fe^{+2} + 3H_2O = Fe(OH)_3 + 3H^+ + e$. (from Levinson, 1974, p. 130).

Rainwater can have a pH of 5,7 due to carbonic acid, and water enriched in H^+ can readily attack silicates. In the vicinity of sulphide-bearing veins the acids may become strong. Waters draining limestone areas can have pH's above 7, while pH's of between 7 and 8 are common for waters draining igneous rocks. Acidic or weakly acidic waters (pH 6) are particularly favourable for the migration of the majority of trace elements. An increase in pH tends to cause precipitation of certain elements in the form of hydroxides. Within environments of relatively high pH values, very low concentrations of certain cations such as Ni^{2+}, Co^{2+}, Zn^{2+} and Ag^{2+} and Pb^{2+} may be considered as favourable indicators of mineralization because, as Beus and Grigorian (1977) suggest, the pH of the surface solutions does not necessarily directly effect the migration of those elements whose solubility is controlled by the formation of hydroxides. Further, in alkaline solutions with pH's greater than 7, several high-valence ions can be transported, generally as complexes. Complex ions are stable to, and soluble at, increased pH conditons, when transport by simple ions would be relatively unimportant. Acidic solutions surrounding orebodies are capable of transporting most cations in the form of sulphate or halogen compounds. The distance of transport depends on, amongst other factors, the increase in the alkalinity of the

solution. Cations such as Cr^{3+}, Ti^{4+}, Th^{4+} and Sn^{4+} can only be transported in strongly acidic solutions as they readily precipitate as the alkalinity increases.

The Eh and pH tend to determine the concentration of an ion in solution and a change in either may cause precipitation. The solubility of most elements and the stability of their compounds is sensitive to the pH of the environment. Only a few elements Na, K, Rb, Ca, Mg, Sr, N, Cl, are capable of being soluble throughout the entire pH range. Other elements have pH limits beyond which they are insoluble, for example, copper becomes insoluble at a pH of 5,3 and zinc at 7,0. Elements tend to be less mobile in alkaline environments by comparison with acidic environments. The limits of pH to which an element will stay in solution therefore causes a separation of the elements resulting in dispersion haloes. Mobility based on pH alone, does not take into account adsorption, the formation of organic and inorganic complexes, other elements and radicals present etc., which could cause immediate precipitation of insoluble minerals, for example, insoluble anglesite which precipitates when sulphate-rich waters encounter oxidizing lead deposits. Agents which are responsible for the precipitation of ions include CO_3^{2-}, PO_4^{3-}. Hydrogen sulphide, and low concentrations of S^{2-} are strong precipitating agents.

The majority of chemical reactions which take place in the supergene zone are accompanied by an exchange of electrons (see secondary enrichment, Section VII) which can be regarded as redox reactions. The electronegativities of the elements are therefore important. Elements such as oxygen, the halogens, Fe^{3+}, Mn^{4+}, Mo^{6+}, Cr^{6+}, As^{5+}, V^{5+}, S^{6+} are all capable of receiving electrons in oxidizing - reducing reactions. Those ions which lose electrons are the reducing agents - they become oxidized. Ions such as Fe^{2+}, Mn^{2+}, Cr^{3+}, S^{2-} are considered to be the most active reducing agents within the supergene environment.

Iron is a common element in the supergene environment. The presence of ferous iron compounds (such as vivianite ($Fe_3P_2O_8 \cdot 8H_2O$), melanterite ($FeSO_4 \cdot 7H_2O$) indicate a reducing environment, whereas limonite ($2Fe_2O_3 \cdot 3H_2O$) and goethite ($Fe_2O_3 \cdot H_2O$) are indicative of an oxidizing environment. In the reduced state Fe^{2+} and Mn^{2+} are mobile in a number of natural environments, but oxidized to the +3 and +4 state respectively, their mobility is greatly reduced. Thus the valence state determines whether they stay in

solution or are precipitated. Figure 32 clearly illustrates that iron and manganese oxides and hydroxide are commonly precipitated under weathering conditions. The presence of these compounds, and organic material has a marked influence on the aqueous migration of trace elements as the precipitation of these compounds with adsorbed trace elements is a common phenomenon. This can lead to apparent anomalous concentrations of metal.

(d) Colloids and Adsorption

Colloidal forms of migration and the phenonenon of adsorption are important in depositing trace elements. In humid climatic conditions the majority of amphoteric elements tend to be transported in the colloidal form. Finely dispersed suspended clay particles, humic organic colloids, hydroxides of iron, manganese and aluminum are capable of carrying trace elements in surface and groundwaters. As such the precipitation of a trace element does not depend on its solubility in solution, but this is controlled by mechanisms capable of precipitating the carrier of the trace element (e.g. water velocity). Thus a number of elements, of which the concentration never reaches saturation point, are dependant upon colloidals for transport and precipitation.

It is therefore obvious that the weathering environment of an area should be understood prior to embarking up on a geochemical exploration programme.

(e) Behaviour of the Selected Elements

NICKEL

The oxidation of Ni^{2+} ions to the Ni^{3+} state is difficult but nickel does tend to be mobile to a certain extent. Weathering may concentrate nickel especially in tropical soils. In saprolites and soils, nickel occurs in nickel ferrous silicate structures (garnierites) due to its high stability in octahedral co-ordination. The supergene ore deposits of nickel are associated with thick lateritic "blankets". The solubility of silver and magnesium in tropical climates is relatively higher than iron or nickel (Fe^{2+} oxidizes to the insoluble Fe^{3+} state), and subsequently through the removal of silica and magnesium nickel becomes concentrated with goethite in the soils (Lelong, 1976).

Figure 9 illustrates the large aqueous stability field of nickel oxides and hydroxides which are relatively soluble as indicated by the large Ni^{2+} field, under alkaline conditions. Nickel does not show a tendency to be mechanically concentrated, and ore deposits tend to undergo supergene enrichment (Section VII).

COBALT

The overall behaviour of nickel and cobalt is very similar and under normal condition (pH 4 to 9) nickel and cobalt are more mobile than iron. The oxidation of Co^{2+} to Co^{3+} is difficult and due to the high Eh required (Figure 10), cobalt tends to become enriched in laterite soils associated with nickel. Cobalt is extracted as a byproduct from nickel deposits, copper-bearing volcanogenic and copper-bearing sedimentary deposits and is almost abiquitous with sulphide deposits. Thus during geochemical exploration programmes anomalous cobalt concentrations are indicative of the presence of sulphide, but it is not indicative of the sulphide-type present.

COPPER

The stability relationships in the $Cu-H_2O-O_2-S-CO_2$ system are little changed by the addition of CO_2 (Figure 13), except that malachite replaces cuprite. Chalcocite is stable over a wide range of pH's in the reducing environment, with covellite appearing at a more acid pH. The stability relationships of copper compounds in the Cu-Fe-S-O-H system at 25^{o}, and 1 atmosphere pressure, are provided in Figure 12. With reference to Figure 13 native copper has a large stability field and the sulphide projects deeply into the acid range under reducing conditions. The diagram illustrates that chalcocite precipitates from acid cupriferous waters when they encounter sulphides under reducing conditions as is likely during supergene enrichment. During weathering of a copper deposit insoluble malachite ($CuCO_3 \cdot Cu(OH)_2$), chrysocolla ($CuSiO_3 \cdot 2H_2O$), azurite ($2CuCO_3Cu(OH)_2$), and dioptase (H_2CuSiO_4), can be formed.

Copper as sulphide can be concentrated mechanically with channel lag conglomerate deposits. It can also occur as a minor constituent within sandstone uranium deposits of which the mechanism of transport is uncertain but is possibly carried attached to the uranium carbonate complex. Secondary enriched zones are an important source of copper within porphyry and other volcanogenic deposits.

LEAD

Unweathered grains of galena commonly occur in transported and *in situ* gossanous material. The insolubility of galena is in part due to the formation of a protective coating of lead sulphate ($PbSO_4$, anglesite) or lead carbonate ($PbCO_3$, cerussite). Both these minerals are insoluble in water. Takahashi (1960) found that in the presence of molybdenum, wulfenite ($PbMoO_4$) tended to be more stable than cerussite in the supergene environment. Galena is possibly oxidized by the presence of ferric sulphate solutions (Anderson, 1930), and is resistent to attack by sulphuric acid and subsequently will be deposited from such solutions in acidic environments. The possibility of mechanically dispersed galena (or secondary minerals thereof) should be borne in mind during geochemical exploration programmes and panning for heavy mineral concentrations might be useful. Due to the fact that lead can occur as insoluble grains within transported material the pulverizing of the sample prior to splitting and analysis is possibly a recommended procedure. Failure to do this could lead to apparently large differences in lead concentration with the same sample.

Figure 15 illustrates the effect of carbon dioxide at a reduced sulphur content. This system resembles oxidation at the surface with PCO_2 approximately that of the atmosphere. The figure clearly illustrates the wide range of pH's over which galena is stable in reducing environments.

ZINC

The relationships between sphalerite, wurtzite and zinc oxide phases in an aqueous system are illustrated in Figure 10. Increasing the concentration of sulphur will expand the field of wurtzite and sphalerite, and decreasing the sulphur concentration will have the opposite effect. Both sphalerite and wurtzite are stable within 3 pH units of neutrality.

Takahashi (1960) suggests that abundant hydrozincite ($2ZnCO_3 \cdot 3Zn(OH)_2$) in the supergene environment possibly forms under dry conditions where carbon dioxide can escape freely into the air, thereby producing a concentration lower than that needed to form smithsonite ($ZnCO_3$). With increasing depth smithsonite would form due to slower rates of diffusion

and the entrapment of carbon dioxide within the rock. At a pH of approximately 7,5, and at saturated pCO_2, smithsonite will probably be formed. Smithsonite is the most stable of the supergene zinc minerals. Hermimorphite ($H_2Zn_2SiO_5$) would tend to form under acidic conditions (pH 4 - 5) where it is more stable than smithsonite or hydrozincite. Takashashi (1960) observed a general supergene paragenetic sequence of smithsonite, hydrozincite and hermimorphite precipitated from solutions containing CO_2 and at a pH of 7 to 8. Cold circulating ground-waters are capable of precipitating willemite (ZN_2SiO_4), and in the presence of vanadium, descloizite [$(Pb,ZN)_2(OH)VO_4$], as coatings within cavities of karst-type lead/zinc deposits.

GOLD

Gold in sulphide deposits may undergo secondary enrichment, but the mechanical concentration of gold rather than chemical concentrations is considered to be of greater importance. Krauskopt (1967) noted that gold should be soluble at 25°C in acid chloride-bearing waters which contain one of several moderately strongly oxidizing agents such as MnO_2, O_2, Fe^{3+} and Cu^{2+}, but appreciably solubility would require higher concentrations of these constituents and greater acidity than commonly found in nature. Under alkaline and neutral conditions appreciable gold solubility occurs in the presence of HS^-.

Anionic species forming stable complexes with gold which might be significant include Cl^-, CN^-, CNS^-, $S_2O_3^{2+}$. Lakin et al. (1971) suggested that gold could be carried in iodine or bromine compounds in ionic form in the zone of oxidation. Kreuter et al. (1958, in Russian, cited in Wedepohl, 1974) suggest that oxidation of sulphides is essential for supergene enrichment of gold and that solutions containing dispersed gold in ferric sulphate - sulphuric adic solutions is the most probable mode of gold transfer. Note that gold tends to occur within sulphides, such as pyrite, as distinct grains, thus decomposition of pyrite could lead to residual deposits of gold. Gold in groundwater could be carried in suspension or in ionic form in bicarbonate-type solution, devoid of Cl^- and SO_4^{2-}.

SILVER

Silver tends to undergo secondary enrichment but due to its siderophile nature might become concentrated in chemically residual deposits. It is possible that where silver is associated with galena, the processes of secondary enrichment will be inhitted due to the formation of protective coatings of secondary minerals around galena.

Silver salts are generally more soluble and more mobile in acidic environments, in alkaline media oxide or hydrated oxide forms may precipitate directly, but the presence of organic matter, manganese and iron will possibly render silver relatively immobile. One of the most important factors governing the geochemical behaviour of silver under low pressure and temperature conditions and which concerns the ratio of Fe^{2+} to Fe^{3+} in solution, is the reaction $Fe^{2+} + Ag^{+} \quad Ag + Fe^{3+}$. In high Fe^{2+} concentrations silver will be precipitated, but in the presence of Fe^{3+} the element remains ionized and mobile. Soluble manganous salts probably affect the behaviour of silver similarly : $2Ag^{+} + Mn^{2+} + 4OH^{-} \quad 2Ag + MnO_2 + 2H_2O$ (Boyle, 1968).

MOLYBDENUM

Under strong oxidizing and weathering conditions various oxymolybdates species are formed. The principle one being wulfenite($PbMoO_4$). In solutions molybdenum occurs in the 6^{+} state and forms $(MoO_4)^{2-}$ ions in alkaline solutions.

TIN

Cassiterite is highly resistant to weathering, subsequently its accumulation in alluvial, residual and possibly placer deposits is to be expected. However, some tin is dissolved in natural waters and according to its oxidation state behaves differently. In the divalent state tin possibly goes into solution as cations, whereas quadrivalent tin is believed to be virtually insoluble and during weathering it would precipitate as hydrolysates. But divalent tin ions are probably unimportant in oxidation because being a strong reducing agent, it can only be present in reducing environments. In certain acidic conditions divalent tin ions can be stable.

TUNGSTEN

Wolframite and scheelite tend to be insoluble in surface waters, but neither experimentation nor observation of natural occurrences permit safe generalizations about the effects of different kinds of solutions or different weathering conditions (Wedepohl, 1974). The insolubility and high density of wolframite and scheelite suggest that they should accumulate in placer deposits, but large concentrations of this sort are uncommon. Residual deposits tend to be economically more important than alluvial and placer deposits. The scarcity of tungsten in alluvial and in particular, placer deposits, is possibly explained by the brittleness of scheelite and wolframite which results in the wide dispersion of very fine particles in fine grained sediments.

Tungstenite should dissolve in slightly acidic solutions according to the following reaction : $WS_2 + 4H_2O \longrightarrow WO_4^{2-} + 2H_2S + 4H^+ + 2e^-$ (Refer Figure 18). The sulphide would be soluble under normal Eh and pH conditions, but tungstenite is a rare mineral and is the only tungsten compound which has a valence of less than +6. It is stable at ordinary temperatures only in unusually reducing conditions.

Tungsten cations can be transported adsorbed to ferric oxide and manganese dioxide. Tungsten minerals are slowly attacked by acid surface waters, especially when associated with weathering sulphide deposits. Scheelite is possibly more soluble in acid than wolframite, but the decay of wolframite is aided by the susceptability of its iron and manganese to weathering. Tungsten released by acid attack is possibly dissolved as HWO_4^-, or as a heteropoly-silicon acid, $H_8Si(W_2O_7)^6$, and partly converted to some form of tungstic oxide. Newhouse (1934) and Dekate (1962) conclude that the behaviour of tungsten released by acid attack depends largely on climate; under semi-arid conditions it forms minerals such as cupritungstite and ferritungstite, in warm humid climate it goes into tungstite and hydro-tungstite if sulphides are present, and is adsorbed on iron manganese oxide etc., if sulphides are absent. Alkaline solution in nature probably have little effect on tungsten minerals.

The chemistry of tungsten in the aqueous and weathering environment has been rather extensively dealt with in order that some conclusion might be drawn as to the possibility of tungsten occurring, as does uranium, in

sandstone. It would appear that while not an impossibility such an occurrence is unlikely.

URANIUM

Under reducing conditions (as was probably the situation in Archaean-times) uraninite can be concentrated as detrital material, probably extremely finely dispersed. Under oxidizing conditions uranium is soluble as the uranyl ion (U^{6+}) and is probably transported to sites of deposition as dicarbonate or tricarbonate complexes. Upon encountering reducing conditions the uranyl ion (U^{6+}) becomes reduced to the relatively insoluble uranous ion (U^{4+}). Thus uranium is a common ore within sandstone deposits where decaying carbonaceous material has provided a reducing environment. It appears that uranium within silicate lattices is virtually unextractable, therefore the uranium found within sandstone deposits is most likely the product of weathered granites or felsic volcanics within which uranium occurred interstitially to the rock-forming minerals.

VII OXIDATION OF SULPHIDE OREBODIES AND SECONDARY ENRICHMENT

Blain and Andrew (1976) have dealt with the subject of sulphide oxidation and gossan formation. The following is essentially a summary of their review paper.

Oxidation via a process of secondary enrichment may upgrade an ore deposit, or perhaps render a subeconomic deposit viable. In the near-surface environment most hypogene mineral assemblages are unstable due to the presence of solutions containing oxygen, carbon dioxide and other species. These oxidizing, or weathering agents, cause sulphides to re-equilibrate electrochemically with the formation of stable secondary minerals. Ions removed from the weathering zone can possibly precipitate at depth in an environment which may become enriched by successive additions.

Usually the primary ore grades upwards into a zone of oxidized secondary sulphides which may or may not be enriched in ore metals. This horizon is overlain by an oxide zone which is leached of ore metals, and which is in turn overlain by a gossan. The transformation of sulphides to secondary minerals releases cations which are either transferred away from the deposit, transormed into insoluble secondary compounds, or enrich the primary ore. Substantial concentrations of iron in the form of goethite or haematite often occur above the water table.

(a) Generalized Profiles

Primary nickel/copper ores associated with ultramafic rocks are connected at depth by a transition zone where pentlandite, and some pyrrhotite, are replaced by violarite, to overlying zones of pyrite-(marcasite)-violarite-chalcopyrite. Above the water-table, the sulphides grades into oxide zones of goethite-haematite-silica, which is capped by a jasperoidal gossan.

Ideally copper and zinc orebodies within acid volcanics consist of a basal supergene sulphide enriched zone, overlain by a precious metal-oxide layer and then an upper carbonate-rich oxide zone. Lead and zinc deposits associated with carbonate rocks are capped by a gossan consisting of silica, haematite and manganese. This is underlain by a zone containing

zinc carbonates and sulphates, plus residual sulphides, which grades downwards into primary ore. Galena is more resistant to weathering than pyrite and sphalerite and may persist at the surface.

Lead-zinc-silver orebodies not associated with carbonate rocks commonly consist of a cerussitic siliceous gossan, an oxide zone dominated by cerussite-smithsonite and silver halides, overlying a zone consisting varying amounts of smithsonite, anglesite, silver sulphosalts and residual sulphides.

(b) The Mechanism of Oxidation of Sulphide Orebodies

Most sulphide orebodies are electrical conductors and during weathering the oxidizing ore releases electrons and becomes positively polarized, and thus forms an anode. At the top of the orebody oxygen dissolved in groundwater is reduced to hydroxyl groupings and the consumption of electrons causes negative polarization in the cathodic region (Figure 33). The flow of current through the orebody is matched by external ionic current flow through the groundwater system with the net migration of positive ions towards the cathode and negative ions towards the anode.

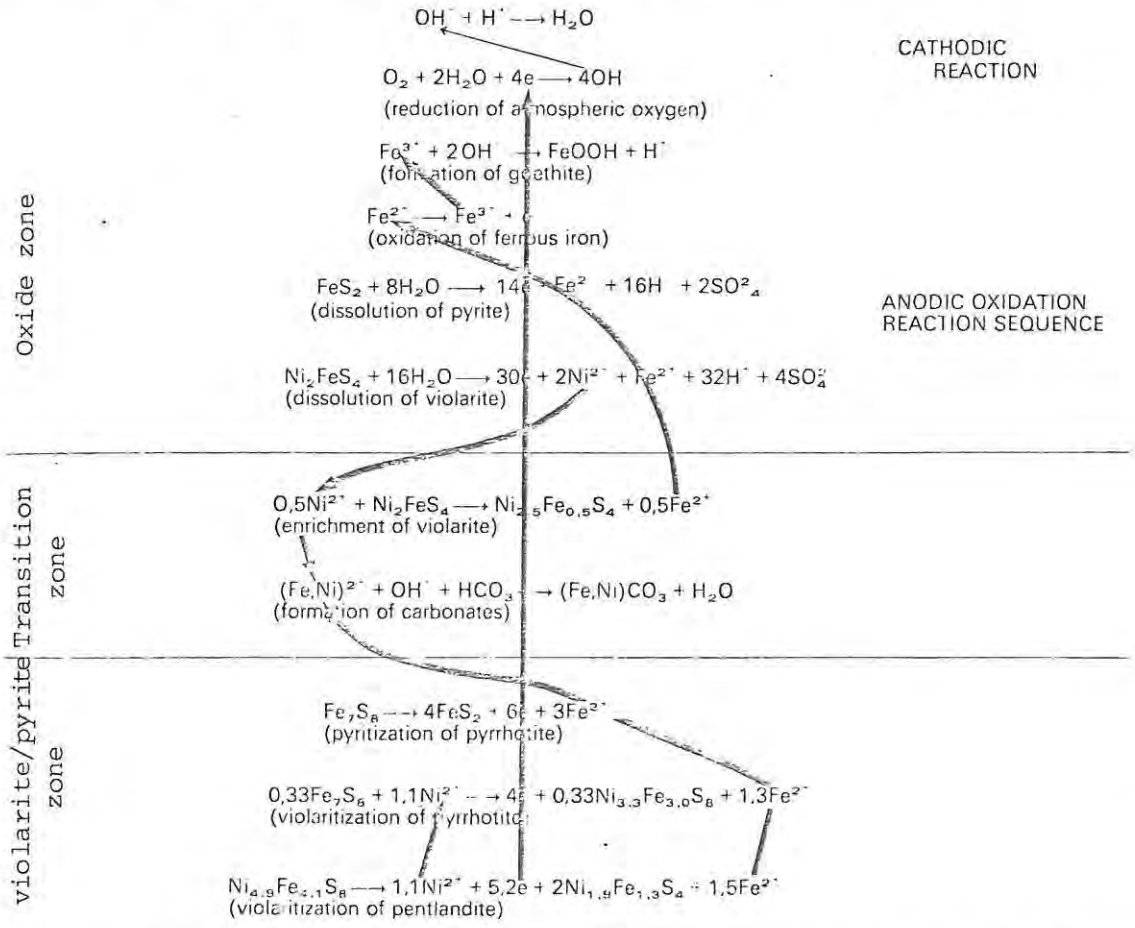


Figure 33. Chemical reactions and their inter-relations during the electrochemical alteration of nickel sulphide bodies in the supergene environment (from Blair and Andrew, 1977 [27]).

In Figure 33 the lowest Eh and deepest supergene alteration occurs where pentlandite is replaced by violarite which is accompanied by a release of iron and nickel ions. The released nickel reacts with surrounding pyrrhotite to form additional violarite. At a higher Eh residual pyrrhotite oxidizes to form pyrite and marcasite. Below the water-table violarite/pyrite (supergene) is stable with pyrite and chalcopyrite (primary).

Figure 34 illustrates that the oxidation process starts immediately above the water table. The dissolution of chalcopyrite (with pyrite) releases copper ions which in the essentially acidic aqueous medium percolate down the profile to the water-table. The copper ions react with chalcopyrite, or bornite, and to a lesser extent with pyrite. These supergene enrichment reactions consume copper, release iron and hydrogen ions and sulphur species giving rise to djurleite, chalcocite and analcite assemblages. Above the water-table, sulphur bound up in minerals, eventually oxidizes to sulphate. The iron released by the dissolution of pyrite and chalcopyrite is generally precipitated as goethite.

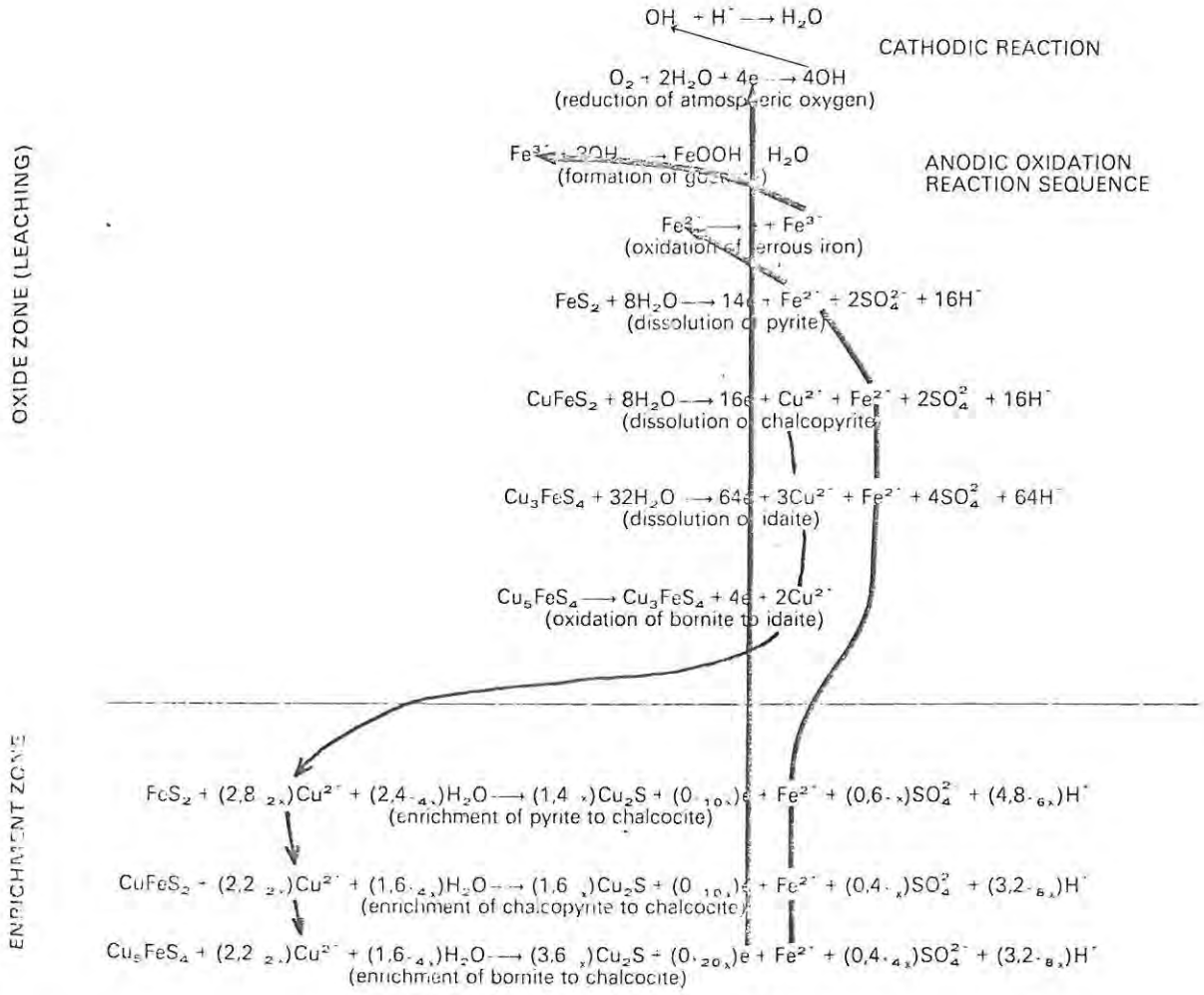


Figure 34. Chemical reations and their inter-relations during the early stages of supergene enrichment of pyrite-chalcopyrite-bornite orebodies.
Note : In the schematic representation of the enrichment reactions, x refers to a very small number which may alter the balance of reactants and products as electrochemical half-cell reactions (from Blain and Andrew, 1977, p. 129).

Sphalerite and galena ores, even in the presence of abundant pyrite, do not give rise to significant zones of supergene enriched sulphides. Alteration appears to be a process leading essentially to the formation of minerals such as anglesite, cerussite and smithsonite. The oxide minerals of tin and tungsten are essentially inert in the oxidizing environment and do not undergo secondary enrichment. Uranium, particularly in porous sandstones, undergoes a process akin to secondary enrichment (see Section VI). Molybdenum is relatively stable within the weathering environment. It does not oxidize readily and tends not to undergo secondary enrichment.

VIII THE METALS IN CERTAIN DEPOSITIONAL ENVIRONMENTS

This section considers the occurrence and deposition of the elements within certain geological environments. The examples cited tend to follow the classification as presented in Section I. When dealing with magmatic deposits the ease with which a melt can reach the surface is emphasised and consideration is given to the possible importance of concepts such as retrograde boiling, the partitioning of elements between various phases, the amount of differentiation undergone by a magma and the possibility that "daughter" melts repeatedly separate from "parent" magmas.

Figure 35 illustrates that the amount of differentiation undergone by a magma possibly determinesthe deposit-type produced. A number of factors are possibly important in determining the composition of an extruded magma :

(i) Rifting would provide easy access to the surface for an undifferentiated magma.

(ii) Blocking a volcanic vent would lead to increased differentiation within the entrapped magma.

(iii) Thick crustal rocks would impede the movement of a magma and differentiation would be enhanced.

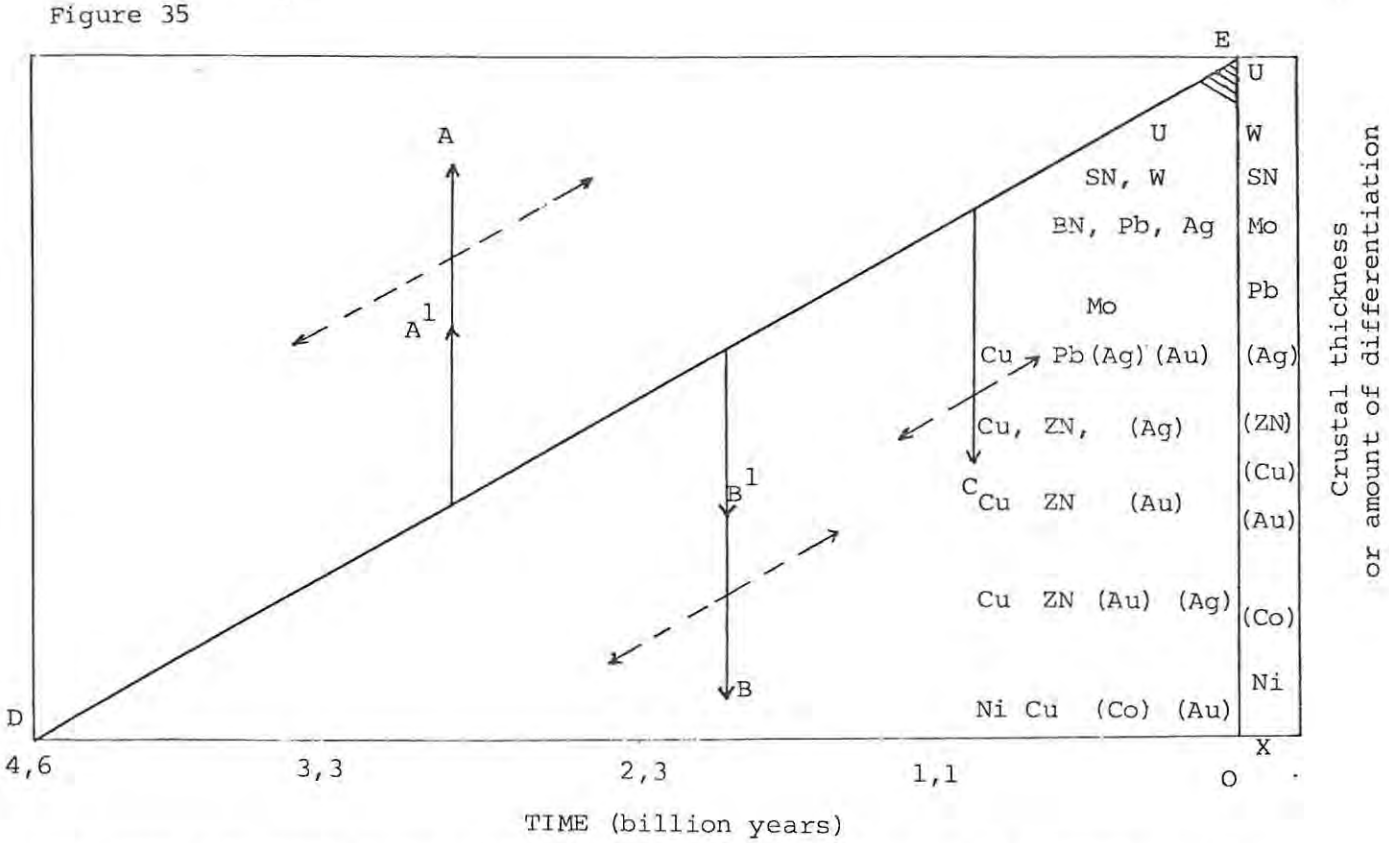
(iv) Repeated separations of "daughter" melts from "parent" magmas would produce final melt of felsic composition.

(a) Orthomagmatic Nickel/Copper Deposits

Due to the high octahedral site preference energy of nickel the crystallization of olivine prior to the development of an immiscible sulphide phase will deplete a magma in nickel. Differentiation will thus cause a depletion of nickel and a relative enrichment of copper in the sulphide phase of the magma.

Those deposits with nickel/copper ratios between 10:1 and 20:1 are dated predominantly between 2,6 and 2,8 billion years, and those deposits within part of the Thompson nickel-belt date 1,7 to 1,8 billion years.

Figure 35



INCREASING DIFFICULTY IN A BASIC MAGMA GAINING ACCESS TO THE SURFACE (A rift at 3,3 b.y. could have produced a Ni/Cu deposit relatively easily, but at 1,1 b.y. a Ni/Cu deposit could only have been formed by a major episode of rifting. Note, positions A, B and C are orbitarily drawn in time as indicated by dashed arrows).

X : the metals in order of increasingly felsic host rocks. NB the brackets indicate that the metal can occur throughout the deposit-types and their position in the column is thus arbitary.

A : indicates that with increased differentiation, possibly due to a blocked volcanic vent, a volcanogenic tungsten deposit could be formed in Archaean.

A^1 : indicates that with less differentiation (than at A) a Cu,ZN(Ag)(Au) deposit might be formed. This also implies that should Pb have been available in the melt, lead could be found in an Archaean volcanogenic deposit.

B : indicates that with rifting ensuring an easy ascent to the surface a Ni/Cu deposit could be formed. With increasing crustal thickness the formation of a Ni/Cu deposit becomes increasingly difficult.

B^1 : indicates that with minor rifting a Cu,ZN,(Ag) or (Au) deposit could be formed.

C : indicates that at a later time a Cu, ZN, (Ag) or (Au) deposit could be formed as a result of a greater amount of rifting.

D-E : line representing increasing crustal thickness with time.

\\\ : domain of porphyry-type deposits. Porphyry-type deposits can occur throughout time but with the advent of plate-tectonics their occurrence markedly increased.

Both these groups of deposits are associated with ultrabasic high-magnesium basaltic rocks which have undergone relatively little differentiation. Extrusion from a vent would give rise to massive high-grade nickel-sulphide deposits, whereas intrusion into country rock and solidification would produce a high-grade but disseminated nickel-sulphide deposit. To form a massive high-grade deposit ascent to the surface must have been relatively fast thereby disallowing the entry of nickel into silicates and causing the gravitative settling and accumulation of the nickel-rich sulphide phases. Evidence of a high temperature of extrusion can be gained from the presence of spinifex textures within the komatiites. This texture probably forms due to a rapid drop in temperature which caused the instantaneous growth of large olivine crystals. The Archaean crust was relatively thin, thus access to the surface could have occurred unimpeded. The deposits within the Thompson nickel-belt are possibly rift-associated, thus the extrusion of a komatiitic basalt was facilitated.

Those deposits with a nickel/copper ratio of 3:1 are characterized by having a sulphide/silicate ratio too great to have formed by fractional crystallization and gravity settling *in situ*. These deposits are associated with rocks which are gabbro-hartzburgite in comparison and their ages range from 1,7 to 2,0 billion years. Intrusion was possibly through a relatively thick crust which caused a certain amount of differentiation and a sympathetic depletion of nickel within the melt. The deposits are possibly the result of tectonic pressure "squeezing" an immiscible sulphide phase into areas of low pressure such as faults and fractures.

Deposits with a nickel/copper ratio of 1:1 or less are found in stable cratonic areas associated with tholeiitic sills and complexes. Under normal conditions fractional crystallization and gravity settling *in situ* would lead to the enrichment of nickel within olivines, and the subsequent relative depletion of the metal within any sulphide phase. The presence of nickel sulphides within the Merensky Reef is the result of this zone developing under conditions of abnormal *in situ* differentiation.

Thus with increasing crustal thickness and with increasing differentiation there is a depletion of the nickel content, and a relative increase in copper within the sulphides of orthomagmatic deposits.

(b) Paramagmatic Deposits

(i) Volcanogenic Deposits

Figures 36, 37 and 38 illustrate the depositional environments of three types of volcanogenic sulphide deposits.

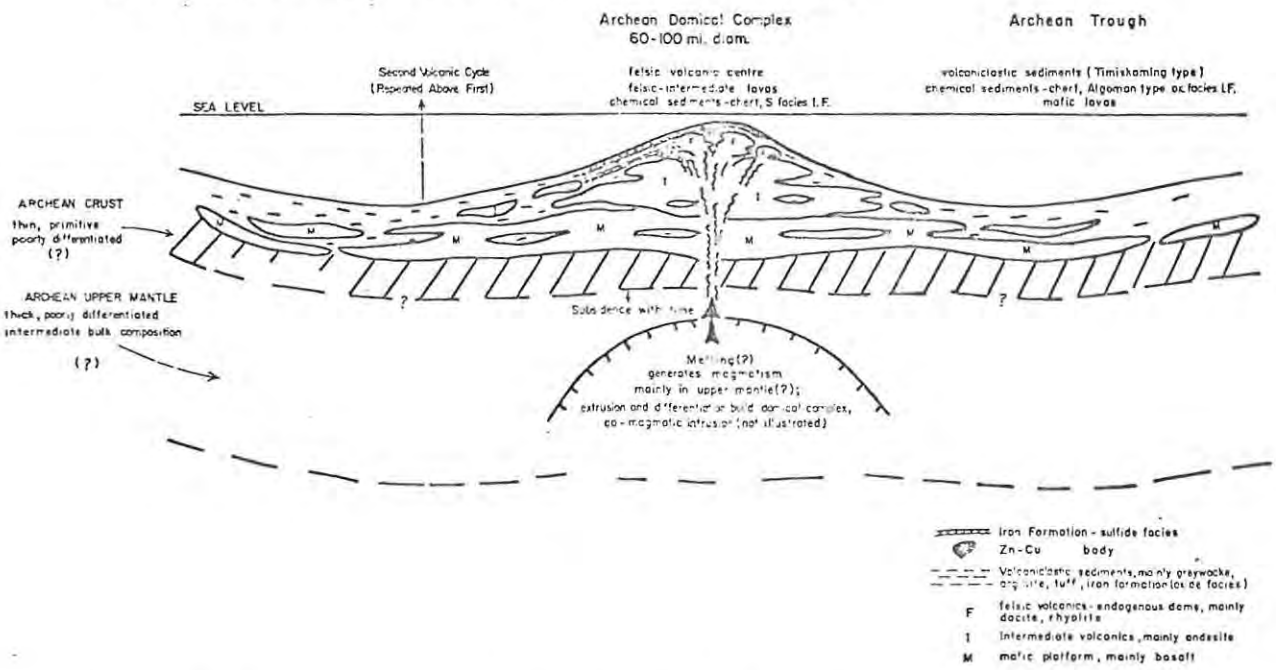


Figure 36. Diagrammatic illustration of an Archaean Cu-Zn volcanogenic massive sulphide deposit (from Hutchinson, 1973, p. 1231).

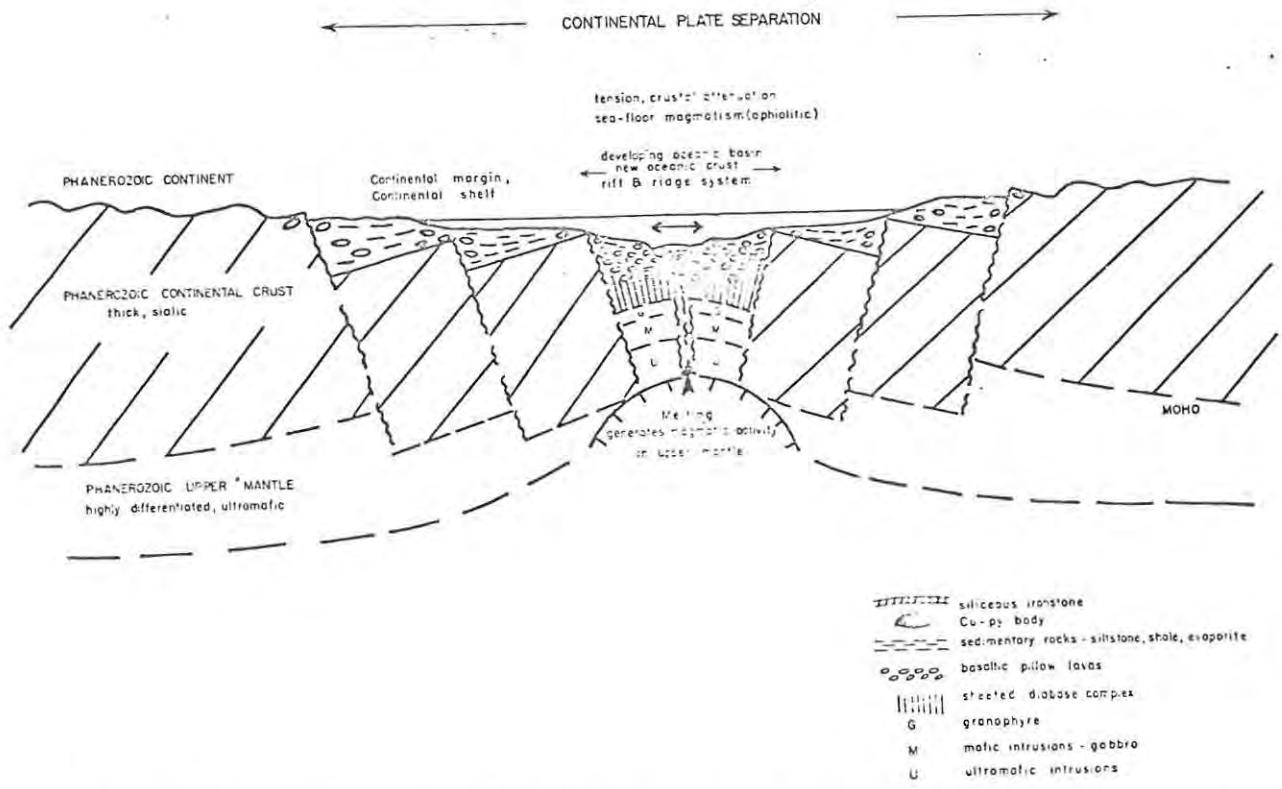


Figure 37. Diagrammatic illustration of a Cupreous pyrite volcanogenic massive sulphide deposit in the Phanerozoic Rifting of oceanic crust (from Hutchinson, 1973, p. 1232).

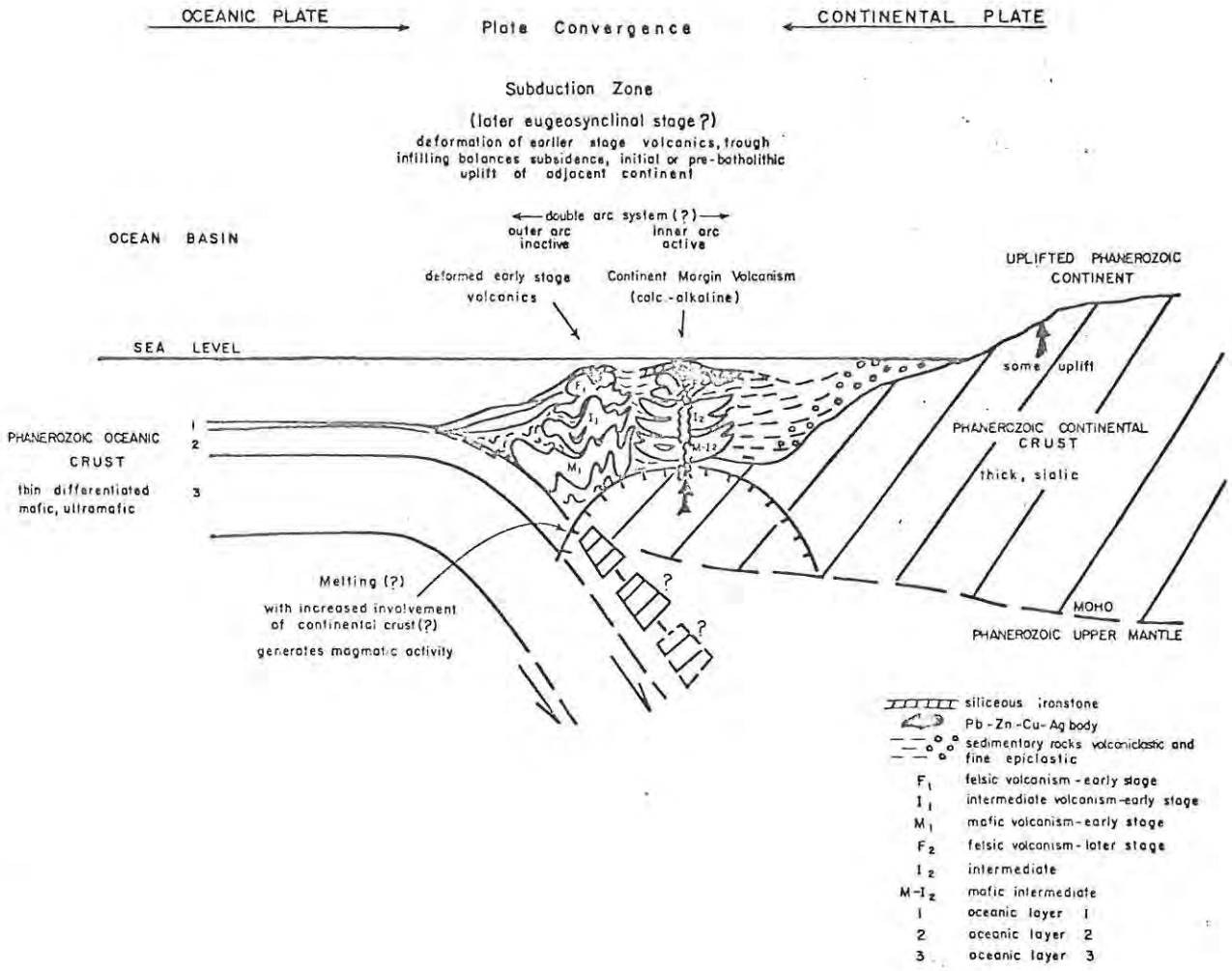


Figure 38. Diagrammatic illustration of a Pb-Zn-Cu-Ag volcanogenic massive sulphide deposit related to a subducting plate (from Hutchinson, 1973, p. 1234).

Rifting and zones of subduction provide a melt with a relatively easy access to the surface. The composition of the rocks associated with volcanogenic deposits is intermediate to felsic. The increase in felsicity compared with orthomagmatic deposits could have been produced by the successive separation of "daughter" melts from "parent" magmas by generation of magma at different depths into the mantle (see porphyry deposits later on), or by the blocking of a volcanic vent thereby also leading to an increase in elements such as Cu, Pb, Zn, (Co), (Ag), (Au) within the final deposit-forming melt.

Volcanogenic deposits are generally underlain by a brecciated pipe-like zone of alteration. This possibly indicates that during the life of the volcano, solidified lava blocked the vent thereby disallowing extrusion of any material. This would cause the melt to differentiate,

and crystallization would proceed until such a time that fluid pressure would overcome lithostatic, or confining pressure. Retrograde boiling would occur, the "plug" would become brecciated, and hydrothermal solutions would stream upwards through the veins and fractures to surface. This process would also explain the fact that volcanogenic massive sulphide deposits tend to be confined to one time-strategraphic horizon within any one volcanic complex.

Copper complexes are possibly less stable than lead or zinc complexes in that so-called stringer zones of the volcanogenic deposits tend to be enriched in chalcopyrite relative to sphalerite or galena. A number of factors ensure that copper stays within the molten portion of a magma, namely : its easy entry into octahedral sites in the melt; its expulsion from ordered octahedral sites within silicate lattices due to distortion effects; the increasing predominance of tetrahedral sites in crystals due to increasing felsicity; and the ability of copper to form soluble stable complexes such as $CuS(HS)_3^{3-}$ and $Cu(HS)_4^{2-}$ which could exist in the melt.

Within seawater (rift controlled basins) transport of copper could possibly occur as one or more of the following complexes : $[Cu(NH_3)_4(H_2O)_2]^{2+}$, $Cu(HS)_3^-$, $CuS(HS)_3^{3-}$ or as the $CuCl_4^{2-}$ complex. Because of the lack of halite and sylvite within volcanogenic deposits, and because the copper occurs as a sulphide, those complexes containing both copper and sulphur are preferred as transporting agents. That native copper (Cu) might behave similarly to the noble metals, gold and silver, and that it tends to be stable as Cu, Cu^+ and Cu^{2+} in certain environments, possibly accounts for the fact that copper occurs in rocks which vary in composition from ultrabasic to felsic.

The strong covalent bonds and subsequent stable compounds which lead forms with oxygen, its relatively large ionic size and charge discrepancies would tend to negate its entry into silicate structures at the expense of elements such as Ba^{2+}, Ca^{2+}, Na^{2+}, K^+ etc. With increasing differentiation and crystallization lead could possibly become bonded with sulphur as the $Pb(HS)_3^-$ or $PbS \cdot nH_2S$ complexes. Lead could be transported as a chloride complex containing enough sulphur to precipitate galena. But the paucity of chloride-bearing minerals tends to negate the transport of lead by these

complexes. It is possible that the chloride ions would, on dissociation enter into solution in seawater, but this would tend to cause a "dumping" effect of the lead. The conclusion drawn is that the exact mechanism of lead transport has yet to be determined, and that the transporting agent is most likely to be one of sulphur complexing.

Divalent zinc can enter Mg^{2+}, Fe^{2+}, Co^{2+}, Mn^{2+} etc. positions during the crystallization of a melt, but because of the stable, soluble tetrahedrally co-ordinated compounds it forms when covalently bonded to oxygen its entry into silicates is inhibited. Because zinc occurs abundantly as sphalerite, zinc is probably transported as a complex containing sulphur, and the bisulphide complex $Zn(HS)_3^-$ might be important. Zinc and iron substitute readily for one another within sulphide phases, which tends to cause the contamination of sphalerite by iron forming the mineral marmatite.

(ii) Porphyry and Hydrothermal Deposits

Magma generation appears to be related to areas of crustal disturbance and with excess differentiation magmas finally generate hydrothermal fluids which deposit the "incompatible" elements such as tin, tungsten, molybdenum and uranium. Porphyry deposits are related to zones of subduction of the oceanic lithosphere. Figure 39 shows the relationship between different porphyry-type deposits and the subducting oceanic plate.

There is an increase in the concentration of potassium in the rocks away from the cratonic edge which is accompanied by an increase in the concentration of the "incompatible" elements within ore deposits. These factors can be explained in terms of distribution coefficients and depth of magma generation. It is possible that the felsic portion of a melt could separate periodically from a parent magma and with each successive separation this felsic portion would become progressibely enriched in the "incompatible" elements. The greater the depth into the mantle that magma generation occurs, the greater the number of occasions this separation can take place before the magma is emplaced into the continental crust. Therefore a magma generated at (A) will produce a final felsic portion with a greater concentration of potassium, tin, tungsten and molybdenum than a magma generated at (B).

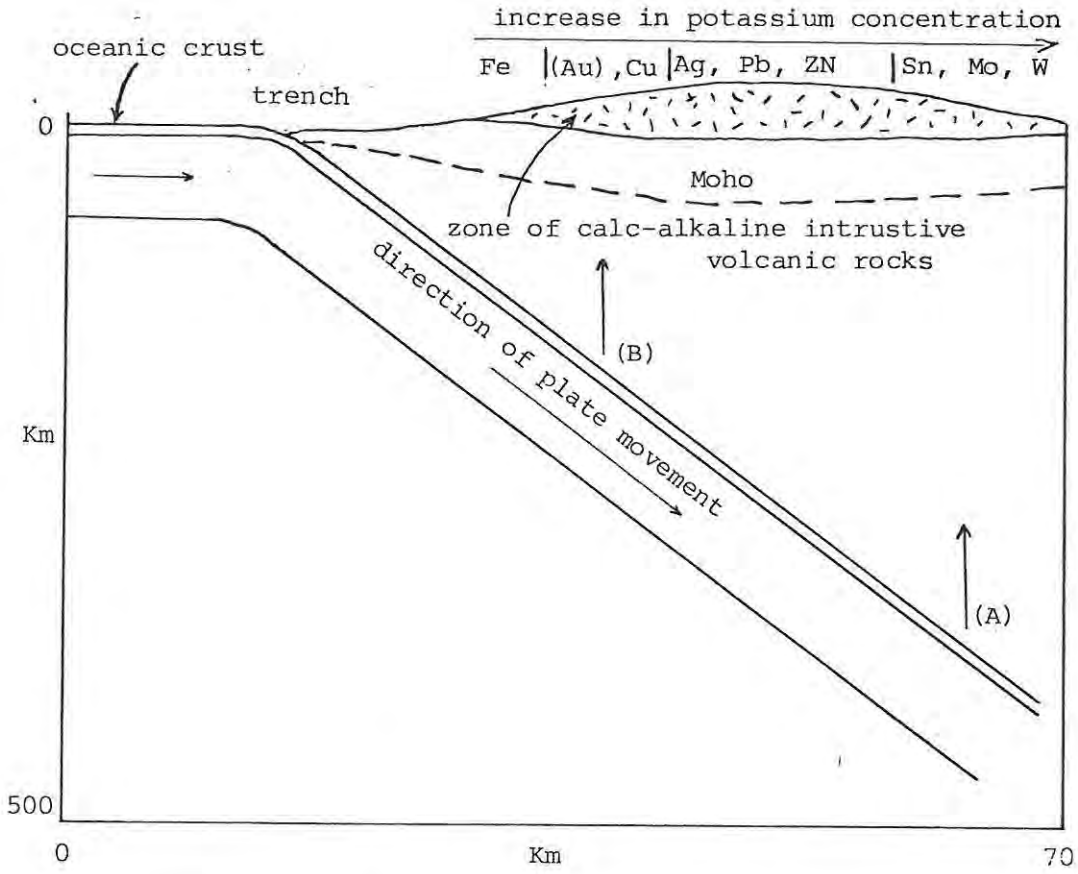


Figure 39 illustrates the differing distances that magmas generated at (A) and (B) will have to move before encountering the crust. The "incompatible" elements increase in concentration away from the cratonic edge (altered from Sillitoe, 1972, p. B14).

Feiss (1978) in a discussion on the concentration of copper in porphyry deposits stressed the importance of the $Al_2O_3/(K_2O+Na_2O+CaO)$ content of the magma, and the Cu^{2+} preference for octahedral rather than tetrahedral sites within a granitic melt or crystal phase. Burns and Fyfe (1964) found that the portion of tetrahedral sites in silicate melts increases with increasing amounts of alkali ions and silica, and with decreasing amounts of alumina. Thus because Cu^{2+} prefers octahedral sites an increase in alkali content indicates that Cu^{2+} will possibly enter the octahedral sites of crystals which are being formed. (The Jahn-Teller effect will be important in negating this process). Conversely with an increase in Al_2O_3 and a decrease in alkali content, the number of octahedral sites within a melt will increase, thus causing the concentration of Cu^{2+} within the molten portion of the magma to increase. During retrograde boiling this Cu^{2+} is released and deposited by hydrothermal fluids in fractures, veins and veinlets.

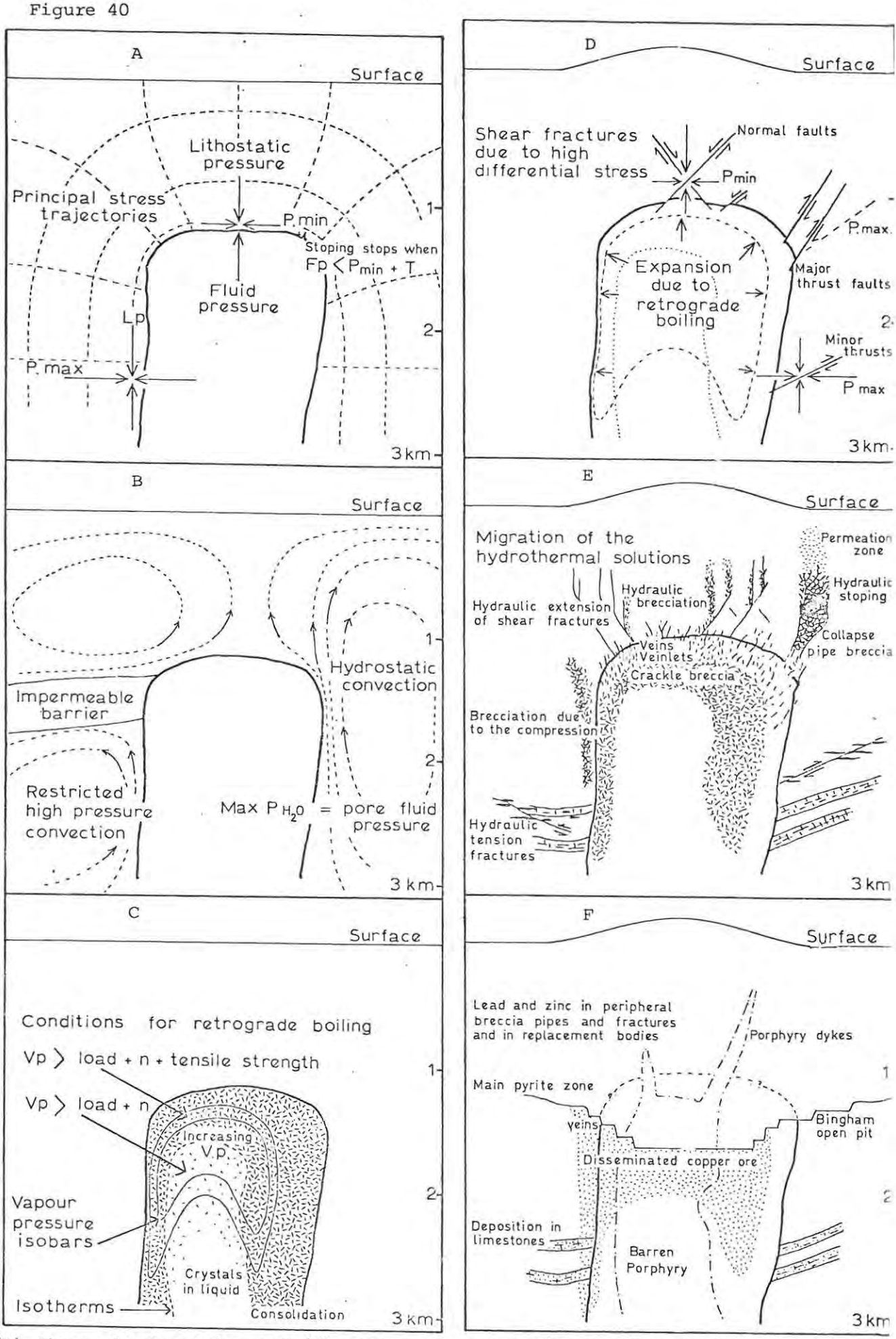
Figure 40 illustrates the importance of retrograde boiling in the deposition of porphyry deposits. A process akin to this possibly occurred during the deposition of volcanogenic massive sulphide deposits, with two important differences ; (i) the volcanic plug would tend to brecciate preferentially to the country rock, and (ii) the hydrothermal fluids associated with the volcanogenic deposits would be extruded subaqueously and not into the country rock.

Hydrothermal fluids are enriched in the "incompatible" elements due to a number of factors. Molybdenum, tin, tungsten and uranium are all characterized by possessing high valence states, thus they tend to form complexes rather easily. The strong nature of the covalent bonds which these elements form with ocygen leads to the formation of molecules such as $(MoO_4)^{2-}$, $(SnO_4)^{4-}$ etc. These molecules are unable to enter into silicate lattices and dissociation of the complex is not readily achieved. Molybdenum, tin, tungsten and uranium will possibly exist at high temperatures in ionic states and at lower temperatures will possibly exist as molecular complexes.

Kelly and Turneaure (1970) found a paragenetic sequence within the tin/tungsten deposits of Bolivia which consisted of (i) an early vein stage in which most tin and tungsten was deposited and (ii) a base metal sulphide stage. They also suggest that the early vein stage was a NaCl-rich brine with a low CO_2 content. Where tin and tungsten minerals occur together the ratio of tungsten/tin often increases towards the intrusive source.

Nekrasov and Bortnikov (1974) found that the order of precipitation of lead and other sulphur-bearing metals in porphyry-type deposits is influenced by temperature, pH, the mass effect of the metals and the presence of other metals in the fluids. At 400°C in a 10% NH_4Cl solution galena cassiterite-teallite and frankeite (amongst other antimony-bearing minerals), were found to be stable in the Pb-Sn-Sb-S system. An increase in the alkalinity of acidic solutions (up to pH 7) was found to change the paragenetic sequence. Tin sulphides and lead sulphostannates are replaced by cassiterite which can co-precipitate with lead. Further, sulphur activity controls the order of deposition. With an increase in the activity of sulphur, sulphide precipitation is predominant and it was demonstrated that a drop in temperature produced the same effect. Thus at 300°C even at low

Figure 40



(A) Stress trajectories and (B) pore water convection systems associated with a stock; (C) crystallization of a stock; (D) Shear fractures, (E) hydraulic fractures and (F) distribution of copper ore associated with a stock which has undergone retrograde boiling (FP = fluid pressure, P min = minimum principal stress, T = tensile strength, Vp = vapour pressure, n = nucleation force (from Phillips, 1973, p. B94).

sulphur activities teallite and frankeite rather than cassiterite will precipitate. Conversely at higher temperatures cassiterite will precipitate readily from solutions despite a high sulphur activity. They also suggest that the Eh of a fluid negligibly affects the order of mineral precipitation.

The accumulation of "incompatible" elements in the residual melts suggests that the accumulation of ore metals in the alkali-rich phase of a silicate melt could be due to heterogeneity as a result of an immiscible liquid phase. These phases would separate and could subsequently be "tapped" by fissures and veins. Ions of the metals tin, niobuim, tantallum and molybdenum and tungsten can be considered as forming network or chain structures within the felsic portion of a melt. Network formers are mostly cations which have a high positive charge, relatively small ionic radii and can bond firmly to oppositely charged anions. It appears that the greater the concentration of network formers the greater tendency to form immiscible phases. Figure 41 indicates the possible importance of flourine concentration in controlling immiscibility (Barth and Rosenquist, 1949; Block and Levin, 1957; and Stemprock, 1963, 1974[1+2]; amongst others).

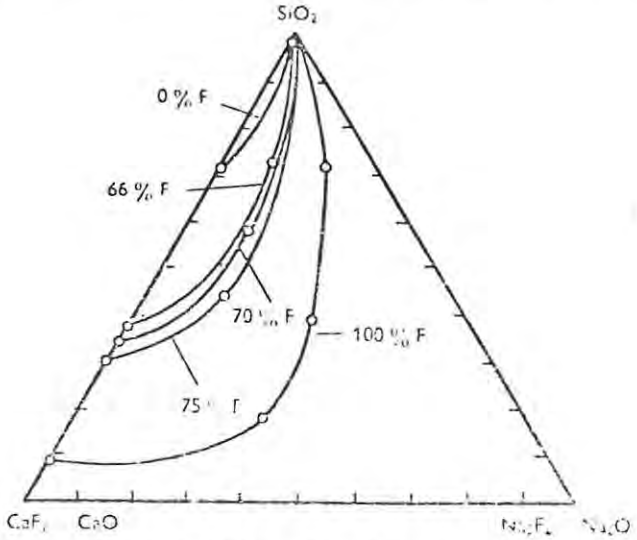


Figure 41. Diagram representing the changes in the ternary system SiO_2-CaO_2-Na_2O at various stages of the replacement of oxygen by fluorine. The region of immiscibility increases by the increase of the content of fluorine (from Stemprock, 1963, p. 304).

Tin can have a stabilizing or modifying effect on the network of ions. Tungsten and molybdenum are network formers in the presence of ions of high charge and Stemprock (1974) concludes that tin belongs to the intermediate oxides which are transitional between network formers and network modifiers.

Metals considered to be network modifiers, Li, Na, K, Ca etc. usually have lower charges than network formers, and tend to bond relatively less strongly to anions than network formers.

Tungsten trioxide and molybdenum dioxide are soluble to a certain extent in silicate melts and may be important in transport. Transport of tin may occur in a number of forms but acido- and aquo-complexes are possibly of significant importance. The complexes which possibly transport tin are $Na_2[Sn(OH,F)_6]$ or the complex ion $[Sn(OH,F)_6]^{2-}$. In deposits containing both flourine and tungsten transport was probably by means of complexes such as an oxyflourotrungstate. In deposits of tungsten not associated with flourine transport could have been by means of the WO_4^{2+} ions or molecular H_2WO_4 and at higher temperatures possibly by an aqueous hexahalide.

Molybdenum tends to bond more strongly to iron and sulphur than tin, tungsten or uranium, and at low temperatures while tin, tungsten and uranium are complexed, soluble and stable, molybdenum will tend to bond with sulphur and with decreasing temperatures will be deposited as molybdenite, possibly disseminated throughout the upper portion of the intrusive body. Any tin, tungsten or uranium present in the system would at this stage be partitioned away from the molybdenum. During differentiation uranium is likely to be in solution and remain stable as the $(U^{6+}O_2)^{2+}$ ion. With decreasing temperatures it would tend to complex with carbonate, $(UO_2)(CO_3)_3^{4-}$ $OUO_2(CO_3)_2^{2-}$ and $[(UO_2)(CO_3)_2(H_2O)_2]^{2-}$ and possibly to a lesser extent with sulphate $(UO_2)(SO_4)_2^{2-}$. Where uranium is found in conjunction with calcite, the complex was most likely of carbonate type.

Anomalous concentrations of nickel with hydrothermal deposits hosting minerals regarded as "late-stage", can be explained by the high stability nickel achieves in octahedral co-ordination. Should a melt of intermediate to felsic composition separate from a basic or ultrabasic magma, and should the "daughter" melt contain a certain amount of nickel, that nickel will tend to remain within the octahedral sites of the melt as the concentration of octahedral sites within the crystallizing portion, due to the increased felsicity, will be relatively low. The nickel will possibly tend to remain octahedrally co-ordinated as isolated structures until extrusion along with the normally "incompatible" elements.

Endogranitic deposits of tin and tungsten apparently did not develop a liquid phase in which the vapour pressure was great enough to overcome the lithostatic or confining pressure. This situation would result in the interstitial crystallization of metals and also result in internal convection of hydrothermal fluids. Once crystallization reached $\pm$ 95 percent these circulating fluids could develop preferred pathways migration. At more advanced stages of crystallization "pipe-like" pathways would develop through which large amounts of fluids could migrate, and within these "pipes" large crystals of tungsten and cassiterite would be deposited. This process explains the tungsten-rich pipes of the Zaaiplaats deposit.

Hydrothermal fluids which developed from melts within which the confining pressure was overcome would migrate through fissures and fractures until a change in environment caused deposition. These fluids can crystallize within veins or become trapped beneath impermeable horizons. Certain deposits within the Rooiberg tin field were deposited, not beneath an impermeable horizon, but fluid migration was discontinued when the fluids (within fractures) encountered a zone of porous sandstone into which the fluids moved and crystallized. This fact could possibly be important from an exploration viewpoint in that certain characteristics of the favourable horizon might be visually recognizable during mine development and exploration drilling.

Deposition from fluids will occur in response to a decrease in temperature, a change in pH (reaction with wall rocks), and due to the crystallization of other phases which will create a change in the environment of migration.

Silver tends to be enriched in volcanogenic deposits such as Broken Hill, Sullivan and Mt. Isa, and is a common secondary metal in the Besshi-type cupreous pyrite deposits. It is also present in porphyry districts, particularly where lead veins are present. Gold tends to occur in Archaean copper/zinc deposits, in island arc porphyry copper deposits and in some nickel deposits. These associations would tend to suggest that the more basic the rocks, those rocks which have undergone relatively less differentiation, and have had an easier access to the surface, are more likely to be enriched in gold than silver. Thus with increasing differentiation, increasing inaccessability to the surface, it would appear that silver tends to become enriched in the melt, possibly bonded to sulphur in a lead-silver-bismuth-sulphide compound.

(c) Residual Deposits

In Section VI the concentration of nickel in laterites was dealt with. These are regarded as typically chemical residual deposits. Detritral residual deposits originate as a result of the mineral of economic interest being more resistant to weathering than their host rocks. Areas of high relief are not conducive to the residual accumulation of minerals as fluvial processes would remove the minerals from the environment of weathering, therefore weathering must be largely chemical in nature, but the accumulation of the economic mineral (due to its resistance to weathering and its high S.G.) would be mechanical.

(d) Deposits with Sedimentary Affiliations

(i) Chemical Deposits

Red Beds copper deposits often consist of chalcocite in association with zones of organic-bearing material. Silver and cobalt are common accessory elements. Rose (1974) suggests that because of the lack of wallrock alteration deposition must have occurred at temperatures below $100^{o}C$. In pure water copper solubilities are low, but in slightly chloride-rich solutions copper chloride (in the Cu^{+} state) complexes might be important as transporting agents, but due to the presence of sulphide, and paucity of chlorine-bearing minerals, sulphide complexes such as $Cu(HS)_3^-$ or $CuS(HS)_3^{3-}$ for example are possibly of greater importance. Further, Cu^{+} might complex more easily with chlorine than Cu^{2+}, but this is no argument that Cu^{+} complexed to chlorine is necessarily an important transporting agent. Also Cu^{2+} is the most likely valence state of copper in the sedimentary environment. The transport of lead in the sedimentary environment could possibly be due to $PbS \cdot 2H_2S$ at neutral pH's and at pH's greater than 7 the $Pb(HS)_3^-$ complex is possibly important. Zinc could possibly be transported as the $Zn(HS)_3^-$ complex.

Renfro (1974) proposed a sabkha model as a possible genetic model (see Figure 42). The sabkha is supplied by landward migrating low Eh, high pH seawater, and by seaward migrating high Eh, low pH terrestrial waters. Decaying algal mats would produce hydrogen sulphide which would act as a

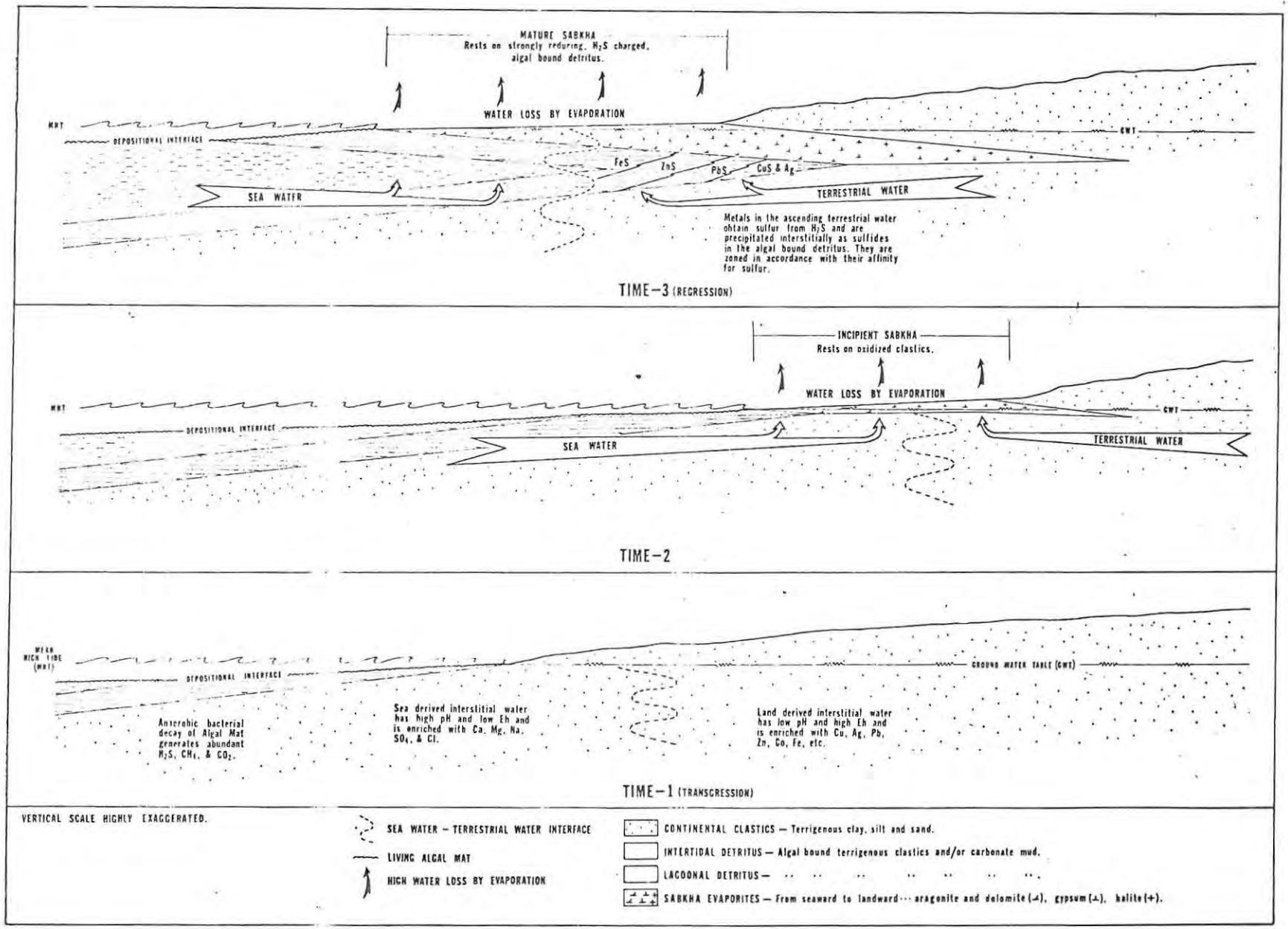


Figure 42. Sequential cross sections illustrating the evolution of a hypothetical, sabkha-type stratiform metalliferous deposit (from Renfro, 1974, p. 40).

precipitating agent for the metals within the seaward migrating waters. That this process could produce deposits of high grade, zonally arranged polymetallic sulphides over an area the extent of the Kupferschiefer or the Zambian Copper Belt is doubtful. This argument is also used against the process, commonly in vogue at present, that bacterial reduction of metal-bearing solutions could produce deposits of this size and nature. Almost certainly fetid conditions did, in certain cases, cause sulphide precipitation, but the euxinic environment produced was more probably due to decaying organic material. Algae in certain environments are capable of trapping or injesting certain metals but it is likely that this process can only be responsible for localized deposits.

The amount of metal within deposits such as the Kupferscheifer, the large areal extent, the zonal arrangement of the metals and the apparent stratigraphic zoning, presents problems with regard to genesis unless a volcanic exhalative source is called upon. Precipitation within predominantly sedimentary rocks would be caused by changes in the environment, such as decreasing temperature, changes in Eh and pH as a result of reaction with other solutions and solids, and the presence of reducing environments.

Uranium is transported in the oxidized hexavalent state (uranyl UO_2^{2+} or the $UO_2(OH)^+$ ion). The mobility of uranium in the presence of CO_3^{2-} is considerably enhanced by the formation of the dicarbonate $UO_2(CO_3)_2^{2-}$ or tricarbonate $UO_2(CO_3)_3^{4-}$ complexes. The presence of reducing environments within reasonably porous sandstone would cause the reduction of the uranyl ion (6+) to the relatively insoluble uranous ion (4+) thus causing the deposition of uraninite (UO_2). Within calcretes the precipitation of carnotite [$K_2O(UO_2)_2V_2O_8 \cdot 3H_2O$] could occur in response to solutions encountering environments with a pH of approximately 6 (Mann[1+2], 1974), an increase in the concentration of uranium or vanadium and possibly due to evaporation of water.

Due to the unsolved problems and complexities related to the genesis and deposition of the Mississippi Valley-type deposits only a few pertinent observations will be made regarding these deposit-types. Regardless of the nature of the ore-transporting agents the acidity of the solution could not have been acidic otherwise dissolution of the limestone and dolomite hosting the deposits would have occurred. Should the transport of the metals

have occurred by a mechanism not containing sulphur, then sulphur for the precipitation of sphalerite and galena must have been derived from elsewhere. Hydrogen sulphide could have been derived from the host rock and as Anderson (1975) suggests, the introduction of the metals, and sulphur must have occurred over reasonably lengthly periods of time, as the hydrogen sulphide within karsts would be insufficient in amount to have precipitated the observed concentration of metal. It is possible that neutral complexes such as $PbS \cdot 2H_2S$ and $Zn(HS)_3^-$ were responsible for ore transport.

The lead deposits in the Transvaal basin of the Northern Cape are associated with the Griquatown fault zone which coincides with fore-reef breccias. The karsts at Berg Aukas are situated within synclinorial warps related to the Grootfontein basement high. It would appear therefore that basement tectonics either during the deposition of sediments, or later, could have been important in the location and formation of breccias and karsts. Introduction of metals was possibly through faults, fractures or zones of brecciated porous host-rock. The structural and chemical traps provided by the karsts would cause precipitation of the metals. Due to the fact that Zn^{2+} can substitute for Mn^{2+}, it is possible that karst deposits are surrounded by an alteration zone which is relatively enriched in zinc. This could be of importance during exploration. The fact that brecciated and karsted dolomites and limestones are possibly related to areas or zones of basement disturbance has important implications with regard to exploration.

(ii) Detrital Deposits

A distinction is made between placer and alluvial deposits on the basis that a true placer deposit is a concentration of metals with a high resistance to weathering within rock units which have undergone a major amount of reworking and sorting resulting in the concentration of the metal. This process is particularly related to those deposits that were laid down by braiding streams. An alluvial deposit implies that the deposit was laid down by sedimentary processes but has undergone little or no subsequent reworking. Resistance to mechanical breakdown within placer and alluvial deposits is gold > cassiterite > wolframite > scheelite.

The concentration of gold (and uranium) within placer deposits such as the Witwatersrand depository is possibly the result of a high energy

environment on the edge of a regressing basin, i.e. the conglomerate and minerals were laid down relatively close to source (Figure 43).

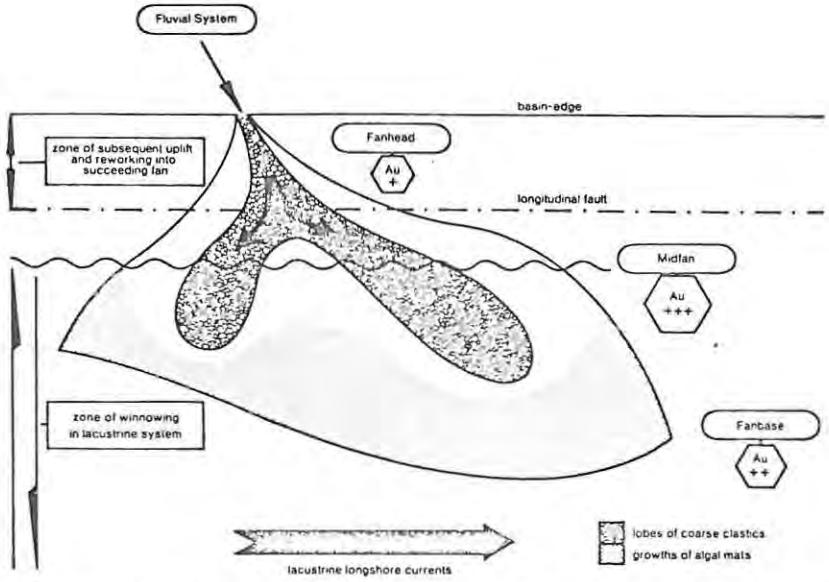


Figure 43 Conceptual model of a Witwatersrand-type goldfield. The fluvial system brings from the source-area unsorted erosional debris which undergoes soting on the fluvial fan in accordance with a hydrodynamic regime radially decreasing in energy away from the apex of the fan. Because of the small grain-size of the gold particles, they are unable to settle, to any marked extent, in the fanhead facies. Optimum conditions for settling occur in the midfan facies. The energy level becomes too low to move detrital particles in any quantity to the fanbase environment. However, gold in solution is precipitated by the algae which grow preferentially in the non-turbulent conditions along the margins and base of the fan (from Pretorius, 1976, p. 17).

Reworking, winnowing and jigging of previously deposited sediment by high energy braiding streams resulted in the sorting and concentration of heavy minerals (Pretorius, 1976, Minter, 1978 Winter Field School provided by Anglo American).

In general alluvial tin deposits are more productive than vein deposits. The source of the cassiterite in the Southeast Asian tin-belt is deeply weathered granite, with deposits being preserved because of the relatively low terrain and subsequent low velocity of water draining the area.

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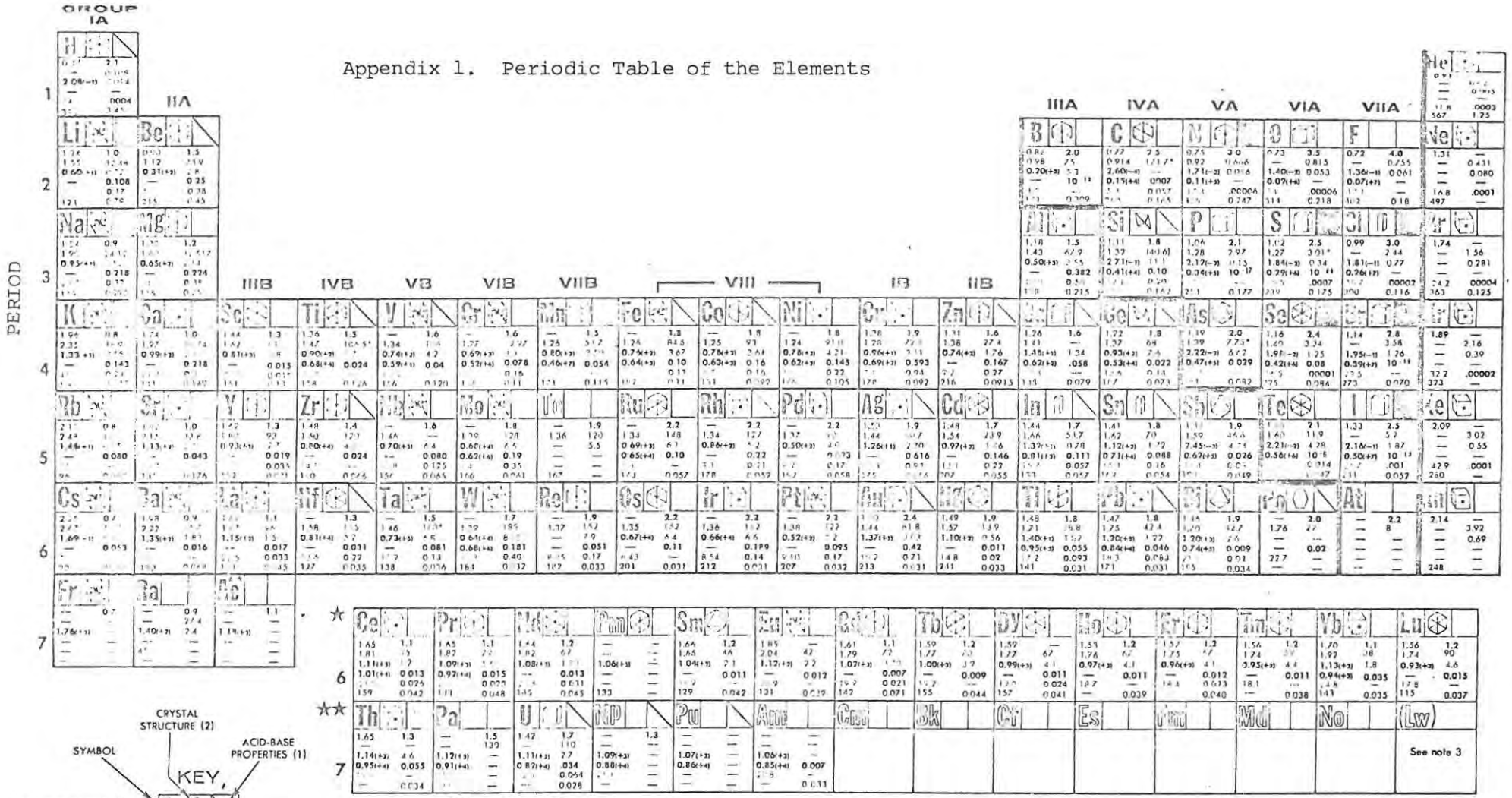
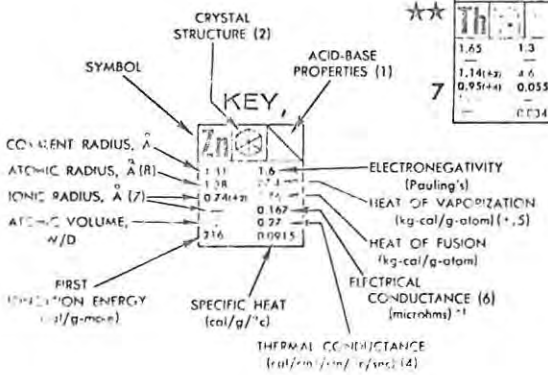
Appendix 1. Periodic Table of the Elements





NOTES: + Element sublimes

(1) For representative oxides (higher valence) of group. Oxide is acidic if color is red, basic if color is blue and amphoteric if both colors are shown. Intensity of color indicates relative strength.

(2) Cubic, face centered; cubic, body centered; diamond; cubic; hexagonal; rhombohedral; tetragonal; orthorhombic; monoclinic.

(3) Proposed, not officially accepted (4) At room temperature. (5) At boiling point.

(6) From 0° to 20°C. (7) Ionic (crystal) radii for coordination number 6.

(8) Metallic radii for coordination number of 12.

(from Sargent, 1967).

Appendix 2. Periodic Table of the elements.

Table of Radioactive Isotopes

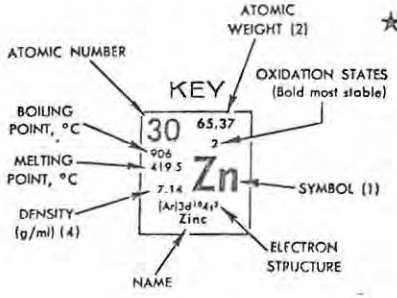
Ac 227(22y)β^-,α
Ag 110(24s)β^-,γ
111(7.5d)β^-,γ
Am241(470y)α,γ,e^-
242(100y)β^-,K,α,γ
243(8000y)α,γ
As 76(26.7h)β^+,γ
77(39h)β^-,γ
At 210(8.3h)K,α,γ
211(7.5h),Kα,γ
Au 198(2.69d)β^-,γ
Ba 131(12d)K,γ
133(7.5y)K,γ,e^-
Bi 210(5d)β^-,α
Bk 245(4.9d)K,α,γ
249(290d)β^-,α,SF
Br 82(36h)β^-,γ
C 14(5600y)β^-
Ca 41(1x10^{5}y)K
45(160d)β^-
47(4.7d)β^-,γ
Cd 115(43d)β^-,γ
Ce 141(32d)β^-,γ
143(33h)β^-,γ
144(285d)β^-,γ
Cf 246(35h)α,γ,SF
249(500y)α,γ,SF
251(700y)γ
Cl 36(3x10^{5}y)β^-
Cm 243(35y),α,γ
245(11000y),α,γ
247(1y)
Co 58(71d),K,β^+,γ
60(5.27y)β^-,γ
Cr 51(27d),K,γ
Cs 134(2.2y)β^-,γ
135(3x10^{6}y)β^-
137(30y)β^-,γ
Cu 64(12.8h)K,β^-,β^+,γ
Es 253(20d)α,γ,SF
254(1y)α,SF
Eu 154(16y)β^-,γ
155(1.7y)β^-,γ
Fe 55(2.9y)K
59(45d)β^-,γ
Fm 255(20h)α
Fr 223(22m)β^-,γ,α
Ga 72(14.1h),β^-,γ
Gd 153(236d)K,γ,e^-
159(18h)β^-,γ
Ge 71(11d)K
H 3(12.3y)β^-
Hf 181(45d)β^-,γ,e^-
Hg 197(65h)K,γ,e^-
203(47d)β^-,γ,e^-
Ho 166(27.3h)β^-,γ
I 129(10^{7}y)β^+,γ,e
131(8.05d)β^-,γ
In 114(50d)γ
Ir 192(74.4d)β^-,γ
K 40(10^{9}y)β^+,K,γ
42(12.4h),β^-,γ
La 140(40.2h)β^-,γ
Lu 176(10^{10}y)β^-,K,γ
177(6.8d)β^-,γ
Md 256(30m)K,SF
Mo 99(67h)β^-,γ
Na 22(2.6y)β^+,K,γ
24(15h)β^-,γ
Nd 147(11.1d)β^-,γ
Ni 63(125y)β^-
59(8x10^{4}y),K
Np 237(2.2x10^{6}y)α,γ
239(2.33d)β^-,γ
Os 191(15d)β^-,γ,e^-
P 32(14.2d)β^-
Pa 231(34000y)α,γ
Pb 211(19.4y)β^-,γ,e^-
202(10^{4}y)L
Pd 103(17d)K,γ
Pm 147(2.6y)β^-
145(25y)K,L,α
Po 210(138.4d)α,γ
209(100y)α,K,γ
Pr 143(13.8d)β^-
Pt 197(18h)β^-,γ
Pu 242(3.8 x 10^{5}y)α,SF
241(13y)β^-,α,γ
239(24300y)α,γ,SF
Ra 226(1620y)α,γ
Rb 86(18.6h)β^-,γ
Re 188(16.7h)β^-,γ
186(3.7d)β^-,γ
Rn 222(3.82d)α
Ru 103(40d)β^-,γ
97(2.9d),K,γ,e^-
S 35(87d)β^-
Sb 122(2.8d)β^-,K,β^+,γ
124(60d)β^-,γ
Sc 46(84d)β^-,γ
Se 75(121d)K,γ
Sm 153(47h)β^-,γ
145(340d)K,γ
Sn 113(119d)K,L,γ,e^-
Sr 90(28y)β^-
89(51d)β^-,γ
85(64d)K,γ
Ta 182(115d)β^-,γ
Tb 160(73d)$\beta^-\gamma$
Tc 99(2x10^{5}y)β^-
97(10^{4}y)K
Te 127(9.3h)β^-
Th 232(1.4x10^{10}y)α,γ,SF
228(1.91y)β^-
Tl 204(3.56y)β^-,K
Tm 170(127d)β^-,γ,e^-
U 238(4.5x10^{9}y)α,γ,SF
234(2.5x10^{5}y)α,γ,SF
235(7.1x10^{8}y)α,γ,SF
233(1.6x10^{5}y)α,γ
W 185(73d)β^-,γ
Y 90(64h)β^-,e^-
Yb 175(4.2d)β^-,γ
169(31d)K,γ,e^-
Zn 65(245d)K,β^+,γ
Zr 95(65d)β^-,γ,e^-
93(9x10^{5}y)β^-,γ

α alpha particle
β^- beta particle
β^+ positron
K K-electron capture
L L-electron capture
SF spontaneous fission
γ gamma ray
e^- internal electron conversion

PERIOD — GROUP IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA, INERT GASES

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1	1 1.00797 1 −252.7 −259.2 0.071 H Hydrogen																	2 4.0026 0 −268.9 −269.7 0.126 He Helium
2	3 6.939 1 1330 108.5 0.53 Li Lithium	4 9.0122 2 2770 1277 1.85 Be Beryllium											5 10.811 3 (2030) — 2.34 B Boron	6 12.0111 ±4,2 4830 3727 2.26 C Carbon	7 14.0067 ±3,5,4,2 −195.8 −210 0.81 N Nitrogen	8 15.9994 −2 −183 −218.8 1.14 O Oxygen	9 18.9984 −1 −188.2 −219.6 1.11 F Fluorine	10 20.183 0 −246 −248.6 1.20 Ne Neon
3	11 22.9898 1 892 97.8 0.97 Na Sodium	12 24.312 2 1107 650 1.74 Mg Magnesium											13 26.9815 3 2450 660 2.70 Al Aluminum	14 28.086 4 2680 1410 2.33 Si Silicon	15 30.9738 ±3,5,4 280w 44.2w 1.82w P Phosphorus	16 32.064 6,4,−2 444.6 119.0 2.07 S Sulfur	17 35.453 ±1,4,5,6,7 −34.7 −101.0 1.56 Cl Chlorine	18 39.948 0 −185.8 −189.4 1.40 Ar Argon
4	19 39.102 1 760 63.7 0.86 K Potassium	20 40.08 2 1440 838 1.55 Ca Calcium	21 44.956 3 2730 1539 3.0 Sc Scandium	22 47.90 4,3 3260 1668 4.51 Ti Titanium	23 50.942 5,4,3,2, 3450 1900 6.1 V Vanadium	24 51.996 6,3,2 2665 1875 7.19 Cr Chromium	25 54.938 7,6,4,2,3 2150 1245 7.43 Mn Manganese	26 55.847 2,3 3000 1536 7.86 Fe Iron	27 58.933 2,3 2900 1495 8.9 Co Cobalt	28 58.71 2,3 2730 1453 8.9 Ni Nickel	29 63.54 2,1 2595 1083 8.96 Cu Copper	30 65.37 2 906 419.5 7.14 Zn Zinc	31 69.72 3 2237 29.8 5.91 Ga Gallium	32 72.59 4 2830 937.4 5.32 Ge Germanium	33 74.922 ±3,5 613* 817 5.72 As Arsenic	34 78.96 6,4,−2 685 217 4.79 Se Selenium	35 79.909 ±1,4,5 58 −7.2 3.12 Br Bromine	36 83.80 0 −152 −157.3 2.6 Kr Krypton
5	37 85.47 1 688 38.9 1.53 Rb Rubidium	38 87.62 2 1380 768 2.6 Sr Strontium	39 88.905 3 2927 1509 4.47 Y Yttrium	40 91.22 4 3580 1852 6.49 Zr Zirconium	41 92.906 5,3 3300 2415 8.4 Nb Niobium	42 95.94 6,5,4,3,2 5560 2610 10.2 Mo Molybdenum	43 (99) 7 — 2200 11.5 Tc Technetium	44 101.07 2,3,4,6,8 4900 2500 12.2 Ru Ruthenium	45 102.905 2,3,4 4500 1966 12.4 Rh Rhodium	46 106.4 2,4 3980 1552 12.0 Pd Palladium	47 107.870 1 2210 960.8 10.5 Ag Silver	48 112.40 2 765 320.9 8.65 Cd Cadmium	49 114.82 3 2000 156.2 7.31 In Indium	50 118.69 4,2 2270 231.9 7.30 Sn Tin	51 121.75 ±3,5 1380 630.5 6.62 Sb Antimony	52 127.60 6,4,−2 989.8 449.5 6.24 Te Tellurium	53 126.904 ±1,4,5,7 183 113.7 4.94 I Iodine	54 131.30 0 −108.0 −111.9 3.06 Xe Xenon
6	55 132.905 1 690 28.7 1.90 Cs Cesium	56 137.34 2 1640 714 3.5 Ba Barium	57 138.91 3 ★ 3470 920 6.17 La Lanthanum	72 178.49 4 5400 2222 13.1 Hf Hafnium	73 180.948 5 5425 2996 16.6 Ta Tantalum	74 183.85 6,5,4,3,2 5930 3410 19.3 W Wolfram	75 186.2 7,6,4,2,−1 5900 3180 21.0 Re Rhenium	76 190.2 2,3,4,6,8 5500 2700 22.6 Os Osmium	77 192.2 2,3,4,6 5300 2454 22.5 Ir Iridium	78 195.09 2, 4 4530 1769 21.4 Pt Platinum	79 196.967 3,1 2970 1063 19.3 Au Gold	80 200.59 2,1 357 −38.4 13.6 Hg Mercury	81 204.37 3,1 1457 303 11.85 Tl Thallium	82 207.19 4,2 1725 327.4 11.4 Pb Lead	83 208.980 3,5 1560 271.3 9.8 Bi Bismuth	84 (210) 4,2 — 254 (9.2) Po Polonium	85 (210) — — (302) — At Astatine	86 (222) 0 (−61.8) (−71) — Rn Radon
7	87 (223) 1 — (27) — Fr Francium	88 (226) 2 — 700 5.0 Ra Radium	89 (227) 3 — 1050 — ★★ Ac Actinium															

★ 6	58 140.12 3,4 3468 795 6.67 Ce Cerium	59 140.907 3,4 3127 935 6.77 Pr Praseodymium	60 144.24 3 3027 1024 7.00 Nd Neodymium	61 (147) 3 — (1027) — Pm Promethium	62 150.35 3,2 1900 1072 7.54 Sm Samarium	63 151.96 3,2 1439 826 5.26 Eu Europium	64 157.25 3 3000 1312 7.89 Gd Gadolinium	65 158.924 3,4 2800 1356 8.27 Tb Terbium	66 162.50 3 2600 1407 8.54 Dy Dysprosium	67 164.930 3 2600 1461 8.80 Ho Holmium	68 167.26 3 2900 1497 9.05 Er Erbium	69 168.934 3,2 1727 1545 9.33 Tm Thulium	70 173.04 3,2 1427 824 6.98 Yb Ytterbium	71 174.97 3 3327 1652 9.84 Lu Lutetium
★★ 7	90 232.038 4 3850 1750 11.7 Th Thorium	91 (231) 5,4 — (1230) 15.4 Pa Protactinium	92 238.04 6,5,4,3 3818 1132 19.07 U Uranium	93 (237) 6,5,4,3 — 637 19.5 Np Neptunium	94 (242) 6,5,4,3 — — Pu Plutonium	95 (243) 6,5,4,3 — — Am Americium	96 (247) 3 — — Cm Curium	97 (247) 4,3 — — Bk Berkelium	98 (251) 3 — — Cf Californium	99 (254) — — — Es Einsteinium	100 (253) — — — Fm Fermium	101 (256) — — — Md Mendelevium	102 (254) — — — No Nobelium	103 (257) — — — (Lw) See note 3 (Lawrencium)



NOTES:

(1) Black — solid.
Red — gas.
Blue — liquid.
Outline — synthetically prepared.

(2) Based upon carbon − 12. ( ) indicates most stable or best known isotope.

(3) Proposed; not officially accepted

(4) Values for gaseous elements are for liquids at the boiling point.

(from Sargent, 1967).

Appendix 3. Average contents of chemical elements in the lithosphere and in its constituent rocks (weight percent) (from Beus and Grigorian, 1977)

Atomic number	Element	Continental lithosphere (excluding sedimentary cover)	Granitic shell	Granite	Granodiorite	Intermediate rocks	Basic rocks	Ultra-basic	Schist	Sedimentary rocks. Sandstone	Carbonate rocks
1	Hydrogen	0,10	0,10	0,06	0,09	0,11	0,12	—	0,40	0,25	0,09
2	Helium	$6 \cdot 10^{-3}$ cm³ per gram of rock weight									
3	Lithium	$2,0 \cdot 10^{-3}$	$3,0 \cdot 10^{-3}$	$3,8 \cdot 10^{-3}$	$3,0 \cdot 10^{-3}$	$2,5 \cdot 10^{-3}$	$1,5 \cdot 10^{-3}$	$0,2 \cdot 10^{-3}$	$6,6 \cdot 10^{-3}$	$1,5 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$
4	Beryllium	$1,5 \cdot 10^{-4}$	$2,5 \cdot 10^{-4}$	$3,5 \cdot 10^{-4}$	$2,5 \cdot 10^{-4}$	$1,8 \cdot 10^{-4}$	$0,4 \cdot 10^{-4}$	$0,2 \cdot 10^{-4}$	$3,0 \cdot 10^{-4}$	$0,n \cdot 10^{-4}$	$0,n \cdot 10^{-4}$
5	Boron	$0,7 \cdot 10^{-3}$	$1,0 \cdot 10^{-3}$	$1,5 \cdot 10^{-3}$	$1,2 \cdot 10^{-3}$	$0,9 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$	$0,3 \cdot 10^{-3}$	$10 \cdot 10^{-3}$	$3,5 \cdot 10^{-3}$	$2,0 \cdot 10^{-3}$
6	Carbon	$1,7\ 10^{-2}$	$3,0 \cdot 10^{-2}$	$3,0 \cdot 10^{-2}$	$3,0 \cdot 10^{-2}$	$3,0 \cdot 10^{-2}$	$2,0 \cdot 10^{-2}$	$1,0 \cdot 10^{-2}$	1,2	1,3	11,0
7	Nitrogen	$2,0 \cdot 10^{-3}$	$2,6 \cdot 10^{-3}$	$2,7 \cdot 10^{-3}$	$2,0 \cdot 10^{-3}$	$2,0 \cdot 10^{-3}$	$3,5 \cdot 10^{-3}$	$1,0 \cdot 10^{-3}$	$54,5 \cdot 10^{-3}$	$13,5 \cdot 10^{-3}$	$0,7 \cdot 10^{-3}$
8	Oxygen	46,6	48,1	48,7	48,0	47,0	44,5	43,7	49,0	51,5	49,2
9	Fluorine	$6,0 \cdot 10^{-2}$	$7,2 \cdot 10^{-2}$	$8,3 \cdot 10^{-2}$	$6,3 \cdot 10^{-2}$	$5,0 \cdot 10^{-2}$	$4,0 \cdot 10^{-2}$	$1,0 \cdot 10^{-2}$	$7,4 \cdot 10^{-2}$	$2,7 \cdot 10^{-2}$	$3,3 \cdot 10^{-2}$
10	Neon	$7,7 \cdot 10^{-8}$ cm³ per gram of rock weight									
11	Sodium	2,3	2,2	2,66	2,78	2,60	1,90	0,18	0,98	0,92	0,25
12	Magnesium	2,4	1,2	0,33	1,10	2,20	4,50	20,50	1,50	0,73	4,60
13	Aluminum	8,1	8,0	7,40	8,60	8,90	8,50	2,40	8,65	2,90	0,96
14	Silicon	27,7	30,9	34,0	30,5	27,5	23,0	20,0	27,5	34,7	3,4
15	Phosphorus	0,10	0,08	0,06	0,11	0,15	0,15	0,05	0,07	0,04	0,05
16	Sulfur	0,03	0,04	0,04	0,04	0,04	0,03	0,01	0,24	0,02	0,12
17	Chlorine	$1,0 \cdot 10^{-2}$	$1,7 \cdot 10^{-2}$	$2,0 \cdot 10^{-2}$	$1,3 \cdot 10^{-2}$	$1,0 \cdot 10^{-2}$	$0,6 \cdot 10^{-2}$	$0,5 \cdot 10^{-2}$	$1,80 \cdot 10^{-2}$	$0,1 \cdot 10^{-2}$	$1,5 \cdot 10^{-2}$
18	Argon	$2,2 \cdot 10^{-5}$ cm³ per gram of rock weight									
19	Potassium	1,8	2,70	3,50	2,52	1,50	0,70	0,05	2,70	1,32	0,28
20	Calcium	4,3	2,5	1,12	2,40	4,60	7,30	3,40	2,00	2,67	32,5
21	Scandium	$2,4 \cdot 10^{-3}$	$1,1 \cdot 10^{-3}$	$0,7 \cdot 10^{-3}$	$1,4 \cdot 10^{-3}$	$2,0 \cdot 10^{-3}$	$3,0 \cdot 10^{-3}$	$1,5 \cdot 10^{-3}$	$1,3 \cdot 10^{-3}$	$0,1 \cdot 10^{-3}$	$0,1 \cdot 10^{-3}$
22	Titanium	0,6	0,33	0,17	0,38	0,60	0,80	0,35	0,38	0,30	0,12

Appendix 3 (continued)

Atomic number	Element	Continental lithosphere (excluding sedimentary cover)	Granitic shell	Granite	Granodiorite	Intermediate rocks	Basic rocks	Ultra-basic	Schist	Sedimentary rocks. Sandstone	Carbonate rocks
23	Vanadium	$1,9\cdot10^{-2}$	$7,6\cdot10^{-3}$	$4,4\cdot10^{-3}$	$8,8\cdot10^{-3}$	$15\cdot10^{-3}$	$25\cdot10^{-3}$	$4,0\cdot10^{-3}$	$13\cdot10^{-3}$	$2,0\cdot10^{-3}$	$2,0\cdot10^{-3}$
24	Chromium	$1,2\cdot10^{-2}$	$0,34\cdot10^{-2}$	$0,1\cdot10^{-2}$	$0,22\cdot10^{-2}$	$0,55\cdot10^{-2}$	$1,7\cdot10^{-2}$	$16,0\cdot10^{-2}$	$0,9\cdot10^{-2}$	$0,35\cdot10^{-2}$	$0,11\cdot10^{-2}$
25	Manganese	0,09	0,07	0,04	0,07	0,12	0,12	0,10	0,08	0,04	0,04
26	Iron	5,7	3,6	1,83	3,30	5,50	8,40	8,70	4,80	2,80	0,85
× 27	Cobalt	$3,4\cdot10^{-3}$	$7,3\cdot10^{-4}$	$1,0\cdot10^{-4}$	$7,0\cdot10^{-4}$	$9,0\cdot10^{-4}$	$48\cdot10^{-4}$	$150\cdot10^{-4}$	$19\cdot10^{-4}$	$0,3\cdot10^{-4}$	$0,1\cdot10^{-4}$
× 28	Nickel	$9,5\cdot10^{-3}$	$2,6\cdot10^{-3}$	$0,45\cdot10^{-3}$	$1,5\cdot10^{-3}$	$5,0\cdot10^{-3}$	$13\cdot10^{-3}$	$200\cdot10^{-3}$	$6,8\cdot10^{-3}$	$0,2\cdot10^{-3}$	$0,2\cdot10^{-3}$
× 29	Copper	$6,5\cdot10^{-3}$	$2,2\cdot10^{-3}$	$1,0\cdot10^{-3}$	$2,6\cdot10^{-3}$	$4,0\cdot10^{-3}$	$8,7\cdot10^{-3}$	$1,0\cdot10^{-3}$	$4,5\cdot10^{-3}$	$0,1\cdot10^{-3}$	$0,4\cdot10^{-3}$
× 30	Zinc	$8,7\cdot10^{-3}$	$5,1\cdot10^{-3}$	$3,9\cdot10^{-3}$	$5,6\cdot10^{-3}$	$7,5\cdot10^{-3}$	$10,5\cdot10^{-3}$	$5,0\cdot10^{-3}$	$9,5\cdot10^{-3}$	$1,6\cdot10^{-3}$	$2,0\cdot10^{-3}$
31	Gallium	$1,7\cdot10^{-3}$	$1,9\cdot10^{-3}$	$2,0\cdot10^{-3}$	$2,0\cdot10^{-3}$	$1,7\cdot10^{-3}$	$1,7\cdot10^{-3}$	$0,15\cdot10^{-3}$	$1,9\cdot10^{-3}$	$1,2\cdot10^{-3}$	$0,4\cdot10^{-3}$
32	Germanium	$1,3\cdot10^{-4}$	$1,3\cdot10^{-4}$	$1,3\cdot10^{-4}$	$1,3\cdot10^{-4}$	$1,3\cdot10^{-4}$	$1,3\cdot10^{-4}$	$1,5\cdot10^{-4}$	$1,6\cdot10^{-4}$	$0,8\cdot10^{-4}$	$0,2\cdot10^{-4}$
33	Arsenic	$1,9\cdot10^{-4}$	$1,6\cdot10^{-4}$	$1,5\cdot10^{-4}$	$1,9\cdot10^{-4}$	$2,0\cdot10^{-4}$	$2,0\cdot10^{-4}$	$1,0\cdot10^{-4}$	$13,0\cdot10^{-4}$	$1,0\cdot10^{-4}$	$1,0\cdot10^{-4}$
34	Selenium	$1,0\cdot10^{-5}$	$1,4\cdot10^{-5}$	$1,4\cdot10^{-5}$	$1,4\cdot10^{-5}$	$1,4\cdot10^{-5}$	$1,3\cdot10^{-5}$	$0,5\cdot10^{-5}$	$5,0\cdot10^{-5}$	$0,5\cdot10^{-5}$	$0,8\cdot10^{-5}$
35	Bromine	$2,0\cdot10^{-4}$	$2,2\cdot10^{-4}$	$1,3\cdot10^{-4}$	$4,0\cdot10^{-4}$	$4,5\cdot10^{-5}$	$3,6\cdot10^{-4}$	$1,0\cdot10^{-4}$	$4,0\cdot10^{-4}$	$1,0\cdot10^{-4}$	$6,2\cdot10^{-4}$
36	Krypton	$4,2\cdot10^{-9}$ cm³ per gram of rock weight									
37	Rubidium	$9,0\cdot10^{-3}$	$18\cdot10^{-3}$	$21\cdot10^{-3}$	$16\cdot10^{-3}$	$11\cdot10^{-3}$	$5,0\cdot10^{-3}$	$0,5\cdot10^{-3}$	$14\cdot10^{-3}$	$6,0\cdot10^{-3}$	$0,3\cdot10^{-3}$
38	Strontium	$3,8\cdot10^{-2}$	$2,3\cdot10^{-2}$	$1,1\cdot10^{-2}$	$4,4\cdot10^{-2}$	$4,5\cdot10^{-2}$	$4,7\cdot10^{-2}$	$0,1\cdot10^{-3}$	$3,0\cdot10^{-2}$	$0,2\cdot10^{-2}$	$6,1\cdot10^{-2}$
39	Yttrium	$2,6\cdot10^{-3}$	$3,6\cdot10^{-3}$	$4,0\cdot10^{-3}$	$3,4\cdot10^{-3}$	$2,9\cdot10^{-3}$	$2,1\cdot10^{-3}$	$n\cdot10^{-5}$	$2,6\cdot10^{-3}$	$4,0\cdot10^{-3}$	$3,0\cdot10^{-3}$
40	Zirconium	$1,3\cdot10^{-2}$	$1,7\cdot10^{-2}$	$1,8\cdot10^{-2}$	$1,6\cdot10^{-2}$	$1,4\cdot10^{-2}$	$1,1\cdot10^{-2}$	$0,45\cdot10^{-2}$	$1,6\cdot10^{-2}$	$2,2\cdot10^{-2}$	$0,2\cdot10^{-2}$
41	Niobium	$1,9\cdot10^{-3}$	$2,0\cdot10^{-3}$	$2,1\cdot10^{-3}$	$2,0\cdot10^{-3}$	$2,0\cdot10^{-3}$	$1,9\cdot10^{-3}$	$1,6\cdot10^{-3}$	$1,1\cdot10^{-3}$	$n\cdot10^{-5}$	$0,3\cdot10^{-4}$
× 42	Molybdenum	$1,3\cdot10^{-4}$	$1,3\cdot10^{-4}$	$1,3\cdot10^{-4}$	$1,2\cdot10^{-4}$	$1,1\cdot10^{-4}$	$1,5\cdot10^{-4}$	$0,3\cdot10^{-4}$	$2,6\cdot10^{-4}$	$0,2\cdot10^{-4}$	$0,4\cdot10^{-4}$
43	Technetium	—	—	—	—	—					
44	Ruthenium	Data not available									
45	Rhodium	Data not available									

Appendix 3 (continued)

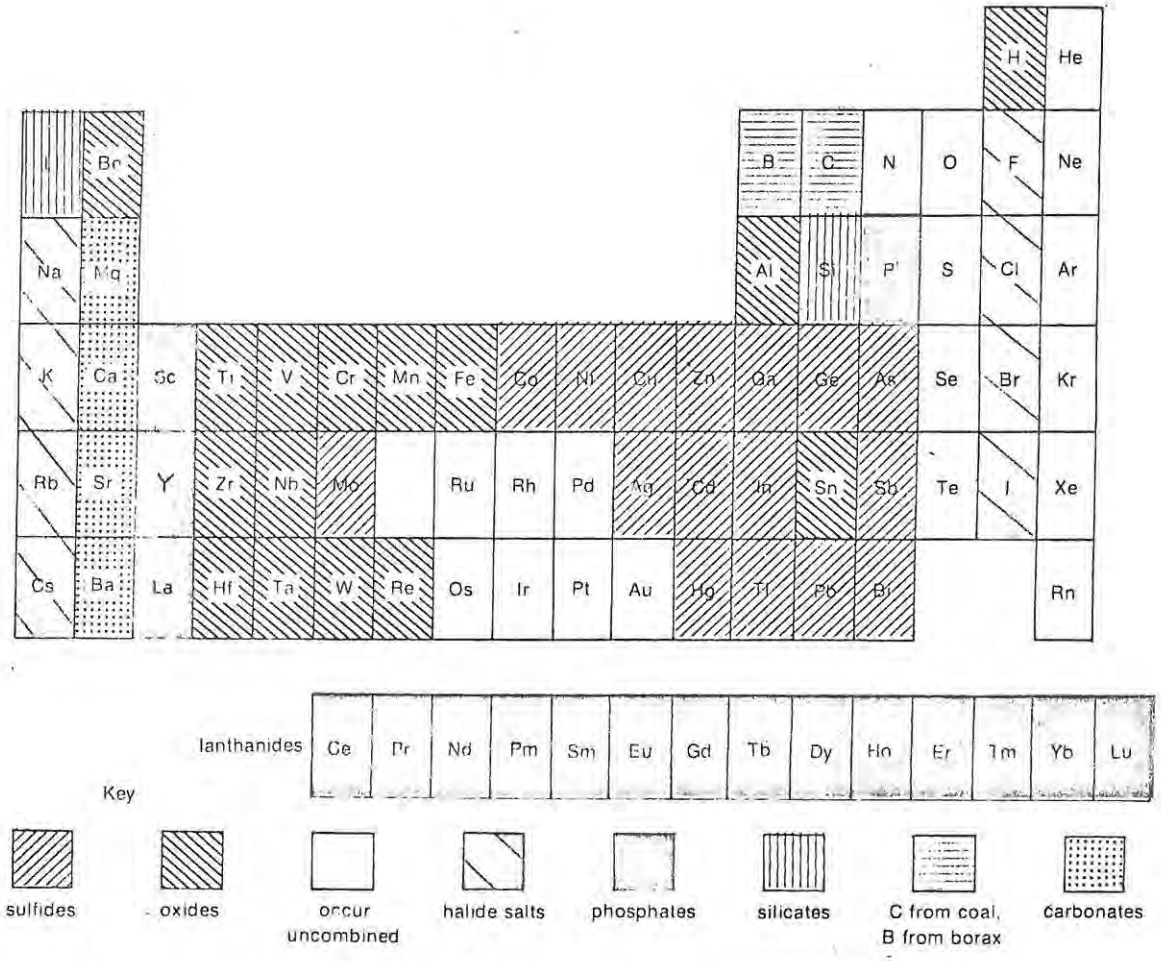
Atomic number	Element	Continental lithosphere (excluding sedimentary cover)	Granitic shell	Granite	Granodiorite	Intermediate rocks	Basic rocks	Ultra-basic	Schist	Sedimentary rocks. Sandstone	Carbonate rocks
46	Palladium	$n \cdot 10^{-7}$	$n \cdot 10^{-8}$	$n \cdot 10^{-8}$	$n \cdot 10^{-8}$	$n \cdot 10^{-7}$	$2{,}0 \cdot 10^{-7}$	$5{,}0 \cdot 10^{-7}$	Data not available		
X 47	Silver	$9{,}0 \cdot 10^{-6}$	$4{,}8 \cdot 10^{-6}$	$3{,}7 \cdot 10^{-6}$	$5{,}1 \cdot 10^{-6}$	$7{,}0 \cdot 10^{-6}$	$11 \cdot 10^{-6}$	$6{,}0 \cdot 10^{-6}$	$7{,}0 \cdot 10^{-6}$	$n \cdot 10^{-6}$	$n \cdot 10^{-6}$
48	Cadmium	$1{,}9 \cdot 10^{-5}$	$1{,}5 \cdot 10^{-5}$	$1{,}3 \cdot 10^{-5}$	$1{,}6 \cdot 10^{-5}$	$1{,}8 \cdot 10^{-5}$	$2{,}2 \cdot 10^{-5}$	$0{,}1 \cdot 10^{-5}$	$3{,}0 \cdot 10^{-5}$	$0{,}n \cdot 10^{-5}$	$0{,}4 \cdot 10^{-5}$
49	Indium	$2{,}3 \cdot 10^{-5}$	$2{,}5 \cdot 10^{-5}$	$2{,}6 \cdot 10^{-5}$	$2{,}4 \cdot 10^{-5}$	$2{,}2 \cdot 10^{-5}$	$2{,}2 \cdot 10^{-5}$	$0{,}1 \cdot 10^{-5}$	$1{,}0 \cdot 10^{-5}$	$0{,}n \cdot 10^{-5}$	$0{,}n \cdot 10^{-5}$
X 50	Tin	$1{,}9 \cdot 10^{-4}$	$2{,}7 \cdot 10^{-4}$	$3{,}0 \cdot 10^{-4}$	$2{,}5 \cdot 10^{-4}$	$1{,}6 \cdot 10^{-4}$	$1{,}5 \cdot 10^{-4}$	$0{,}5 \cdot 10^{-4}$	$6{,}0 \cdot 10^{-4}$	$0{,}n \cdot 10^{-4}$	$0{,}n \cdot 10^{-4}$
51	Antimony	$2{,}0 \cdot 10^{-5}$	$2{,}0 \cdot 10^{-5}$	$2{,}0 \cdot 10^{-5}$	$2{,}0 \cdot 10^{-5}$	$2{,}0 \cdot 10^{-5}$	$2{,}0 \cdot 10^{-5}$	$1{,}0 \cdot 10^{-5}$	$15 \cdot 10^{-5}$	$0{,}n \cdot 10^{-5}$	$2{,}0 \cdot 10^{-5}$
52	Tellurium	$1{,}0 \cdot 10^{-7}$	$1{,}0 \cdot 10^{-7}$	$1{,}0 \cdot 10^{-7}$	$1{,}0 \cdot 10^{-7}$	$1{,}0 \cdot 10^{-7}$	$1{,}0 \cdot 10^{-7}$	$0{,}n \cdot 10^{-7}$	$10 \cdot 10^{-7}$	Data not available	
53	Iodine	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-7}$	$5 \cdot 10^{-7}$	$5 \cdot 10^{-7}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$2{,}2 \cdot 10^{-4}$	$1{,}7 \cdot 10^{-4}$	$1{,}2 \cdot 10^{-4}$
54	Xenon	$3{,}4 \cdot 10^{-10}$ cm^3 per gram of rock weight									
55	Cesium	$2{,}0 \cdot 10^{-4}$	$3{,}8 \cdot 10^{-4}$	$5{,}0 \cdot 10^{-4}$	$2{,}0 \cdot 10^{-4}$	$1{,}5 \cdot 10^{-4}$	$1{,}1 \cdot 10^{-4}$	$n \cdot 10^{-5}$	$5{,}0 \cdot 10^{-4}$	$n \cdot 10^{-5}$	$n \cdot 10^{-5}$
56	Barium	$4{,}5 \cdot 10^{-2}$	$6{,}8 \cdot 10^{-2}$	$8{,}4 \cdot 10^{-2}$	$4{,}5 \cdot 10^{-2}$	$3{,}8 \cdot 10^{-2}$	$3{,}3 \cdot 10^{-2}$	$0{,}4 \cdot 10^{-4}$	$5{,}8 \cdot 10^{-2}$	$n \cdot 10^{-3}$	$1{,}0 \cdot 10^{-3}$
57	Lanthanum	$2{,}5 \cdot 10^{-3}$	$4{,}6 \cdot 10^{-3}$	$5{,}5 \cdot 10^{-3}$	$4{,}0 \cdot 10^{-3}$	$3{,}0 \cdot 10^{-3}$	$1{,}5 \cdot 10^{-3}$	$n \cdot 10^{-5}$	$9{,}2 \cdot 10^{-3}$	$3{,}0 \cdot 10^{-3}$	$n \cdot 10^{-4}$
58	Cerium	$6{,}0 \cdot 10^{-3}$	$8{,}3 \cdot 10^{-3}$	$9{,}2 \cdot 10^{-3}$	$8{,}0 \cdot 10^{-3}$	$6{,}5 \cdot 10^{-3}$	$4{,}8 \cdot 10^{-3}$	$n \cdot 10^{-5}$	$5{,}9 \cdot 10^{-3}$	$9{,}2 \cdot 10^{-3}$	$1{,}2 \cdot 10^{-3}$
59	Praseodymium	$5{,}7 \cdot 10^{-4}$	$7{,}9 \cdot 10^{-4}$	$8{,}8 \cdot 10^{-4}$	$7{,}5 \cdot 10^{-4}$	$6{,}2 \cdot 10^{-4}$	$4{,}6 \cdot 10^{-4}$	$n \cdot 10^{-5}$	$5{,}6 \cdot 10^{-4}$	$8{,}8 \cdot 10^{-4}$	$1{,}1 \cdot 10^{-4}$
60	Neodymium	$2{,}4 \cdot 10^{-3}$	$3{,}3 \cdot 10^{-3}$	$3{,}7 \cdot 10^{-3}$	$3{,}2 \cdot 10^{-3}$	$2{,}7 \cdot 10^{-3}$	$2{,}0 \cdot 10^{-3}$	$n \cdot 10^{-5}$	$2{,}4 \cdot 10^{-3}$	$3{,}7 \cdot 10^{-3}$	$4{,}7 \cdot 10^{-3}$
61	Promethium	—	—	—	—	—	—	—	—	—	—
62	Samarium	$6{,}5 \cdot 10^{-4}$	$9{,}0 \cdot 10^{-4}$	$10{,}0 \cdot 10^{-4}$	$8{,}5 \cdot 10^{-4}$	$7{,}5 \cdot 10^{-4}$	$5{,}3 \cdot 10^{-4}$	$n \cdot 10^{-5}$	$6{,}4 \cdot 10^{-4}$	$1{,}0 \cdot 10^{-3}$	$1{,}3 \cdot 10^{-4}$
63	Europium	$1{,}0 \cdot 10^{-4}$	$1{,}4 \cdot 10^{-4}$	$1{,}6 \cdot 10^{-4}$	$1{,}4 \cdot 10^{-4}$	$1{,}2 \cdot 10^{-4}$	$0{,}8 \cdot 10^{-4}$	$n \cdot 10^{-5}$	$1{,}0 \cdot 10^{-4}$	$1{,}6 \cdot 10^{-4}$	$0{,}2 \cdot 10^{-4}$
64	Gadolinium	$6{,}5 \cdot 10^{-4}$	$9{,}0 \cdot 10^{-3}$	$10{,}0 \cdot 10^{-4}$	$8{,}5 \cdot 10^{-4}$	$7{,}5 \cdot 10^{-4}$	$5{,}3 \cdot 10^{-4}$	$n \cdot 10^{-5}$	$6{,}4 \cdot 10^{-4}$	$1{,}0 \cdot 10^{-3}$	$1{,}3 \cdot 10^{-4}$
65	Terbium	$1{,}0 \cdot 10^{-4}$	$1{,}4 \cdot 10^{-4}$	$1{,}6 \cdot 10^{-4}$	$1{,}4 \cdot 10^{-4}$	$1{,}2 \cdot 10^{-4}$	$0{,}8 \cdot 10^{-4}$	$n \cdot 10^{-5}$	$1{,}0 \cdot 10^{-4}$	$1{,}6 \cdot 10^{-4}$	$0{,}2 \cdot 10^{-4}$
66	Dysprosium	$4{,}6 \cdot 10^{-4}$	$6{,}5 \cdot 10^{-4}$	$7{,}2 \cdot 10^{-4}$	$6{,}1 \cdot 10^{-4}$	$5{,}2 \cdot 10^{-4}$	$3{,}8 \cdot 10^{-4}$	$n \cdot 10^{-5}$	$4{,}6 \cdot 10^{-4}$	$7{,}2 \cdot 10^{-4}$	$0{,}9 \cdot 10^{-4}$
67	Holmium	$1{,}3 \cdot 10^{-4}$	$1{,}8 \cdot 10^{-4}$	$2{,}0 \cdot 10^{-4}$	$1{,}8 \cdot 10^{-4}$	$1{,}5 \cdot 10^{-4}$	$1{,}1 \cdot 10^{-4}$	$n \cdot 10^{-5}$	$1{,}2 \cdot 10^{-4}$	$2{,}0 \cdot 10^{-4}$	$0{,}3 \cdot 10^{-4}$
68	Erbium	$2{,}6 \cdot 10^{-4}$	$3{,}6 \cdot 10^{-4}$	$4{,}0 \cdot 10^{-4}$	$3{,}2 \cdot 10^{-4}$	$2{,}8 \cdot 10^{-4}$	$2{,}1 \cdot 10^{-4}$	$n \cdot 10^{-5}$	$2{,}5 \cdot 10^{-4}$	$4{,}0 \cdot 10^{-4}$	$0{,}5 \cdot 10^{-4}$

Appendix 3 (continued)

Atomic number	Element	Continental lithosphere (excluding sedimentary cover)	Granitic shell	Granite	Granodiorite	Intermediate rocks	Basic rocks	Ultra-basic	Schist	Sedimentary rocks. Sandstone	Carbonate rocks
69	Thulium	$0,2 \cdot 10^{-4}$	$0,3 \cdot 10^{-4}$	$0,3 \cdot 10^{-4}$	$0,3 \cdot 10^{-4}$	$0,2 \cdot 10^{-4}$	$0,2 \cdot 10^{-4}$	$n \cdot 10^{-6}$	$0,2 \cdot 10^{-4}$	$0,3 \cdot 10^{-4}$	$0,4 \cdot 10^{-5}$
70	Ytterbium	$2,6 \cdot 10^{-4}$	$3,6 \cdot 10^{-4}$	$4,0 \cdot 10^{-4}$	$3,2 \cdot 10^{-4}$	$2,8 \cdot 10^{-4}$	$2,1 \cdot 10^{-4}$	$n \cdot 10^{-5}$	$2,6 \cdot 10^{-4}$	$4,0 \cdot 10^{-4}$	$0,5 \cdot 10^{-4}$
71	Lutecium	$0,8 \cdot 10^{-4}$	$1,1 \cdot 10^{-4}$	$1,2 \cdot 10^{-4}$	$1,0 \cdot 10^{-4}$	$0,8 \cdot 10^{-4}$	$0,6 \cdot 10^{-4}$	$n \cdot 10^{-5}$	$0,7 \cdot 10^{-4}$	$1,2 \cdot 10^{-4}$	$0,2 \cdot 10^{-4}$
72	Hafnium	$2,6 \cdot 10^{-4}$	$3,5 \cdot 10^{-4}$	$3,9 \cdot 10^{-4}$	$3,2 \cdot 10^{-4}$	$2,8 \cdot 10^{-4}$	$2,2 \cdot 10^{-4}$	$0,5 \cdot 10^{-4}$	$2,8 \cdot 10^{-4}$	$3,9 \cdot 10^{-4}$	$0,3 \cdot 10^{-4}$
73	Tantalum	$1,0 \cdot 10^{-4}$	$2,1 \cdot 10^{-4}$	$2,5 \cdot 10^{-4}$	$1,8 \cdot 10^{-4}$	$1,2 \cdot 10^{-4}$	$0,5 \cdot 10^{-4}$	$0,2 \cdot 10^{-5}$	$0,8 \cdot 10^{-4}$	$n \cdot 10^{-6}$	$n \cdot 10^{-6}$
X74	Tungsten	$1,1 \cdot 10^{-4}$	$1,9 \cdot 10^{-4}$	$2,2 \cdot 10^{-4}$	$1,7 \cdot 10^{-2}$	$1,2 \cdot 10^{-4}$	$0,7 \cdot 10^{-4}$	$0,1 \cdot 10^{-4}$	$1,8 \cdot 10^{-4}$	$1,6 \cdot 10^{-4}$	$0,6 \cdot 10^{-4}$
75	Rhenium	$7,0 \cdot 10^{-8}$	$7,0 \cdot 10^{-8}$	$6,7 \cdot 10^{-8}$	—	—	$7,1 \cdot 10^{-8}$	—	—	—	—
76	Osmium	—	Data not available		—	—	—	—	—	—	—
77	Iridium	$2,0 \cdot 10^{-8}$	$1,5 \cdot 10^{-8}$	$1,0 \cdot 10^{-8}$	—	—	$2,2 \cdot 10^{-8}$	—	—	—	—
78	Platinum	—	Data not available		—	—	$1,0 \cdot 10^{-5}$	$2,0 \cdot 10^{-5}$	—	—	—
X79	Gold	$1,7 \cdot 10^{-7}$	$1,2 \cdot 10^{-7}$	$0,8 \cdot 10^{-7}$	$1,2 \cdot 10^{-7}$	$2,8 \cdot 10^{-7}$	$3,6 \cdot 10^{-7}$	$6,0 \cdot 10^{-7}$	$n \cdot 10^{-7}$	$n \cdot 10^{-7}$	$n \cdot 10^{-7}$
80	Mercury	$4,6 \cdot 10^{-6}$	$6,6 \cdot 10^{-6}$	$6,7 \cdot 10^{-6}$	$6,7 \cdot 10^{-6}$	$7,5 \cdot 10^{-6}$	$6,5 \cdot 10^{-6}$	$6,4 \cdot 10^{-6}$	$6,6 \cdot 10^{-5}$	$7,4 \cdot 10^{-6}$	$4,5 \cdot 10^{-6}$
81	Thallium	$0,7 \cdot 10^{-4}$	$1,8 \cdot 10^{-4}$	$2,3 \cdot 10^{-4}$	$1,5 \cdot 10^{-4}$	$1,0 \cdot 10^{-4}$	$0,2 \cdot 10^{-4}$	$0,6 \cdot 10^{-5}$	$1,4 \cdot 10^{-4}$	$0,8 \cdot 10^{-4}$	$n \cdot 10^{-6}$
X82	Lead	$0,9 \cdot 10^{-3}$	$1,6 \cdot 10^{-3}$	$1,9 \cdot 10^{-3}$	$1,5 \cdot 10^{-3}$	$1,2 \cdot 10^{-3}$	$0,6 \cdot 10^{-3}$	$0,1 \cdot 10^{-3}$	$2,0 \cdot 10^{-3}$	$0,7 \cdot 10^{-3}$	$0,9 \cdot 10^{-3}$
83	Bismuth	$0,8 \cdot 10^{-6}$	$1,0 \cdot 10^{-6}$	$1,0 \cdot 10^{-6}$	$1,0 \cdot 10^{-6}$	$0,8 \cdot 10^{-6}$	$0,7 \cdot 10^{-6}$	$0,1 \cdot 10^{-6}$	Data not available		—
84	Polonium	—	—	—	—	—	—	—	—	—	—
85	Astatine	—	—	—	—	—	—	—	—	—	—
86	Radon		Data not available								
87	Francium	—	—	—	—	—	—	—	—	—	—
88	Radium		Data not available								
89	Actinium	—	—	—	—	—	—	—	—	—	—
90	Thorium	$7,3 \cdot 10^{-4}$	$1,4 \cdot 10^{-3}$	$1,7 \cdot 10^{-3}$	$1,2 \cdot 10^{-3}$	$8,5 \cdot 10^{-4}$	$4,0 \cdot 10^{-4}$	$4,0 \cdot 10^{-7}$	$1,2 \cdot 10^{-3}$	$1,7 \cdot 10^{-4}$	$1,7 \cdot 10^{-4}$
91	Protactinium	—	—	—	—	—	$1,0 \cdot 10^{-4}$	$1,0 \cdot 10^{-7}$	$3,7 \cdot 10^{-4}$	$4,5 \cdot 10^{-5}$	$2,2 \cdot 10^{-4}$
X92	Uranium	$1,5 \cdot 10^{-4}$	$2,6 \cdot 10^{-4}$	$3,0 \cdot 10^{-4}$	$2,5 \cdot 10^{-4}$	$2,0 \cdot 10^{-4}$	—	—	—	—	—

x = elements dealt with in this dissertation

Appendix 4. Natural sources of the elements. The soluble halide salts are found in the ocean or in solid deposits. Most of the noble gases are obtained from air.



(from Masterton and Slowinski, 1977, p. 163).