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A REVIEW OF THE ECONOMIC GEOLOGY OF TUNGSTEN

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ABSTRACT

A description of the geochemistry of tungsten is given. The geochemical properties of tungsten have a strong influence on its mineralogy, distribution and abundance in crustal rocks and rock-forming minerals, and its migration/deposition within the ore-forming and supergene environments. The behaviour of tungsten during migration, from source to site of deposition, within the crust is discussed in some detail and environments considered favourable to the concentration of tungsten ore minerals are suggested.

All major types of tungsten ore deposit are described with emphasis placed on those of greater economic importance. Characteristic features of each type of deposit are particularly emphasized in order to provide clear guidelines to exploration.

Hydrothermal, pyrometasomatic and stratabound tungsten deposits present themselves, economically, as the most important exploration targets.

The recently developed concept of syngenetic stratabound tungsten mineralisation is outlined. Exploration for deposits of this type should be aimed predominantly, but not exclusively, at volcano-sedimentary sequences of Lower Palaeozoic age, particularly within regions known to contain occurrences of Sb and Hg.

Tungsten deposits commonly contain concentrations of one or more of the following metals: Sn, Sb, Bi, Mo, Au and Ag. The presence and possible extractive value of these metals, together with commonly associated metal impurities such as As, must always be taken into account in a feasibility study.

INTRODUCTION

- 1 -

Tungsten is a metallic element with the highest melting point $(3410^{\circ} + 20^{\circ}C)$ of all metals and all elements except carbon. It is exceeded in density (19.35 gm/cc) only by rhenium and metals of the platinum group. In order of abundance it is the fifty fourth element in the Earth's crust.

Tungsten is a metal of great industrial and strategic importance. It is valued, in particular, for the hardness and wear resistance of its carbide and as an additive in the manufacture of tool steels to which it imparts high temperature hardness and tensile strength.

At present supplies of tungsten and, more important, the stability of prices, are dependent to a large degree on the scale of sales of the metal from China and the releases from the United States General Services Administration stockpile. China and North Korea possess over half of the known world resources of tungsten and, with the U.S.S.R., account for about 50 percent of world production. Their erratic marketing policies have a disrupting effect on world supplies and thus also prices.

For economic and, to some extent, for strategic reasons, therefore, this review was undertaken to provide a comprehensive knowledge to exploration companies currently, or otherwise, engaged in an investigation of tungsten mineralisation. The review is submitted in partial fulfillment of the requirements for the degree of M.Sc. Exploration Geology at Rhodes University, Grahamstown, S. Africa. A period of approximately ten weeks duration was spent preparing and writing this review.

1.0

THE GEOCHEMISTRY AND MINERALOGY OF TUNGSTEN

- 2 -

A knowledge of the geochemistry of tungsten may provide useful information towards an understanding of the behaviour of the metal during its migration and eventual deposition in the earth's crust. A discussion of the geochemical properties of tungsten may, therefore, provide useful guidelines in locating and evaluating deposits of the metal. Unfortunately, however, there is a scarcity of reliable geochemical data on tungsten in the literature, particularly in relation to its abundance and distribution in the crust.

Until the early 1960's, and to some extent since that time, the most commonly utilized technique for tungsten analyses was the spectrographic method. This low sensitive method, however, is incapable of measuring to a reliable accuracy very small, parts per million (p.p.m.), values of the element. The spectrographic method has since been superceded by the much more sensitive radiochemical neutron activation technique. Although this accurate technique for tungsten analyses has been available since the early 1960's, there still remains little reliable information. This could be accounted for by either a lack of recent studies, or by an actual lack of published data.

2.1 The Crystal Chemistry of Tungsten

Tungsten belongs to group VI, and occurs along the sixth row of the periodic table. Its atomic number is 74 and atomic weight 183.85. Naturallyoccurring tungsten is a mixture of 5 stable isotopes whose main characteristics are listed below. No appreciable separation of the isotopes occurs in natural processes or would be expected for an element such as tungsten with so slight a percentage difference in its atomic masses (table 1).

TABLE 1

Stable Tungsten Isotopes

Mass Number	Abundance - Weight Percentage
180	0.135
182	26.41
183	14.4
184	30.64
186	28.41

2.0

The atomic radius of tungsten is 1.46 Å and is similar (\pm 12 Å) to the atomic radii of Al, Zn, Nb, Mo, Tc, Ru, Pt, Pd, Ta, Re, Rh, Os, Ir, Sn and U.

Tungsten, like molybdenum, has a wide range of oxidation states and may have valencies of 2-, 1-, 1+, 2+, 3+, 4+, 5+ and 6+. However, the lowest oxidation states (2-, 1-, 1+) occur only in organometallic compounds.

The ionic radius of \underline{W}^{4+} is 0.68 Å and is close (+12 Å) to the ionic radii of V^{3+} , Mn^{3+} , Fe^{2+} , Co^{3+} , Ni^{2+} , Ge^{2+} , Mo^{4+} , Tc^{4+} , Ru^{4+} , Rh^{3+} , Pd^{4+} , Sn^{4+} , Te^{4+} , Ta^{5+} , Re^{4+} and Bi^{5+} .

The ionic radius of \underline{W}^{6+} is 0.65 Å and is close (+12 Å) to the ionic radii of v^{4+} , v^{5+} , Mn^{4+} , Fe^{3+} , Co^{3+} , Ni^{3+} , Ga^{3+} , As^{3+} , Nb^{5+} , Mo^{6+} , and Sb^{5+} .

The ionization potentials (in e.v.) of tungsten are: $W^{1+} - 7.98$; W^{1+} to $W^{2+} - 17.7$; W^{2+} to $W^{3+} - 24.8$, and W^{3+} to $W^{4+} - 35.36$; thus there is an increase in the value of the ionization potential toward the higher valencies.

The electron configuration of the tungsten atom is: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^4 6s^2$. The configuration of the outermost, or valence, electrons is $5d^4 6s^2$. In order to describe the electron configuration of the tungsten atom in more detail it is convenient to draw comparisons with the electron configuration of the molybdenum atom. Such a comparison will, hopefully, elucidate the differences in chemical behaviour of the two elements.

There is a considerable difference in the electronic configurations of tungsten and molybdenum, (Barnard, A., 1968 - cited in Barabanov, V.F., 1971). The energy levels of orbitals 4s, 4p, 5s, 5p, and 6s are similar in both elements, but the energy levels of 4d, 4f, and 5d orbitals of tungsten are considerably lower than the energy levels of corresponding orbitals in molybdenum. In tungsten the energy level of the 4d orbital is much lower than that of the 5s orbital but in molybdenum the energy levels of these orbitals are nearly equal. The energy level of the 4f orbital in tungsten is lower than the energy levels of 5p, 5d, and 6s orbitals, while in molybdenum it is much higher. Finally, the energy level of the 5d orbital in tungsten is lower than that of the 6s orbital, but in molybdenum it is higher. The energy levels of the atomic orbitals in molybdenum are as follows: $2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 3d \rightarrow 4s \rightarrow 4p \rightarrow 4d \rightarrow 5s$ nearly equal

and in tungsten: $2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 3d \rightarrow 4s \rightarrow 4p \rightarrow 4d \rightarrow \underbrace{5s \rightarrow 4f \rightarrow 5p}_{nearly equal} \rightarrow 5d \rightarrow 6s$

Thus, the valence electrons of Mo and W are in (n-1) <u>d</u> and <u>ns</u> - orbitals, but in molybdenum their energy levels are nearly equal, while in tungsten they are different. The 5d⁴ 6s² valence electrons in tungsten are at a considerable distance from the nucleus and are effectively screened by the 4f¹⁴ electrons. As a result, the third ionization potential of tungsten (W^{3+}) is smaller than that of molybdenum (Mo³⁺) by as much as 3.05 e.v., and the fourth by 5.17 e.v., etc.



Fig. 1 Stability diagram of tungsten compounds, - total sulphur versus oxygen fugacities at 627°C. (modified after Krauskopf, 1965).

Taken from Stemprok, 1977

The ionization potential is a measure of the minimum energy required to remove an electron from an atom, therefore, the ionization potential is also a measure of the stability of the electronic structure of the atom. The ionization potential values of tungsten increase toward the higher valencies which explains why the highest valency +6 is the most stable form. The +6 state would only be unstable under extreme reducing conditions e.g. conditions in which chondritic meteorites formed. The difference between the ionization potential values, and hence the relative stabilities, of tungsten and molybdenum is the most likely explanation (Barabanov, 1971) for the tendency of tungsten to form oxygen compounds and the tendency of molybdenum to form compounds with sulphur. That tungsten has an affinity to form oxide compounds is suggested by Krauskopf (1965) who calculated the stabilities of tungsten sulphide (WS2) and tungsten oxides (fig. 1). It can be seen from fig. 1 that the tungsten oxides occupy a predominant part of the W-S-O diagram, thus indicating a very small field of tungstenite stability.

2.2

The Mineralogy of Tungsten

The compounds of tungsten that have been identified as naturallyforming minerals are both small in number and relatively simple in composition. Table 2 lists twenty, positively identified tungsten mineral species (Krauskopf, 1970). It was suggested in the description of the electronic configuration of the tungsten atom, and from the values of its oxidation potential, that the element should preferentially form oxide compounds i.e. exhibit lithophile characteristics. This suggestion is corroborated by the composition of the identified tungsten minerals (table 2). Except for the very rare sulphide, all the minerals are tungstates or forms of the oxide. Of the twenty minerals listed only scheelite, and the three minerals of the wolframite group, have any quantitative, or economic importance. The top eleven minerals in table 2 are usually recognised as primary minerals, whereas the bottom nine are secondary and limited to zones of weathering.

Tungsten Sulphides

The only naturally-occurring tungsten sulphide is the rare species tungstenite (WS₂). The rarity of this mineral is explained by the strong affinity of tungsten for oxygen and by the chemical instability of tungsten sulphides.

TABLE 2

- 6 -

MINERALS OF TUNGSTEN

Mineral	Composition
Wolframite group	
Huebnerite	$MnWO_{A}$ (O-20 atomic - % Fe)
Wolframite	(Fe, Mn)WO ₄ (20-80 atomic - % Fe)
Ferberite ^a	FeW0 ₄ (80-100 atomic - % Fe)
Scheelite	CaWO4
Seyrigite	Ca (W, Mo)O4 (WO3 ca. 28%)
Cuproscheelite	(Cu,Ca)WO4
Sanmartinite	$(Zn, Fe, Ca, Mn) WO_4$
Tungstenite	ws ₂
Russellite	(Bi ₂ W)O ₃
Scheteligite	(Ca,Fe,Mn,Sb,B,Y) (Ti,Ta,Nb,W) (0,OH) 7
Yttrocrasite	(Y,Th,U,Ca) ₂ (Ti,Fe ₃ ⁺ ,W) ₄ O ₁₁ (?)
Stolzite	PbWO4
Chillagite	Pb (W,Mo)04 (WO3 21.1 - 29.5%)
Raspite	PbWO
Tungstite	WO3 H2O (?)
Hydrotungstite ^b	WO3 2H20
Cuprotungstite	Cu ₂ WO ₄ (OH)
Ferritungstite	$Ca_2Fe_2^{2+}Fe_2^{3+}(WO_4)_7 9H_2O$
Anthoinite	Alwo40H H20
Yttrotungstite	Hydrated Y tungstate

^a Ferberite pseudomorphous after scheelite is sometimes called reinite.

^b Amorphous hydrotungstite is called meymacite

Taken from Krauskopf (1970)

Tungstenite usually exhibits an earthy or foliated habit. It is dark lead-grey in both colour and streak. It has a hardness of 2.5 (Mohr Scale) and a S.G. of 7.4.



Fig. 2 The crystal structure of tungstenite, WS₂. The trigonal-prismatic co-ordination of S atoms around a tungsten atom is shown by dotted lines, the hexagonal unit cell by full lines.

Taken from Krauskopf, 1970

Tungstenite shows a close crystallographic resemblance to molybdenite (fig. 2). The crystal structure is hexagonal and contains a series of double triangular-shaped sulphide layers. The sulphide layers are stacked one above the other, with interlayer van der Waals bonds between adjacent sulphur atoms. The geometry of the hexagonal layers provides interstices which are occupied by tungsten atoms. The tungsten atoms display a trigonal-pyramidal co-ordination geometry with the sulphur atoms of the adjacent layers (Krauskopf, 1970).

Tungsten Oxides (Tungstates)

Two principal isostructural groups of tungstate compounds are known as minerals and are typified by the wolframite and scheelite groups.

The wolframite group contains compounds with fairly small divalent cations such as Fe^{2+} , Mn^{2+} (and occasionally Zn^{2+}) in six-fold co-ordination with $(\text{WO}_A)^{2-}$.

Scheelite contains the larger divalent cation Ca^{2+} in eight-fold co-ordination with $(WO_A)^{-2}$.

<u>Wolframite Group</u>. This group is typified by wolframite, a tungstate of iron and manganese (Fe, Mn) WO_4 . Fe²⁺ and Mn²⁺ substitute for each other in all proportions and a complete solid solution series exists between <u>ferberite</u> (Fe WO_4), and huebnerite (Mn WO_4). Schröcke, 1960 (cited in Krauskopf, 1970) has shown, however, that complete solid solution 'mixing' of the wolframite group is only possible above 400°C. Although quantitatively less important, Zn^{2+} and Mn^{2+} also form a solid solution series producing the mineral sanmartinite (Zn, Mn) WO_4 . Small amounts of Ca and Mg may substitute for Fe²⁺, Mn^{2+} and Zn^{2+} . W may also be replaced by varying amounts of Nb and Ta.

The minerals of the wolframite group are all monoclinic. The monoclinic structure is based on a hexagonal close-packed arrangement of oxygen atoms, with all cations located in octahedral sites. As shown in fig. 3 these octahedra form zigzag edge-shared chains, with the tungsten chains alternating with the 2^+ metal chains.



Fig. 3 The crystal structure of wolframite, (Fe, Mn) WO₄. The view is nearly along the octahedral chain direction parallel to the monoclinic c axis (the a axis is vertical). Shaded octahedra contain W, unshaded octahedra contain (Fe, Mn). The monoclinic unit cell is shown in light lines. Taken from Krauskopf (1970). The wolframite group minerals form prismatic crystals (fig 4) which are commonly tabular or bladed; crystal faces are striated parallel to the c-crystallographic axis. A massive or columnar habit is also quite common. The minerals possess a perfect cleavage which is parallel to the clinopinacoid crystal face. They also have a hardness of 4-4.5 and a S.G. of 7.0 - 7.5 (which is higher with an increasing iron content). Ferberite is black, huebnerite is brown and the streak varies from dark grey to brown. The minerals have a submetallic lustre which is brilliant on cleavage surfaces but dull on other surfaces.





Scheelite

Fig. 4 Wolframite

<u>Scheelite Group</u>. Scheelite is a member of a naturally-occurring isostructural series of the type MXY_4 where Y is oxygen, X may be tungsten or molybdenum, and M may be calcium or lead, thus producing the minerals scheelite (Ca WO_4), stolzite (Pb WO_4), powellite Ca Mo O_4 and wulfenite (Pb Mo O_4). Although commonly occurring as an almost pure chemical species, scheelite is capable of incorporating variable amounts of the powellite (Ca Mo O_4) component to form a complete solid solution series (Hsu & Galli, 1973). This is readily recognised (in the field) by the distinctive change in fluorescent colours from blue when scheelite is pure to yellow when it contains more than a few percent of molybdenum. Solid solution between scheelite and wolframite is limited to a fraction of a percent at ordinary temperatures, but becomes extensive at temperatures over $600^{\circ}C$, (Grubb, 1967 - cited in Krauskopf, 1970).

Scheelite is tetragonal in crystal form. Within the structure Ca²⁺ occur in eightfold co-ordination with the WO₄ tetrahedra (fig. 5). The crystals are usually simple dipyramids (fig. 4) which can be modified by other and less symmetrical pyramidal faces. Scheelite can have a massive, granular, reniform or columnar habit. It possesses a distinct cleavage parallel to pyramidal (III) faces and has an uneven or brittle fracture.

The mineral is usually pale yellow or pale brown in colour and has a vitreous or adamantine lustre. Scheelite has a hardness of 4.5-5 and a S.G. of 5.9-6.1.



Fig. 5 The crystal structure of scheelite, c_{aWO}_{4} . The WO₄ groups are indicated by tetrahedra, and the Ca⁺ions by spheres. The eightfold co-ordination of one Ca⁺ is shown by dashed lines; the tetragonal unit cell is outlined in full lines.

<u>Other Minerals</u>. Three of the most common hydrated oxide minerals from weathering zones have the composition WO_3 : n H₂O i.e. tungstite with n = 1, hydro-tungstite with n = 2, and meymacite with n \gg 2.

3.0 THE ABUNDANCE AND DISTRIBUTION OF TUNGSTEN IN THE CRUST

Tungsten is one of the rarer elements in the earth's crust i.e. it is the fifty fourth most abundant element. Fersman, 1959 (cited in Barabanov, 1971) was one of the first geochemists to recognise that although tungsten is a rare element it is dispersed in crustal rocks. He stated that tungsten not only occurred in minerals such as scheelite and wolframite but was also situated within the crystal lattices of many rock-forming minerals. The average crustal abundance of tungsten was estimated by Taylor, S.R. (1964) at 1.5 ppm. A similar figure (1-1.3 ppm) was suggested by Krauskopf, 1970 (based on compilations of Wiendl's, 1968, analyses), and by Beus, 1972 (1.1 ppm). Abundance of tungsten in rock-forming and accessory minerals

Although there is little available quantitative data on the abundance of tungsten in minerals, acceptable estimates have been made from several sources. Krauskopf (1970) suggests that quartz and feldspar seldom contain more than 2 ppm tungsten and often have less than 1 ppm. In table 3 more precise estimates of average tungsten content in quartz and feldspar are given.

TABLE 3

Minowal	Tungsten content ppm						
	after Ivanova, G.F. (1967)	after Dekate Y.G. (1967)					
Quartz	0.1 - 2.1	0.2					
Microcline	0.9 - 1.5	0.2 - 0.8					
Plagioclase	1.0 - 1.2	0.8 - 2.8					
Biotite	8.0	1.5 - 2.6 (gneisses					
Sphene	16.0	< 7.5 (aplites)					

Tungsten content in some rock-forming minerals

Data and estimations on the average content of tungsten in amphibole, pyroxene and olivine minerals are not available. However, the estimated small total concentration of tungsten in mafic and ultramafic rocks (table 4) indicates that the tungsten content of these minerals is generally less than 1 ppm. Of the abundant minerals in igneous rocks mica appears to commonly contain the most tungsten. Concentrations of 5-50 ppm are common, and muscovite in altered granites adjacent to tungsten deposits contains locally as much as 500 ppm tungsten. Table 3 gives two estimates of the average content of tungsten in biotite. It is possible that tungsten substitutes for the octahedrally-sited aluminium in the muscovite crystal lattice and for aluminium and/or iron²⁺ in the biotite lattice.

Considering the similarity of certain geochemical properties and ionic radii of tungsten, niobium, tantalum, tin, bismuth, iron, titanium, manganese and molybdenum, it is not unexpected to find tungsten in close primary association with minerals containing these elements. Accessory iron oxide and titanium minerals commonly have tungsten values greater than 10 ppm. Table 3

gives two calculated values of the tungsten content in the titaniferous mineral sphene. Niobium and tantalum minerals (e.g. columbite), which typically occur in pegmatites, may contain 1% or more tungsten due to the substituion of W^{6+} for Nb⁵⁺ and Ta⁵⁺ (Rankama and Sahama, 1952). The manganese oxide minerals psilomelane and cryptomelane locally (e.g. in hot spring environments) contain large amounts of tungsten. Tourmaline, a common mineral constitutent of granitic pegmatites, has also been reported (Dekate, 1967) to contain anomalously high values of tungsten. The tungsten content of the tin mineral cassiterite is commonly high (Hosking, 1973). Tungsten may substitute for Sn^{4+} and be incorporated in the cassiterite lattice, or it may occur as exsolution 'bodies' in the tin mineral. The magnitude of the tungsten content in cassiterite, a resistate species, is important in that it could have a profound effect on the nature of secondary dispersion patterns of tungsten (Hosking, 1973). Furthermore, it may provide evidence for the type of primary deposit form which the cassiterite was derived, and this could indicate the nature of the primary tungsten deposits to be expected in the vicinity. As outlined above, compounds of tungsten and molybdenum commonly exhibit isomorphism which sometimes leads to solid solution systems e.g. the scheelite-powellite series.

It is important to be able to distinguish primary elemental/mineralogical associations from secondary associations. For example, a close elemental relationship between W^{6+} and Sn^{4+} may be largely a result of deposition of late Sn^{4+} (cassiterite) around earlier deposited W^{6+} (wolframite) e.g. in the South Crofty Mine, Cornwall, early wolframite-bearing veins are intersected by later cassiterite-bearing veins, (Hosking, 1964 - cited in Hosking, 1973).

Abundance of tungsten in igneous rocks

Hawkes and Webb (1962) state that the average tungsten content of igneous rocks is 2 ppm. A more recent compilation of tungsten analyses carried out by Beus, 1972 (cited in Beus and Grigorian, 1977) suggests that the average is 1.18 ppm.

Although most general estimates of the tungsten content in the main igneous rock types indicate that rocks of granitoid composition contain the highest values, it is striking that the differences are only slight and often only vary by a single order of magnitude. This is an unexpected conclusion when it is considered that most of the known tungsten deposits show a close spatial relationship with igneous rocks of granitoid composition.

An average tungsten value of 1.5 ppm for granitic rocks was given by Vinogradov, 1962 (cited in Barabanov, 1971). This seems to be a representative value and is in agreement with the 2.0 ppm value given by Taylor (1964), and the 1.55 ppm value by Wiendl, 1968, (cited in Krauskopf, 1970). Simon, 1972 (cited in Helson et al., 1978) undertook a detailed analytical study (utilizing the neutron activation method) of the Southern Californian batholith and calculated a somewhat lower average tungsten value of 0.44 ppm. From data on the concentration of tungsten in various granites associated with tungsten mineralisation, Ivanova, 1963 (cited in Štemprok, M, 1977) came to the conclusion that the average tungsten content in unaltered biotite granites does not depend on the presence or absence of tungsten mineralisation.

Beus (1972) suggests that the average tungsten content of igneous rocks of intermediate, basic and ultrabasic composition (without specifying the nature of emplacement of the rocks in question) is 1.2, 0.7 and 0.1 ppm respectively. The data by Turekian and Wedepohl (1961) give an average of 0.7 ppm tungsten for basalts while Vinogradov (1962) gives 1 ppm. For ultrabasic rocks Turekian and Wedepohl (1961) give an average of 0.77 ppm tungsten and Vinogradov (1962) gives 0.1 ppm. Data by Ukharov and Rasskazova, 1974 (cited in Stemprok, 1977) on the concentration of tungsten in ultrabasic rocks largely confirms the data by Vinogradov (1962) and Beus (1972). This data is presented in table

TABLE 4

	Ukhanov and Rasskazova, 1974;	cited in Stemprok	(1977).
District	Rock	W ppm	Number of Samples
Ural	harzburgite	0.1 - 0.5	2
Ural	harzburgite	0.5	1
W. Sayan	harzburgite	0.2	1
E. Sayan	dunite	0.1	1
Tuva	harzburgite	0.2	1
Kamchatka	harzburgite	not. det.	l
Yakutiya	kimberlite	0.9 - 1.3	5
	peridotites	0.3	2
	garnet pyroxenite	0.25	1
	eclogite	0.3	1

Contents of tungsten in ultrabasic rocks (compiled from Ukhanov and Rasskazova, 1974; cited in Stemprok (1977).

If the data in table 4 is representative, it suggests that kimberlite, relative to other ultrabasic rock types, is likely to contain high values of tungsten.

Helson et al. (1978) determined, by the neutron activation method, the tungsten content of a number of volcanic rock types from various tectonic environments (table 5).

TABLE 5

	Sample of Type & Number	Mean	Median	Range
I	Oceanic environment			
	Ocean floor basalts 8 (9) ⁺	0.16(0.23)	0.13(0.15)	0.05-0.29(0.84)
	Subalkaline ocean island basalts 18	0.30	0.28	0.08-0.54
	Alkaline ocean island basalts 10	0.60	0.60	0.18-1.13
	All oceanic rocks** 42	0.43	0.32	0.05-1.81
II	Subduction zone environment			
	Island arc basalts 9 (12)*	0.17(0.27)	0.17(0.19)	0.09-0.34(0.67)
	Island arc andesites 11 (13)*	0.24(0.43)	0.20(0.23)	0.10-0.75(1.49)
	Continental margin basalts 12	0.58	0.40	0.18-1.85
	Continental margin andesites 7	0.96	1.05	0.19-1.74
	All subduction zone rocks** 44	0.52	0.27	0.09-1.85
III	Continental Environments			
	Subalkaline basalts 6	0.36	0.30	0.23-0.53
	Alkaline basalts 24	1.29	1.35	0.17-2.65
	All continental rocks** 38	0.97	0.85	0.01-2.65

Distribution of W (ppm) in basalts and andesite

* Values in parenthesis include samples with anomalous values

- ** These values include felsic differentiates, ultramafics, etc.
 - Taken from Helson et al., 1978.

Helson et al. derived a number of conclusions from this study:

 a) alkaline basalts generally have a higher tungsten content than subalkaline basalts and a greater range of dispersion;

- b) ocean floor basalts and island arc basalts have a similar tungsten content and have amongst the lowest recorded values;
- c) island arc andesites contain less tungsten than subalkaline oceanic island basalts;
- continental margin andesites have a higher tungsten content than their island arc equivalents.

Vinogradov et al., 1968 (cited in Helson et al., 1978) proposed that mafic volcanic rocks have a tendency to have a higher tungsten content than their plutonic equivalents. However, the tungsten content of the basalts analysed by Helson et al. are lower than the tungsten contents of the mafic intrusive rocks determined by Vinogradov et al.

Abundance of tungsten in metamorphic rocks

It is apparent from the dearth of information on the tungsten content of metamorphic rocks that little reliable information is known.

Dekate (1967) analysed various types of metamorphic rocks, of Precambrian age, from India and reported an anomalously high (3.7 ppm) average content of tungsten. Jeffery, 1959 (cited in Krauskopf, 1970) also obtained unusually high (5.83 ppm) average tungsten values from a study of Precambrian metamorphic rocks from Uganda. In table 6 the results of the analyses of Dekate (1967) and Jeffery (1959) are listed. If the tungsten values of the metasedimentary rocks in table 6 are compared with the tungsten values of the comparable, but unmetamorphosed, sedimentary rocks in table 7 an obvious correlation exists between them. Thus tungsten attains conspicuously higher values in rocks derived from clastic sediments than from rocks derived from carbonates. Phyllitic and schistose rocks containing graphite can be seen to contain particularly high average contents of tungsten. This would suggest an initial enrichment of the element in the original graphitic sediment. The high tungsten values for metamorphic equivalents of mafic igneous rocks (Jeffery's "amphibolites", and Dekate's "metabasic rocks") do not correlate, however, with the earlier quoted tungsten values of basaltic rocks, and so are difficult to explain. On the basis of the results of Jeffery (1959) and Dekate (1967) it is highly improbable that a representative crustal average of the tungsten content of metamorphic rocks could be obtained.

TABLE 6

Rock	Number of Analyses	Range	Average	Locality	Refere	ence
Phyllite	19	0.3 - 15.7 ^a	4.7	Uganda	Jeffery	(1959)
Mica schist	5	1.2 - 4.8	2.5	Uganda	п	n
Other schists	5	0.5 - 6.2 ^b	2.7	Uganda	n	n
Pelitic schists			2.6	India	Dekate	(1967)
Graphitic phyllite	40	8 - 86	22.8	Uganda	Jeffery	(1959)
in n			22.2	India	Dekate	(1967)
Quartzite	8	0.2 - 10.4 ^C	3.4	Uganda	Jeffery	(1959)
н			0.5	India	Dekate	(1967)
Marble	3	0.5 - 0.8	0.7	Uganda	Jeffery	(1959)
п.			0.4	India	Dekate	(1967)
Amphibolite	5	2.7 - 6.3	4.0	Uganda	Jeffery	(1959)
Metabasic rocks			6.8	India	Dekate	(1967)
Charnockite			0.6	India	Dekate	(1967)

^a 3 samples with high concentrations omitted : 28.5, 89.9, and 128.0 ppm ^b 2 samples with high concentrations omitted : 12.5 and 25.0 ppm ^c " " " " : 33.8 and 38.6 ppm

Abundance of tungsten in sediments and sedimentary rocks

Table 7 (after Wiendl, 1968) is a compilation of numerous data on the tungsten content of sediments and sedimentary rocks. The data indicates that the average abundance of tungsten in sedimentary rocks is 1 - 2 ppm. Wiendl (1968) notes that the average abundance of tungsten in carbonate rocks, as with meta-carbonate rocks, is significantly less (0.6 ppm) than the average values of clastic sedimentary rocks (1.7 ppm). Beus (1972) confirms the value (0.6 ppm) for carbonate rocks. Wiendl, 1968 (cited in Krauskopf, 1970) points out that tungsten is equally abundant in sandstones and shales and explains this fact by suggesting that the element in sandstones is concentrated in the heavy minerals and/or in the argillaceous matrix.

Consistent tungsten values of 1 - 2 ppm for the analyses of marine sediments, have been recorded by various authors: (Vinogradov, 1962; Turekian and Wedepohl, 1961; Rankama and Sahama, 1952). Significantly higher tungsten - 17 -

Rock	Number	Abundance,	ppm W	Locality	Reference
	of analyses	range	average		
Shales and clave.					
Shale, average			1.8	World	TUREKIAN and WEDEPOHL (1961)
Clays and shales, average			2.0	World	VINOGRADOV (1962b)
Shale, average			1.9	World	HORN and ADAMS (1966)
Clay	Composite of 7,614 samples		1.8 (SW)	Russian platform	VINOGRADOV et al. (1958)
Shales and clays			1.5 (C)	India	Dekate (1967)
Shale, siltstone, mudstone	23	1.2—9.0ª	3.8 (C)	Uganda	Jeffery (1959)
Sandstones:					
Sandstone, average			1.6	World	TUREKIAN and WEDEPOHL (1961)
Sandstone, average			1.6	World	HORN and ADAMS (1966)
Sandstone and quartzite			1—2	World	Реттіјонм (1963)
Sand	Composite of 6,107 samples		1.6 (SW)	Russian platform	VINOGRADOV et al. (1958)
Sandstone			1.5 (C)	India	Dekate (1967)
Ferruginous sand- stone and clay			4.3 (C)	India	Dekate (1967)
Sandstone	5	1.2—5.5 ^b	3.6 (C)	Uganda	Jeffery (1959)
Carbonate rocks: Carbonate rocks, average			0.6	World	TUREKIAN and Wedepohl (1961)
Carbonate rocks, average			0.56	World	HORN and ADAMS (1966)
Limestone and dolomite			0.4 (C)	India	Dekate (1967)
Limestone	4	0.2-0.7	0.48 (C)	Uganda	Jeffery (1959)
Organic sedimentary r	ocks:				
Coal ash	596	40—440	90 (S)	West Virginia	HEADLEE and HUNTER (1953)
Anthracite ash	÷	8—90	(?)	Pennsyl- vania	NUNN et al. (1953)
Carbonaceous			2.5 (C)	India	Dekate (1967)
shale and lignite					
Modern marine sedin	ments:				
Deep-sea clay, average		1—10	38- L	World	WEDEPOHL (1961)
Ocean clay, average			1.1	World	HORN and ADAMS (1966)
Deep-sea sediments	4	3.18-5.35	4.5 (N/R)	Mid- Pacific	Amiruddin and Ehmann (1962)
Red clay	5	16—18	17 (C)	NE Pacific	ISAYEVA (1960)
Bottom sediments	145	5—70	12—20 (C)	Okhotsk Sea	Isayeva (1960)
Clay and sand		15—40	(?)	Near Kamchatka	· Petelin and Ostroumov (1961)
Arenaceous and argillaceous sediments		10—130		Black Sea	Pilipchuk, Volkov (1966)
Deep-sea carbonate		0.1—1.0		World	TUREKIAN and WEDEPOHL (1961)
Ocean carbonate			0.11	World	HORN and ADAMS (1966)
Acid-soluble part of Mn nodules		50—100			Riley and Sinhaseni (1958)

Taken from Krauskopf, 1970

a 2 samples with high concentrations omitted: 15.1 and 50.7 ppm,
b 1 sample with high concentration omitted: 33.8 ppm.

values for deep sea/oceanic sediments are given (table 7) by Amiruddin and Ehmann, 1962, (3.18 - 5.35 ppm) and by Isayeva, 1960, (5 - 70 ppm). Krauskopf (1970) suggests that the high tungsten values of deep sea/oceanic sediments may owe their derivation to a local volcanogenic source. Iron and manganese rich sediments in the vicinity of high tungsten values, in particular, indicate an association to a volcanogenic source.

Dekate (1967) states that tungsten is preferentially concentrated in the B-horizon of certain Indian soils. Furthermore, he notes that the tungsten content of soils in mineralised areas can reach 29 times background values. Holman and Webb, 1957 (cited in Krauskopf, 1970) report the results of a geochemical study of deep tropical soils in Uganda. The results of their analyses indicate a regional geochemical background for tungsten of 4 - 6 ppm with an increase to 6 - 12 ppm in the vicinity of mineralisation.

4.0 THE MIGRATION AND DEPOSITION OF TUNGSTEN

The Migration and Deposition of Tungsten in Crustal Rocks

Concentrations of tungsten ore-bearing minerals (wolframite and scheelite) have been identified in intrusive igneous (acid to intermediate composition), metamorphic, volcano-sedimentary and sedimentary rocks as well as within the supergene zone. In particular a spatial (and commonly assumed genetic) relationship exists between many wolframite deposits and granitic to intermediate intrusive rocks. In order to formulate sound theories on the oreforming processes of tungsten, and hence to hopefully provide guidelines for the search for such deposits, it is, therefore, important to discuss the critical constraints that govern the migration and deposition of tungsten from a melt to an ore-depositional environment.

In crustal rocks tungsten on average occurs only in trace amounts (approximately 0.1 percent). This low concentration (and thus low thermodynamic activity) of the element, therefore, often prevents it (e.g. within a magma) from reacting with other ions etc., and forming phases in which it is a major constituent. In such circumstances tungsten must, therefore, be accommodated as a minor component in early rock-forming minerals, in melts, or in separating fluid phases. In minerals, trace amounts of tungsten may be present as:

- a) occluded zones trapped during rapid crystallization;
- b) interstitial defects in the host mineral lattice;
- c) solid solutions substituting for atoms of the host phases.

The trace amounts of the small highly charged tungsten ion W^{+6} are, however, incompatible with most common silicate mineral lattices and so they either remain in the melt or enter a separating fluid phase. The partitioning of trace amounts of tungsten between minerals and melts may result in changes in trace concentrations of several orders of magnitude during fractional magmatic crystallization or during partial melting processes. This thesis is supported by a slight enrichment of the element in granitic relative to mafic and ultramafic igneous rocks.

A fractionated or partially-melted magma, containing the incompatible tungsten W^{+6} ions would move upward in the earth's crust and be accompanied by the separation of a fluid phase when $P_{TOTAL} < P_{FLUID}$. The coexistence of magma and fluid results in a further partitioning of elements between the two phases. That tungsten partitions into the fluid phase is suggested by the predominant number of tungsten-bearing hydrothermal deposits. Furthermore, Tugarinov and Naumov (1972) state that observations of fluid inclusions from 59 wolframite and scheelite deposits in the USSR indicated that 99 percent of the fluids responsible for mineralisation were liquids and not gases.

Foster, 1973 (cited in Foster, 1978) studied the behaviour of tungsten (experimentally) in aqueous granitic environments and demonstrated that, for the system granite - H_2O :

- i) at $P_{H_2O} = 1000 2000$ bar and temperature at 800-850°C, up to 6000 ppm W can enter a water-saturated granitic melt.
- ii)

the tungsten-content of a granitic melt is probably a function of a_{H_00} in the melt:

WO_X (scheelite) $+ nH_2^{O}$ (magma) $\Rightarrow WO_X \cdot nH_2^{O}$ (magma)

and the equilibrium constant:

$$K = \frac{{}^{a}WO_{X} \cdot nH_{2}O}{{}^{a}_{H_{2}O}}$$

Foster (1973) applied this experimental work to a study of the partitioning of tungsten between granitic melts and aqueous chloride-rich fluids. The components and the experimental conditions that he applied in this exercise, and the results that he obtained, are summarized in table 8 . The results indicate that the partition coefficient (K_w^P) values for 1 M KCl solutions that equilibrated with the synthetic granite Ab 30 Or 30 Q40 reveal a marked concentration of tungsten into the aqueous phase. Furthermore, the $K^{\rm P}_{\!\scriptscriptstyle \rm W}$ is not directly related to temperature. Foster, therefore, demonstrates from this experimental work that tungsten readily enters a chloride-rich aqueous fluid co-existing with a silicate melt compositionally close to the ternary minimum of the system Ab-Or-Q.

TABLE 8

Run No.	Composition of granitic fraction	Molarity of Na2WO4 solution	Molarity of KC1 solution	Temp (°C)	Duration (days)	K _W ^P
KP17	Adamellite	see below*	1	852	5	2,1 x 10 ⁻²
KP4	Adamellite	0,1	1	860	5	1,5 x 10-2
KP18	Adamellite	0,01	1	870±2	16	6.0×10^{-2}
KP23	Ab30Or30Q40	0,01	1	809±4	17	5,7
KP30	Ab30Or30Q40	0,01	1	784±3	18	6,3
KP31	Ab30Or30Q40	0,01	1	850±1	7	3,9
KP33	Ab30Or30Q40	0,01	1	815±1	11	6,8
KP70	Ab30Or30Q40 .	0,01	· 0,5	857±2	10	0,4

The partition coefficient K^P_W of tungsten between siliceous melts and a coexisting aqueous phase ($P_{H20} = 1 \text{ kb}$).

*Run KP17 comprised a 1M KC1 aqueous solution in equilibrium with the leucocratic fraction containing 3900 ppm W as scheelite ground to minus 200 mesh. The calculations of K_W^P were based on 70% fusion (assumed 70 wt %) for KP17 and KP4 and 75% fusion for KP18. $K_{W}^{P} = (moles W/kg fluid)/(moles W/kg melt).$

Taken from Foster (1978)

That tungsten may readily enter a chloride-rich aqueous phase under experimental conditions is borne out by fluid inclusion studies which commonly suggest that chlorine-rich brines were responsible for tungstenbearing hydrothermal mineralisation. Kelly and Turneaure (1970) for example, did a fluid inclusion study of a number of Bolivian tin/tungsten deposits and conclude that the ore-bearing hydrothermal fluids must have been complex

NaCl-rich brines with a low CO₂ content. Furthermore, they report that during the early and main mineralisation of cassiterite and wolframite the salinities of the brines must have reached values as high as 46 weight percent. The salinity, however, became diluted and decreased to only a few weight percent during the deposition of the later ore fluids. Shepherd et al. (1976) studied the fluid inclusions in the Carrock Fell (England) tungsten deposit and also conclude that the fluids responsible for mineralisation were predominantly NaCl-rich brines. The Na/K atomic ratios of the Carrock Fell 'brines' were reported to range from 17 to>114.

The widespread occurrence of fluorine-bearing minerals (fluorite, apatite etc.) with greisen/pegmatite mineralisation suggests that fluorine complexes play an active role in the transport of tungsten. Kelly and Turneaure (1970) have also identified fluorine in many fluid inclusions and state that the fluorine is in sufficient quantity to have transported much of the tin/tungsten as fluor-hydroxyl complexes.

Neumann (1973) predicted the order of thermal stabilities of oxyhalides of the type WO_2 R₂ at all temperatures of geological interest:

$$WO_2 F_2 > W P_2 Cl_2 > WO_2 B_2 > WO_2 I_2$$

This order would suggest that oxyboro- and oxyido-tungsten complexes are relatively insignificant in the transport of tungsten because of their instability. The boron-bearing mineral tourmaline is, however, a common constituent of tungsten greisen/pegmatite deposits. Although it appears that oxyfluoro-tungsten complexes are the most important agencies of tungsten transportation, Foster (1977) states that the chloro-complexes are significantly more important, in most tungsten ore-bearing environments, than the fluorocomplexes. This certainly appears to be true for the Archean hydrothermal tungsten deposits of Rhodesia as fluorine-bearing minerals in this environment are rarely present (Foster, 1977).

That chlorine anions (Cl⁻) are strongly concentrated in the hydrothermal phase is suggested by the work of Koster van Groos and Wyllie, (1969) and Holland, (1972). Stormer and Carmichael (1971) suggest that the concentration of Cl⁻ in the fluid phase is enhanced by a high magmatic a_{sio_2} (a is the activity or concentration). Furthermore, Koster van Groos and Wyllie (1969)

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report that fluorine anions (Fl⁻) are retained by a simple albite melt in the system Na Al Si₃ O_8 - NaF - H₂O. In hydrothermal fluids derived from a melt of the latter composition it is, therefore, probable that $P_{\rm HF} < P_{\rm HCl}$ and so most of the available tungsten in the system would be transported as chloro-complexes.

The ready transport and ease of mobility of tungsten in chloride solutions at sub-magmatic temperatures has been demonstrated by Ravich and Yastrebova, 1961, and Foster 1973 (cited in Foster, 1977). However, the Russian workers used high density chloride brines in their experiments which are not applicable to many ore-bearing environments. Foster (1973) demonstrated that scheelite solubility, in dilute aqueous KCl solutions buffered with the solid phase assemblage K-feldspar-muscovite-quartz at 1000 bar, increases almost exponentially from approximately 200 ppm at 350°C to more than 1000 ppm at 550°C (fig. 6). Furthermore, the solubility of scheelite is a function of $P_{\rm HCl}$ which is buffered by the silicate minerals according to the reaction:

$$^{3}/_{2}$$
 KAl Si₃ O₈ + H⁺ = $^{1}_{2}$ K Al₂ Si₃ O₁₀ (OH)₂ + 3 Si O₂ + K⁺

If this equation applies to a natural situation then it may represent the high temperature alteration process as involved in greisenization.



Fig. 6 Scheelite solubility in aqueous KCl solutions at 1,000 bar (A) and 2,000 bar (B) total pressure and buffered by the assemblage quartz—K-feldspar—muscovite. Taken from Foster (1977).

The ability of tungsten to become mobile, and hence its ability to migrate, in the partitioned fluid phase depends not only on the solubility of its compounds but also on their stability in specific physicochemical environments. In order to be transported over a considerable distance a migrating tungsten compound, or dissociated ionic species of the element, must not react with certain components in the solution otherwise insoluble minerals may be formed. An aqueous transporting medium, from source to site of deposition, must possess diverse physicochemical characteristics (Beus, 1977). Differences in chemical characteristics of the fluid medium are usually expressed by a general tendency (from source to site) toward an increase in alkalinity as a result of interaction with (alkali mineralbearing) enclosing rocks. Tungsten belongs to the amphoteric group of elements. This group of elements are characterized by average values of electronegativity ranging from 190 to 270 k. cal./g - atom, which enables them to exhibit both alkaline and acidic properties depending on the composition of the enclosing solutions. This ability, therefore, enhances the mobility of tungsten in that it enables the ion (W^{+6}) to form stable complex compounds which can be transported through solutions of different chemical composition. The general formula of a complex tungsten compound could be given schematically as:

where B is an alkaline element (k, Na, Ca); and A is the electronegative added (Cl, F, B, I). This complex would dissociate in aqueous solutions accordingly:

$$\mathbf{B}_{m} \begin{bmatrix} \mathbf{W} \mathbf{A}_{n} \end{bmatrix} \rightleftharpoons_{m}^{\mathbf{B}^{+}} + \begin{bmatrix} \mathbf{W} \mathbf{A}_{n} \end{bmatrix}^{m-}$$

In order to obtain some idea of the behaviour of mobile tungsten complexes in aqueous solutions whose composition is continually changing, it is worthwhile considering certain properties of the complex compounds, inferred from the law of mass action. The stability of complex ions in a solution is determined by the value of the so-called instability constant of the complex, C_{in}, which is expressed by the equation:

$$\frac{a_{M}}{a_{MA}} = C_{in}$$

where ^aMA_n is the activity of a complex tungsten ion on the solution, ^aM is

the activity of the dissociated complexing tungsten cation; and a^n_A is the activity of the added anions (Cl⁻, Fl⁻).

Assuming an invariable value for the instability constant C_{in} , an increase in the activity of the added anions relative to ^aM in the solution, contributes to the stability of the complex, by suppressing the activity of the dissociated ions of the complexing tungsten metal. Consequently, a medium with an increased activity of the added anions is the most favourable environment for the transport of the tungsten complexes in the aqueous (e.g. hydrothermal) medium. Accordingly, a decrease in the activity of the added anions in the solution, relative to ^aM, leads to the decomposition of the tungsten complex radical $\begin{bmatrix} M & A_n \end{bmatrix}$ because of the necessity of a simultaneous increase in the activity of the dissociated cations of the metal ^aM. A situation that could lead to such instability would be if a solution that contained fluoro-tungsten complexes came into contact with carbonate rocks. This would lead to the removal of fluorine as the solid phase (fluorite, CaF₂) resulting in an increase in the activity of the tungsten radical which would then become unstable and be precipitated.

Consequently, decomposition of tungsten complexes during processes involving changes in the composition of the aqueous solutions, which in turn may determine the possibility of isolating the complexing tungsten metal in a solid phase, may generally be caused by two factors:

- a) reaction of the dissociated ions of the complex with certain components of the solution;
- b) hydrolysis of the complex as a result of an increase in the pH of the solution.

It was originally thought that tungsten was transported, by a hydrothermal/pegmatitic solution, from a melt to a site of deposition as a single volatile tungsten halide or oxyhalide (e.g. WF_6 , WCl_6 , $WOCl_4$). However, volatile halides are very unstable, and they readily hydrolyse, especially when changes in pH values occur i.e. $WF_6 + 3H_2O \rightleftharpoons WO_3 + 6$ H F. Ivanova (1966) computed equilibrium constants between volatile tungsten halides/oxyhalides and the principal components of tungsten-bearing solutions (water, alkali, metals, silica) for pressures of one to 1000 atom, temperatures from 25-500^oC and pH from 1 - 10. These computations showed that the partial pressures of WCl_6 , WF_6 , $WOCl_4$, WOF_4 , WO_2Cl_2 and WO_2F_2 are very low under these conditions (10⁻¹¹ - 10⁻²³ atm), and bearing in mind that these compounds are very unstable, it must be concluded that they cannot be transported in significant quantities either in the liquid or gas phase.

Uncertainty, however, remains as to the particular ionic complexes or compounds of tungsten that play the principal roles in transportation at different ranges of temperature, pressure and composition. Krauskopf (1970) suggests that in slightly acid conditions tungsten may be carried in the presence of Ca^{2+} , Fe^{2+} and Mn^{2+} as the simple tungstate WO_A^{2-} , or at a higher temperature as the relatively undissociated compounds H2 WO, and Na, WO,. Foster (1977) tentatively suggests that the main aqueous tungsten species is in the hydrated form of molecular H2 WO4. Furthermore, Foster suggests that at sub-critical temperatures (i.e. $< 400^{\circ}$ C and P_{H,O} < 1000 bar) ionic tungsten species will be dominant although WO₄²⁻ may also be stable in concentrated brine solutions above 350-400°C. Another possible form of tungsten transportation in silica-containing solutions could be the heterpoly-tungsten acids, particularly H₈ Si (W₂O₇)₆. Gundlach 1967 (cited in Barabanov, 1971) has shown that the neutralization of acid solutions of this compound (H_{g} Si (W207);) at 'ordinary' temperatures (concentrations : 1.4% WO2 and 0.12 M Ca^{2+} , Fe^{2+} , or Mn^{2+}) gives a precipitate of Fe WO₄ at pH 5.9, Mn WO₄ at 6.7, and Ca WO_A at 7.4 (fig. 7) Their experiments also show that the compound is stable at least to temperatures of 300°C.



Fig. 7 Order of separation of tungstates in neutralization of solutions of silico-tungstic heteropolyacids with NaOH solution (after H. Gundlach, 1967).

1.
$$H_8[si(W_2O_7)_6]$$
; 2. $H_8[si(W_2O_7)_6] + Fe^{2+};$
3. $H_8[si(W_2O_7)_6] + Mn^{2+};$ 4. $H_8[si(W_2O_7)_6] + Ca$

Taken from Barabanov (1971)

Foster (1978) has constructed a flow diagram to depict the behaviour of tungsten in a cooling chloride-rich fluid (fig. 8). The data on which this diagram is based has been drawn from various sources:

- a) field and experimental observations of the Richardson's Kop (Rhodesia) hydrothermal tungsten deposit;
- b) theoretical observations on the stability of,
 - i) H₂WO₄ (Foster, 1973)
 - ii) polytungstates (Kepert, 1962; Aveston, 1964; Ivanova and Khodakovskiy, 1968; Barabanov, 1971).

 $pH > neutral : [WO_2]_{a0}^{2-} + [c_a]^{2+} \longrightarrow SCHEELITE$ pH~neutral. : [HW6021]=+ [Fe2+/Mn2+]= WOLFRAMITE pH < neutral. : $\left[H_3 W_6 O_{21}\right]_{aq}^{3-} + \left[F_e\right]_{aq}^{2+} \longrightarrow FERBERITE$ SCHEELITE decreasing [H,WO] ag WOLFRAMITE *emperature* Fe - sulphides Fluid pH increases. Hydrolysis and hydration. Nat/K* increases. become effective WOLFRAMITE Fe - sulphides low for WCI6 Jag SCHEELITE [WO3. nH20] melt [W] rock

Fig. 8

Foster (1978) however, admits that this flow diagram is probably an oversimplification for what geologically would be a complex interplay of the parameters indicated. Foster suggests that four inter-related parameters in particular, will largely control the transport, and the order and site of deposition, of wolframite and/or scheelite. The critical parameters would be temperature, fo_2/f_{s_2} , $a_{ca}^{2+/}$ ($a_{Fe}^{2+} + Mn^{2+}$), and pH. That Eh has not been included as an important parameter can probably be explained by the fact that the solubility characteristics of tungsten, unlike many other metals, are not complicated by the possibility of reduction to a lower form of valence. This is because redox potential values in most environments within the crust are believed to rarely fall low enough to reduce the stable tungsten valence +6 (Krauskopf, 1970). The experimental data, on which the flow diagram is based, indicates (Foster, 1978) that a maximum deposition of tungstate minerals should occur between the temperature range 350 - 450°C. Foster, however, considers that hydrothermal fluids are unlikely to be saturated with tungsten at these temperatures. He suggests that deposition is probably restricted to sub-critical temperatures where P_{HC1} is relatively low, HCl is partially dissociated, and ionic tungstates exist in solution. Table 9 lists various geothermal results indicating depositional temperatures of a number of tin/tungsten deposits and illustrates the wide depositional temperature range (200 - 530°C) for scheelite/wolframite mineralisation. This would indicate that temperature is not a critical causative factor in the deposition of tungsten minerals.

With respect to the chemical environment of tungsten migration, it is necessary to stress the role of the enclosing rocks as they are responsible for changes in the chemical composition of the mobile aqueous solutions and for the progress of the chemical reactions within the solutions.

Highly siliceous rocks, such as quartzite or sandstone, generally do not cause major changes in the composition of the aqueous solutions, and therefore, do not favour rapid decomposition of the mobile tungsten complexes or deposition of tungsten minerals. When these rocks interact with alkaline solutions, this sometimes results in feldspathization.

Siliceous and alkaline igneous and metamorphic rocks, relatively enriched with strong bases (Na, K, Ca), which interact with the mobile aqueous solutions, are generally the sources of bases for the solutions. The extent of the removal of bases from rocks is determined by the relative activity of TABLE 9

Fluid inclusion temperatures for tin and tungsten deposits

Source	Mineral .	Method ¹	Temperature °C	Locality	Reference
Wolframite – cassiterite – quartz,	Quartz	Н	295 - 510 PS	Central and	Kelly and Turneaure (1970)
Wolframite – cassiterite – quartz, plutonic setting.	Quartz Cassiterite	H H	390 - 480 PS 225 - 530 PS 338 - 510 PS	Cordillera Real, Bolivia.	Kelly and Turneaure (1970)
Tourmaline – cassiterite – quartz.	Tourmaline Cassiterite	HD HD	390 P 390 P	St. Austell, Cornwall. St. Austell, Cornwall.	Smith (1949) Smith (1949)
Quartz – chalcopyrite – quartz.	Quartz Quartz Chalanguaitz	HD HD	370 P 345 P	St. Austell, Cornwall. South Crofty, Cornwall.	Smith (1949) Smith (1949)
Questa esseritarita	Wolframite	D D H	260 P 260 P	South Crofty, Cornwall.	Smith (1949) Smith (1949)
Quartz – cassiterite Quartz (post-cassiterite)	Quartz Quartz Cassiterite	н	300 - 314 250 - 390	Cornwall.	Sawkins (1966) Bradshaw and Stovel (1968)
Quartz – chalcopyrite Quartz – fluorite – sulphides	Quartz Quartz and fluorite	H H	245 — 310 260 – 410 PS	Cornwall. Rex Hill Mine,	Bradshaw and Stoyel (1968)
Greisen and vein wolframite	Quartz, fluorite,		205 – 302 PS	Tasmania. Transbaykaliya,	Groves et al. (1970) Naumov and Ivanova (1971)
and cassiterite deposits Quartz – wolframite vein	beryl and cassiterite Fluorite	H H	350 – 375 PS	U.S.S.R. Kazakhstan, U.S.S.R.	Naumov and Ivanova (1971)
Quartz – wolframite – cassiterite vein.	Quartz, cassiterite and beryl	н	277 – 314 PS	Chukotka, U.S.S.R.	Naumov and Ivanova (1971)
Greisen and vein deposits	Quartz, topaz, cassiterite, fluorite, beryl and huebnerite	н	205 – 400 PS	Mongolia.	Naumov and Ivanova (1971)
Quartz – wolframite	Quartz and	HD	280 – 360 PS	Erzgebirge.	Naumov and Ivanova (1971)
Greisen	Wolframite, quartz	нр	280 - 330	Transbaykaliya, USSR	Sushchevskaya and
Quartz – feldspar – huebnerite veins Quartz – huebnerite – scheelite veins	2 2	HD HD	260 - 390 ?PS 230 - 420 ?PS	Buluktay, U.S.S.R. Buluktay, U.S.S.R.	Kosals and Dmitriyeva (1973) Kosals and Dmitriyeva (1973)
Quartz – huebnerite – sulphide veins Various	2	HD HD	260 - 340 ?PS 200 - 450 ?PS	Buluktay, U.S.S.R. Various.	Kosals and Dmitriyeva (1973) Tugarinov and Naumov (1972)

¹H – homogenization temperatures D – decrepitation temperatures

 ^{2}P - pressure correction applied S - salinity correction applied

the acids in the aqueous solutions. If the acidity of the solutions is high, this may lead to the greisenization of the rocks. The interaction of acidic hydrothermal solutions with rocks of this general composition, therefore, leads to a gradual increase in the alkalinity of the solutions. This has a negative effect on the stability of the tungsten complexes thus contributing to the precipitation of tungsten ore minerals (usually wolframite) from solution.

Basic and ultrabasic igneous rocks are low in alkalis (K, Na) but are relatively rich in Ca. Ca, as discussed earlier, reacts with fluorine (F1⁻) to produce fluorite. Therefore, Ca-bearing rocks could have a decomposing effect on fluoro-tungsten complexes carried by the aqueous fluids. Basic and ultrabasic rocks, therefore, may be responsible for tungsten ore mineralforming reactions which may result in accumulations of the ore minerals.

Carbonate rocks which are rich in Ca promote important changes in the composition of solutions and lead to the neutralization of the acid solutions interacting with them, especially if these solutions contain Fl. The zone of interaction (skarn) of hydrothermal fluids with carbonate rocks is often a well-defined reaction barrier where mobile tungsten complexes decompose and precipitate the tungsten ore mineral scheelite. If the ore-bearing solutions, however, are alkaline in composition rather than acidic, the calcium-bearing carbonate rocks may not in themselves be the principal factor in the deposition of tungsten ore minerals (Barabanov, 1971). Ryzhenko, 1965 (cited in Barabanov, 1971) demonstrated that, if tungsten is transported in alkaline solutions, the precipitation of tungsten in the form of scheelite requires a decrease in pH of the solutions to 6 or 7. The carbonate rocks themselves cannot totally account for the decrease in pH. The alkalinity of the solutions is decreased, during skarn formation, mainly by fixation of the alkali elements (K, Na) present in the solutions as a result of sericitization of plagioclase and amphibolitization of pyroxenes (Ryzhenko, 1965). At the same time calcium, liberated from minerals such as calcic plagioclase, reacts with available tungsten complexes to form, and precipitate, scheelite.

The Behaviour of Tungsten in the Supergene Zone

Most geochemical investigations related to tungsten dispersion and migration in the supergene zone are devoted to the mechanical and chemical properties of the main ore minerals scheelite and wolframite, and their alteration products.

It is generally accepted that scheelite and wolframite minerals are fairly insoluble in the pH range (about 7-9) of most surface waters. That these minerals also possess high values of S.G. suggests that they should be capable of accumulating as placer deposits. However, large alluvial concentrations of tungsten minerals are very uncommon. Eluvial deposits of tungsten, formed by in-situ weathering and concentration, are quantitatively and economically more important than alluvial deposits. The scarcity of alluvial tungsten placer deposits is usually explained by the brittleness and good cleavage of scheelite and wolframite minerals which leads to their disintegration into very fine particles which become widely dispersed during sedimentary processes. Varlamoff (1971) states that the mineral alteration products of scheelite and wolframite 'strongly affect the mechanical resistance' of these primary tungstates, so that they cannot survive for more than several hundred metres of alluvial transportation. According to Varlamoff, the products of alteration can be dispersed and transported for distances of tens of kilometres.



Fig. 9 The behaviour of tungsten minerals in the zone of weathering. Taken from Hosking, 1973, (after Hosking, 1970)

In fig.9 Hosking (1973) attempts to depict the outline of the behaviour of tungsten minerals in the zone of weathering. Under acidic surface water conditions, particularly in environments of weathering sulphide deposits, scheelite and wolframite minerals are slowly decomposed. It is in the form of these products of decomposition, rather than as the primary minerals, that the dispersion and migration of tungsten begins in the supergene zone (Varlamoff, 1971). Under acidic surface water conditions scheelite is commonly considered to be more soluble than the minerals of the wolframite group even though the decomposition. With reference to the thermodynamic data given by Urusov et al. (1967), Krauskopf (1970) suggests that for the reaction:

 $Me WO_4 + 2H^+ \implies Me^{2+} + WO_3 + H_2O$

where Me²⁺ may be Ca, Mn or Fe,

- alteration of scheelite to tungstite should take place in solutions near neutrality;
- ii) alteration of huebnerite to tungstite should take place in slightly acid solutions; and
- iii) alteration of ferberite to tungstite should take place in strongly acidic (pH range 2-3) solutions.

According to Krauskopf (1970) the above conclusions are in accord with observations on the solubility of the three tungstate minerals obtained under both natural and laboratory conditions. Apart from tungstite other forms of tungstic acid, formed during the alteration of primary tungstates, include hydrotungstite and ferritungstite. All three secondary minerals are commonly inconspicuous, and difficult to identify, especially when they are mixed with limonite and jarosite. If Pb and Cu sulphides are present the secondary minerals stolzite and cuprotungstite may form.

Dekate (1967) suggests that the type of tungsten alteration product depends largely on climate. He suggests that under semi-arid conditions the main (i.e. most stable) alteration products should be anthoinite, cuprotungstite, and ferritungstite; whereas under hot, humid, tropical conditions the dominant alteration products should be tungstite and hydrotungstite. Varlamoff (1971) states that in the zone of weathering around tungsten deposits, particularly in hot, humid, tropical environments, tungsten alteration minerals may represent as much as 50 - 75 percent of all tungsten-bearing minerals.

The dispersion of tungsten in near-surface solutions is shown by the existence of "haloes" in soils around tungsten deposits. Tungsten haloes, however, are much narrower than associated molybdenum haloes. This could be explained by differences in mobility of the two elements and their complexes. However, Krainov et al. (1965) explain the limited amount of dispersion and subsequent secondary enrichment of tungsten by the trapping of most dissolved tungsten by adsorption on Fe and Mn oxides.

Szalay and Szilagyi (1967) have demonstrated that when waters carrying vanadate and molybdate anions come into contact with peat, the peat reduces them to cationic forms. The cations so produced are then available for adsorption by a cation-exchange process. Eskenazy suggests that such a mechanism may explain the commonly recorded high values of tungsten for coal and peat deposits, considering the similarity of tungsten to molybdenum.

5.0 WORLD DISTRIBUTION OF TUNGSTEN DEPOSITS

Most of the major tungsten deposits of the world occur near the continental margins of countries that border the Pacific Ocean. Such countries include China, North and South Korea, Thailand, eastern Australia and the western part of North America and Canada. Other important tungsten deposits occur in the U.S.S.R., Brazil, Portugal, France and Austria. World tungsten reserves and identified resources are indicated in table 10 ; and the world tungsten production (concentrates) for 1973, with estimated production capacities, are given in table 11 . From tables 10 and 11 it is clear that China is by far the world's major tungsten producer and possesses the largest reserves of the metal.

Tungsten deposits are not uncommonly found in the same areas, and even in the same orebody, as economically important concentrations of tin, molybdenum, antimony and bismuth minerals. According to Hosking (1973) all the tin provinces known to him contain tungsten-bearing deposits, and the overwhelming majority of the tin provinces contain economically exploitable concentrations of tungsten. However, the degree of importance of the tungsten deposits in the tin provinces varies enormously. For instance the tin fields in the Northern

TABLE 11

	Reserves	Other 1	Total	
orth America:				
United States	238	720	958	
Ceneda 2	476	700	1,180	
Mexico	2	5	7	
Other	2	5	7	
Total 2	718	1,430	2,150	
outh America:		1	-	
Bolivia	87	185	272	
Brazil	40	95	135	
Other	3	5	8	
Total	130	285	415	
urope:				
France	1	5	6	
Portugal	22	65	87	
U.S.S.R.*	350	700	1,050	
Other	з	5	8	
Total 2	376	775	1,150	
nca	-		- In-	
Rhodesia, Southern	10	10	20	
Rwanda	5	5	10	
South-West Alrica, Territory of	3	5	8	
Zaire, Republic of	3	5	8	
Other	- 2	5	7	
Total	23	30	53	
sia	1.0	1.0		
Burma	70	155	225	
China. People's Republic of	2,100	4,000	6,100	
Japan	5	10	15	
Korea				
North *	250	300	550	
Republic of	101	175	276	
Malaysia	32	75	107	
Theiland	40	35	75	
Total ²	2,600	4,750	7,350	
ceania:				
Australia	76	210	286	
New Zealand	1	5	6	
Total	77	215	292	

World tungsten production, 1973, and capacity, 1973, 1974, and 1980 (Thousand pounds of tungsten content)

Capacity Production in 1973 1973 1974 1980 * North America: United States 7.575 9 200 9 300 9 600 4,750 4,900 Canada 4,594 4,650 767 Mexico 900 900 500 600 700 Other 348 Total 1 13,284 15,300 15,600 16,100 - ----South America: Argentina Bolivia 155 200 250 300 4,815 4,950 5,000 5,100 Brazil 2.097 2 700 2 800 3 000 1,753 1,900 1,950 2,080 Peru Total 1 8.820 9.750 10,000 10.500 Europe: Austria 100 200 400 1,750 1,950 France 1,532 1,600 -----Portugal 4.000 4.000 3,333 1,200 789 1,200 1,200 Spain Sweden U.S.S.R.* 600 570 800 16,500 16,500 16,300 16,500 United Kingdom . 10 15 15 Total 1 22.528 24.000 24,400 25.000 Africa: Rhodesia, Southern 330 450 350 200 700 700 750 Rwanda 570 South-West Africa, Territory of 49 100 50 40 Zaire, Republic of 240 300 300 531 700 700 700 Other 6 20 20 20 2.270 2 120 2.010 Total 1.735 Asia Burma 1,102 1,200 1,250 1,400 China, People's Republic of * 17,600 17,600 17,600 17,600 India 2/ 30 40 50 2,750 Japan 2.072 2,500 2,500 Korea: North * 4,800 4.800 4.800 4,750 5,100 200 4,965 5,000 5,000 15 100 150 5,736 6,500 5.500 3.000 Total 1 36,264 37,700 36,800 34,900 Oceania; 3,800 Australia 2.687 3,000 3,400 New Zealand 10 20 30 Total 2,689 3,010 3,420 3.830 World total 1 85,320 91,900 92,300 92.300

* Estimate. 1 Derived from U.S. Geological Survey Professional Paper 820, 1973 (5). 2 Data may not add to totals shown owing to rounding.

> * Estimate. * Data may not add to totals shown due to rounding.

Transvaal and in S.W. England have produced little, if any, tungsten in the past. It should be noted, however, that potential may still exist in such tin-fields for the discovery of economically important tungsten deposits. For instance in Devon, S.W. England, the Hemerdon wolframite deposit has recently been evaluated and it is now thought to have important economic value. Hosking (1973) reports that the tin-fields of China and the U.S.S.R. contain considerable deposits of both tin and tungsten. Within mixed tin/tungsten provinces the
distribution of tungsten may, or may not, broadly coincide with that of tin. In the S.E. Asian tin province, for example, the closest associations of tin and tungsten are to be found in Tavoy and the Shan States of Burma, and the immediately adjacent parts of Thailand. The Indonesian parts of the tinbelt, however, are markedly deficient in tungsten, with only one small producer known (Hutchinson and Taylor, 1978).

Tin/tungsten provinces are spatially, and probably genetically, related to zones of batholith intrusions within orogenic belts. For instance the Chinese and Bolivian tin/tungsten belts are aligned along batholiths of Mesozoic age.

The age of rocks associated with tungsten deposits ranges from Precambrian to Tertiary. However, it is evident that the majority of economically important tungsten deposits occur in rocks of Mesozoic to Tertiary age. One possible explanation for this is that deposits have a greater probability of preservation in the younger rocks than in the older ones. The tendency of many tungsten deposits to be preferentially located in the highest parts of intrusives implies a greater susceptibility to erosion and, therefore, a lesser chance of survival in the older rocks.

Schuiling (1967) has compiled a number of maps (e.g. fig.10) showing the distribution patterns of tin occurrences in Europe, Africa, N. America and S. America. Considering the common association of tungsten and tin deposits, these maps may have significant value in exploration for tungsten as well as for tin deposits. For example, the tin/tungsten deposit of Abu Dom, Sudan (Almond, 1967), which lies within a logical extension of one of Schuiling's tin belts, was discovered after the preparation of the maps in question.

The position of tin-tungsten-fluorite deposits in the framework of the theory of plate tectonics has been considered by Mitchell and Garson (1972). They suggest that, within the circum-Pacific region, such deposits occur in the vicinity of former destructive plate margins and were emplaced during the opening of marginal basins above migrating Benioff zones.



Fig. 10 Position of Tin-belts on a reconstruction of the continents.

Taken from Schuiling, 1966 Continental fit after Bullard et. al. (1965)

TYPES OF TUNGSTEN DEPOSIT

Economic concentrations of tungsten minerals can occur in various types of mineralised environments. A knowledge of these environments and an appreciation of the geological characteristics of the different types of tungsten deposit may be useful when searching for and evaluating such deposits. Certain types of tungsten deposit are more commonly of economic importance than others. A greater understanding of the characteristics of the different types of deposit may, therefore, be useful in the assessment of the economic potential of a mineralised environment or of an individual deposit.

6.1 Pyrometasomatic/Skarn¹ Tungsten Deposits

These deposits are a major source of tungsten which is predominantly recovered as the mineral scheelite. Scheelite deposits of this type invariably occur in carbonate-rich rocks that have been metasomatically altered by material derived from an intrusive mass of granitoid composition. Skarn tungsten deposits are, therefore, found to be spatially related to the contact zones of granitoid intrusive bodies.

It is generally assumed in the literature that the tungsten in these deposits has been derived, as a late-stage residual product, from the granitic magma. However, a pre-existing concentration of tungsten in the intruded country rocks should not be discarded as a possible source of the metal. The heat generated from an intrusive body enables metamorphic (isochemical) and metasomatic reactions, and recrystallization, to take place in the contact zone of the intruding body. It must be noted, however, that contact metamorphism alone cannot give rise to tungsten mineralisation, for at least part of the essential material that forms the deposit is introduced extraneously from the magma.

Footnote: 1. The term 'skarn' as applied in this review refers to hightemperature metasomatic replacement of carbonate-rich rocks by the transport of materials from a cooling plutonic body (usually of granitoid composition). The term 'tactite', often used in the literature, was introduced by Hess (1919) and is usually restricted (especially in the N. American literature) to skarns containing the tungsten mineral scheelite.

6.0

As mentioned earlier intruded rocks rich in Ca²⁺, such as limestones, dolomites and rocks of ultrabasic composition, tend to be particularly 'reactive' on contact with magma, and aqueous solutions, derived from an intruding granitoid pluton. Furthermore, reactions involving the release of Ca²⁺ and CO₂ from the 'reactive' rocks can lead to the decomposition and precipitation of tungsten complexes carried by the intrusive material. The Ca^{2+} and CO_{2} of the 'reactive' rocks react with, and are metasomatically replaced by, elements such as Si, Al and Fe during skarn formation. Skarn formation takes place, therefore, within an alteration halo, or aureole, in the peripheral margin immediately adjacent to the plutonic body and along minor aphophyses (dykes, sills etc.) of the intruding mass. Skarn formation within the country rock itself is commonly referred to as 'exoskarn' and that within the outer margin of the plutonic body as 'endoskarn'. Tungsten mineralisation has been recognised within both of these skarn types. Deposits occurring in 'exoskarn' tend to be the more 'productive' however. Hydrothermal veins that lead from a pluton and transect the country rocks are often responsible for local skarn formation and tungsten mineralisation. Hosking (1973) is of the opinion that, "many so-called pyrometasomatic/skarn deposits are simply hydrothermal tungsten deposits which happened to have developed largely by metasomatic processes, in calc-silicate hornfels".

The mineralogical character of the skarn deposit must depend in part on the composition of the intruded rock and in part on the nature and amount of the components contributed by the invading granitic magma. Perry (1969) has studied the effects of contact metamorphism/metasomatism on the formation of skarn zones at the Christmas porphyry copper deposit in Arizona. Perry identified, and outlined in table 12 , a number of contact metamorphic/metasomatic mineral assemblages that relate to the alteration of rocks of different original composition. Table 12 could serve as a guide to comparable alteration zones associated with skarn tungsten deposits. Perry notes, however, that the assemblages outlined in table 12 are not diagnostic of any one of the three contact metamorphic facies which, in order of increasing temperature, are: albite-epidote hornfels, hornblende hornfels, and pyroxene hornfels. TABLE 12

Outline of Contact Metamorphic Mineral Assemblages

- I. System CaO-MgO-SiO₂-CO₂-H₂O
 - A. Siliceous Rocks-Excess SiO₂
 - 1. Dolomitic
 - a. Tremolite-quartz
 - b. Diopside-quartz
 - 2. Cherty Limestone
 - a. Wollastonite-quartz
 - b. Quartz
 - B. Calcareous Rocks-Deficient SiO2
 - 1. Dolomite
 - a. Dolomite
 - b. Tremolite-calcite
 - c. Tremolite-dolomite-calcite
 - d. Tremolite-dolomite
 - e. Diopside
 - f. Diopside-calcite
 - g. Diopside-wollastonite-calcite
 - h. Brucite-calcite
 - 2. Linnestone
 - a. Calcite
 - b. Calcite-wollastonite
 - 3. Limestone-Fe2O3. Al2O3 impurity
 - a. Wollastonite-garnet-calcite
 - b. Diopside-garnet-calcite
 - C. Shales and Siltstone
 - 1. K₂O Absent
 - a. Diopside-quartz
 - b. Diopside-wollastonite-quartz
 - c. Diopside-garnet
 - 2. K₂O Present

- -

- a. Diopside-phlogopite-quartz
- II. System K2O-(Al2O3,Fe2O3)-(FeO,MgO)-
 - SiO₂-H₂O
 - A. Muscovite-quartz
 - B. Andalusite-muscovite-quartz \pm orthoclase
 - C. Andalusite-biotite-quartz ± orthoclase
 - D. Biotite-quartz
 - E. Phlogopite-quartz-orthoclase

Taken from Perry (1969)

Fig. 11 (after Perry, 1969) illustrates the development of skarn formation, and associated mineralisation, in favourable lithological horizons at the Christmas mine. It can be seen from fig. 11 that skarn development in certain 'favourable' lithological units extends outward from the contact for greater distances than other less 'favourable' units. The development of Mg-skarn, for instance, varies from a maximum of 1,000 feet in the Martin Formation to a minimum of just over 150 feet in part of the Naco Formation.



Fig. 11 Generalized stratigraphic relationships Christmas mine ore bodies: South side.

Taken from Perry (1969)

Apart from the characteristic calc-silicate minerals (listed in table 12) of skarn zones other typical, commonly associated, mineral species include: magnetite, molybdenite, gold, arsenopyrite, chalcopyrite and pyrrhotite.

In many tungsten skarn deposits scheelite occurs as part of a solid solution series with the molybdenum mineral powellite $(CaMoO_4)$. Hsu and Galli (1973) have studied various tungsten deposits and suggest that combined mineralogical and chemical studies indicate that, in general, the scheelite-powellite solid solution series is depleted in the powellite component when molybdenite is present in the deposit. This suggestion is supported by the thermodynamically-based phase diagrams, figs. 12 and 13, which show that there is a wide overlapping field of stability for both scheelite and molybdenite in terms of oxygen and sulphur fugacities (fo_2, fs_2) . However, contact metasomatic

-

environments of tungsten mineralisation are commonly accompanied by diverse values of fo_2 and fs_2 , due mainly to the varied nature of the intruded lithologies (Hsu and Galli, 1973). For a given concentration of molybdenum in the ore fluid, different mineral assemblages can develop as a consequence of different physical-chemical conditions. Hsu and Galli suggest that an oxidizing environment of mineralisation (high fo_2 and/or low fs_2) favours the formation of powellite-rich scheelite, whereas a more reducing environment (low fo_2 and/or high fs_2) will produce a purer scheelite along with molybdenite.



Fig. 1.2 Stability relations of some molybdenum compounds as functions of f_{0_2} and f_{8_2} at 800°K and 2000 bars. Field boundaries of iron compounds are located for reference. The dashed lines are inferred field boundaries for powellite. Normal crustal condition in terms of f_{0_2} and f_{8_2} is also shown. A very narrow stability field for $M_{0_2}S_3$ between Mo and M_0S_2 is omitted.



FIG. 13 Stability relations of some tungsten compounds as functions of f_{0_2} and f_{s_2} at 800° K and 2,000 bars. Field boundaries of iron compounds are located for reference. The dashed lines are inferred field boundaries for scheelite. Stability field of molybdenite in terms of f_{0_2} and f_{s_2} from its association with iron oxides and iron sulfides is also shown.

Tungsten mineralisation in skarn formations cannot occur in the absence of an efficient 'plumbing system', as large amounts of material have to be transported to and from the centre of deposition (Hosking, 1973). The physical and chemical properties of the 'contact' rocks, <u>at the time when mineralisation</u> is a possibility, will provide important constraints on the efficiency of this plumbing system. According to Perry (1969), "skarn formation is not regarded as a ground preparation stage that increases the permeability and porosity for later mineralisation, although both permeability and porosity are increased as a result of skarn formation".

Collins (1977) compares scheelite-bearing and scheelite-barren skarn formation in the Brown's Lake-Lost Creek area of south-western Montana. He found that the two types of skarn formation showed differences in physical appearance, petrography and geochemistry. Although the two skarn-types show some similarities in their mineralogy (i.e. both are rich in garnet and pyroxene) the scheelite-bearing skarn has a dark brown colouration whereas the scheelite-barren skarn has a beige colour. Such a difference in colour is probably a reflection of chemical composition, i.e. the garnet and pyroxene minerals of the scheelite-bearing skarns are Fe-rich, whereas those of the barren skarns are Al- and Mg-rich. Collins also determined that the scheelitebarren skarn possesses random mineralogical and chemical trends across its width. In contrast the scheelite-bearing skarn shows a gradual increase in percent total garnet toward the intrusive contact, and the composition of both garnet and pyroxene shows a smooth sinusoidal variation in major oxide content across each zone.

Collins (1977) suggests that scheelite-bearing skarn formed from the alteration of relatively pure marble and the scheelite-barren skarn formed from a less pure carbonate rock rich in Al and Mg. He tentatively suggests that the Al and Mg in the latter skarn type contaminated and inhibited metasomatic reactions that involved oxides such as those of tungsten. This would explain the lack of scheelite in skarns of such composition. According to Collins the literature indicates that other skarn tungsten deposits possess some, if not many, of the above characteristics and he suggests that these characteristics could be used as guides to exploration and evaluation. In connection with possible compositional 'favourability' of pre-skarn carbonate rocks to metasomatic replacement, Hosking (1973) is of the opinion that 'dirty' carbonate beds in a sequence are the most susceptible to skarn formation and hence also (as a result of an increase in porosity/permeability) the most favourable to scheelite mineralisation.

Apart from chemical properties, other important factors likely to have an effect on the movement of mineralising fluids through the 'contact' rocks, would be the magnitude and duration of a 'tectonic stress field' prevailing at the time of mineralisation. Pre- and/or syn-mineralisation tectonic stresses could be responsible for fracturing, tensional features, etc. that could provide channel-ways and increase permeability to mineralising fluids. Hobbs and Elliott (1973) state that scheelite mineralisation is rarely uniformly distributed throughout zones of skarn formation. Furthermore, they state that in many skarn tungsten deposits scheelite occurs in well-defined 'ore shoots' or is more concentrated along certain bands in the skarn than in others. They suggest that the zones of scheelite concentration may be restricted by factors such as permeability, fracturing and other local controls. They do not mention, however, that bands of scheelite mineralisation may represent pre-existing syngenetic deposits.

The shape and attitude of skarn tungsten deposits can vary considerably and are related to a number of controlling factors. The most important factors relate to the amount and disposition of rock units, in the contact zone of an intruding pluton, that are favourably susceptible to metasomatic replacement. Skarn tungsten deposits are commonly tabular in shape and bounded by sharp contacts. Hobbs and Elliott (1973) mention that some skarn tungsten deposits do not have a direct contact with an igneous body. They quote the example of the Tem Piute deposit in Nevada where the tungsten ore body is parallel to, but separated from, an igneous contact by several hundred feet of barren strata.

Irregularities in igneous contacts are often sites of enlarged and enriched tungsten skarn ore bodies, e.g. Pine Creek mine, California (Gray et. al. 1968); Nevada Scheelite mine, Mineral County, Nev., (cited in Hobbs and Elliott, 1973). Irregularities may have acted as traps to mineralising fluids and/or as sites of intense metasomatism. Morgan (1975) compares the character of skarn formation at different localities in the contact zone of the Round Valley Peak Granodiorite in Sierra Nevada, California. He suggests that the mineralogical characteristics and intensity of skarnitization are strongly influenced by the geometry of the pluton-wall rock interface. Fig. 14 (after Morgan, 1975) is a schematic vertical section through the Round Valley Peak Granodiorite and indicates the apparent positions of three tungsten skarn deposits. From fig.14 it can be seen that the McGee Lakes skarn deposit underlies an overhanging 'wall' of granodiorite rock. Morgan suggests that this deposit would have formed under conditions characterized by high temperatures



Fig. 14 Schematic vertical section of the Round Valley Peak Granodiorite showing the apparent relative positions of the skarn deposits and the differing pluton-wall rock geometry. Straight arrows represent upward migration for late-stage magmatic fluids; curved arrows show paths of migration for metamorphic fluids.

Taken from Morgan (1975)

and by a fluid environment relatively rich in 'metamorphic' CO₂. Morgan tentatively suggests that these conditions produced a 'highly' oxidized skarn with most of the iron present in andradite garnet (i.e. an andradite-rich skarn). The Laurel Lakes deposits, however, were formed at the pluton-roof rock contact. Morgan suggests that this environment would produce a more 'reduced' skarn with most of the iron present in hedenbergite (i.e. a hedenbergite-rich skarn). Although these suggestions are speculative, the mineralogical characteristics of skarn rocks may provide a useful guide by enabling the relative position of tungsten skarn mineralisation, within the contact zone of a pluton, to be determined. If such determinations are possible and valid they may prove useful in outlining tungsten mineral zones of greater economic potential.

Major production of tungsten from skarn deposits in the U.S.A. have come from the Pine Creek mine, Inyo County, Calif. (Bateman, 1965; Gray et. al. 1968); the Mill City district, Pershing County, Nev.; various deposits in the Osgood Range, Humboldt County, Nev. (Hobbs and Clabaugh, 1946; Hotz and Willden, 1964); and the Brownes Lakes and Calvert Creek deposits in Beaverhead County, Mont. Major occurrences of tungsten-producing skarn formations outside the U.S.A. occur at the Flat River area in the Northwest Territories, Canada and on King Island, Tasmania. The Sangdong tungsten deposit in South Korea, which is described in the next section as a syngenetic/stratabound deposit, has been described by many authors as a pyrometasomatic skarn deposit.

The <u>Bishop district</u> (fig. 15) is situated in east-central California. The geology and tungsten mineralisation of this district have been described in detail by Bateman (1965). Although over fifty tungsten prospects are known in the district only one mine, the Pine Creek mine, has been in production in recent years. This section concentrates mainly on a description of the geology and mineralisation of the Pine Creek mine and surrounding area; the latter is referred to as the Mount Tom quadrangle.



Fig. 15 Map showing location of the Bishop tungsten district, California. Taken from Gray et. al. 1968. Virtually all the tungsten deposits in the Bishop district occur in skarn formation situated in close contact with intrusive igneous masses. Skarn formations containing tungsten deposits often occur as 'roof pendants' or remnants of older rock lying wholly within a younger igneous body. Such igneous bodies are commonly of granitic composition but in a few cases igneous bodies of gabbroic composition are host to 'roof pendants' that contain skarn tungsten deposits e.g. those deposits of the Deep Canyon area.

The pre-Tertiary geology in the Bishop district consists of a series of metasedimentary and metavolcanic rock remnants which have been intruded by plutonic rocks of various compositions. The metasedimentary rocks include marbles, hornfels, metachert and quartzites. These rocks are generally considered (Gray et. al. 1968) to be of Palaeozoic age. The marble rocks, from which mineralised skarn formation is believed to have derived, are commonly white-to-bluish grey in colour and frequently interbedded with pelitic hornfels. The metavolcanic rocks are probably of Mesozoic age and include metarhyolites, metadacite, metalatites and meta-andesites.

Contact metamorphism and metasomatism of the sedimentary and volcanic rock sequence took place in Mesozoic times as a response to the intrusive igneous activity. This event was succeeded by pneumatolytic and hydrothermal activity which is believed (Gray et. al. 1968) to be responsible for much of the metasomatic alteration, and most of the tungsten mineralisation, in the skarn formations.

In the Bishop district almost 75 percent of all tungsten deposits are in skarn formation that has a direct contact with granite, while 10 percent are in skarn that is in contact with granodiorite.

The Pine Creek mine is a major producer of tungsten, molybdenum and copper. It is located along the western edge of the main marble of the Pine Creek pendant. Tungsten ore bodies have been found along the marble - Tungsten Hills Quartz Monzonite contact for a length of approximately 2.5 miles and vertically for an elevation of about 3,700 feet. The surface geology over the main part of the Pine Creek mine is shown in fig. 16.



Fig. 16 Surface geology of Pine Creek Mine and Vicinity

10

Throughout the mineralised area ore bodies are numerous and show varied characteristics. Some ore bodies, for instance, are unusually large and extend hundreds of feet both vertically and horizontally.

Gray et. al. (1968) give a number of factors which have influenced the location of tungsten deposits of economic value. The main control to

mineralisation, of which there are few exceptions, is the contact of the marble with the Tungsten Hills Quartz Monzonite. In addition, ore-forming traps were formed by irregularities in the intrusive rock contact. The form and character of the original bedding in the marble has influenced the shape of some ore bodies. Impervious barriers, such as beds of hornfels, locally restricted the migration of mineralising fluids. Unmineralised boudins of hornfels within the ore bodies can, depending on their number, considerably increase the amount of waste dilution. There is no evidence that pre-ore faulting has controlled economic tungsten mineralisation in the Pine Creek mine.

The Pine Creek ore bodies all contain tungsten ore shoots, but only the upper parts of two of them contain molybdenum ore shoots. Some of the molybdenum ore shoots may contain as much tungsten as the tungsten ore shoots. Gray et. al. (1968) cite the following details which refer largely to the Main ore body of the Pine Creek mine, "The configurations of the ore shoots were determined by assays: cut-off grades of 0.4 percent of WO_3 and 0.4 percent of MOS_2 were assumed. The assay data indicated that the tungsten ore shoots contained an average of about 0.7 percent WO_3 with the grade of different shoots ranging from 0.6 to 1 percent. The tactite outside the tungsten ore shoots contained an average of 0.24 percent of WO_3 , and the tungsten ore shoots not coextensive with molybdenum shoots contained about 0.2 percent of MOS_2 . The molybdenum shoots in the upper part of the main ore body contained an average of about 1 percent of MOS_2 , plus substantial amounts of copper".

Gray et. al. suggest that scheelite deposition in the Pine Creek ore bodies took place in two stages. The first stage was probably penecontemporaneous with the formation of skarn. Late-stage scheelite occurs with quartz in veins that cut the skarn. Scheelite mineralisation is almost always associated with quartz, fluorite and apatite. The scheelite grains are usually anhedral and range in size from about 20 microns to a few millimetres. The majority of the scheelite fluoresces a pale creamy colour but some, perhaps 10 percent, has a pale blue fluorescence attributed to a low molybdenum content.

The Donut ore body (fig. 17), one of the North ore bodies at Pine Creek, mine, has been described in detail by Gray et. al (1968). They suggest that this ore body may serve as a standard for comparison with other ore bodies, as it appears to possess typical mineralogical and zoning characteristics.



Fig. 17 Horizontal Section, showing the relationship of the Donut Ore Body to the Main Ore Zone of the North Ore Body.

Taken from Gray et. al. (1968)

The Donut ore body occurs as a rim of mineralised skarn formation around a marble inclusion within the surrounding granitic rocks. The dimensions of this marble inclusion, including the skarn formation, are about 200 feet in height by about 130 feet in its greatest horizontal dimension. Relic bedding, along which scheelite is commonly found, is preserved throughout both the marble and the skarn formation. Gray et. al. suggest that the continuous rim of skarn formation around the marble suggests that pyrometasomatic replacement of marble took place at an almost equal rate around the entire inclusion. The small and completely enclosed nature of the remnant suggests that a temperature gradient was not a significant factor in the formation of the ore body. Gray et. al. suggest that a chemical gradient was responsible for the observed features. They demonstrated that, within the concentric lithological units of the ore body, there is an increase in iron content and a decrease in calcium content from the marble to the granitic rock. These zones are shown in table 13.

TABLE 13

Sequence of rock types encountered in the ore bodies

		1.0		
Marble		1		
Calc-silicates			p I	
Light-coloured Tactite	5u 1	ŋ	sin -	е. Н
Normal Tactite	asi	Ŭ	Cu	
Amphibole Tactite	M		inc	
Epidote Tactite	i		I V	V
Silicified Quartz Monzonite				
Quartz Monzonite				

Dawson and Dick (1978) report the results of a survey in <u>S.E. Yukon</u>, Canada, devoted to a study of tungsten-bearing skarn deposits. The geological characteristics of several deposit types are described and these should prove useful as prospecting guides.

The survey examined skarn deposits in the following areas: Macmillan Pass, South Nahanni-Flat River, Tillei Lake, Hyland River, Frances River and Rancheria.

Most deposits studied are located within the Selwyn Fold Belt in southern Yukon and Mackensie, but the deposits near Rancheria occur in the northern Omineca Crystalline Belt. The skarn deposits in the former area are hosted by upper Proterozoic to late Palaeozoic miogeosynclinal sedimentary rocks, which consist mainly of inter-bedded shale and carbonate formations.

Numerous plutons intrude the rocks of the Selwyn Fold Belt. Skarn

deposits are often, but not always, closely associated with the plutonic intrusions. As a group the plutons are all early to mid-Cretaceous in age, are notably discordant to regional structural trends, and have steeply dipping contacts. The plutons are predominantly of quartz monzonite composition, and biotite is generally more abundant in the rock than hornblende. The plutons appear to have been emplaced in relatively unmetamorphosed rocks in that they show well developed contact metamorphic aureoles.

Spatial relationships between pluton and skarn vary from proximal to distal. Skarns may occur as: xenoliths within the outer zones of the plutons; semi-concordant bodies developed in calcareous rocks immediately adjacent to the plutonic contact; essentially conformable units many tens to hundreds of metres away from the contact; and, discordant, fracture-controlled vein and replacement bodies that may be many kilometres removed from exposures of granitic rock. In migmatitic terrains skarns may develop in calcareous beds adjacent to conformable granitic bodies, without apparent or temporal relationship to discordant plutonic or hypabyssal rocks.

Dawson and Dick (1978) were able, based on ore element assemblages, to successfully classify 19 of the 22 deposits (table 14) which they studied. Further comparisons on the basis of host rock age and lithology, degree of regional metamorphism, and hydrothermal alteration of associated plutons reinforced this classification.

TABLE 14

No	Name (s)	Metals	Coordinates
1.	Mactung	W, Cu (Zn, Mo)	63°17 130°09
2.	Clea (Omo)	W, Cu (Zn)	62°46 129°52
3.	Lened (Nip)	W, Cu (Mo)	62°22 128°38
4.	Cantung	W, Cu (Zn)	61°57 128°15
5.	Nar	Zn, Pb, Cu, Ag (W)	62°01 129°53
6.	Narchilla	and the second second	
	(Ptarmigan Creek)	Zn, Pb, (W, Cu)	61°57 129°52
7.	Woah	W (Mo, Zn)	61°51 129°11
8.	Tai	W (Zn, Cu, Mo)	61°49 129°00
9.	Tanya	W (Cu, Zn, Pb, Ag)	61°48 128°54
10.	Zeus (Log)	Zn, Pb (W, Cu)	61°52 128°58
11.	Chap	Zn, Pb, (W, Cu)	61*52 128*53
12.	Ron	Zn, Pb (Cu, Ag)	61°27 128°30
13.	Firtree	Zn, Pb (W, Ag)	61*25 128*27
14.	Blackjack	Zn, Pb (W, Ag)	61*22 128*23
15.	Max (Bm)	W + Zn Pb Ag Cu	61°16 128°41
16.	Glenna-Miko	Zn, Pb (W, Cu)	61°16,128°35
			(61'15 128'30)
17.	Bailey	W, Cu	60'46 128'51
18.	Hundere (Ritco)	Pb, Zn (Ag)	60'31 128'53
19.	Atom	Zn, Pb (Cu, Ag, Bi)	60°11 131°13
20.	Bom-Munson	Zn, Pb, Ag (Sn, Cu,	60°09 131°12
		W, Mo)	(60°09 131°15)
21.	Bar (Dan)	Zn,Pb,Ag, (Cu, Sn)	60'10 131'08
22.	Mid-Nite	W, Mo (Zn, Pb, Ag)	60°20 130°42
		The second se	(60°20 130°41)

Skarn deposits and occurrences

Taken from Dawson and Dick (1978)

Four groups of skarn deposits were recognised and a comparison of some of their characteristics are tabulated in table 15.

TABLE 15

Group	Ore Element Assemblage	Hostrock age, lithology	Regional Metamorphism	Alteration of pluton	Examples
T	W, Cu (Zn, Mo)	€ to D carbonates, interbedded shale	Relatively unmetamorphosed terrane	Border phases argillized; locally greisened, tourmalinized	Mactung (1), Clea (2), Lened (3), Cantung (4), Bailey (17)
н	W, Mo (Zn, Pb, Cu)	Late P limestone xenoliths, screens	(not served)		Woah (7), Tai (8), Tanya (9), Mid-Nite (22)
m	Zn, Pb (W, Cu, Ag)	Late P limestone beds in quartz-biotite schist	Helatively Metamorphosed terrane	Plutons Relatively Unaltered	Nar (5), Narchilla (6) Zeus (10), Chap (11), Ron (12), Fir Tree (13), Blackjack (14), Max (15) Glenna-Miko (16)
IV	Zn, Pb, Ag (Cu, Bi, Sn)	DM carbonates, inter- bedded shale			Atom (19), Bom- Munson (20), Bar (21)

A comparison of some characteristics of 22 skarn deposits

Taken from Dawson and Dick (1978)

In summary, the important characteristics of the four groups of skarns recognised by Dawson and Dick are:

i) Group 1 - W, Cu (Zn, Mo) skarns

This group of deposits in which scheelite and chalcopyrite are the main ore minerals includes most of the economically significant deposits studied in the survey in question. These skarns are associated with an arcuate belt of small discordant plutons in S.E. Yukon and S.W. Mackenzie. Host rocks are the first thick limestone beds, usually Lower Cambrian, that occur above a relatively unmetamorphosed Upper Proterozoic clastic succession. The common morphology of a W, Cu skarn is a more or less concordant body localized some tens to hundreds of metres above a shallowly dipping intrusive contact.

With the exception of one ferberite occurrence at Mactung, scheelite is the only tungsten mineral in Group 1 skarns. Scheelite commonly occurs unevenly disseminated in dark green calc-silicate skarn. W:Cu ratios at Mactung and Cantung range from 6:1 to 7:1. In general the Group 1 skarns contain more copper than the other groups. Sphalerite is associated with some scheelite at Cantung and Clea, and in the former occurrence locally attains significant grade. Pyrrhotite is abundant in all W, Cu skarns, and tends to increase with increasing tungsten content. Pyroxene (diopsidehedenbergite) and garnet are the main calc-silicate minerals in the skarn. Actinolite, quartz, biotite, chlorite, epidote, vesuvianite and wollastonite are subordinate but locally extensive.

ii) Group II - W, Mo (Zn, Pb, Cu) skarns

This group of deposits, in which scheelite predominates over molybdenite, occupy a linear belt of calcareous screens and xenoliths of U. Proterozoic age, that extend for 60 km. along the N.E. margin of the Mount Billings Batholith.

Group II skarns generally have a garnet-rich sulphide-deficient composition. Scheelite and the silicate minerals of the skarn (garnet, pyroxene and quartz) display characteristic foliate textures.

iii) Group III - Zn, Pb (W, Cu, Ag) skarns

This group of deposits are found in a belt of relatively high grade metamorphic and migmatitic rocks bordering the northern and eastern flanks of the Mount Billings Batholith. The deposits are typically concordant bodies, a few metres thick and up to hundreds of metres long. They are developed in thin, continuous calcareous beds in Upper Proterozoic metasedimentary rocks adjacent to small, conformable, intrusive bodies of granitic composition. According to Dawson and Dick (1978) the stratiform morphology and distance from discordant intrusive contact suggest a synmetamorphic age of mineralisation.

iv) Group IV - Zn, Pb, Ag (Cu, Bi, Sn) skarns

These skarn deposits occur in late Palaeozoic metasedimentary rocks adjacent to the Cassiar Batholith. They are relatively rich in epidote, magnetite, and tourmaline and deficient in scheelite. The assemblage of minerals that contains Sn, Be, Bi, Mo and F may be characteristic of skarns associated with the Seagull phase (early Cretaceous) of the Cassiar Batholith.

Fig. 18 , after Dawson and Dick (1978) is an attempt to illustrate several skarn types.



Fig. 18 Idealized section showing several types of skarn deposits (i.e. Woah, Tai, etc.) in the Tillei Lake area.

Taken from Dawson and Dick (1978)

Dawson and Dick (1978) list a number of general observations, derived from their study, which may be useful in prospecting for skarn tungsten deposits:

- a) although the large W, Cu skarns contain pyrrhotite, the association of pyrrhotite with scheelite may not be essential for economic W concentrations;
- b) biotite-rich skarns occur only with W, Cu (Group I) mineral assemblages;
- scheelite occurs with many different calc-silicate and biotite skarn mineral assemblages;
- d) garnet-rich skarns generally contain scheelite, whereas base-metal skarns are low in garnet (as well as W) relative to W-Cu and W-Mo skarns;
- e) Wollastonite-bearing skarns do not contain base metals, and only rarely contain scheelite;
- f) epidote-rich skarns are common only in regionally metamorphosed terrain.

Stratabound Tungsten Deposits

It was not until the mid 1950's that this type of tungsten deposit was recognized. However, since that time a considerable amount of research on syngenetic, stratabound, tungsten mineralisation has taken place. This work has led to the revision of many early concepts on tungsten mineralisation, and to a reinterpretation of the genesis of a number of tungsten deposits.

Pargeter, 1954 (cited in Reedman, 1966) from his work in Ruhiza, Uganda, was one of the first geologists to recognise the stratigraphic control on, and stratabound nature of, tungsten mineralisation. The enclosing rocks, and hence also the tungsten deposits themselves, described by Pargeter, are of Precambrian (Karagwe-Ankolean) age. Pargeter noted ovoid ferberite nodules aligned along distinct bedding planes, and at one locality the nodules were restricted to a single 4" thick sandy phyllite horizon over a strike length of 140'. Pargeter (1954) also recorded reinite crystals (i.e. ferberite psuedomorphous after scheelite) lying along the bedding of the enclosing phyllites and flattened perpendicular to bedding.

Jeffery, 1959 (cited in Reedman, 1966) found that the graphitic phyllites of Ruhiza Mine were consistently enriched in tungsten compared with the average content of Karagwe-Ankolean age rocks of other lithologies. Graphitic phyllites from other ferberite deposits in the region, and from localities where no tungsten mineralisation was known, also showed an enrichment and the analyses suggested a positive correlation between the tungsten and the carbon content of the phyllites.

On the evidence of their work both Pargeter (1956) and Jeffery (1959) suggested the possibility that tungsten (ferberite) had been deposited syngenetically with the enclosing phyllitic rocks. Subsequent work, largely by Magnee and Aderca, 1960 (cited in Tanner, 1972) and Reedman (1966) demonstrated an overall stratigraphic control for the distribution of similar deposits in S.W. Uganda and Rwanda. Furthermore, Reedman (1966) identified concretions and nodules of ferberite from deposits other than Ruhiza which provide further evidence for the syngenetic theory.

Tweto (1960) recognised stratabound tungsten (scheelite) mineralisation in Precambrian-age calc-silicate and amphibolitic gneisses in Colorado and

6.2

Wyoming, U.S.A. The scheelite mineralisation, particularly that associated with the calc-silicate gneissic rocks, resembles metasomatic skarn-type mineralisation. However, although granitic intrusive bodies are abundant throughout the gneissic terrain, only minor amounts of scheelite are spatially related to the granitic rock contacts. Unlike skarns, the calc-silicate rocks do not vary in their form or composition for a distance of many miles from an intrusive contact. Furthermore, the calc-silicate rocks show no pattern of zoning, as is typical of skarns, but form part of a varied lithological sequence. The metamorphic banding in the calc-silicate rocks, (interpreted by Tweto as an original sedimentary feature), is conformable with the stratification of the scheelite deposits. Scheelite is commonly accompanied by molybdenum (in the form of powellite) in most of the deposits. The scheelite takes a variety of forms, ranging from minute anhedral specks to large enhedral crystals weighing 20 to 45 pounds. One of the consistent features of the deposits is the erratic nature of the distribution of the scheelite in the calc-silicate rocks. In a given locality, scheelite generally occurs in some single variety of calc-silicate rock almost to the exclusion of all others.

According to Tweto (1960), the formation of the scheelite segregations took place as a result of the mobilization of syngenetic concentrations of tungsten during granitization and regional metamorphism of sedimentary rocks.

Stratabound scheelite/sibnite mineralisation was first recognised in Sardinia, Italy, in the early 1960s by Maucher A. and a team of research workers from Munich University, Germany.

A stibnite/scheelite ore horizon was found to be restricted to one lithological unit of Lower Palaeozoic (Ordovician-Silurian) age. This unit consists of graphitic schists which alternate twice with horizons of tuffaceous and limestone rocks.

Two types of stratabound stibnite - scheelite mineralisation were identified (Angermeier, 1964 - cited in Maucher, 1976):

a) 'concordant' ore layers and lenses, b) 'discordant' veinlets.

The 'concordant' ore is the most important type with respect to size, scheelite content and frequency. It consists of massive to banded streaks and lenses of mostly fine-grained stibnite with irregularly dispersed stringers and patches of scheelite. The concordant ore is restricted to one lithostratigraphic horizon, the so-called "upper graphite schist" which is up to 10 metres thick. The lower part of the "upper graphite schist" contains various layers of sericitized quartz-porphyry and tuffaceous rocks. Maucher (1976) suggests that these layers owe their origin to submarine volcanogenic activity. The ore-bearing horizons are also restricted to the lower part of the "upper graphite schist" and the bulk of the ore occurs near to, or upon, the horizons of volcanic rocks. The ore layers, though tectonically deformed and sheared into lenses, still display primary features. Their original thickness according to Maucher (1976), changes within short distances, corresponding to the original submarine topography that existed during deposition; a maximum thickness of 1.5 metres was attained in basins and channels. Sedimentary structures such as rhythmic bedding, cross-bedding and 'soft-sediment' folds are locally still recognizable in the massive or banded 'stibnite-only' ore. Scheelite/stibnite ore, however, consists largely of alternating layers of massive ore with intercalated scheelite bands.

The coeval sedimentation of the ores is not only proved by the sedimentary structures. Maucher (1976) states that tectonic measurements prove that both ore and host rocks have undergone the same tectonic deformations, of which the oldest is of Variscan age. The ore must therefore be pre-Variscan. Any genetic relationship, therefore, to the syn- or post tectonic Variscan granites must be excluded.

The 'discordant' stibnite/scheelite mineralisation cross-cuts Variscan structures and so must clearly have been deposited syn- or post Variscan. Discordant mineralisation is bound to fissures or faults extending from the "upper graphite schist" into the underlying limestone or tuffaceous beds. The ore veins are generally narrow, short and of low grade. Unlike the stibnite, the scheelite is usually only found within or very near the 'primary' concordant beds, therefore it is still stratabound within the 'favourable' horizon. The ore veinlets do not show any dependence upon the Variscan granites or any younger igneous phenomenon.

Based on the described characteristics of the Sardinian deposits Maucher (1965) formulated a syngenetic conception model to explain the stratabound tungsten-stibnite mineralisation. He and his co-workers then carried out an investigation of similar deposits in other parts of Europe.

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Maucher (1976) notes that a re-investigation of scheelite mineralisation in the Uludag region of Turkey revealed that the previously described (Van der Kaaden, 1958 - cited in Maucher, 1976) skarn scheelite deposits, near the Uludag granite, showed indications of a syngenetic origin. He suggests that the scheelite ore horizons (which occur within marbles and amphibolites) are stratabound to folded reaction skarns and have not been emplaced epigenetically. Furthermore, the ore horizons are not restricted to, or dependent upon the nearby granite but are also found at a great distance from the granite contact. The scheelite content is, therefore, pre-tectonic and pre-granite.

That the re-interpretations of the genesis of the Sardinian and Turkish W-Sb-(Hg) deposits suitably agreed with the syngenetic, stratabound concept, induced Maucher and his co-workers to undertake a detailed investigation of the known W-Sb-Hg deposits in the Alps.

The investigations extended over a distance of more than 500 km., from Switzerland to Austria, and discovered more than 50 previously unknown scheelite occurrences. All the deposits were found in rocks of Lower Palaeozoic age. In some deposits scheelite was found to occur as fine disseminations in metasedimentary and basic metavolcanic rocks. The scheelite content of such deposits is generally very low. Maucher (1976) suggests that deposits such as these, containing fine-grained disseminations of scheelite, are typical of areas that have only undergone low grades of metamorphism. In deposits which have been subjected to high grades of metamorphism (e.g. to amphibolite facies) the scheelite commonly occurs as coarse-grained (10-20 mm. diameter) porphyroblasts. The metamorphosed scheelite-bearing rocks resemble typical scheeliteskarn formations. However, they have not been formed as a result of contact metasomatism and many of them occur at a considerable distance from granitic contacts. Furthermore, the majority of the scheelite-bearing formations do not contain carbonate rocks or minerals (Maucher, 1976).

The economically most important stratabound scheelite deposit discovered in the Alps by Maucher and his co-workers is the Felbertal deposit (fig. 19) which is located near Mittersill in Austria. Höll, 1977 (fig. 20) gives a detailed description of this deposit. The scheelite-bearing horizon of the Felbertal deposit is more than 300 metres thick. It comprises the lower part of an over 1500 metre thick metavolcanic sequence. The rocks most closely associated with scheelite ore are quartzites, chromium-rich hornblendites and amphibolites.

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Fig. 19 Ore deposits of the Sb-W-Hg formation in the Eastern Alps.

Taken from Höll, 1977.



Fig. 20 Schematic cross sections through the scheelite-bearing series of the eastern and western field of the Felbertal ore deposit.

Taken from Höll, 1977, (after Höll, 1973)

A volcanic origin for these metamorphic rocks is indicated by their distinctive geochemistry and by relict pyroclastic textures. According to Holl (1977) the Cr-rich hornblendites, characterized by high Ca and high Mg as well as low Al and low alkali metal content, show striking similarities to "komatiitic" volcanic rocks (of presumed primary mantle origin) of Archean greenstone belts. Holl further suggests that the quartzitic rocks, that occur within the orebearing horizon, may represent metamorphosed chert rocks which may owe their origin to siliceous submarine volcanogenic exhalations. In the eastern Felbertal ore-field, quartzites are particularly important host rocks (fig.21). Scheelite occurs as laminae, bands etc. in the quartzitic rocks in amounts that average 3-4% WO₃. The ore grade in a particular ore horizon is proportional to the number of quartzitic horizons present.



Fig. 21 Selective restriction of scheelite (3) to layers of quartzites (2) among metadiabases (1). Felbertal deposit.

Taken from Deninsenko, V.K. and Rundkvist, D.V. 1978

Scheelite, scheelite-powellite and wolframite, in varying amounts, occur throughout the ore horizons at Felbertal. The ore horizon also occasionally contains minerals such as: pyrrhotite, magnetite, hematite, ilmenite (mostly metamorphosed to rutik and anatase), pentlandite, chalcopyrite, tetrahedrite, sphalerite, molybdenite, tungstenite, bismuthite, silver and gold-rich silver (electrum), pyrite and rare arsenopyrite and cassiterite. Crystals of beryl (emerald and aquamarine) have also been found. Maucher (1977) states that geochemical studies have revealed that contents of Be, W, Mo, Bi, Ag and Au are typically present above their clarke in the ore unit. Maucher further states that the metavolcanic rocks (especially those of basic composition) contain anomalously high values of these elements.



Fig. 22 Arrangement of scheelite mineralisation conformable with bedding in graphite-rich limestone. Kleinarltal deposit. 1. graphite-rich limestone; 2. scheelite; 3. late calcite-dolomite veinlets.

Taken from Deninsenko, V.K. and Rundkvist, D.V. 1978

Another important scheelite deposit that was discovered by Maucher and his co-workers in the Austrian Alps is the Kleinarltal deposit (fig. 19). In this deposit scheelite mineralisation is best developed within graphitic carbonate rocks, graphitic slates and quartzites (Maucher, 1976). Scheelite occurs as disseminations and as thin veinlets. Fig. 22 illustrates the distribution, and conformable nature, of scheelite mineralisation in graphitic carbonate rocks from the ore horizon at Kleinarltal.

The main aspects of Maucher's conceptual model (Maucher, 1965 cited in Maucher, 1976) for syngenetic, stratabound Sb-W-Hg mineralisation, together with the important characteristics of this type of deposit, are outlined below:

- a) stratabound Sb-W-Hg deposits owe their origin to submarine, eugeosynclinal volcanic activity. The deposits were laid down contemporaneously, and thus conformably, with volcanic and sedimentary material;
- b) the majority of the known deposits are of Ordovician and Silurian age; therefore it is considered that the deposits of this type are 'time-bound'. (Since the discovery of the European stratabound Sb-W-Hg deposits various descriptions of similar deposits of Precambrian age have been reported, so it is possible that there are at least two favourable 'time-bound' periods of Sb-W-Hg mineralisation);
- c) the most favourable host rocks to mineralisation are amphibolites, hornblendites, quartzites, graphitic schists and minor carbonates;
- a metamorphic grade varying from greenschist to amphibolite facies appears to be characteristic of most of the important deposits discovered;
- e) metamorphism of the Sb-W-Hg deposits caused a separation of the metals according to their relative mobilities. Thus Hg, which is the most mobile, migrates further than the other two metals. W, the least mobile, migrates the least distance. Sb, though of intermediate mobility, possesses mobility characteristics that more closely resemble those of W. It is, therefore, more common to find Sb in close association with W than with Hg.
- f) the higher the grade of metamorphism the more coarse-grained will be the scheelite grains and the more likelihood of scheelite being mobilized into discordant veins etc.

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g) anomalously high values of Sb, Bi, Be, Hg and Au are commonly associated with stratabound tungsten mineralisation.

Since the discovery of the stratabound scheelite deposits in the Alps a number of similar deposits notably in Yugoslavia, Czechoslovakia, Greece, U.S.S.R. and Norway have been re-interpreted as stratabound, syngenetic deposits.



Fig. 23 Position of tungsten-bearing stratiform deposits in the Bindal region of Northern Norway. 1. biotite and biotite-hornblende gneisses; 2. calc-silicate gneisses; 3. marble and skarn horizons in metamorphic rocks (a) and in xenoliths of the latter among granitoids (b); 4. diorites; 5. para-autochthonous granites; 6. syenites and monzonites; 7. Bindal granites; 8. sectors with identified tungsten mineralisation.

Taken from Skaarup, 1974

According to Skaarup (1974) scheelite mineralisation in the Bindal region of Northern Norway (fig. 23) has been formed either in 'mobilised' quartz veins or along zones of skarn rocks. The mineralisation can be traced over a distance of tens of kilometres along boundaries between various varieties of gneisses. The gneisses are usually calc-silicate and biotite hornblende types. Skaarup suggests that scheelite mineralisation may be an expression of the metamorphism of pre-existing concentrations of tungsten within volcanogenicsedimentary sequences. Skaarup has determined that skarn formation took place most extensively during the peak of metamorphism and migmatization, which was attained near the Bindal massif. The granites in the region appear to have had no direct influence on the development of the scheelite-bearing skarn rocks, and in fact granite pegmatite veins cross-cut the skarn as well as the gneissic rocks. Furthermore, according to Skaarup it is not possible to identify 'pathways' from the granitic rocks to the zones of skarn formation along which magmas/fluids etc. could have introduced tungsten and the other components of the skarn formation. In the skarns and gneisses, at certain localities in the Bindal region, scheelite mineralisation is clearly associated with zones of disseminated sulphides (mainly pyrrhotite) in the host hornblende-biotite gneiss. Skaarup suggests that such zones can be compared to sulphide zones of 'exhalitivesedimentary' origin, formed from concentrations of metals (and sulphur) from volcanic emanations.

The stratabound character and Caledonian (Ordovician-Silurian) age are an indication that the scheelite occurrences in the Bindal area may be another example of syngenetic Sb-W-Hg mineralisation (in which Sb and Hg may be missing as a result of intense metamorphism), formed along an 'active' continental margin in the Caledonian fold belt.



Fig. 24 Map of geologic structure of tungsten-ore region of Orsdalen, Southern Norway. 1. Hiadal migmatite series; 2. granitized gneisses; 3. Orsdal charnockite gneiss series; 4. Orsdal charnockite gneiss series with numerous amphibolite seams; 5. assumed overthrust zone; 6. tungsten-bearing horizon.

Taken from Deninsenko, V.K and Rundkvist, D.V., 1978

In the Orsdalen region of Southern Norway there is a further example of stratabound tungsten mineralisation. In this region according to Urban, 1971 (cited in Deninsenko and Rundkvist, 1978) stratabound tungsten-molybdenum mineralisation of Precambrian age occurs within an horizon of graphite-bearing amphibolite rocks. This horizon is traceable for several kilometres (fig. 24). The ore-bearing horizon occurs within an intensely metamorphosed and granitized sequence of rocks which includes such rock types as gneisses, granitegneisses, migmatites and charnockites. According to Urban, tungsten and molybdenum were deposited syngenetically within volcanic host rocks of basic composition (now converted to amphibolites), as primary mineral constituents. Furthermore, Urban suggests that basic volcanic rocks were deposited within a sequence of geosynclinal sedimentary rocks.

The Sangdong scheelite deposit, South Korea, though long interpreted as a classical skarn tungsten deposit, shows close similarities to many of the above described stratabound tungsten deposits and, in particular, to the Felbertal deposit in the E. Alps. The scheelite ore in the Sangdong deposit is stratabound, time-bound and genetically-related to six very extensive, but thin, metavolcanic horizons (now converted by metamorphism to hornblende-biotite quartzitic rocks) which are inter-bedded with metapelitic beds (Kim, 1976; Maucher, 1976). Kim (L976) suggests that there is no evidence in the Sangdong area to indicate that granites have had any influence on the initial scheelite formation. The main ore zone displays well-preserved sedimentary fabrics. Regional metamorphism of this volcanogenic-sedimentary (Kim, 1976) sequence has caused local melting and remobilisation of quartz and scheelite into small (several decimetre long) discordant veins. However, it is noteworthy that these small veins are only ore (scheelite)-bearing adjacent to the six main orebearing horizons. Very small amounts of pyrrhotite, chalcopyrite, magnetite, ilmenite, hematite, molybdenite and bismuthite occur sporadically throughout the ore beds and veins.

Further examples of stratabound tungsten deposits, but of Precambrian age, have been described from Southern Africa.

Cunningham et. al. (1973) recognise, and have described, stratabound tungsten deposits in Rhodesia that belong to two widely separated time-intervals in the Precambrian (fig. 25).

The oldest stratabound deposits were identified from rock sequences of Lower Bulawayan age (about 2900 m.y.). They occur within an inter-bedded sequence of volcanic rocks of mafic/ultramafic composition, tuffaceous rocks, and minor arenite, argillite and carbonate rock formations. The rocks have been metamorphosed to greenschist, and in places, to the amphibolite facies. According to Cunningham et. al. scheelite mineralisation, within this rock sequence and within different greenstone belts throughout the country, occurs at horizons of differing rock compositions. The scheelite-bearing horizons at different deposits in the Bulawayan formation consist of: a)skarn rocks, b) jaspilitic iron formations, c) iron-poor quartzites. The different horizons contain varied amounts of Fe (as sulphides and/or oxides), Sb, Au and As.



Fig. 25 Distribution of tungsten and gold occurrences in the Bulawayan and Piriwiri formations in Rhodesia.

Taken from Cunningham et. al., 1973

A syngenetic origin for the scheelite mineralisation in certain deposits is indicated by well-preserved sedimentary features such as rhythmic layering, slump-structures, graded bedding and early diagenetic brecciation (Cunningham et. al., 1973). The tungsten content of many of the Rhodesian stratabound deposits is low and is often of subordinate economic value to the associated gold content.

The second period of stratabound tungsten mineralisation described by Cunningham et. al. (1973) from Rhodesia took place during the deposition of the Piriwiri formation (1950 m.y.). The Piriwiri formation is predominantly composed of a sequence of argillaceous rocks which are inter-bedded with lesser amounts of arenaceous and basic volcanic rocks. The rocks have been most intensely metamorphosed and partially granitized in the region of the Zambezi mobile belt (fig. 25), where they have been converted to biotite-tourmaline schists and gneisses. In the region of Tschontonda-Kamativi a persistent tungsten-bearing horizon (10-20 metres thick) extends for a distance of about 60 km. The mineralisation consists of wolframite and scheelite disseminated in sheared quartz-tourmaline rocks. According to Cunningham et. al. the tungstenbearing horizon is stratiform and it traces the outline of isoclinal folding in the rock sequence. At certain places along the strike length of the tungstenbearing horizon the rock sequence has been granitized. However, this has not led to major mobilisation and redeposition of the tungsten. Outside the tungsten-bearing horizon adjacent pegmatites and quartz veins do not contain tungsten minerals. Many tungsten deposits in Rhodesia are of distinct hydrothermal origin and are closely related to granitic rock contacts. Whether or not these hydrothermal deposits represent granitized and remobilised syngenetic stratabound deposits is, however, debatable.

Cunningham et. al. (1973) tentatively suggest that the scheelite-bearing stibnite/cinnabar deposits of the Murchison Range, S. Africa were originally stratabound, and timebound to the same time-interval as the Rhodesian tungsten deposits of lower Bulawayan age.

A syngenetic/stratabound origin has been recently ascribed to a number of tungsten deposits in the northwestern Cape Province, S. Africa (Stumpfl, 1977). Several occurrences of ferberite-quartz veins occur in a 130 metre thick rock unit known as the 'Wolfram Schist'. This unit forms part of a succession of gneissic rocks which have been dated at $1213^{+}22$ m.y. (Stumpfl, 1977). The tungsten-bearing 'Wolfram Schist' unit can be traced over a distance of 40 km. in the Concordia granite gneiss massif. The quartz-ferberite veins are concordant with, and arranged parallel to, the schistosity of the enclosing rocks. The main rock-forming minerals of the 'Wolfram Schist' are quartz,

plagioclase, garnet, biotite, cordierite and sillimanite. Minor ore minerals in the 'Wolfram Schist' include: chalcopyrite, scheelite, pyrite, molybdenite and sphalerite. Stumpfl (1977) states that the distinct stratabound nature of mineralisation and the grade of metamorphism suggest remobilisation of preexisting tungsten concentrations. He tentatively suggests that the original tungsten concentrations in the 'Wolfram Schist' occurred within a sequence of volcanic and sedimentary rocks. Stumpfl believes that the tungsten deposits in the 'Wolfram Schist' show similarities to, and may be analogous with, the stratabound tungsten deposits of the E. Alps.

Cunningham et. al. (1973) briefly describe a further stratabound tungsten deposit in Southern Africa. This deposit is situated near Okahandja in S.W. Africa and consists of stratiform scheelite mineralisation in 'calc-silicate' metamorphic rocks of Damaran Supergroup (about 600 m.y.) age.

From the above descriptions of stratabound tungsten deposits in Southern Africa it is evident that at least four periods of tungsten mineralisation (? primary/syngenetic) took place at approximately the following times: 2900 m.y.; 1950 m.y.; 1213 m.y.; and ?600 m.y. Although these periods of time could be used as guides to investigation of stratabound tungsten mineralisation, it would be inadvisable to restrict exploration to rock formations of these ages. It has been shown that stratabound tungsten mineralisation occurs predominantly within inter-bedded sequences of basic volcanic and argillaceous sedimentary rocks. Again, it would be inadvisable to restrict investigation to rock sequences of this nature, for a number of stratabound tungsten deposits occur within sequences of quite different rock types.

In spite of the differences in the geological environment of deposition, age, mineralogy and other features, stratabound tungsten deposits have a number of common characteristics:

- a) they are restricted to definite stratigraphical and/or lithological horizons;
 - b) the ore zones are conformable with the enclosing rock sequences;
 - c) the ore zones are usually thin but laterally extensive along strike.

In a number of cases, the syngenetic nature of tungsten mineralisation has been reliably demonstrated.

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Hydrothermal Tungsten Deposits

Hydrothermal tungsten deposits are widely distributed and account for more than three quarters of the known world reserves of the metal. The great bulk of these reserves, however, are concentrated in the extensive tungsten province of southeastern China.

In common with skarn tungsten deposits most hydrothermal tungsten deposits are spatially and possibly genetically related to plutonic rocks of granitic composition. Furthermore, like skarn deposits they commonly occur either within the border zones of plutons or in the adjacent intruded country rocks. Unlike the lithological environments favourable to the deposition of skarn deposits i.e. carbonate-rich rocks, the majority of hydrothermal tungsten deposits occur within siliceous sedimentary and/or igneous rocks or their metamorphic equivalents.

Scheelite and the wolframite minerals are usually amongst the earliest minerals to be deposited in a hydrothermal deposit. Often they pre-date associated cassiterite, as is generally the case in the S.E. Asian deposits; however, they do occasionally post-date cassiterite, e.g. S.W. England (Hosking, 1973). Because tungsten minerals occur paragenetically early in lode and vein deposits they are commonly fractured, brecciated or mylonitized, and cemented by one or more of the later introduced minerals.

That scheelite and the wolframite minerals tend to form early in the paragenetic sequence means that polymineralic tungsten-bearing deposits are often difficult to beneficiate and this may severely restrict their value. Hosking (1973) notes that at the Mawchi and Hermyingyi mines, Burma, the wolframite and cassiterite were so intergrown that it was necessary to sell a mixed concentrate the components of which were subsequently separated by chemical means.

It is traditional to sub-divide hydrothermal deposits, according to temperature of formation and level of emplacement in the crust, i.e. hypo-, meso-, epi-, and xeno-thermal. Based on this style of classification fig. 26 (after Hosking, 1971) is an attempt to illustrate the relative environments in the crust of the types of hydrothermal tungsten deposits. Hosking (1973) believes, however, that this scheme of classification has limited practical use to the field geologist. The writer shares this opinion and for the purpose of this review the following classification, taken from Hosking (1973) will be adopted:



THEME. THE J O TUNGSTEN DEPOSITS: VARIATIONS - 69

÷

C 03 % in this beds

03-50

WO3 Content, %] Percentage of grid output

U - Uncommon

L E G E N D 5 - ord sediments

R - Rare

Converturities

C - Common

55

.

52

0.2
- i) Tungsten deposits spatially and possibly genetically-related to granitic intrusives:
 - a) Early (high-temperature ?) deposits
 - b) Late (low-temperature ?) deposits
- ii) Tungsten deposits spacially and possibly genetically-related to granitic effusives and high-level granitic plutons:
 - a) Xenothermal deposits
 - b) Hot spring deposits
- i) Tungsten deposits spatially and possibly genetically-related to granitic intrusives
 - a) Early (high-temperature ?) deposits

Tungsten deposits of this type generally occur as mineralised vein lode-swarms and stockworks, particularly in and around 'high spots' (cusps) of granitic masses, and as lodes and pipes flanking granitic 'ridges'. Fig. 27 is a simplified sketch illustrating cusp-like features formed on the upper surface of a granitic cupola.



MAIN BODY OF BATHOLITH

Fig. 27 Simplified section attempting to illustrate the relationship between granitic 'cusps' and emanative centres of mineral-isation.

Hosking (1973) states that cusp-like structures along ridges of granitic bodies are so often spatially-related to important economic deposits of tungsten (and tin) that they must be considered important features capable of localizing a concentration of the metal. The plateau granites of Nigeria apparently lack 'cusps', are flat-topped and are characterised by widely dispersed, uneconomic tin/tungsten mineralisation, (Mackay et. al., 1949 cited in Hosking, 1973). This would support, albeit in a negative sense, the thesis that 'cusps' on the surfaces of granitic bodies are important structures in which economic quantities of tin/tungsten minerals may be concentrated.



Fig. ²⁸ The Primary Cassiterite and Wolframite Deposits of Portugal Taken from Hosking, 1973 (after J.M. Catelo Neiva, 1943)



Fig. 29 The distribution pattern of the mineralised areas containing tin and commonly tungsten, and of the zones of most markedly negative Bouguer anomalies. The material on which this map is, in part, based, has been derived from Dines (1956, figs 3a and 3b) and from Bott, Day and Masson-Smith (1958, fig. 2).

Taken from Hosking, 1973

Hosking (1973) holds the view that the ridge/cusp pattern on the original surface of a granitic intrusive is due to the invaded rocks behaving as a mould to intrusive material. He believes that antiformal structures, preexisting in the invaded rocks, gave rise to 'ridges', whilst 'cusps' developed where two antiforms of distinctly different orientation intersected. Hosking also believes that cusp-like structures could have formed at the intersection of an antiform and a major fault or even at the intersection of two major faults of widely differing orientation. The distribution of 'cusps' has been shown to be structurally-controlled both in Portugal (fig. 28) and S.W. England (fig. 29). Assuming that 'cusps' represent emanative sites of tin/tungsten mineralisation, then a distribution pattern of known 'cusps' in a region could be used to indicate sites of buried cusps and hence possible sites of economic deposits of tungsten.

Tin and tungsten mineralisation may be confined to the apices of granitic

cusps, and take the form of lode and vein swarms (e.g. Cligga, Hemerdon in S.W. England, Mawchi in Central Burma), or it may be partly in the cusps and partly in the invaded rocks (as at Hermyingyi, S. Burma), or finally it may be entirely in the invaded rock outside the cusp (as at Aberfoyle, Tasmania, and Panasqueira, Portugal) (Hosking, 1973).

Granitic cusp structures may also play an important role in the localization and concentration of tin/tungsten mineralisation in xenothermal (i.e. porphyry-type) deposits, e.g. Bolivia (Hosking, 1973); Mount Pleasant porphyry deposit (see fig. 33), New Brunswick (Parrish and Tully, 1978).

Hydrothermal tungsten-bearing deposits occurring within, or close to granitic cusps and ridges display a considerable variation in size, shape, tenor, mineralogy and structural complexity. They often consist of sub-parallel vein-swarms which commonly dip steeply, are rarely above 4 cm wide, and are usually bordered on both sides by zones of alteration (greisenization). Blake and Smith (1970) state that tin/tungsten mineralisation in the Herberton region, Queensland, Australia, is only associated with one of several granitic intrusives, the Elizabeth Creek intrusive, and this intrusive is the only one which contains zones of greisenization. Greisens are common, particularly where the granite is mineralised, and occur as both veins and irregular bodies; they are made up mainly of quartz and a pale mica (probably muscovite). Blake and Smith believe that all the greisens were probably formed during the late phases of the solidification of the Elizabeth Creek intrusive. Although vein swarms occur in the Krantzberg wolframite deposit, Omaruru, S.W. Africa, the ore bodies all occur within true stockwork bodies that consist of dense networks of mineralised fractures located along contact zones between schist and granite rocks. Greisenization is also a common form of alteration of true stockwork deposits e.g. the Krantzberg deposit.

Where lodes or veins occur in granitic rocks the latter are commonly kaolinised, often largely as a result of hypogene rather than supergene processes. In such a situation a high recovery of wolframite from the mined ore may be very difficult to achieve on account of the high concentration of clay in the mill feed. The amount of kaolinite associated with a tungsten deposit must, therefore, be taken into consideration in an evaluation.

According to Hosking (1973) the mineralogy of these hydrothermal tungsten deposits is very variable. Quartz is the dominant non-metallic gangue mineral,

and the dominant tungsten species is wolframite although scheelite may be present in considerable quantity. Cassiterite and arsenopyrite/loellingite are virtually always present in considerable concentrations. Molybdenite is rarely absent and can occur in appreciable quantities. Tourmaline, topaz, fluo-apatite and sericite and gilbertite micas are common non-metallic gangue minerals in these deposits. The deposits may also contain one or numerous other non-metallic and metallic mineral species.

Table 16 (after Ikonnikov, 1975, Chong, 1976) is a classification of tungsten deposits in S.E. Asia and shows the variety of mineral species that can be encountered in hydrothermal deposits.

TABLE 16

	Class and subgroup	Mineralogy	Geological environment	Examples of localities
1	. Quartz hydrothermal vei	n type (Southern Kiangsi type)		
	la. Tungsten-tin in greisen	<pre>cassiterite-wolframite, scheelite, chalcopyrite, molybdenite ,<u>quartz</u>.</pre>	vein swarms in greisenized granite. Ore grade is low	Nan Ling range of South Kiangsi; Mawchi and Hermyingi in Burma. Mae Sariang in Thailand
	1b. Wolframite-quartz veins	wolframite (ferberite). quartz, with minor cassiterite, molybdenite, base-metal sulphides, stibnite, hematite.	veins in metasediments at top parts of granites, or some distance from the granites	The most important ore type of the Nan Ling Range of South Kiangsi. Khao Soon (Thailand) Chendrong and Tunku Mahkota (Peninsular Malaysia)
Ì.	<pre>lc. Scheelite-wolframite quartz veins</pre>	scheelite, wolframite, quartz, with minor cassiterite, and base-metal sulphides.	small deposits related to granite and granodiorite.	Nan Ling Range of South Kiangsi, China.
	1d. Tungsten-antimony- gold deposits	quartz, barite, scheelite, stibnite, native gold.	gently dipping veins	Nan Ling Range, South Kiangsi, China.
2.	Scheelite deposits in skarns	garnet. diopside, <u>scheelite</u> , cassiterite, base- <u>metal</u> sulphides, fluorite.	granite-limestone meta- somatic contact zones	Southeast Hunan in China. Doi Mok in Thailand;Kramat Pulai in Malaysia
3.	Wolframite-scheelite- sulphide veins	fine grained (<10mm) wolframite, <u>scheelite</u> , with base-metal sulphides	large deposits of reticulated fissure veins in Mesozoic sandstones near granite contacts	Eastern Kwangtung, Chin
4.	Placer deposits	wolframite, cassiterite gold	residual, eluvial, alluvial. Always <5 or 6 km from the source. Tungsten dies off much more rapidly than tin.	Nan Ling Range of Southeast China.
	(After Ikonniko	v 1975, Chong 1976)		

Classification and occurrence of Southeast Asian tungsten deposits

Taken from Hutchison and Taylor, 1978

The most important classes of hydrothermal deposit, from a production viewpoint for the whole S.E. Asian region, are la. and lb. (Hutchison and Taylor, 1978). Class ld. belongs to the late (low-temperature?) type of hydro-thermal tungsten deposit in the classification adopted here.

According to Hosking (1973), "marked primary mineralogical zoning of individual hydrothermal tungsten deposits is never seen although at depth ore minerals may give rise to minerals such as quartz and tourmaline. This statement is substantiated by Blake and Smith (1970) who conclude, from an extensive study of the tin/tungsten deposits in the Herberton region, that zoning in individual deposits is not obvious and is often misleading.

There is, however, evidence of regional zoning in tungsten ore-bearing fields and this zoning can be a useful aid in exploration (Hosking, 1973). In most cases tungsten deposits occur either within a granitic intrusive or close to the intrusive contact. Fig. 30 (after Hosking, 1973) illustrates the close relationship between primary tungsten deposits and granitic intrusive rocks in the Kinta Valley, Malaya. The tungsten, iron and lead/zinc zones all parallel the N-S granite contacts of the Main and Kledang ranges, with the tungsten zones restricted to the contact areas.





Metal Zones in the Kinta Valley Based on data taken from the mineral distribution map (1966) of the geological survey of Malaysia.

Taken from Hosking, 1973, (after Hosking, 1969)

Blake and Smith (1970) recognize four regional zones of mineralisation in the Herberton district; these are: 1) tungsten, 2) tin, 3) copper and 4) lead. The type of rock that hosts mineralisation does not appear to appreciably affect the relations of one zone of mineralisation to the others. The tungsten zone is the innermost one and is almost entirely located in the Elizabeth Creek granite. The principal ore mineral is wolframite and also present are arsenopyrite, molybdenite, bismuthinite and other less abundant sulphides and, in places, a little cassiterite and scheelite. The principal gangue minerals are quartz, mica, fluorite, topaz together with minor beryl, monazite and tourmaline. This type of mineralisation is found most frequently in vertical to steeply dipping greisen veins in the Elizabeth Creek granite. Some wolframite is also found in flat topaz-greisen bodies in granite, in quartz veins and pipes in both granite and hornfels rocks, and in chlorite lodes in hornfelsed sedimentary rocks in the tin zone.

Taylor (1971) says that, although the concept of zoning in the Herberton field is valid, spaces barren of any mineralisation at all lie between mineralised areas of a given zone. Blake and Smith (1970) suggest, however, that the zoning pattern has been made less clear by intrusions of later, and unmineralised, granites into the rocks of the district.

Impounding structures invariably play an important role in the localization of economic quantities of tungsten in hydrothermal deposits of this type. The importance of cusp-like structures and ridges on the surface of major intrusive bodies of granitic composition, as features capable of impounding mineralising fluids, has been stressed.

Faulting within a mineralised region may provide channel-ways to mineralising fluids and also provide a barrier(s) to mineralisation. According to Hosking, 1973, "the unusual richness of the top-of-cusp Mawchi deposits may well have been due in part to the canalisation of the ore-forming agents which were liberated, during the consolidation of the deep granitic magma, into the cusp by the impounding action of the pre-lode wrench (?) faults which bound the ore zone to the north and south." Pre-lode wrench faults commonly occur in strongly mineralised hydrothermal areas, and Hosking (1973) believes that these faults are important features capable of impounding mineralising fluids. Hosking suggests that these important features should always be looked for (e.g. during photogeologic studies), particularly during target selection.

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Carbonate horizons in a lithological sequence may form effective chemical as well as physical barriers to mineralising fluids. The Mawchi tungsten ore deposit in Burma for instance is partially sealed by a roof of limestone rock. (Hobson, 1940-41 - cited in Hosking, 1973). Hobson believes that the limestone formed a chemical barrier to the upward progress of ore fluids when they entered the area and thereby aided the ore-forming process. Where the area into which the ore fluids entered was not covered by limestone, the fissures are numerous, but thin, and the tungsten/tin ore ceases to be concentrated enough for profitable mining.

The angle of an intrusive/wall-rock contact may also be important in impounding and concentrating ore-bearing fluids. At the Krantzberg wolframite mine, S.W. Africa, ore-bearing quartz-topaz greisens are located along the contact zones between schist and granite rocks. The contact between these two rock types dips at an average angle of 55°. It is believed (Nord-Mining Report) that, at such an angle of dip, the schist rocks acted as a barrier to orebearing solutions. This barrier largely restricted the movement of oresolutions to within the fracture zones of the granite thus producing zones of alteration (greisenization) and mineralisation (wolframite ore). That the schist contact acted as an impounding structure to mineralising solutions is shown by the fact that only the fractures in the granite near the contact contain economically exploitable amounts of wolframite; greisen veins away from the contact either lack, or have a very low, wolframite content.

The wolframite ore bodies at the Krantzberg mine tend to have an irregular shape. As shown in fig. 31 the ore bodies tend to taper, and inter-finger, from the intrusive contact to within the granite.

The Krantzberg wolframite ore bodies generally contain some or all of the following ore minerals: wolframite (ferberite), arsenopyrite, chalcopyrite, pyrite, magnetite and very small amounts of molybdenite and bismuthinite. Small amounts of scheelite and powellite also occur in places. The arsenic content of the ore and hence also of the concentrate, is within the limits (?5pph) considered generally acceptable for such a product. The main gangue minerals are quartz and topaz, with lesser amounts of orthoclase, muscovite, fluorite and minor tourmaline.



NOT TO SCALE

Fig. 31 A generalised section of one of the ore bodies in the Krantzberg wolframite mine, S.W. Africa.

Taken from Nord-Mining Report

Wolframite (ferberite) varies considerably in grain size, and is distributed erratically in the Krantzberg ore bodies. For these reasons a method of metre-grid sampling is used in the mine for grade control. The Kranzberg greisen ore bodies have an average in-situ grade of between 0,3 to 0,6 percent WO₃.

b) Late (low temperature ?) deposits

This type of tungsten hydrothermal deposit is quantitatively and economically less important than the type described in the preceding sub-section. An important difference between the two deposit types lies in their characteristic mineralogies. In contrast to the above-described deposits, these deposits typically contain scheelite with gold and/or stibnite. Late (low temperature ?) tungsten deposits may be found not only in tungsten provinces which are lacking or impoverished in tin, such as those of the Western Cordillera, U.S.A., but also within tin/tungsten provinces. In the latter they tend to be found at a considerable distance from sites of early (high temperature ?) tin/tungsten deposits.

At Yellow Pine, Idaho, deposits of this type, which contain economic concentrations of tungsten, gold, silver and antimony, were formed essentially by replacement along shear zones in quartz monzonite rock. Cooper, 1944 (cited in Hosking, 1973) suggests that mineralisation in the Yellow Pine deposits took place in the following three stages:-

- introduction of sericite, quartz, alkali feldspar, pyrite, arsenopyrite and gold;
- 2) introduction of carbonate, quartz and scheelite;
- the deposition of stibnite together with silver, quartz, pyrite and carbonates.

According to Hosking (1973) the Raub deposit of Western Malaysia constitutes a further example of this type of deposit. The Raub ore bodies, which have been worked for gold, occur in intensely faulted carbonaceous shale, and are situated within the vicinity of a granite-porphyry intrusive body. Coldham, 1946, (cited in Hosking, 1973) suggests that the "Raub ore bodies have been formed by hydrothermal solutions, partly as vein-filling of the compression and tension faults and partly by replacement of the country rock". According to Coldham the approximate composition of the ore was as follows:

- a) quartz and schist 50% to 80% : quartz predominant.
- b) $CaCO_3 15 30\%$.
- c) MgCO₂ about 2.0%.
- d) arsenopyrite, chalcopyrite, pyrite 1 5.0% : average about 2.5%.
- e) carbonaceous matter a maximum of 0.5%.
- f) stibnite and scheelite small amounts.

The Raub deposit occurs in a gold belt located between the eastern and western tin/tungsten belts of West Malaysia. Although the deposit lacks economic quantities of tungsten, Hosking, 1973, believes that other similar deposits within this gold belt may contain exploitable amounts of the metal.

ii) Tungsten deposits spacially and possibly genetically-related to granitic effusives and high-level granitic plutons

a) Xenothermal deposits

Xenothermal deposits are associated with high level plutons and their related effusives. Most of the known tungsten deposits of this type also contain the tin mineral cassiterite as the predominant ore mineral. Xenothermal tin/tungsten deposits possess striking similarities to porphyry copper deposits and have in fact been designated (Sillitoe et. al, 1975) 'porphyry tin' deposits.

Although xenothermal tin/tungsten deposits have been described principally from known deposits in Bolivia, other deposits of this type elsewhere include the Climax molybdenum/tungsten mine, Colorado, and the Mount Pleasant tin/tungsten mine, New Brunswick, Canada.

Xenothermal tungsten mineralisation occurs principally as fracture fillings and replacements in stockworks and breccia zones. The mineralogy of xenothermal deposits is usually complex and consists of a wide variety of high- and low-temperature minerals. Typical high-temperature minerals, such as cassiterite, wolframite, scheelite, magnetite, specularite and molybdenite are found with minerals characteristic of low-temperature environments, such as the silver sulfosalts. Gangue minerals include such diverse associations as orthoclase, tourmaline, topaz, augite, diopside, phlogopite, apatite and alunite; but beryl, spodumene and other high-pressure minerals are not formed in the xenothermal environment. Complex ores such as these may require special (expensive)treatment during beneficiation if a high recovery of tungsten is to be achieved.

The composition of the host rocks in the xenothermal environment is an important factor in determining the site of deposition of hydrothermal ore minerals. Where breccias and stockworks form in carbonate rocks the composition of the host would undoubtedly be a major factor in the deposition of scheelite.

In describing additional features of xenothermal tin/tungsten deposits it is convenient here to compare and contrast certain features of these deposits with similar features of porphyry copper deposits. This will hopefully provide additional, and possibly important, guidelines to exploration.

Sillitoe et. al. (1975) list a number of features considered to be characteristic of both porphyry copper and porphyry tin/tungsten deposits.

- a) Mineralisation is centred on small (commonly 1-2 km²) calc-alkaline porphyry stocks (cupolas) of intermediate composition.
- b) The stocks are believed to be subvolcanic in character and are considered to have formed beneath the vent regions of volcances (c.f. Sillitoe, 1973). Coeval volcanic rocks are preserved adjacent to several deposits.
- c) The stocks possess sharp contacts with their wall rocks, but contacts are complicated by the presence of numerous dykes and sills.
- d) Thermal metamorphic aureoles are narrow and of low grade.
- e) Hydrothermal intrusion breccias post-date the consolidation of the associated stocks. The larger breccia bodies carry significant tonnages of ore unrelated to vein structures.
- f) The stocks and adjacent wall rocks have undergone pervasive hydrothermal alteration. Both lateral and vertical alteration zones, each possessing characteristic mineral assemblages, are centred on the host stocks (fig. 32).
- g) Lead-, zinc-, silver-, and barium-bearing veins commonly occur peripheral to the stockwork and disseminated mineralisation.

Sillitoe et. al. (1975) also note several differences between porphyry copper and porphyry tin/tungsten deposits.

- a) Supergene enrichment is an important characteristic of porphyry copper deposits but is absent from porphyry tin/tungsten deposits.
- b) Potassium silicate alteration (c.f. Lowell and Guilbert, 1970) has not been identified in the Bolivian deposits despite its frequent occurrence in porphyry copper deposits.
- c) The stocks associated with porphyry tin/tungsten deposits commonly have the form of an inverted cone. In contrast, the majority of porphyry copper stocks have a dominantly cylindrical form.



Fig. 32 An idealized reconstruction of a porphyry tin deposit, using observations from the Bolivian tin province.

Taken from Sillitoe et. al., 1975.

The simplified sketch in fig. 32 (after Sillitoe et. al. 1975) is an attempt to represent the nature and dimensions of the hydrothermal system that applies to Bolivian porphyry tin/tungsten mineralisation.

A good example of a xenothermal or porphyry tungsten deposit, in which tungsten is the prime ore mineral, is the Mount Pleasant deposit(s) in New Brunswick (Parrish and Tully, 1978).

At Mount Pleasant disseminated and stockwork mineralisation is associated with a late Carboniferous rhyolite porphyry stock margined by coeval lavas. A central zone, with potassium silicate alteration is characterized by wolframite, molybdenite, and native bismuth. Outward this gives way to feldspar-destructive alteration with cassiterite, and farther out to disseminated zinc-copper-lead mineralisation. Fig. 33 (after Parrish and Tully, 1978) is an idealised section across the Mount Pleasant area and outlines several ore zones.

The largest of the porphyry-tungsten deposits in the Mount Pleasant area is the Fire Tower tungsten zone. This deposit contains wolframite, molybdenite and bismuth minerals as disseminations and veinlets in a moderately to highly silicified and brecciated rhyolite porphyry known locally as tuffite. The Fire Tower zone contains about 25 million tons of rock grading o.1% Mo, 0.2% W, 0.1% Bi and about 5.0% fluorite (Parrish and Tully, 1978).

Within the Fire Tower tungsten zone there are at least two highergrade bodies. One of these bodies, the Western Body, is about 500 feet long by 200 feet wide and contains 3 million tons of rock grading 0.15% Mo, 0.36% W and 0.11% Bi, extending from the -100-ft. elevation to just above the +300-ft. elevation. The minerals are coarser-grained than in the surrounding lower grade rocks. The limits of the high-grade body are assay walls which, according to Parrish and Tully, are easily defined on the assay plans. Metal content ranges from 0.4% W (or more) to less than 0.20% within the tuffite, with very few high grade assays appearing in the walls of the body. The wall rocks grade about 0.14% W. The tungsten content drops markedly below the tuffite as the 'unfavourable' (post-ore?) rock is encountered.



Fig. 33 Idealized section across the Mount Pleasant mining area.

Taken from Parrish and Tully, 1978.

At the Climax porphyry molybdenum deposit (Wallace et. al., 1968) wolframite (huebnerite) and cassiterite occur in small but recoverable amounts, disseminated widely throughout the ore body. Although the grade of the tungsten is only a few hundredths of one percent, and thus is far below the economic cut-off for tungsten alone, the huebnerite is recovered as a byproduct of the very large scale mining for molybdenum. Xenothermal tungsten-bearing deposits, such as those outlined above, commonly contain important economic quantities, and grades, of two or more of the following metals: W, Sn, Mo, Bi and Ag. Deposits of this type may constitute an important, and economically worthwhile, exploration target in regions containing preserved high level intrusives and other features considered to be characteristic.

b) Hot-spring deposits

6.4

Lindgren (1922) reports the occurrence of a hot-spring deposit at Uncia, Bolivia which contains a high concentration of tungsten. He states that the deposits of the springs are predominantly calcareous (calc-tufa), are about 30 metres thick, and extend over an area of about 10 acres. In places the calc-tufa contains beds of barite, calcite and manganese (predominantly psilomelane). Lindgren reports that little to no tungsten was recorded in the purer calcareous and siliceous material of the tufa but an average quantity of 0.5 percent WO_3 was found to be present in the psilomelane. Lindgren concludes that the tungsten is not present as any definite mineral but was precipitated as a colloid together with manganese dioxide. If it is true that tungsten occurs in colloidal form, then it would not be amenable to physical methods of separation. Therefore, in spite of a high average content of WO_3 (0.5%), it would probably not be economical to separate the tungsten by chemical means (Lindgren, 1922).

Similar deposits to the above occur at both Golgonda and at Sodaville, Nevada and have been described by Kerr (1946).

Pegmatite Tungsten Deposits

It is apparent from the literature that economic quantities of tungsten are rarely to be found in pegmatites. Shcheglov and Butkevich (1977), for instance, state that, "commercial tungsten deposits of the pegmatite type are unknown in the Soviet Union". Hosking (1973) believes that on the rare occasions when high concentrations of tungsten (and many other heavy minerals) are reported for pegmatites, they probably owe their origin to ore-bearing hydrothermal solutions which intruded the pegmatite some time after it had formed. Hosking suggests that because pegmatites are generally more susceptible to fracturing than the surrounding rocks in which they are emplaced, explains why pegmatites are often preferred sites for hydrothermal mineral deposition. However, despite the latter point Hosking (1973) states that, "pegmatites have never contributed more than very modestly to the world production of tungsten concentrates".

That pegmatites in general do contain tungsten, albeit in sub-economic quantities, is indicated by Shcheglov and Butkevich (1977) who state that tungsten-bearing pegmatites have been found in all of the rare-metal provinces of the Soviet Union. A study of the pegmatite provinces of Southern Africa (von Knorring, 1970) has shown that the content of tungsten minerals in pegmatites is generally less than that of minerals such as cassiterite, columbite and tantalite.



Fig. 34

Taken from Hosking, 1973 (after Cotelo Neiva, 1944)

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In tungsten-bearing pegmatite deposits containing exploitable amounts of cassiterite the tungsten content may have economic significance. The Adoria pegmatite, Portugal, described by Neiva, 1944, (cited in Hosking, 1973), is an example of such a deposit and its mineral content is shown in fig. 34. According to Neiva the 'heavy minerals' (including wolframite) were deposited in the already crystalline Adoria pegmatite, by hydrothermal solutions.

Hosking (1973) sums up the conclusions reached by stating, "... beyond reasonable doubt the chances of finding pegmatites containing such tonnages of tungsten minerals, that these alone would attract any but small operators, are slight", and he continues, "the chances of finding economically interesting stanniferous pegmatites containing minor wolframite which can be recovered as a by-product during the recovery of cassiterite are probably somewhat better, but even these deposits are rarely of interest to large mining companies".

6.5

Endogranitic Tungsten Deposits

Endogranitic tungsten deposits are rare and as far as the writer is aware, no known commercial deposits of this kind exist.

According to a translated report by Alexandrov (1962), a number of tungsten-bearing districts in the U.S.S.R. and in the Auvergne, France, contain rhythmically-banded, often dyke-like, rocks of granitoid composition. The banding consists of zones of granitic rocks intercalated with quartz zones and zones consisting predominantly of albite, biotite and wolframite. The central part of the dykes are often occupied by pegmatoid bodies. It is stated by the author of the paper in question that, "the rhythmically-banded granitoid bodies are known only in massifs with which tungsten and molybdenum deposits are associated genetically. This may indicate that the 'banded granitoids' represent a regular stage of ore-bearing intrusions. An occurrence of these granitoids may be used as an indicator in prospecting for tungsten and molybdenum deposits".

Hosking (1973) commenting on the above paper states that, "such deposits are clearly not economic sources of tungsten". Hosking further states that, "whilst spectacular banded granitoids are known in S.W. England, they are, nevertheless, very rare and not a single one contains wolframite, although many, but usually small, tungsten deposits are known and have been worked there". Tungsten-bearing endogranitic pipes are unusual features and are restricted to a few of the many tungsten provinces of the world.

Pipes of this kind occur in the Potgeitersrus tinfields (Zaaiplatts area), S. Africa (Strauss, 1954). These pipes, together with related flat lenticular ore bodies are presently mined for tin (cassiterite) but the tungsten (mainly scheelite) is not recovered. The pipes show great complexity in shape and attitude within 275 metres of the upper contact of the Bobbejaankop granite, fig. 35 (a plug-like intrusive in the 'Main Granite'). The pipes are roughly cylindrical bodies up to 12 metres in diameter (mean 1-2 metres) and vary in length from 7-1000 metres. (Hunter, 1973). Scheelite also occurs as disseminations throughout the upper part of the Bobbejaankop granite and possibly also in the overlying Lease Granite.



Fig. 35 The geology of the Bushveld Granites in the Zaaiplaats area.

6.6 Tungsteniferous brines and evaporites

Tungsten is known to be enriched in alkaline brines, or the evaporites derived from them, of certain present day or ancient lakes that occur in arid regions. Boyle, 1969 (cited in Hosking, 1973) reports the occurrence of 'high' concentrations of tungsten found in certain arid region lakes of the Soviet Union. Carpenter and Garrett (1959) describe what is probably the best example of this type of deposit, the Searles Lake deposit, California.

This dry lake is located in the basin formed by the Argus and Slate ranges in the northeastern corner of the Mojave Desert (fig. ³⁶). It consists of a massive evaporite deposit, about 35 sq. miles in area, varying in thickness from O-120 ft. and containing more than 3 billion tons of 'salt'. All but the central 8 sq. miles of this deposit is overlain by 'mud'. About 50 percent of the evaporite consists of a dense brine and this is worked for its boron and lithium content. The brine also contains about 70 ppm WO₃ which Carpenter and Garrett believe is in the form of a complex heteropoly ion, $(M_X W O_2)^{n-}$, where M may be boron, arsenic or phosphorous.

According to Carpenter and Garrett the low grade of tungsten is far below the saturation concentrations that would allow a solid phase of tungsten to crystallize out. Although the concentration of tungsten in the evaporite is low, and no efficient extraction method has yet been designed, these brines must be considered a major resource for future consideration, because the large volume of brines contain approximately 170 million lb. of WO₃ (i.e. 8.5 million units), i.e. more than half the known reserves of the U.S.A. (Carpenter and Garrett, 1959).

Searles Lake is situated within a part of the Pleistocene Owens River interior drainage system which covers an area which contains many primary tungsten deposits and includes the Bishop tungsten district (fig. 36). It would seem, therefore, that the tungsten in the Searles Lake deposit probably resulted from the leaching of these primary deposits. However, leaching may not be the only source of tungsten for numerous springs in the area, at least one of which is known to carry anomalous amounts of tungsten, may also have contributed to the total tungsten content of the lake.

6.7

Tungsten-Bearing Placer Deposits

The term 'placer' is generally applied in this section to cover the more specific terms alluvium, eluvium and colluvium.



Fig. 36 Relation of tungsten deposits to former Owens drainage system. Taken from Carpenter and Garrett, 1959.

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Tungsten-bearing placer deposits of economic importance are relatively insignificant worldwide and constitute only a minor proportion of the world's total production of the metal. Tungsten (only) placer deposits contrast sharply, from an economic point of view, with the economicallyimportant tin placer deposits.

Tungsten-bearing placers are predominantly eluvial and colluvial. They are rarely alluvial on account of the good cleavage and brittle nature of wolframite and scheelite minerals, features which lower their resistance to abrasive action. When true alluvial deposits occur they tend to be restricted to those parts of the drainage system which are close to the primary source (Varlamoff, 1971) or to beaches adjacent to primary tungsten deposits. Wolframite and scheelite minerals can only survive for some distance (i.e. over several hundred metres) in the alluvial environment if they occur as intergrowths within resistate gangue minerals such as quartz. Raeburn and Milner (1927) note that near the Widnes wolframite mine in southern Burma an eluvial deposit contains wolframite and cassiterite in the ratio of 24:1. From the site of this deposit (a position about 1500 ft. up a mountain-side) to a position on the valley floor, the ratio of wolframite to cassiterite, in panned concentrates, is reduced to the extent that the content of the two minerals becomes equal.

Shcheglov and Butkevich (1977) state that cassiterite-wolframite and wolframite placers are the most widely distributed and best developed tungsten placer deposits in the U.S.S.R. The Omchikandya deposit (fig. 37) in the Yakutian region is one of the largest cassiterite-wolframite placers in the Soviet Union. According to Shcheglov and Butkevich primary contact metasomatic (skarn) tungsten deposits rarely form commercial placer deposits.

Shcheglov and Butkevich (1977) state that the average wolframite content of the commercial tin-tungsten placer deposits in the U.S.S.R. varies from $10-20 \text{ kg/m}^3$ with a minimum of 0.3 kg/m².



Fig. 37 Structure of the Omchikandya tungsten placer deposit. 1) biotite granites; 2) weathering crust; 3) clay with sand and pebbles; 4) mud with rubble, pebbles, and seams of peat; 5) rubble and pebbles with clay filler; 6) lenses and veins of ice; 7) slope deposits of loam and sandy loam with rubble; 8) peat; 9) quality portion of placer; 10) valueless portion of placer.

Taken from Shcheglov and Butkevich, 1977.

7.0 EXPLORATION FOR TUNGSTEN DEPOSITS - GENERAL ASPECTS AND TECHNIQUES

It is clear from the descriptions in the preceding section that any exploration programme searching for economically worthwhile deposits of tungsten should be aimed primarily, but not exclusively, at the hydrothermal (particularly the early high? temperature and xenothermal types), pyrometasomatic/skarn, and stratabound (particularly those of Palaeozoic age) deposits. Most of the important characteristics of these deposits have been given and it is hoped that these will provide the basic guidelines to an investigation of tungsten deposits of economic value.

Hosking (1973) outlines various types of exploration programme for tungsten, together with various procedures that may be carried out at each stage of these programmes.

If the drainage pattern of a region is considered to be sufficiently 'dense' then a geochemical survey involving the systematic panning and analysis (for W and associated elements e.g. Sn, As, Be and Mo) of the heavy concentrates of stream sediments, is a useful reconnaissance method in outlining areas anomalously high in tungsten. If scheelite is present in the panned concentrates then a useful technique of analysis and estimation of grade utilizes the portable short-wave U.V. lamp. Under the lamp scheelite fluoresces a bright blue-white to creamy-yellow and the degree of yellow fluorescense is controlled by the amount of molybdenum in the mineral structure. A person experienced in the use of this technique can detect very small amounts of scheelite and estimate grade quite accurately.

Hosking (1973) suggests that areas outlined by stream sediment sampling as being anomalously high in tungsten should be followed up by geochemical soil surveys. One such soil survey is reported by Cachau-Herreillat and Prouhet (1971). This survey led to the discovery of the Salau skarn tungsten deposit in the French Pyrenees. The soil samples that were taken during this survey were analysed for W, Mo, Pb, Zn, Cu, As, P and F. (fig. 38). Tungsten shows a marked anomaly (fig. 38) that is closely restricted to the outcrop of the Salau deposit and to the down-stream network of channels leading from the deposit. The background values for tungsten are below 5 ppm, and the skarn deposit is clearly defined by values which grade up to 100 times background i.e. 500 ppm. The other metals show clear but smaller anomalies which do not enlarge the target.

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Fig. 38 Geochemical results of soil samples for Tungsten, Fluorine, Arsenic and phosphorus. Taken from Cachau-Herreillat and Prouhet, 1971.

The metalloids show increasingly larger anomalies in the order As-P-F (fig. ³⁸). The enlargement of the target area is up to 500 metres for fluorine, without any field indication of hydrothermal alteration. Cachau-Herreillat and Prouhet (1971) suggest, therefore, that the metalloid elements appear to be good indicators in regional prospecting for granitic intrusions and their associated ore deposits.

Hosking (1973) suggests that map research, photo-geological and field studies should be undertaken, before or during detailed soil sampling programmes, to ascertain the presence of indicative features of tungsten mineralisation such as granitic cusps and granite/limestone contacts etc. Hosking further suggests that rapid semi-quantitative analysis of gossanized outcrops may help assess the potential of a possible target. Stanton (1970) has developed a rapid method for tungsten determination, which has adequate sensitivity for the determination of tungsten in soils, stream sediments and rocks. Quin and Brooks (1972) describe a technique of even greater sensitivity developed specifically for the determination of tungsten in vegetation. Hosking (1973) describes three simple field tests for the identification of tungsten:

- a) Ammonium Hypophosphate test
 - 1. Mix powdered substance with 3 to 4 volumes ammonium hypophosphate in a silica crucible.
 - 2. Heat until a melt is obtained (strong smell).
 - 3. Add few drops of water to hot turbulent melt.
 - A product like blue ink indicates that tungsten is probably present.

b) Zinc/HCl streak test

- 1. Make a heavy streak of the mineral on an unglazed tile.
- 2. Place a small pile of zinc dust on the streak.
- 3. Add several drops conc.HCl to get a vigorous reaction between HCl and the zinc.
- 4. Wash off powder with water.
- 5. If streak has turned blue, tungsten is present,

or

boil powder in conc.HCl for 15 minutes - a yellow solution that turns blue on addition of zinc indicates tungsten.

c) Staining of Concentrates

This method is particularly useful in obtaining a qualitative indication of proportions of wolframite and scheelite in pan concentrates.

- Boil 2 to 5 grams concentrate for about 20 minutes in solution of 25 ml HCl, 15 ml HNO₃ and 60 ml water.
- 2. Wolframite and scheelite grains become yellow.
- Pick out yellow grains and remove yellow coating with ammonia. White grains are scheelite, dark grains are wolframite.

Geophysical methods may be applicable to the selection of geological environments in which tungsten deposits might logically exist. Broad regional studies by means of airborne radiometric and gravity surveys may be useful in identifying variously anomalous rock bodies that are known to relate to possible environments of ore deposition. It is possible that such measurements could locate igneous contacts and provide information on the location and depth of buried plutons and cupolas, and delineate tungsten-associated granites that have a relatively high radioactivity. The ability of geophysical methods to locate buried granitic cusps may be in doubt as Hosking (1973) states, "Geophysicists have all claimed that, in general, the cusp is likely to constitute too small a target to be located, unless it is quite close to the surface". Detailed geophysics may, however, be applied in the detection of ore zones or individual ore bodies. Many skarn tungsten deposits, for instance, contain a considerable amount of magnetite and/or pyrrhotite. The presence of these minerals may, therefore, enable such deposits to be detected by magnetic methods. Furthermore, tungsten deposits commonly contain sulphide minerals; therefore, by utilizing electrical methods it may be possible to detect such a deposit.

Detailed geological field-work such as mapping, structural analysis etc. are obviously important aspects that must be undertaken in the surface evaluation of a tungsten deposit. The compiling of fracture density maps may prove particularly useful in the evaluation of a xenothermal/porphyry tungsten deposit.

Where sub-surface information is needed pitting, trenching and drilling

may be appropriately employed. However, the brittle nature of tungsten minerals and their frequently very patchy distribution within a deposit can cause problems in sampling trenches, pits and drill core etc. It is important for instance, when sampling a trench or channel, to be sure that the sampling surface has been cleaned of loose material. This is particularly important in trench sampling where almost indiscernible 'wash' into trenches can give completely misleading results. To minimise spurious results the trench, channel and surface sample should be as large as is practically possible. Furthermore, when channel sampling it is preferable that the width of the channel should be equal to its depth.

The method of sampling diamond and percussion drill material is highly problematical. That tungsten mineralisation is commonly patchily distributed in a deposit suggests that the size of any drill sample is considerably limited and likely to give a spurious result. The sampling of drill material is, therefore, of little use in establishing grade of mineralisation.

One method which may be used in the grade control of a tungsten ore body involves the point-counting of ore minerals. Solomon and Brooks (1966) have employed this method of assaying wolframite at Story's Creek Mine, Tasmania.

8.0

TUNGSTEN PRICES AND GRADES

In order to place tungsten in economic perspective, the following exploration for the assessment of in situ value of tungsten ores is given:

The Mining Journal of April 15, 1977, quotes the tungsten price on the LME as:

Wolframite/Scheelite (65%) \$178 to \$183 per tonne unit WO₃ Say \$180,00 per tonne where \$1-00 = R1.15 i.e. 6.8 tonnes of 66.2% WO₃ concentrate would realise $6.8 \times 66.2 \times \frac{180}{1.15} = R70,459-00$ 1.15 or the in situ value of a 0.2%W ore body would be

$$\frac{180}{1.15} \times \frac{W}{WO_3} \times 0.2 = R 24-73$$
where $\frac{W}{WO_3} = 0.79$

SUMMARY OF CONCLUSIONS

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- a) Exploration should be aimed primarily, but not exclusively, at the hydrothermal (particularly the early high? temperature and xenothermal types), pyrometasomatic skarn, and stratabound tungsten deposits.
- b) Hydrothermal and skarn tungsten deposits are spatially and possibly genetically related to plutonic rocks of granitic composition.
- c) Hydrothermal mineralisation is commonly centred upon the roof zones, or within cusps, of small (1-2 km²) granitic cupolas. Such zones of mineralisation are thus susceptible to denudation. Granitic cusps tend to be located at the intersection of two antiformal axes, at the intersection between an antiform and a major fault or even at the intersection of two major faults of widely differing orientation.
- d) Both scheelite and the wolframite minerals form paragenetically early in primary deposits. Polymineralic tungsten-bearing deposits are, therefore, often difficult to beneficiate and this may severely restrict their value.
- e) Wall rock alteration is indicative of hydrothermal tungsten mineralisation, particularly the alteration zoning associated with xenothermal deposits. Where lodes or veins have been kaolinized a high recovery of wolframite from the mined ore may be very difficult to achieve.
- f) Tungsten deposits commonly contain concentrations of one or more of the following metals : Sn, Sb, Bi, Mo, Au and Ag. The presence and possible extractive value of these metals must be taken into account in a feasibility study. As is also commonly found associated with tungsten deposits but there is a limit to the content of this element above which the concentrate is either unacceptable for sale or would be heavily penalised.

- g) Zoning of individual primary hydrothermal tungsten ore bodies is rarely, if ever, present. Regional zoning, however, is often clear and can be a useful aid in exploration. In most cases tungsten deposits occur either within a granite intrusive or close to the intrusive contact.
- h) Impounding structures are important in localising mineralisation and should always be investigated. Low angle intrusive contacts are more likely to be associated with high concentrations of tungsten minerals than high angle ores. Carbonate horizons may act as both chemical and physical barriers to migrating ore fluids. The position where an intrusive rock forms an 'overhang' to adjacent carbonate contact rock may have been a site of intense metasomatic replacement and scheelite mineralisation.
- Skarn tungsten mineralisation is commonly stratabound to one or more horizons which may extend for several hundred metres from a granitic contact.
- j) Late, low? temperature hydrothermal tungsten deposits often contain Au and Sb. The tungsten content in mines of this type of deposit is commonly of subordinate value to that of the associated Au.
- k) The density of fractures is often a good indication of hydrothermal tungsten mineralisation i.e. fractures tend to become more dense toward a deposit. Fracture density maps may be particularly useful in evaluating xenothermal (porphyry) tungsten deposits.
- Tungsten deposits are by and large small, and large disseminated deposits are rare. Climax molybdenum mine produces tungsten as a by-product but the grade of tungsten alone does not warrant mining.
- m) Tungsten ore minerals are commonly patchily distributed in hydrothermal veins and lodes. For this reason the estimation of grade is often difficult during mining and evaluation.
- n) Stratabound tungsten deposits are often found associated with Sb and Hg and within volcano-sedimentary sequences. The majority

of the economically important deposits of this type are of Ordovician and Silurian age. Exploration for this type of deposit should be aimed primarily, but not exclusively, at eugeosynclinal sequences within Lower Palaeozoic fold mountain belts e.g. an investigation of Ordovician/Silurian strata in the Caledonian belt of northern Europe, or of rocks of similar age in the Tasman geosyncline of eastern Australia.

- o) Stratabound tungsten deposits that have been subjected to low grades of metamorphism commonly consist of disseminations of fine-grained scheelite. In environments of higher .grades (amphibolite facies and higher) of metamorphism, scheelite tends to form coarse grains and becomes mobilized into veins and small fissure fillings. Such veins, however, often remain stratabound to a particular horizon.
- p) Despite a number of differences between stratabound tungsten deposits, i.e. in age mineralogy, lithological setting etc., they all have a number of characteristics :
 - (i) they are restricted to definite stratigraphical and/or lithological horizons;
 - (ii) the ore zones are conformable with the enclosing rock sequences;
 - (iii) the ore zones are usually thin but laterally extensive along strike.
- q) If a drainage pattern of a region is considered to be sufficiently 'dense' then a geochemical survey involving the systematic panning and analysis (for W, Sn, As, Be and Mo) of the heavy concentrates of sediments, is a useful method (particularly in reconnaissance) of outlining areas anomalously high in tungsten. If scheelite is present as a heavy concentrate it can be assayed quite accurately by means of a U.V. lamp. Night prospecting for scheelite (over ground outlined during the day) using a U.V. lamp is a useful method of surface evaluation.

ADDENDUM

It was felt at the time of writing the section on the skarn tungsten deposits that a description of the King Island Scheelite deposits would have been superfluous in that similar features were displayed and described from the Bishop district, California, and from the Yukon, Canada. However, on reflection, and for the sake of completion, a description of the important King Island Scheelite deposits of Tasmania should provide additional useful detail on skarn tungsten mineralisation.

King Island Scheelite Deposits

King Island lies off the northwest coast of Tasmania and is about 35 miles long by 20 miles wide at the maximum. The scheelite deposits are located in the south-east corner of the island in the vicinity of the town of Grassy.

Scheelite is mined by the open cut method and total production since commencement of mining operations (1912-15) to mid-1972 is estimated at 5,670,000 tonnes of ore averaging 0.53 percent tungstic acid (WO₃) (Danielson, 1977). In 1971, about 287,000 tonnes of ore were milled producing about 1,600 tonnes of concentrates containing roughly 1,200 tonnes of WO₃.

Scheelite mineralisation is found within a sequence (approx. 200 metres thick) of ?Late Proterozoic/?Early Cambrian dolomitic siltstones, shales and conglomerates which have been locally contact metamorphosed by granitic intrusives of Devonian/Carboniferous age. This sequence of sedimentary rocks, referred to as the 'mine series', is unconformably overlain by a sequence of volcanic rocks of undetermined thickness (Danielson, 1977). The local stratigraphic sequence (after Knight and Nye, 1953) in the mine area is given by Danielson, 1977. This sequence has been divided into mappable zones which are listed below in descending stratigraphic order:

- B lens hangingwall hornfels; 10-20 m; strongly jointed actinolitebiotite hornfels
- B lens; 25-30 m; a banded sequence of biotite-pyroxene hornfels, marble, grossularite, pyrrhotite, variable scheelite

Hangingwall hornfels; 5-50 m; strongly jointed, purplish black, biotite-actinolite hornfels

- Pyroxene-garnet hornfels; 2-15 m; a blotched green (diopside) and pink (grossularite) hornfels containing calcite ovoids up to 15 cm diameter; variable scheelite
- Upper C lens; 0-12 m; principal ore horizon; andradite skarn, marble, minor pyroxene-grossularite hornfels
- Marble marker; 1-5 m; barren or weakly mineralised marble, pyroxenegrossularite-biotite hornfels
- Lower C lens; 6-15 m; weakly banded andradite skarn, and pyroxene hornfels
- Banded footwall beds; 7-30 m; banded (1-5 cm) marbles, pyroxenebiotite-grossularite hornfels; variable scheelite
- Biotite-pyroxene hornfels; 20-30 m; thinly banded (0.5-1.0 cm) biotite-pyroxene-actinolite hornfels
- Lower Metavolcanics; 5-8 m; tremolite-phlogopite-chlorite-magnetite rock

The scheelite ore bodies occur in skarn rocks which have probably formed either by selective metasomatic replacement of limestone beds (Danielson, 1977) or represent syngenetic deposits (Burchard, 1977). Scheelite mineralisation, which is largely stratiform and stratabound, is finely disseminated as idiomorphic grains (0.05-0.2 mm) predominantly in an andradite-clinopyroxene-quartz host and, to a lesser extent, in clinopyroxene-andradite-plagioclase-titanite rock. Scheelite also occurs as coarse grains, up to 2.0-5.0 cm, exhibiting coarse crystallinity on joint planes and in quartz filled tension gashes. The ore lenses and beds can be traced for several 100 m. along strike and decrease in thickness and grade down dip approaching the intrusive contact. That there is no evidence of any tungsten concentration gradient around the intrusive argues against a metasomatic origin for the scheelite mineralisation.

The molybdenum content of the tungsten sales concentrate, which averages 70-75 percent WO₃, is of the order of 2.0-2.5 percent molybdenum. No wolframite or cassiterite have been detected (Danielson, 1977) although the tin content of the scheelite sales concentrate varies up to 0.01 percent tin. Sulphides present are mainly pyrite, arsenopyrite, pyrrhotite, chalcopyrite and molybdenite. Principal gangue minerals are garnet, carbonate, quartz and apatite.

Burchard (1977) is of the opinion that the tungsten content of the King Island scheelite deposits was not epigenetically introduced. He believes the tungsten was deposited syngenetically with certain beds of the volcanosedimentary 'mine series'. Burchard suggests that tungsten mineralisation is genetically related to basaltic volcanic rocks which occur at the base and at the top, and also as thinner strata, throughout the entire sequence of the 'mine series'. Evidence for a syngenetic mode of origin and a close relationship with volcanic activity, is the relict bedding (accentuated by rapid alternations of barren and mineralised beds) and high Ti, Ni and Cr content of several of the scheelite-rich clinopyroxene bands.

Danielson (1977) proposes, however, that the close connection between structural controls and the loci of tungsten ore deposition suggests that the ores, though largely stratabound, are not remobilised syngenetic deposits. He believes that, "mineralisation has resulted from infiltration and diffusive metasomatic replacement of carbonate horizons, the solutions having entered the 'mine series' along zones of major dislocation". I would like to give special thanks to Prof. Bob Mason for his helpful comments, guidance and co-operation throughout the preparation of this review.

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MARINE

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