

Some Aspects of Tungsten Mineralogy and Geochemistry*

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Abstract: Though tungsten minerals have been mined for over fifty years in Korea, which has become one of the worlds largest tungsten producers since 1951, knowledge of their mineralogy and geochemistry is somewhat limited to the school of tungsten students.

There is a considerable amount of literature throughout the world on the tungsten mineralogy, the geochemical behaviour of tungsten, the nature of tungsten deposits and geological environments for tungsten mineralisation. Commonly known tungsten minerals such as scheelite and wolframite belong to one of two series, the scheelite or the wolframite series, as the primary tungsten minerals. Secondary tungsten minerals are known rather rare, however, some of them plays an important role of exploration guide in search for tungsten deposits.

The geochemistry of tungsten is imperfectly known, and apparently the behaviour of tungsten in geological processes has been the subject of few studies. Recently, some aspects of the fundamental geochemistry of tungsten has been worked out and compiled the data in broad the up to date by many authors.

In order to facilitate the better understanding and future exploration of tungsten deposits, an attempt has been made to summarise the existing knowledge of the fundamental geochemistry of tungsten, together with its common geochemical association with various types of tungsten deposits.

1. INTRODUCTION

Since tungsten was discovered in 1781 by K. W. Scheele, the value of tungsten plays such an important role in the modern heavy industries, especially the strategic industries, as one of the essential alloy metals, which are of vital importance during times of world trouble. Bateman (1950, Economic Mineral Deposits, p. 598) has expressed the situation of tungsten in a simple sentence "the more trouble, the more tungsten".

Tungsten is a brilliant, white metallic element with a physico-chemical property of the greatest tensile strength for all known metals, so-called 'a feast and famine metal'. Therefore it has suffered from wild swings in demand which produced shortages and frantic prospecting followed

by overproduction and tumbling prices as wars and peace have alternated over this century.

Most of the known major tungsten deposits of the world occur in the Asiatic continent and other less important deposits are found in South America and western Europe. In particular Korea has been known as one of the most important tungsten producer, next to China, in the world.

In this paper an attempt has been made to summarise the existing knowledge of the fundamental mineralogy, geochemistry and type of tungsten ore deposits with geochemical associations, in order to facilitate the further exploration of new tungsten deposits. The data for molybdenum, which appears to be relevant in view of its common association with tungsten has been summarised by the writer (Kim, S. Y., 1973 and later published in the Journal of the Korean Institute of Mining Geology, vol. 9, p. 177-212, 1976).

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2. SOME ASPECTS OF TUNGSTEN MINERALOGY

2-1. General Statement.

Tungsten minerals found in nature usually occur in the form of oxide or tungstate compounds with predominantly iron, manganese and calcium. The most notable exception is the only tungsten sulphide mineral, tungstenite, an extremely rare mineral.

More than twenty tungsten minerals appear in mineralogy books, of which twelve are usually primary minerals and the rest are limited to the weathered zone, as secondary minerals. All the primary tungsten minerals belong to one of two series, the wolframite series or the scheelite series, and are of major importance. Secondary tungsten minerals are rather rare and are not significant sources of tungsten. However, some of them are common minor constituents of many oxidised zones, and are a guide in the search for hypogene deposits. The fluorescence characteristics and behaviour of tungsten minerals in the zone of weathering are also briefly considered.

2-2. Primary Tungsten Minerals

Primary tungsten mineralogy is fairly simple, and is listed in Table 1.1. (Krauskopf, 1970 and Kerr, 1946). Of twelve minerals listed, only scheelite and the three minerals of the wolframite group are commonly found and are the main sources of tungsten. Therefore, the wolframite and scheelite groups are briefly discussed below. Cuproscheelite was formerly classed as calcium, copper tungstate, being analogous to cuprotungstite, but it is shown to be a mixture of a basic copper tungstate (cuprotungstite) and scheelite which has been reported as a common occurrence in the Copiapo mine, north-western Chile (Sillitoe, et al, 1970).

Sanmartinite is known only at San Martin, Argentina, where it is an alteration product of

Table 1.1 The Primary Minerals of Tungsten

Group	Minerals	Composition
Wolframite	Huebnerite	FeWO_4
	Wolframite	$(\text{Fe, Mn})\text{WO}_4$
	Ferberite	MnWO_4
Scheelite	Scheelite	CaWO_4
	Seyrigite	$\text{Ca}(\text{Mo, W})\text{O}_4$
	Powellite	CaMoO_4
Sub-Scheelite	Cuproscheelite	$(\text{Cu, Ca})\text{WO}_4$
	Sanmartinite	$(\text{Zn, Fe, Ca, Mn})\text{WO}_4$
Others	Tungstenite	WS_2
	Russellite	$(\text{Bi}_2\text{W})\text{O}_3$
	Scheteligite	$(\text{Ca, Fe, Mn, Sb, Y})(\text{Ti, Ta, Nb, W})_2(\text{O, OH})_7$
	Yttrocrasite	$(\text{Y, Th, U, Ca})_2(\text{Ti, Fe}^{3+}, \text{W})_4\text{O}_{11}(\text{?})$

scheelite (Little, 1959). Both species are restricted to the oxidized zone of porphyry copper deposits. Tungstenite is the only species of tungsten sulphide, occurring as a dark-grey mass exhibiting minute scales, resembling graphite, and containing about 61.5% of WS_2 . Its occurrence is known at only one locality, the Emma mine, Utah (Kerr, 1946).

All the others are little more than mineralogical curiosities.

2.2.1. The Wolframite Group

The Wolframite group comprises an isomorphous series from one end member, iron tungstate, ferberite, to the other end member manganese tungstate, huebnerite, with the intermediate member wolframite. Hess and Schaller (1914) have examined more than 300 analyses of minerals of the wolframite group throughout the world, and proposed the following definitions for the members of the wolframite series, based on compositional variations, as summarised below:

Minerals	% FeWO ₄	% MnWO ₄
Ferberite	80—100	0—20
Wolframite	20—80	20—80
Huebnerite	0—20	80—100

The minerals of the group crystallise in the monoclinic system, commonly with short prismatic or wedge-shape crystals. In nature, the occurrence of end members ferberite and huebnerite is comparatively rare whilst wolframite is common.

Solid solution relations of the wolframite series have only partly worked out. Hess and Schaller (1914) claimed that there exists an essentially complete and continuous series of mixtures of manganese iron tungstates ranging from pure ferberite to pure huebnerite, but Reedman (1967) states that Leutwein (1953) has questioned this conclusion and suggested that a gap exists in the series with pure huebnerite being nearly always secondary. Schrocke (1960) claimed that continuous solid solution is exhibited only at temper-

atures over about 400°C.

The composition of natural minerals of the wolframite group appears from published analyses to be rather widely variable and is shown in Table 1.2.

The wolframite group commonly occurs in hydrothermal quartz and pneumatolytic pegmatite veins or in contact skarn aureoles with granite intrusions. It is commonly associated with copper, molybdenum and tin. In Korea, wolframite is the most common, occasionally close to ferberite in composition, predominantly in hydrothermal quartz veins or in many places in contact aureoles and is associated with copper or molybdenum but not with tin. It is less commonly found in pegmatites.

The composition of any given member of the wolframite series is characterised by the ratio of the content of huebnerite molecule to the content of ferberite molecule; the so-called H/F coefficient. Similarly, if only the FeO and MnO compositions of the mineral are known, the ratio MnO/FeO gives an approximation to the

Table 1.2. The Chemical Compositions of Natural Minerals of the Wolframite Group(a)

Group	Ferberite			Wolframite			Huebnerite			
	Sample No. (b)	68	83	89	26	43	63	2	15	17
		Original analyses (%)								
WO ₃		76.20	75.55	74.13	76.01	74.78	76.57	75.58	75.36	76.50
FeO		19.19	21.31	23.15	9.81	13.80	18.98	0.24	2.66	4.40
MnO		4.48	2.37	0.56	13.90	9.36	4.90	23.40	19.50	18.50
CaO		—	0.26	1.28	1.19	Tr	0.70	0.13	—	0.20
SiO ₂		—	—	0.71	—	0.30	—	0.62	1.70	0.70
MgO		0.80	0.51	—	—	Tr	Tr	—	—	—
Total		100.67	100.00	100.29	100.91	100.12	100.15	100.02	99.22	100.30
		Recalculated analyses (%)								
FeWO ₄		80.8	89.6	97.4	36.6	59.2	78.3	0	11.6	19.1
MnWO ₄		19.2	10.4	2.6	63.4	40.8	21.7	100.0	88.4	80.9
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Specific gravity		—	7.07	6.405	7.230	—	—	7.177	—	7.20

Source a) Hess and Schaller (1914) P24-35. Among about 100 analyses, the writer selected randomly, to illustrate the end members and intermediate compositions.

b) Sample numbers refer to the above paper.

H/F coefficient. It has been suggested that the ratio is a guide to the conditions for ore formation (Hoskings and Polkinghorne, 1957 and many others) but this has not been verified.

2.2.2. The Scheelite Group

The scheelite group exists also within a series of a large number of isomorphous or polymorphous solid solution compounds. It belongs to the series formed by the anionic substitution, $(\text{WO}_4)^{2-}$ for $(\text{MoO}_4)^{2-}$ or by the cationic substitution, Ca^{2+} for Pb^{2+} , with tetrahedral coordination, producing anisodesmic compounds. The former represents the scheelite-powellite series, essentially a complete solution of two end members, scheelite (CaWO_4) and the powellite (CaMoO_4), with intermediate member, seyrigite ($\text{Ca}(\text{Mo}, \text{W})\text{O}_4$). The latter is the stolzite-wulfenite series, with partial substitution of Pb for Ca between scheelite and stolzite, and also powellite and wulfenite.

Chemical analyses of members of the scheelite-powellite series in nature show a range which covers large portion of the region between theoretical pure scheelite ($\text{CaO}=19.4\%$; $\text{WO}_3=80.6\%$) and pure powellite ($\text{CaO}=28.0\%$; $\text{MoO}_3=72.0\%$). Kerr (1946) suggested the following compositional definitions for the members of the scheelite-powellite series, as listed below.

Solid solution between scheelite and wolframite has been worked out by Grubb (1967), who concluded that it is limited to a fraction of

Minerals	MoO ₃ (%)
Scheelite	0—23
Seyrigite	24—34
Powellite	35—72

a per cent at ordinary temperatures, but becomes extensive at temperatures over 600°C. Chang (1967) also stated that complete solid solutions exist in the systems $\text{CaWO}_4 - \text{SrWO}_4$ and $\text{CaWO}_4 - \text{PbWO}_4$ above 825°C, respectively.

Scheelite is the most important tungsten mineral in Korea and the United States. It is tetragonal, colourless to white, usually yellowish white, brittle, and exhibits clear fluorescence, usually bluish white when irradiated by ultraviolet lamp. It is predominantly found in contact metamorphic or metasomatic deposits associated with calc-silicate skarn minerals, or pegmatite and quartz veins with a variety of minerals. However, seyrigite and powellite are not common in nature. Hsu and Galli (1973) have investigated more than 100 specimens from various deposits of the western U. S. A. and reported that most scheelite contains CaMoO_4 mole% upto 20%, but it is unusual to find members of the seyrigite-powellite series with over 60 mole% powellite. A nearly pure end-member was reported by Knopf (1921) from the vugs of an altered zone of rhyolite at the Divide mine, Nevada, and by Battey and Moss (1962) also from vugs in phonolite, Traprain Law, Scotland.

Table 1.3 The Chemical Compositions of Natural Scheelite Group

Minerals	Scheelite					Powellite			
	1(a)	2(a)	7(a)	3(b)	4(c)	9(c)	4(b)	I(d)	I(d)
Sample No.									
CaO	18.96	18.87	19.68	19.7	18.99	18.68	27.2	27.8	27.8
WO ₃	77.0	76.4	77.08	80.5	80.43	80.20	4.4	10.9	11.6
MoO ₃	Tr	0.96	1.87	0.1	—	—	68.0	61.9	61.7
SrO	—	—	—	—	0.33	0.92	—	—	—
Total	95.96	96.77	98.63	100.2	99.75	99.81	99.6	100.6	101.1

a) Vermaas (1952)

c) Barraclough and Reay (1970)

b) Easton and Moss (1966)

d) Battey and Moss (1962)

The composition of the scheelite-powellite series appears from published analyses to be rather variable and is listed in Table 1.3.

2-3. Secondary Tungsten Minerals

Most primary tungsten mineral species may be decomposed in the oxidised zone due to alteration or weathering, though in many near-surface environments they are sufficiently inert to form placers.

Table 1.4. The Secondary Tungsten Minerals.

Stolzite-wulfenite series	
Stolzite	PbWO ₄ (Tetragonal)
Chillagite	Pb(Mo, W)O ₄
Wulfenite	PbMoO ₄
Raspite	PbWO ₄ (Monoclinic)
Oxides	
Tungstite	WO ₃ ·H ₂ O (or H ₂ WO ₄)
Hydrotungstite	WO ₃ ·2H ₂ O (or H ₂ WO ₄ ·H ₂ O)
Cuprotungstite	Cu ₂ WO ₄ (OH) ₂
Ferritungstite	Ca ₂ Fe ²⁺ Fe ³⁺ (WO ₄) ₇ ·9H ₂ O
Anthoinite	AlWO ₄ OH·H ₂ O
Yttrotungstite	Hydrated Y tungstate
Pseudomorphs	
Reinite	Pseudomorph of ferberite after scheelite
Alkinitite	Pseudomorph of wolframite after scheelite.

These secondary tungsten minerals occur as hydrous compounds, except for the stolzite-wulfenite series, and are listed in Table 1.4.

Most species indicated in Table 1.4 have only been recorded from one, or two localities, whilst anthoinite is only found in workable amounts in Uganda and adjacent countries, occurring intimately associated with ferberite and a few other tungsten species (Hosking, 1973). Anthoinite is found as white, earthy masses and is a product of the alteration, perhaps under supergene conditions in the altered zone of scheelite.

Ferritungstite occurs in many localities of the United States (Kerr, 1946), of Africa (Reedman, 1967) and Malaysia (Hosking, 1973). It forms earthy coatings composed of hexagonal plates with a yellow ochreous ore pale yellow to brownish yellow colour, similar to those of hydrous tungstite oxide, tungstite. Goldschmidt (1954, p. 559) states that there is a rather frequent occurrence of the tetragonal stolzite as a secondary mineral in cassiterite deposits. However, Hosking (1965) observed that it is not common in the Malay tin-belt, and tungstite the only secondary species which is common, although possibly ferritungstite may have been misiden-

Table 1.5. The Chemical Composition of Secondary Tungsten Minerals

	1	2	3	4	5	6	7	8	9
CaO	—	0.7	—	0.25	2.2	6.03	—	0.54	—
PbO	48.6	5.95	—	—	—	—	—	—	—
FeO	—	—	—	—	—	—	—	1.21	—
Fe ₂ O ₃	—	—	0.6	0.69	9.3	7.33	0.18	4.14	0.08
Al ₂ O ₃	—	—	14.8	16.41	4.6	—	—	—	—
MoO ₃	0.8	39.2	1.3	—	—	—	—	—	—
WO ₃	49.3	—	74.1	73.23	75.5	72.61	91.3	86.2	80.31
SiO ₂	0.3	—	—	0.73	0.8	—	0.96	—	6.65
H ₂ O	—	—	9.1	8.7	8.3	7.52	7.46	7.72	12.52
Total	99.0	99.4	99.9	100.01	100.7	100.0	99.90	99.81	99.56

1. Stolzite (Easton and Moss, 1969).
2. Wulfenite (Easton and Moss, 1966).
3. Anthoinite (Easton and Moss, 1966).
4. Anthoinite (Reedman, 1967).
5. Ferritungstite (Reedman, 1967).

6. Ferritungstite (Reedman, 1967).
7. Tungstite (Kerr and Young, 1944).
8. Tungstite (Kerr and Young, 1944).
9. Hydrotungstite (Kerr and Young, 1944).

tified. The chemical composition of the secondary tungsten minerals from published analyses is shown in Table 1.5.

The general characteristics of the secondary species of tungsten minerals are quite similar to those of secondary molybdenum minerals, for example, anthoinite resembles crystalline aluminum molybdate, tungstite is similar to molybdate and ferritungstite to ferrimolybdate, which are widely observed in the oxidised zones or supergene enrichment zones of porphyry copper or molybdenum deposits elsewhere (Kim, S. Y., 1973). Thus it may be possible to integrate on an intimate knowledge of these secondary minerals developed from the primary minerals by supergene processes, to search for the hypogene deposits.

2-4. Fluorescence of Tungsten Minerals

Fluorescence is defined as the ability of a substance to absorb invisible wave lengths of light, particularly ultraviolet and to emit visible wave lengths during the irradiation. This is a particularly valuable aid in prospecting and for distinguishing valuable ore minerals with characteristic fluorescence.

Of all tungsten-bearing minerals, only scheelite fluoresces when irradiated with short-wave ultraviolet light, with wave lengths of 2000 to about 3000Å. However, its fluorescent colour varies due to the presence of minute quantities of chemical impurities. The effect upon the fluorescent colour of scheelite of variable amounts of impurities has been investigated by Greenwood (1943), McLaren (1943), Vermaas (1952) and Kononov (1968).

Pure scheelite fluoresces a strong blue but generally with an increasing molybdenum content the colour changes to pale blue through white to yellow, as listed in Table 1.6.

Greenwood (1943) noted that manganese content in scheelite produces a trend similar to that of molybdenum, but is less consistent. Hosking

Table 1.6. Molybdenum Content and Fluorescent Colour of Scheelite

Colour.	MoO ₃ (%)		CaMoO ₄ (%)	
Blue	0 (a)	0 (b)	0 (c)	0 (d)
Pale blue	0.01-0.2	0.01-0.03	0.1-0.4	0.12
Cream	0.3	—		0.39
White	0.35-1	0.54	0.5-10	0.52
Pale yellow	+1.0	0.96	1.0	1.62
Yellow		1.87	1.0	2.46-16.81

(a) McLaren (1943)

(b) Vermaas (1952)

(c) Hosking (1973)

(d) Kononov (1968)

(1965) stated that the comparatively, rare cuproscheelite always fluoresces yellow-green, and also malayaite (CaO·SnO₂·SiO₂) usually fluoresces yellowish, a colour which may well have caused it to be mistaken, on occasion, for molybdenum-rich scheelite or powellite.

The fluorescent colours of certain other minerals commonly resembling those of scheelite and which may be associated with scheelite are listed in Table 1.7.

It is noteworthy that lichen which is so abun-

Table 1.7. The Principal Fluorescent Minerals Associated with the Scheelite(modified from Little, 1959)

Minerals	Fluorescent Colour
Apatite-usually non-fluorescent	green, gray blue, orange
Calcite-usually fluorescent	white, yellow, green, blue
Fluorite-occasionally fluorescent	green, grey, blue, cream
Hydrozincite	bright blue to cream
Petroleum (oil)	strong blue, yellow or green
Quartz-usually non-fluorescent	
but rose quartz	pale purple
smoky quartz	brownish yellow
Rhodochrosite	brownish, grey
Willemite	bright green, reddish brown
Wulfenite	green
Zincite	bright green

dant on most out crops will usually react to the ultraviolet lamp with a bright bluish white fluorescence, whilst with mineral oil which is commonly splashed onto the fresh rock underground, has strong blue or yellow to green fluorescence.

3. SOME ASPECTS OF THE GEOCHEMISTRY OF TUNGSTEN.

3-1. General Statement

Goldschmidt (1954) and Rankama and Sahama (1952) express the fact that the geochemistry of tungsten is imperfectly known, and apparently the behaviour of tungsten in geological processes has been the subject of few studies. It is common to find the results of trace element studies of rocks and soils, in which the data of many elements are presented, whilst those of tungsten are lacking. According to Ginsburg's (1960, p. 176) observation, the lack of knowledge about the geochemistry of tungsten doubtless stems from the relative low sensitivity of the spectrographic method for tungsten, perhaps a few thousands of one per cent.

Recently, some aspects of the fundamental geochemistry of tungsten have been worked out in part, Krauskopf (1970) has compiled most of the up to date geochemical data relating to tungsten distribution in various geochemical materials and geochemical behaviour of tungsten in various geological processes on the basis of its thermodynamic evaluation and solubility products. Barabanov (1971) has also reviewed the theoretical aspects of the geochemical characteristics of tungsten compounds.

3-2. Geochemical Character of Tungsten.

Tungsten (or more accurately, tungsten trioxide WO_3) was discovered in 1781 by the famous Swedish chemist Karl Wilhelm Scheele (1742-1786), who separated the oxide by treating the mineral tungstenite, later named scheelite, with different acids. The actual metal is not

found in nature, but was isolated by two Spanish brothers, J.J. and F. d' Elhuyar in 1773, by reduction of WO_3 with carbon.

Tungsten is a brilliant, white metallic element with the following physico-chemical properties (Krauskopf, 1967 and 1970; Barabanov, 1971; Smith and Curtis, 1972):

- a) Periodic system: Group VI-B, along with Cr, Mo, U.
- b) Atomic number and weight: 74 and 183.92
- c) Atomic radii: 1.26Å (4-cord.), 1.31Å (8-cord.), 1.41Å (12-cord.)
- d) Natural stable isotopes: 180 (0.1), 182(26.4), 183 (14.4), 184 (30.6), 186 (28.4) (abundance, wt%)
- e) Ionic radii: 0.70 Å (W^{4+} in 6-cord.), 0.62 Å (W^{6+} in 6-cord.), 0.59Å (W^{6+} in 4-cord.)
- f) Electron shells: 2, 8, 18, 32, 12, 2
- g) Valences: 2, 4, 5, 6
- h) Electron configuration: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^2, 4d^6, 4d^{10}, 4f^{14}, 5s^2, 5p^6, 5d^4, 6s^2$
- i) Type of lattice: body-centred cubic
- j) Specific gravity and hardness: 9.50 and 6.5 to 7.5
- k) Melting and boiling points: $3,410^\circ C \pm 20^\circ C$ and $5,900^\circ C$
- l) Electronegativity : $W^{+6}, 1.7$
- m) Ionization Potential (eV): $W^0 - W^+, 7.89$; $W^+ - W^{2+}, 17.7$; $W^{2+} - W^{3+}, 24.08$ and $W^3 - W^{4+}, 35.36$
- n) Approximate ionic character of bond with oxygen (%): $W^{6+}, 57$
- o) Chemical reactions: dissolved only in a mixture of hydrofluoric and nitric acids.

The most important properties of tungsten are its strength and hardness at elevated temperature, and its melting and boiling points are higher than those of any other metal. Its tensile strength is the greatest for all known metals. Also its specific gravity is the same as that of gold and is exceeded only by iridium, osmium,

platinum and rhenium. It forms alloys with many metals and becomes elastic and ductile but retains its rigidity at very high temperature. Tungsten alloyed with carbon is only marginally less hard than diamond and is used for cutting and drilling in machine tools and mining rock bits. In pure or substantially pure metallic form, the filaments of electric lamps and the distributor points of motor cars are well known uses of tungsten in our daily life.

3-3. Geochemical Distribution of Tungsten

Geochemically, tungsten is strongly lithophile and weakly siderophile, with no chalcophile tendency (Goldschmidt, 1958).

The cosmic abundance of tungsten has been estimated as 0.1–0.2 atoms W per 10^6 atoms of Si, which is in good agreement with values of 0.11 or 0.14 ppm obtained by neutron activation from an average of 16 chondrites (Amiruddin and Ehmann, 1962), and is shown in Table 2.1. They conclude that tungsten possesses definite siderophilic properties with some lithophile characters in meteoritic matter.

Table 2.1. Abundance of Tungsten in Meteorites and Tektites

Samples	Number of analyses	Abundance (ppm)	Analytical method
Iron meteorites	5	1.16(0.78–1.45)	Neutron activation
Chondrites	16, 29	0.14(0.08–0.19)	"
Achondrites	6, 13	0.07(0.005–0.12)	"
Troilite	3	0.016(0.013–0.02)	"
Tektites	4	1.63(1.12–2.35)	"
Cosmic		0.11–0.14	Estimated

3.3.1 Tungsten Distribution in Igneous Rocks.

The abundance and distribution of tungsten in various igneous rocks was reported as early as 1933 by von Hevesy and Hobbie (Sandell, 1946) who found 69 ppm in average of 282 igneous rocks from central Europe, 83 ppm in granites and 24 ppm in mixture of gabbros and norites.

Later, Sandell (1946) claimed that the figures of von Hevesy and Hobbie are higher than might be expected, and suggested that the average tungsten content may be approximately 1.5ppm for silicic and intermediate rocks. He found that tungsten decreases regularly with an decrease of silica content in granites from 2.4 ppm with 76.8% SiO_2 , 1.6 ppm with 73.0% SiO_2 , 1.5ppm with 72.2% SiO_2 to 1.1 ppm with 68.2% SiO_2 .

Regional differences have been seen in tungsten abundances in igneous rocks from various parts of the world and some of the data are summarised in Table 4.2. However, it has been shown that the abundance of tungsten in granitic rocks ranges from 1.4 ppm to 2.4 ppm (except for 3.4 ppm from Dekate) and older analyses (pre-1946) of tungsten in normal igneous rocks are almost certainly in error. Generally the tungsten content of igneous rocks increases with increasing SiO_2 , a feature which is characteristic also of Mo and Sn in igneous rocks (Kim, S. Y., 1973). Several studies have been made concerning the abundance of tungsten in granites and are summarised in Table 2.2.

Table 2.3 indicate that at least to some extent the tungsten contents of mineralised granitic rock are higher than those of unmineralised granitic rocks. Wung (1969) notes that the granite in Hunan, the second largest tungsten province in the southeastern China contains 0.1~0.3% tungsten and 0.1~0.7 % tin based upon spectrographic analyses and these figures greatly exceed the average Clark values (1.5×10^{-4} for tungsten and 3×10^{-4} for tin) of these elements in the acidic igneous rocks. He further noted that due to their intense autometamorphism (or deuteric alterations) the rocks contain large quantities of muscovite, fluorite, topaz and tourmaline. He concludes that the primitive magma of the granite was extraordinarily rich in W, Sn and other metallic elements, as well as H_2

O, F, B and other volatile elements, and this responsible for the tungsten mineralisation. Ivanova (1963 and 1969), however, generalised from her extensive work in eastern Siberia that normal granites in regions of tungsten mineralisation are not enriched in the metal; only rocks that have been altered (muscovitised), show anomalous concentration. She concluded that tungsten accumulates in muscovite during the early stages of greisenisation, but in later stages it forms an independent mineral, wolframite. Here, the Mo/W ratio in the greisenised granite is apparently lower than that of the unaltered granite, and molybdenum minerals are practically absent from the greisen and quartz veins. A similar conclusion is reached by Sotnikov and Izyumova (1965) with regard to granites associated with deposits in the Altai Mountains.

Jeffrey (1959) found from his study of tungsten content in rock forming minerals in Uganda that tungsten is not associated with quartz and feldspar in granitic rocks, but appears predominantly in the accessory minerals and muscovite in accord with the observations by Ivanova (1969) (Table 2.4). This suggests that appreciable quantities of tungsten may be removed from the margin by the crystallisation of accessory minerals, otherwise the concentration of this element will rise until primary minerals of tungsten can crystallise. Thus, the appearance of primary minerals of tungsten is characteristic of the late hypothermal stage of granite emplacement, and wolframite ores of this type are known to occur elsewhere in the world.

Recently Nanking University, Department of Geology, China (1974) has studied the granitic rocks of different geological periods of south-eastern China, one of the major tungsten provinces, and the genetic relations of the granites and tungsten deposits. According to their study (Table 2.5 and Table 2.6), the contents of

tungsten and tin of all granites from different geological ages are of slightly higher than the average value of these two elements in granitic rocks and their values increase progressively towards the younger granite ages, whilst the content of molybdenum gives no distinct trend of progressive enrichment. It is explained that the low content of tungsten in the early Caledonian is due to the latter being at the beginning stage of migmatitisation and granitisation. They also have demonstrated that the content of tungsten (together with Sn, Be, Nb and Ta) increases progressively with the development of successive

Table 2.1. Abundance of Tungsten in Meteorites and Tektites

Samples	Number of analyses	Abundance (ppm)	Analytical method.
Iron meteorites	5	1.16(0.78-1.45)	Neutron Activation
Chondrites	16, 29	0.14(0.08-0.19)	" "
Achondrites	6, 13	0.07(0.005-0.12)	" "
Troilite	3	0.01(0.013-0.02)	" "
Tektites	4	1.63(1.12-2.35)	" "
Cosmic		0.11-0.14	Estimated.

Table 2.2. Abundance of Tungsten in Igneous Plutons According to Various Authors

Authors	Average W (ppm)				Locality
	Granite	Diorite	Gabbro	Dunite	
Sandell (1946)	1.5	1.2	—	—	N. America
Kuroda (1956)	1.6	1.2	—	—	U. S. & Canada
" (1956)	2.0	—	—	—	Japan
Vinogradov (1958)	2.4	1.6	1.0	0.33	U. S. S. R.
Jeffrey (1959)	1.4	—	6.3	10.4	Uganda
Studenikova (1960)	2.0	—	—	—	U. S. S. R.
Turekian (1961)	2.2	1.5	0.77	0.7	World
Ivanova (1963)	1.8	1.1	—	—	U. S. S. R.
Ivanova (1969)	2.1	—	—	—	U. S. S. R.
Dekate (1967)	3.7	—	—	—	India
Lyakhovich (1969)	1.5	—	—	—	U. S. S. R.
Levashev (1972)	1.9	1.9	—	—	U. S. S. R.

granites and finally it forms the present deposits.

Table 2.3. Abundance of Tungsten in Some Granites Associated with Tungsten Mineralisation

Authors.	W(ppm)	Remarks
Jeffrey (1959)	8.0	6 Samples from Uganda
Ivanova (1963)	6.4	29 Samples from muscovite granite in E. Transbaikal
Hosking (1965)	6.5	31 Samples from Carmensell Granite, S. W. England.
Reedman(1967)	7.0	9 Samples from Mubende Granite, W. Uganda
Chi, T. K. (1965)	83.6	6 Samples of granite from Kiangsi, China
Wung (1969)	1000-3000	10 Samples of granite from Chin-tao Hunan, China
Levashev(1972)	6.5-16	11 Samples from Primorye granodiorite, U. S. S. R.

In contrast it appears also that the levels of tungsten of granites from two or three different geological ages are almost consistent and there is no concentration in the latest stage of the altered zones, though the ages of the granites are similar to those of the granites of southeastern China (Silverman, et al, 1974; Ishihara, 1971; and Shibata and Ishihara, 1974).

3.3.2. Tungsten Distribution in Sedimentary Rocks.

Tungsten shows about the same average abundance in sedimentary rocks as in igneous rocks,

Table 2.4. Tungsten in Rock-forming Minerals

Minerals	(1)	W ppm	Remarks
Quartz		0.1	granite(a)
Quartz	6	1.0-1.6	granite
Quartz	1	5.6	greisen
Feldspar		0.1	granite
Feldspar	10	0.9-2.6	granite
Feldspar	2	6.5-10	granite in W ore zone
Muscovite	1	0.4	schist (a)
Muscovite	11	14-70	granite
Muscovite	8	41-120	granite in W ore zone
Muscovite	2	510	greisen
Biotite	1	6	biotitegneiss (a)
Biotite	4	5	granite
Hornblende	21	1.2-13	granite (b)
Pyroxene	5	1.2-4.0	granite (b)
Sphene	1	3.0	granite (b)
Garnet	1	0.4	granite (b)
Magnetite	4	1.6-3.6	granite (b)

(1) Number of samples analysed.

(a) From Jeffrey (1958)

(b) From Levashev (1972)

The rests are from Ivanova (1969)

Table Variations in the Amounts (in ppm) of Tungsten in Different Stages (Facies) of Some Representative "multiple-staged" Granite Bodies

Granite Body	First Stage	Second Stage	Third Stage
Kiangsi 455	7.0	8.9	70
Hunan 487	100	100	360

with a range from 0.4-3.8 ppm (Table 2.7). Jeffrey (1959) studied non-calcareous sedimentary rocks of Uganda, and reported that a mean

Table 2.5. Contents of the Principal Ore-forming Elements in the Granites of the Successive Geologic Age (in ppm)

Elements	Hsueh-fengian ^(a)	Early Caledonian	Late Caledonian	Indo Sinian ^(b)	Early Yenshanian ^(c)	Late Yenshanian ^(d)	
						1	2
W	1.9(3)	1.3(6)	2.1(20)	2.5(5)	7.6(21)	8(4)	4.1(4)
Sn	7.4(19)	5.4(26)	9.7(34)	8.7(34)	2.5(50)	20(6)	5.2(22)
Be	1.55(5)	1.8(6)	4.0(6)	7.4(13)	9.8(5)	13.1(10)	4.9(21)
Mo	1.1(19)	0.20(15)	2.0(28)	0.45(39)	2.3(68)	0.4(6)	0.8(3)

(a) 900-840m. y.

(b) 230-180m. y.

(c) 180-160m. y.

(d) 130 m. y.

The numbers in parentheses denote the number of samples analysed.

tungsten content 3.6 ppm, was determined in both arenaceous and argillaceous rocks. As with most heavy metals, the concentration in carbonate rocks is notably less than in clastic sedimentary rocks. Sandstone and quartzite contain 1.6 ppm, at least as abundant as which seems anomalous, since quartz and feldspar in igneous rocks are usually as low as 0.1–0.4 ppm. Wedepohl (1968) considers that this is due to the fact that tungsten in sandstones is concentrated greatly in the heavy minerals or in clay minerals.

Little is known of the abundance of tungsten in carbonaceous sediments, including coals, although these are known to concentrate many other heavy metals, such as Fe, W, U, and Mo. The analysis of coal ashes from the coalfields of the eastern United States reveal a wide 8–440 ppm (Headlee and Hunter 1953; Nunn et al, 1953). Korolev and Derbaremdiker (in Reedman, 1967, p.58) has described a brown coal deposit in Russia where the coal contained as much as 400 ppm tungsten; and the interbedded sandstones and silts 14 and 40 ppm, respectively, which accords with data from the United States. Recently, the Geological and Mineralogical Institute of Korea has explored the belt of Uranium–Vanadium bearing carbonaceous shale in the central part of Korea, and the writer analysed three rocks which were found to contain about 180 ppm Mo and 70 ppm W. This evidence suggests that in certain circumstances tungsten behaves as a biophile element in much the same way as molybdenum is known to behave, particularly in conditions where other heavy metals are enriched.

Dekate (1967) notes that tungsten is preferentially concentrated in the B horizon of Indian soils, and it is enriched as 28 times in the soils of mineralised area. Holman and Webb (1957) reports a regional background over unmineralised rock of 4–6 ppm W, increasing to 6–12 ppm near tungsten deposits and to 20–40 ppm directly

over an ore body, ranging upto 100 ppm at a depth of 45 cm in thick tropical soils in Uganda. These few data lead to a conclusion that tungsten is slightly enriched in the B horizon or lower A horizon of normal soils and that it forms well defined haloes in soils around ore deposits.

3.3.3. Tungsten Distribution in Metamorphic Rocks

Jeffrey (1959) and Dekate (1967) have studied the metamorphic rocks in Uganda and India, respectively and their data are summarised in Table 2.8. Their studies suggest that metamorphic rocks contain roughly twice as much tungsten as their igneous and sedimentary equivalents. These authors do not describe the relati-

Table 2.7. Abundance of Tungsten in Sedimentary Rocks

Rocks	Number of Analyses	W. ppm.	Locality
Shale		1.8	World (a)
		2.0	World
		1.9	World
		1.5	India, with clay (d)
		23 3.8	Uganda, with siltstone and mudstone (e)
Clay	7,614	1.8	Russian platform (b)
Sandstone		1.6	World, (a) and (b)
Sand	6,107	1.6	Russian platform (b)
Sandstone		1.5	India (d)
		5 3.6	Uganda (e)
Carbonate Rocks		0.6	World, (a) and (b)
Limestone and Dolomite		0.4	India (d)
Limestone	4	0.48	Uganda (e)
Coal ash	596	90(40–440)	West Virginia (f)
Anthracite ash		8–90	Pennsylvania (g)
Lignite & shale		2.5	India (d)

(a) Turekian and Wedepohl (1961)

(b) Vinogradov (1958 and 1962)

(c) Horn and Adams (1966)

(d) Dekate (1967)

(e) Jeffrey (1959)

(f) Headlee and Hunter (1953)

(g) Nunn et al (1953)

Table 2.8. Abundance of Tungsten in Metamorphic Rocks

Rocks	W (ppm)	Number of Analyses	Range	Ave- rage	Rem- arks
All metamorphic rocks				3.7	(b)
All metasedimentary rocks				2.3	(b)
Phyllite	19		0.3-15.7	4.7	(a)
Mica schist	5		1.2-4.8	2.5	(a)
Other schist	5		0.5-6.2	2.7	(a)
Pelitic schist				2.6	(b)
Graphitic phyllite	40		8-86	22.8	(a)
				21.2	(b)
Quartzite	8		0.2-10.4	3.4	(a)
				0.5	(b)
Marble	3		0.5-0.8	0.7	(a)
				0.4	(b)
Amphibolite	5		2.7-6.3	4.0	(a)
Metabasic rocks				6.8	(b)

(a) Jeffrey (1959)

(b) Dekate (1967)

onships of their samples to tungsten mineralisation in surrounding rocks but since their works were preliminary studies of tungsten ore deposits, it seems possible that their material was contaminated from widespread tungsten mineralisation of the Precambrian basement in both countries which are approximately similar to those of the Precambrian tungsten mineralised belts in Colorado, U. S. A. as described by Tweto (1960).

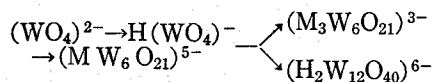
However, their data for metasedimentary rocks, bear out the general relationship noted for the original sedimentary types (see Table 2.7). Tungsten is conspicuously higher in rocks derived from clastic sediments than in those from carbonates. The most striking are the high values for phyllites and schists containing graphite, the graphite being derived from the organic matter which has an initial enrichment of tungsten.

3-4. Geochemical Behaviour of Tungsten in the Various Geologic Processes

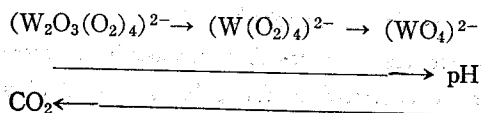
Tungsten geochemistry is very complex, since tungsten may have valences of +1, +2, +3,

+4, +5, and +6. It is generally known that tungsten has acid properties in the higher valence states and basic properties in the lower states. The lower oxidation states of tungsten are unstable and therefore univalent and bivalent tungsten occur only in halides.

Barabanov (1971) states that tungsten has a strong tendency to form complexes, and as a result, there are various heteropoly-, aquapoly-, and isopoly- tungsten compounds. He also notes that under normal conditions the existence in solution of particular tungsten ions is certainly dependant upon the pH of the medium. In alkaline solutions with pH greater than 8, the monotungsten ions, $\text{H}(\text{WO}_4)^-$, are in equilibrium and in neutral solution with pH 8 to 6 it forms the hexa-tungstate ions, $6\text{H}(\text{WO}_4)^-$. In acid solutions with pH from 6 to 4 only the $(\text{HW}_6\text{O}_{21})^{5-}$ ions are stable, and with further decrease in pH, in very dilute solutions, these ions are transformed into $(\text{H}_3\text{W}_6\text{O}_{21})^{3-}$ ions. Thus, with increase in concentration of hydrogen ions in the solutions the tungstate ions form hydrogen-tungstate ions.



Whilst in weakly acid and weakly alkaline, in the presence of strong oxidisers, as hydrogen peroxide, the tungstate ions are transformed into peroxytungstate ions containing peroxide groups (O_2). The evolution of tungsten-bearing solutions with decrease in the concentration of active oxygen and increase in pH may be represented as follows:



This clearly shows the strong affinity of tungsten for oxygen in acid environments and the gradual weakening of this affinity with increase in alkalinity.

3.4.1. The Behaviour of Tungsten in Magmatogenic Processes

Tungsten minerals in nature are commonly associated with fluorine bearing minerals, fluorite, mica and topaz, and occur in quartz and pegmatite veins near or within igneous plutons. It is traditionally assumed that tungsten is often enriched in volatiles and is transported in the form of a halogen compound (Helgeson, 1964). But it is known that 'one of the principal properties of fluorines' is the ease with which they hydrolyse. Hydrolysis of tungsten produces oxyfluorides, WOF_4 and WO_2F_2 or monohydrate of $\text{WO}_3(\text{WO}_3\text{H}_2\text{O})$.

Krauskopf (1970) states that in a crystallising magma that contains appreciable tungsten, the tungsten should be concentrated in the water rich residual solutions. The marked difference in properties between W^{6+} and the major ions of silicate minerals, together with the demonstrated scarcity of tungsten in the common silicates, indicates that the element will favour a water-rich phase rather than the crystallising silicate minerals.

According to the calculations from thermodynamic data (Ivanova, 1966 and Krauskopf, 1957 and 1964), volatile tungsten compounds should not be present in the water-rich phase in appreciable amounts. In order speculations, many tungsten halides and oxyhalides like WF_6 , WOF_4 , WOCl_4 , which are assumed to be volatile, are often called upon to transport tungsten. However, equilibria involving these compounds and water are displaced so far toward the oxide that their presence in a gas phase is impossible (Krauskopf, 1964). Ivanova (1966) computed equilibrium constants of all reactions between tungsten halides and oxyhalides and the principal components of the tungsten-bearing solutions (water, alkali metals, silica) for pressures of one to 100 atm, temperatures from 25 to 500°C and pH from 1 to 10. The results showed that

the partial pressures of all tungsten compounds are very low as 10^{-11} to 10^{-23} atm. These imply that they cannot be transported in significant quantities either in the liquid or gas phase.

Krauskopf (1970) suggests that in slightly acid solutions tungsten can be carried in small but appreciable amounts in the presence of Ca^{2+} , Fe^{2+} , and Mn^{2+} , perhaps as the simple tungstate ion WO_4^{2-} , or at higher temperatures as the relatively undissociated compounds H_2WO_4 and Na_2WO_4 . As noted earlier by Barabanov (1971), the increase in the activity of monomer ions WO_4^{2-} in the solution, paralleling an increase in alkalinity, creates conditions favourable for precipitation of Fe and Mn tungstates. Gundlach (1967) has investigated the stability of silicotungstic acid $\text{H}_4(\text{Si}(\text{W}_3\text{O}_{10})_4\text{H}_2\text{O})$ at elevated temperatures and pressures and at different pH values in the presence of Fe, Mn and Ca. Pure silicotungstic acid remained completely stable at 200°C and 20 atm, nor was it dissociated into $(\text{SiO}_4)^{4-}$ and $(\text{WO}_4)^{2-}$ ions in the presence of Fe, Mn and Ca. He also observed that the stability of silicotungstic acid increases with increase in pressure and is preserved in aqueous solutions to temperatures of 250–300°C. If Fe, Mn and Ca are present in the solution, the tungstates of these cations are precipitated in, the order of increasing solubility: $\text{FeWO}_4 < \text{MnWO}_4 < \text{CaWO}_4$, and begin with crystallisation of FeWO_4 at pH 5.9, MnWO_4 at pH 6–7 and CaWO_4 at pH 7.3. In addition, Ivanova and Khodakovskiy (1968) pointed out that an oxyfluoride complex may contribute to the solubility in solutions where the concentration of F^- is exceptionally high.

Bryzgalin (1958 and 1960) has shown that scheelite forms readily by reaction between Na_2WO_4 solutions and calcic plagioclase at higher temperature, provided the solution is no more than weakly alkaline, and also notes a faintly alkaline solution in the presence of

calcite at 250° and 500°C will decompose wolframite and deposit tungsten as scheelite. Further he showed that tungsten is precipitated in skarns not only by the calcium of marbles but also by the calcium released from pyroxenes, amphiboles, and calcic plagioclases.

From these observations it seems clear that tungsten is carried in ore forming solutions chiefly as tungstate ion, tungstic acid, sodium tungstate, or a heteropoly-acid, and the relative amounts of these is dependent upon temperature, pH and the silica content of the solution, in conjunction with the primary or secondary sources of bivalent Ca^{2+} , Fe^{2+} and Mn^{2+} .

3.4.2. The Behaviour of Tungsten in Sedimentary Processes

A few scattered analyses for tungsten only have been published in reports on recent marine sediments and therefore the knowledge of its distribution, mode of accumulation and occurrence is little known.

Amiruddin and Ehmann (1962) obtained 4.5 ppm W in a core from the mid Pacific, and noted that their four analyses indicate a steady downward increase in tungsten concentration, from 3.2 ppm within 16 cm of the sediment-water interface to 5.4 ppm at a depth of 3.7 metres. Similarly, Isayeva (in Reedman, 1967, p. 56) found that most of the bottom sediments of the Okhotsk Sea contain between 8 and 16 ppm W and that the content tended to increase slightly with depth to about 24 ppm at 27 metres below the sediment-water interface. High concentrations (16–24 ppm W) near to the Kurile Island arc were associated with concentrations of titanomagnetite; tungsten was associated with iron and manganese hydroxides. Deketa (1967) reported that an abnormal concentration of tungsten was found in ferruginous sandstone and shales in India containing 4.3 ppm W, and was correlated with the ease of absorption of tungsten on ferric and manganese oxides, which

is in accord with a similar correlation suggested by Isayeva's observation.

It appears from these works that tungsten may accumulate as a constituent of heavy minerals in clastic sediments as noted by Jeffrey (1959) or by co-precipitation or absorption with hydroxide of manganese and iron as noted by Isayeva and Deketa (1967). The latter processes are known from quantitative experiments of Kraymov et al (1965) who showed that if a solution containing 100 ppm W in the form of WO_3^{2+} is maintained at a pH between 6 and 7, 60%–80% of tungsten is absorbed on either ferric oxide or manganese dioxide.

Despite the fact that tungsten under most natural conditions is stable in its highest valence, +6, and its oxide, WO_3 is nearly insoluble in neutral and weakly acid solution but readily soluble in alkaline solutions. Also the primary tungsten minerals are regarded as being rather stable and occasionally accumulate as placer deposits, containing predominantly ferberite and less huebnerite but seldom scheelite. However, the scarcity of tungsten placers compared with tin placers is commonly explained by the extreme brittleness of scheelite and wolframite, which leads to their breakdown into very fine particles that become widely dispersed in fine-grained sediments; or that tungsten goes into solution during the weathering process.

It is well known that when acid is added to an alkaline solution the oxide is precipitated, generally as a hydrate, or it may form a colloid. Tungstates of most divalent metals are insoluble in natural and alkaline solutions but in acid they are decomposed with formation of the oxide.

Khodakovskii and Mishin (1971) indicate that the solubility of scheelite decreases as temperature rises, at least to 100°C, but the apparent decrease reverses at higher temperature according to the calculations of solubility product shown in Table 2.9. Urusov et al (1967) have com-

Table 2.9. Solubility Products of Tungsten Minerals from 25° to 350°C

Temperature	°C	25°	50°	100°	150°	200°	250°	300°	350°
-log K_{CaWO_4}	(a)	8.74	8.54	8.55	9.02	9.80	10.80	11.95	13.21
-log K_{MnWO_4}	(b)	9.06	9.07	9.48	10.23	11.27	12.51	13.90	15.33
-log K_{FeWO_4}	(b)	15.00	14.72	14.69	15.06	15.75	16.67	17.76	19.00

(a) Khodakovskii and Mishin (1971)

(b) Chernyshev and Ivanova (1969)

piled solubilities of other tungstates and free energies of formation of tungsten compounds which are shown in Table 2.10 and Table 2.11, respectively. These indicate that in general at least the order of solubilities of scheelite, ferberite and huebnerite agrees with the relative solubilities of three minerals noted by several observers (Gannett, 1919 and Gundlach, 1967); Scheelite being most soluble, huebnerite slightly less, ferberite considerably less.

Table 2.10 Solubilities of Tungstates

Compound	Temperature, °C	Solubility (g/l)	Log of solubility product
MgWO ₄		high	
SrWO ₄	25	0.03	-8.17
BaWO ₄	25	0.0096	-9.25
MnWO ₄	25	0.0166	-8.85
FeWO ₄	25		-9.2
CuWO ₄	25		-12.8
PbWO ₄	25		-12.9, -15.0(2)

Data from Urusov et al (1967).

Table 2.11. Free Energies of Formation of Tungsten Compounds (in Kcal/mole at 25°C)

	Latimer (1952)	Khodakovskii & Mishin (1971)	Urusov et al (1967)
WO ₄ ²⁻	-220	-222.5±1.0	
CaWO ₄	-368.7	-366.7	-364.7±0.5
MnWO ₄			-287.8±1.0
FeWO ₄			-259.8±2.0
WO ₃	-181.2	-182.63	
WS ₂	-47.5		

Goldberg (1965) suggests a general average of 0.001 ppb W and a residence time for tungsten in the ocean of about 1,000 years. Udodov

and Parilov (1961) report that of 2,223 samples from Siberian streams and lakes only 18 had detectable tungsten, ranging from 0.8–4.0 ppb W. These indicate seawater is markedly under-saturated with respect to the common compounds of tungsten, in common with the compounds of other rare metals. Krauskopf (1956) suggests that tungsten in seawater was probably mainly removed by organic reactions.

Tungsten is also reported to concentrate in the alkaline waters and brines of certain inland lakes. Krainov et al. (1965) found that high concentrations of tungsten appear in some mine-water increases with an increase of pH, particularly in deep alkaline water which contain 100–300 ppm W. Carpenter and Garrett (1959) noticed as much as 40–64 ppm W in the brines of Searles Lake in California.

In general, the tungsten content in natural waters increase with temperature, pH and with total dissolved solids, and is highest in areas of tungsten mineralisation.

4. MAJOR TYPES OF TUNGSTEN DEPOSITS AND GEOCHEMICAL ASSOCIATIONS

There is a considerable amount of literature throughout the world on the behaviour of tungsten, the nature of tungsten deposits and geological environments for tungsten mineralisation.

Kerr (1947), Bilibin (1968) and Hosking (1973) present summaries of tungsten deposits describing various types and their major characteristics, particularly in U.S.A., U.S.S.R., south-east Asia, south-western England and

Portugal. They have classified the tungsten deposits into the following seven types: 1. Tungsten-bearing banded granitoids. 2. Pegmatite/aplite deposits, 3. Pyrometamorphic deposits, 4. Hydrothermal deposits, 5. Tungsteniferous brines and evaporites, 6. Stratabound and allied deposits, and 7. Placers. Only the following three types are of major economic importance and are briefly considered below.

1) Hydrothermal Vein Lodes Associated with Granites

A great majority of tungsten deposits are essentially of wolframite-bearing quartz vein lodes, associated with tin, molybdenum and copper, accompanying intense wall-rock alteration. They are genetically related to the granitic intrusions and their distributions are usually confined to within typical tin-tungsten-bearing granite metallogenetic provinces (Sn-W belts of southwestern England, Cornwall to Panasqueira, Portugal; western Malaysia, northern Thailand to Mawchi in central Burma; and Hunan to Kangsi in south-eastern China).

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

2) Contact-metamorphic Skarn Deposits Associated with Granites

These tungsten deposits are scheelite-bearing skarn deposits, associated with calc-ferromagnesian silicate skarn minerals, accompanying the metamorphic replacement. They are also genetically related to hydrothermal infiltration derived from the adjacent granitic rocks, and they are usually confined to calcareous sediments in contact with granitic intrusions. Pyrometamorphic deposits in which there are no visible granite intrusions near the deposits may be genetically similar. Only a few deposits are economically exploited up to date and these are Tyrny-Auz, U. S. S. R. (Nesterenko, 1960 and Bryzgalin, 1958), King Island, Australia (Edwards, et al.,

1955 and Large, 1971), Bishop, California (Gray, et al., 1968) and Tempiute, Nevada, (Busek, 1967), U. S. A. The main elements concentrated are W, Mo, Re, Sc, rare-earths, Bi, Cu, Pb, Zn, Fe, S, As, Au, Ag, B, and F.

3) Stratabound Deposits Associated with Metavolcanic Rocks.

There are several distinct varieties of stratabound deposits in different associations. One is widely found in Uganda, consisting mainly of ferberite and locally scheelite and anthoinite from quartz veins and breccia zones within graphitic schist of the Precambrian basement, situated in anticlinal formations. This graphite schist contains also considerable amounts of nodular ferberite, ranging from several millimetres to one centimetre in diameter, locally so plentiful that the rock can be mined for tungsten (Jeffery, 1959 and Reedman, 1967). Many scheelite-bearing strata-deposits were known in Precambrian gneisses basement, associated with calcareous shales and skarn bands (Tweto, 1960; Collins and Kester, 1969; and Cunningham, et al., 1973). Another type recently found in the eastern Alps and described as time- and stratabound deposits, is mainly of scheelite associated with Sb-Hg minerals, occasionally with molybdenite and bismuthinite. These scheelite-bearing deposits are always in very similar rock types related to metavolcanics, and are all in Lower Palaeozoic rocks (Maucher, 1972; Hoell and Maucher, 1972; Zhelyaskova-Panajotova, et al., 1972 and Skaarup, 1974).

The principal elements concentrated are not clearly known except for the main element of W, but are common of Sb, Hg, Sr, Ba, and rare elements.

For geochemical prospecting, tungsten is an excellent indicator of its deposits and can be used in all types of geochemical surveys based on soils, tills, and stream sediments. Tungsten compounds are relatively insoluble in natural

settings as noted above, and hence water surveys are generally not effective. Exceptions to this may prevail where the waters are alkaline since the element exhibits an increased mobility under such conditions. Spring precipitates, especially those containing manganese, are often enriched in tungsten in terrains containing its deposits. Vegetation surveys may also be useful since some plants take up considerable of the element. Some bogs especially if enriched in

manganese commonly contain high amounts of tungsten in the vicinity of tungsten deposits. Good ancillary indicators of tungsten include Sn, Mo, and Bi. The effectiveness of the other elements noted above that are concentrated with tungsten are relatively unknown. Those which are most common in tungsten deposits, including B, Fe, As, Li, and Cu are useful indicators in some districts.

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중석의 광물학적, 지화학적 고찰

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要 約

중석은 우리나라에서 40여년간 개발되어 1951년 이후 세계 굴지의 중석 생산국의 하나로 등장했으나 중석에 대한 광물학적 및 지화학적 지식은 이들을 다루고 있는 전문가에게도 극히 제한되어 이해되고 있다.

중석에 대한 광물학, 지구화학적인 활동특성, 중석광상의 특징과 광화작용의 지질적인 환경 등에 관한 연구논문이 세계적으로 상당량 발표되어 있다. 일반적으로 잘 알려진 중석광물 중 회중석과 흑중석은 일차광물로 회중석계 열 및 흑중석계 열 광물 중의 하나에 불과하며 이외 이차광물은 극히 드물게 산출되나 이들은 중석광물을 탐사하는데 중요한 자료가 되기도 한다. 반면 중석에 대한 지구화학적 지식은 아직도 불완전하게 알려져 있고 지질과정에 있어 중석의 활동 특성은 연구단계에 있다. 최근 중석의 기초 지구화학연구가 많이 진전되어 여러 학자들에 의하여 그 자료가 정리되어 발표되고 있다.

중석광상을 보다 더 이해하고 앞으로 효율적인 탐사를 위하여 현재까지 알려진 중석에 대한 지구화학적 기초 연구와 중석광상에 수반되는 원소들을 요약한다.