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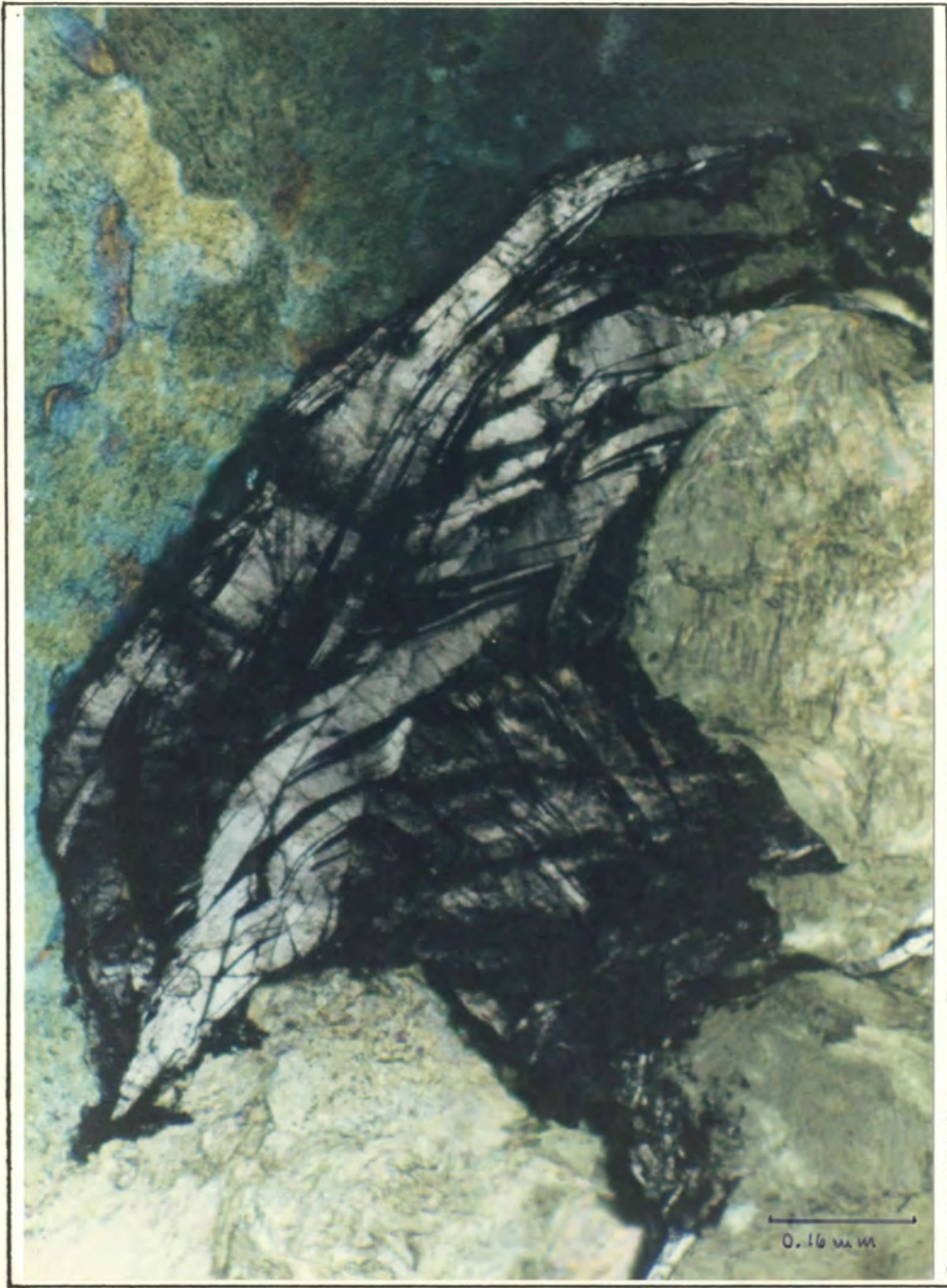
MOLYBDENUM MINERALIZATION WITH EMPHASIS
ON PORPHYRY SYSTEMS. GENESIS AND EXPLORATION

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Dissertation submitted in partial fulfilment of the requirements for the degree of Master of Science (Mineral Exploration) at Rhodes University.

This dissertation was prepared in accordance with specifications laid down by the University and was completed within a period of eight weeks full-time study.

January 1986



FRONTISPIECE : MOLYBDENITE (Mo S_2) : THE MAIN SOURCE OF MOLYBDENUM

ABSTRACT

Mo became very important in the last century, because of its sophisticated properties and its use in the new technology of alloys.

Porphyry systems (porphyry Cu-Mo and Mo) contribute a significant proportion (90 - 95%) to the Mo world's production. This type of deposit is associated mainly with Phanerozoic orogenic belts. Above 87% of the world resources are in the American Circumpacific belts, both Andean and Cordilleran. Ore grade in porphyry Cu-Mo range from 0,005 to 0,04% Mo, whereas in porphyry Mo grades range from 0,08 to 0,75% Mo.

These deposits are associated with a magmatism which shows an evolution from calcic in island arcs, to calc-alkaline in magmatic back arcs, with an increase of the Mo content in the same direction.

Porphyry Mo deposits display several features in common with porphyry Cu deposits. Similarities include nature of host rock intrusives, hydrothermal alteration patterns and distribution of ore minerals. An interesting difference is found in the Re contents of the molybdenite mineral. This element is higher in the molybdenites of porphyry Cu, than in those of the porphyry Mo.

The ore genesis process begins within enriched zones of the upper mantle and involves partial melting, magma differentiation, liquid state thermogravitational diffusion, magma convection and boiling. These processes progressively concentrate Mo in the fluids, which are released at some stage, into sulphidic hydrothermal systems, under complex geologic-tectonic conditions involving fracturing, brecciation and hydrothermal alteration. Major concentrations of the ore mineral are always associated with potassic alteration, and with late magmatic-early hydrothermal stages (Chilean and Western North American porphyries).

Geological mapping and a close understanding of alteration and mineralization patterns, and litho-geochemistry are important tools for the exploration of porphyry Mo deposits. Geochemical prospecting, using soils, vegetation and water as sampling media, and regional aeromagnetic, gravity surveys, aerial photography and remote sensing, are useful methods for the detection of "blind" porphyry Mo deposits.

CONTENTS

	Page
1.0 INTRODUCTION	1
2.0 THE ELEMENT : MOLYBDENUM	3
2.1 History and Production	3
2.2 Uses and properties	4
2.3 Geochemical Characteristics	4
2.4 Mineralogy and Crystallography	5
2.5 Polytypes of Molybdenite	6
2.6 Molybdenum in Meteorites and Lithosphere	7
2.7 Molybdenum in the Exogenic and Endogenic Cycles	11
3.0 TYPES OF MOLYBDENUM DEPOSITS AND THEIR CLASSIFICATION	13
3.1 Porphyry or Disseminated Deposits	14
3.2 Metamorphic Deposits	14
3.2.1 Contact metamorphic type	14
3.2.2 Stratabound metamorphic type	14
3.3 Quartz Veins	16
3.4 Pegmatite and Aplite dykes	18
3.5 Bedded Deposits in Sedimentary Rocks	18
3.6 Wulfenite Deposits in Sedimentary Rocks	19
4.0 GEOTECTONIC SETTING AND DISTRIBUTION	20
4.1 Introduction	20
4.2 Passive Continental Margins and Interior Basins settings	22
4.3 Orogenic Belts and Magmatic Ores	24
4.3.1 Asia	24
4.3.2 Europe	28
4.3.3 America	29
4.4 Island Arc	29
4.5 Intracontinental Rifts	30
4.6 Collision Related Settings	32
5.0 MOLYBDENUM ASSOCIATED WITH PORPHYRY TYPE DEPOSITS AT CONVERGENT PLATES BOUNDARIES	34

	Page
5.1 Introduction	34
5.2 Subduction Related Environments : Andean Type and Island Arc Cu-Mo Deposits	34
5.2.1 Andean type	34
Chilean porphyries	37
El Salvador and Chuquicamata deposits	42
5.2.2 Island arc porphyry deposits	48
5.3 Continental Setting Related to Inactive Subduction zones	50
5.3.1 Porphyry Cu-Mo in western North America	51
5.3.2 Porphyry Mo deposits	55
A - Classification	58
B - Climax type, Urad-Henderson deposit	60
C - Quartz-Monzonite type, Endako deposit	69
5.3.3 An Unusual Occurrence of Porphyry Mo in New Zealand	75
6.0 GENETIC ASPECTS	77
6.1 Origin of the Fluids	77
6.2 Solubility and Transport	77
6.3 Concentration and Deposition	79
6.4 Relationships between Magmatism, Subduction and Molybdenum deposits	80
6.5 Ore Genesis of Climax Type Molybdenum Deposits	81
6.6 Ore Genesis of Quartz-Monzonite type Molybdenum Deposits	83
7.0 EXPLORATION CRITERIA	85
7.1 General	85
7.2 Geotectonic Setting and Type of Magmatism, Guidelines	85
7.3 Geochemical Criteria	87
7.4 Geophysical Criteria	88
7.5 Aerial Photography and Remote Sensing	89
8.0 CONCLUSION	91
ACKNOWLEDGEMENTS	92
REFERENCES	93

LIST OF FIGURES

Fig. No.		Page
2.1	Three main polytypes of MoS_2 . Projected on (1120)	7
2.2	Mo-content in different intrusive rocks	9
2.3	Mo-content in different extrusive rocks	9
2.4	Mo-content in different intrusive and extrusive igneous rocks	10
2.5	Eh-pH diagram of the system $\text{MO-S-H}_2\text{O}$ for $\text{Mo} = 10$ and standards conditions	12
3.1	Block diagram of the south Ore Body, Pine Creek Mine	16
3.2	Paragenetic sequence of veins minerals of the Questa deposit	17
4.1	World Cu-Mo porphyry deposits related to main Phanerozoic and Precambrian orogenic belts	20
4.2	Ratio of % Mo to the length of the corresponding sector of the belt	21
4.3	Suggested facies distribution across a continental margin setting	23
4.4	Uranium deposits in the Athabasca sandstone and Wollaston Fold Belt, Saskatchewan	24
4.5	European-Asian Cu-Mo porphyries related to tectonic	27
4.6	Geological map of the Oslo region showing Molybdenite in graben prepared by Prof. F.M. Vokes and Dr. P.M. Ihlem	31
4.7	Mineralization associated with postulated zones of Keweenawan rifting in the Lake Superior area, Canada	32
5.1	Distribtuion of the porphyry Cu/Mo	36
5.2	Schematic model of the effect initial H_2O and CO_2 contents of melt, in reservoirs with sulphur and metals to form porphyry copper deposits	37
5.3	Tertiary volcanism and related age of Chilean porphyry W deposits	38
5.4	Simplified geological map of the El Salvador (Indio Muerto) district, Chile	44

Fig. No.		Page
5.5	Geology of Chuquicamata Porphyry copper	46
5.6	Lithology, alteration and mineralization at Chuquicamata, Chile	47
5.7	Relative abundance of Cu, Mo and Au in porphyry copper deposits in Pacific and Caribbean island arc area	49
5.8	Hypothetical plate tectonic model, relating metallogeny and convergence plate	51
5.9	Batholiths, thrust belts, and porphyry copper belts of the southern Cordilleran Orogen	52
5.10	Distribution of porphyry deposits in the Canadian Cordillera	54
5.11	Distribution of molybdenum-bearing province in North America	56
5.12	Climax section 16 showing generalized geology and ore zone	61
5.13	Geological sketch of the Urad and Henderson ore bodies Colorado	66
5.14	Henderson alteration zone	66
5.15	Geologic map of Central British Columbia	70
5.16	Geology of Endako Area	73
5.17	Alteration mineralization at Endako or deposit	74
5.18	Diagram illustrating chronology of accretionary events for New Zealand	76
6.1	Eh and T^0 conditions, from early crystallization to hydrothermal stage	78
6.2	Diagrammatic representation of alteration assemblage in a granite Mo system	80
6.3	Schematic representation of the relationship between stockwork Mo deposits, porphyry Cu deposits and arc magma chemistry in a convergent plate margin setting	82
6.4	Summary of possible and probable sources of granitic magmas associated with prophyry deposits	82
7.1	General geological patterns for exploration in Cu-Mo and Mo porphyries	86
7.2	Relationships between thick sialic crust and pronounced gravity lows and high grade Mo deposit	89

LIST OF PLATES

Plate No.		Page
5a	Concentrations of molybdenite along veinlets walls, in the Urad-Henderson stockwork	63
5b	Molybdenite and pyrite in veins of Bruthen stockwork Mo prospect, Australia	63
5c	Red Mountain Porphyry with silicification and sericitization, Urad-Henderson Mine	68
5d	Henderson Granite, displaying sericitic and argillic alteration. Urad-Henderson Mine	68

LIST OF TABLES

Table No.		Page
2I	Mo historical supply-demand growth 1901-1980	3
2II	Chemical and physical properties of molybdenum	4
2III	Ionic radii of the Mo together with a group of other principal elements	5
5I	Mo reserves on resources at Chilean porphyry Cu/Mo deposits	37
5II	Molybdenum-bearing porphyry type deposits of the United States	53
5III	Stockwork and breccia Mo deposit classification based in Magma Series	58
5IV	Porphyry Mo deposits, classified in Climax type and Quartz Monzonite type	59
5V	Comparison of types of Porphyry Mo deposits	59
5VI	Stages of mineralization of Mo deposits in Canada	71

1.0 INTRODUCTION

Molybdenum has been known for at least 2000 years before its discovery in 1788. The metal however became significant in the economy of the world only in the present century. The progress of science and technology discovered its sophisticated properties and found adequate ways to use them.

Molybdenum (Mo) is an element that is scarce in the earth's crust since its average crustal content is at around 1,5 ppm. Mo is classified as a "chalcophile" element which also exhibits behaviour as a "lithophile" element (in its chemical valence 6).

Mo is found in metallic groups associated with sulphur and oxygen in a direct relationship with metallogenic belts in orogenic environments. Most of the molybdenum deposits are related to calc alkaline magmatism in acid to intermediate igneous rocks. Its content increases uniformly from mafic to felsic rocks, clearly increasing in acid hypabysal rocks. This ranges from 0,4 ppm in basic rocks to 2,3 ppm in acid rocks.

Most of the Mo reserves (90 - 95%) and a similar percentage in terms of production, have their source in disseminated porphyry deposits, as a primary ore or by-product. Deposits are associated with Phanerozoic orogenic belts, mainly of the Cenozoic era. Around 87% of world resources belong to the American Circumpacific belts, both Andean and Cordilleran, with approximately 50% of the world total falling within the United States, 20% within the Chilean sector, and 14% within the Canadian sector. Minor occurrences of Mo deposits are restricted to contact metamorphic and quartz veins associated with Sn and W.

Unlike most of the rest of the metals, the supply and demand of Mo has steadily increased because of its new uses. Its future supplies are plentiful because successful exploration results in the last twenty years have proven the existence of large reserves, most of them restricted to porphyry ore types.

The purpose of this dissertation is to present a review of the geology of Molybdenum, its general geochemical characteristics, tectonic settings,

classification of ore deposits, genesis and guides for exploration.

In the following chapters chemical elements will be referred to in their abbreviated forms.

2.0 THE ELEMENT: MOLYBDENUM

2.1 History, Production and Resources

In ancient Greece, Aristoteles called "molybden" the grey, lead-like substance, and until the middle of the XVIII century, it was commonly confused with galena or graphite.

Successive investigations by German chemists, led in 1778 the Swedish pharmaceutical-chemist, Karl Wilhelm, to show that molybdenite and graphite are different mineralogic species. Later, in 1782, Hjelms recognised the new metallic element, and called it molybdenum. In 1893, Moissan obtained metallic Mo of high purity, 99,98%, which permitted to calculate its atomic weight, electric conductivity and other physical, chemical and mechanical properties.

The recorded world Mo production began only in the first years of this century, and its important industrial uses, only since the late 1920's. The first known producers were Australia, United States, Norway and Japan, until the Climax Mine was developed in 1924 (Table 2.1).

Table 2.1. Historical Mo supply - demand growth (Sutulov, 1978)

Period	Table output (mt of Mo)
1901 - 1920	3 378
1921 - 1940	98 165
1941 - 1960	477 449
1961 - 1980 (estimated)	11417 000

The western hemisphere contains more than 3/4 of the resources and production. Until 1977 the total of Mo produced and consumed was 1 720 000 tons. United States have supplied 1 200 000 tons or slightly over 70%, Canada has produced about 165 000 tons of Mo or 10%, while Chile, another large producer, has supplied about 123 000 tons of Mo and thus supplied almost 7,2% of the world's demand. Today, with the Henderson Mine in operation and with a number of porphyry copper mines recovering Mo as a by

product, there is security for the Mo supplies at least for the next 100 years.

2.2 Uses and properties

Mo is a comparatively soft silver white metal characterized by a high relative density of 10,2; a high melting point of $2620 \pm 20^{\circ}\text{C}$, high thermal and good electrical conductive properties and is resistant to corrosion and chemical action (Table 2.II).

These properties mean that it is considered as one of the most important elements in the steel industry.

Table 2.II Chemical and Physics properties of Mo (Venegas, 1981)

Número Atómico	42
Peso Atómico	95,95
Densidad	10,2 g/cm ³
Punto de Fusión	2.610 °C
Punto de Ebullición	4.830 °C
Conductividad Térmica	0,346 cal/seg. cm/°C
Coefficiente de Dilatación (entre 25 - 100 °C)	$4,9 \times 10^{-5}/^{\circ}\text{C}$
Resistencia Eléctrica	$24,6 \times 10^{-6}$ ohm a 800 °C
Calor de Vaporización	142 K cal/mol.
Calor de Atomización	157,5 K cal/mol a 25 °C

2.3 Geochemical Characteristics

Mo is a metallic element of the Group VI of the Periodic Table, and it has an atomic number 42, with an electronic configuration of 2-8-18-13-1; Mo

chemically it occurs in values of +2, +3, +4, +5 and a maximum value of +6. Only values of +4 and +6 are of importance in the nature. Mo has six stable isotopes, with masses of 92, 94, 95, 96, 97, 98 and 100 in proportions that vary between 9,04% (Mo^{94}) and 23,78% (Mo^{98}). Its average atomic mass is 95,94.

It has an ionic radii of $0,68\text{\AA}$ and $0,65\text{\AA}$, tetravalent and hexavalent, respectively. In Table 2.III it is indicated the ionic radii of the Mo together with a group of other principal elements (Uzkut, 1974).

Table 2.III Ionic radii of the Mo and other elements (Uzkut, 1974)

Element (Ion)	Atomic Radius	Ionic Radius (\AA)			Electro- negativity
		C	W	Λ	
Fe^{2+}	1.26	0.83	0.80	0.74	1.7
Al^{3+}	1.43	0.57	0.55	0.51	1.5
Fe^{3+}	1.26	0.67	0.67	0.64	1.8
Ti^{4+}	1.47	0.64	0.60	0.68	1.6
Mo^{4+}	1.39	0.68	0.68	0.70	1.6
W^{4+}	1.39	0.68	0.68	0.70	1.6
Re^{4+}	1.37	—	—	0.72	1.8
Zr^{4+}	1.60	0.87	0.80	0.79	1.5
U^{4+}	1.52	1.05	1.05	0.97	1.4
V^{5+}	1.34	0.4	—	0.58	1.9
Ta^{6+}	1.46	—	—	0.68	1.7
Nb^{5+}	1.46	0.69	—	0.69	1.7
Cr^{6+}	1.28	0.35	0.52	0.52	2.2
Mo^{6+}	1.39	—	0.65	0.62	2.1
W^{6+}	1.39	—	0.65	0.62	2.0
U^{6+}	1.52	—	—	0.80	1.9
Re^{7+}	1.37	—	—	0.56	2.2

2.4 Mineralogy and Crystallography of the Molybdenum minerals

Molybdenite MoS_2 , wulfenite Pb MoO_4 , powellite Ca MoO_4 or Ca (Mo, W) O_4 and ferrimolybdate $\text{Fe}_2 (\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O} + \text{Fe MoO}_4 \cdot \text{OH} \cdot 3\text{H}_2\text{O}$ are the most common Mo minerals. Other Mo minerals are considered as curiosities, like jordisite, amorphous mineral, hemusite $\text{Cu}_6 \text{Mo Sn S}_8$, ilsemannite $\text{Mo}_3 \text{O}_8 \cdot \text{H}_2\text{O}$, eosite Pb (Mo, V) O_4 , lindgrenite $\text{Cu}_3 (\text{MoO}_4)_2 (\text{OH})_2$, iriginite $\text{U(MoO}_4)_2 (\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and seyrigite (molybdoscheelite : Ca (W, Mo) O_4).

The most important Mo mineral is molybdenite, which is the only independently occurring mineral of any importance. Its theoretical composition is 59,9% Mo and 40,1% S. It contains trace elements such

as Re, Ti, Bi, W, Fe, Ge, Se, Te, Cr, Ag, V, Hg and Pt.

Molybdenite has the following diversities :

Mineral : $A x_2$ sulphide type

Crystalline system : Hexagonal

Symmetry class : $6/m, 2/m, 2/m$

axial ratio : $a : c = 1 : 3,899$

type of cell : P unit cell, with $a = 3,16$, $c = 12,32$

content : $Z = 2$

crystalline structure : Octahedral MoS_6 linked by forming parallel layers to (0001). These layers are related to other weak links between the sulphur of each contiguous cells, thus giving a perfect basal foliation.

2.5 Polytypes of Molybdenite

The crystal structure of molybdenite contains a number of double sulphide layers (S - Mo - S). Stacked on one another with interlayer van der Waals contacts between sulphur atoms. The crystals are consequently very soft and folial, very similar in mechanical properties to graphite (both are excellent lubricants).

Hexagonal molybdenite is the most common polytype in the nature (2H1, spatial group $P6_3/mmc$) and consists of two layers for unit cell. The rhomboedric (3R, spatial group $R3m$) is the less common and consists of three layers of unit cell (Figure 2.1).

Commonly molybdenite is made up of 2H1 and 3R polytypes (Chukhrov et al. 1968), and mixtures of the two. The stability conditions of the two forms in terms of temperature and compositions have been studied by Clark (1970).

Evidence suggests that 3R type shows a high content of impurities, with rhenium (Re) being the most common. Its variations range between 1 ppm to more than 5000 ppm. It is possible to establish a direct relationship between the Re content and the 3R molybdenite (Ayres, 1974). The same characteristic is valid for Ti, Bi, W and Fe. The 2H polytype, is relatively pure (Chukhrov, op cit).

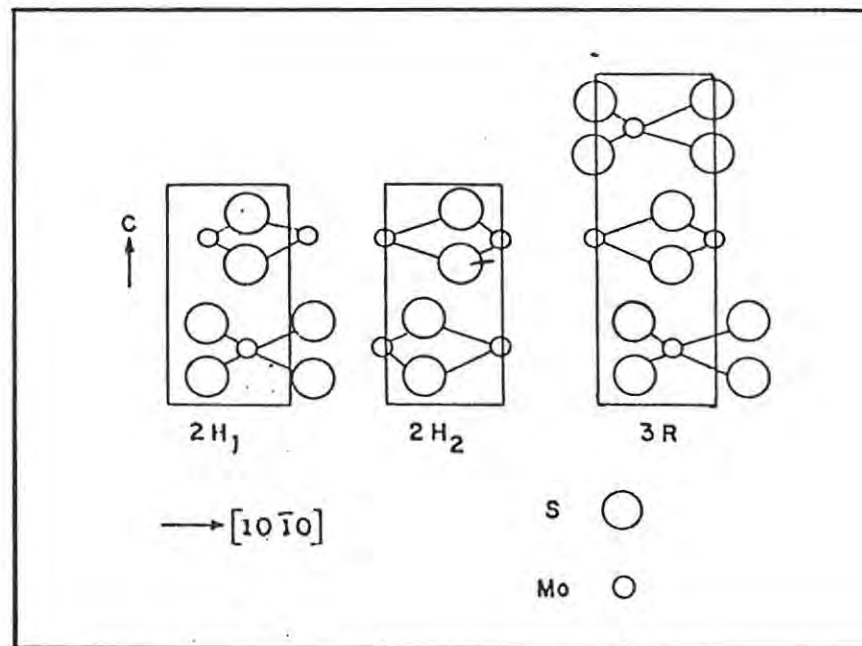


Figure 2.1 Three main polytypes of MoS_2 . Projected on (1120).
(Newberry, 1979)

The Re occurrence in molybdenite can be economically important because of its high concentration of this element in porphyry copper deposits.

The Re^{+4} and W^{+4} have the geometric and electric configurations which allow them to substitute the Mo^{+4} in molybdenite. But only Re is present in it because W^{+4} has a high affinity with the oxygen.

2.6 Molybdenum in Meteorites and Lithosphere

2.6.1 Molybdenum in meteorites

Meteorites provide a valuable source of information with respect to the geochemical nature of the elements and allow inferences as to the elements' distributed in the interior of the earth.

Mo contents in meteorites, according to Kuroda and Sandell (1954), are as follows :

Chondrites (lithites)	1,6 ppm
Silicate phase of chondrites	0,6 ppm
Sulphide phase of chondrites	6,0 ppm
Metallic phase of chondrites	8,0 ppm
Siderite phase	15,0 ppm

Subsequent studies of Murthy (1963), Wetherill, (1964) and Smales et al., (1968), give values of 6,8 , 10,4 and 7,3 ppm respectively which are very similar to the values of the metallic phase of the chondrite.

According to the above distribution Mo is considered to have siderophile characteristics. Also Mo of sulphophile nature is confirmed by enrichment in Mo (6 ppm) in the sulphide (troilite) phase.

2.6.2 Molybdenum in igneous rocks

According to Uzkut (1974), the Mo content in igneous rocks is as follows :

ultrabasic rocks	0,4 ppm
Basic rocks :	
Gabbro	0,78 ppm
Basalt	1,40 ppm
Intermediate Rocks :	
Diorite	0,9 ppm
Quartz - Diorite	1,2 ppm
Andesite	1,7 ppm
Rhyodacite and Dacite	1,9 ppm
Acid Rocks :	
Granodiorite	1,7 ppm
Granite	2,4 ppm
Rhyolite	2,3 ppm
Alkaline Rocks :	
Syenite	4,0 ppm
Carbonatites	50,0 ppm

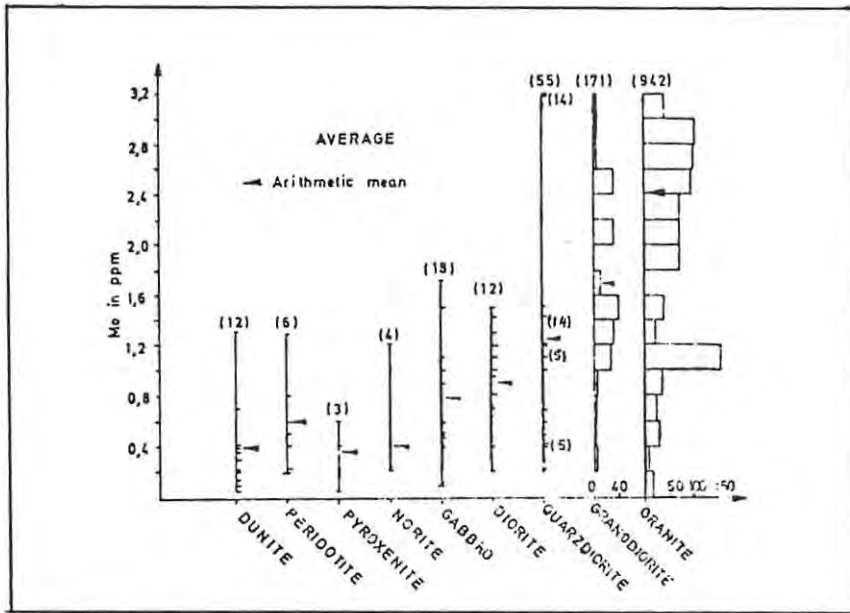


Figure 2.2 Mo - Content in different intrusive rocks from (Uzkut, 1974)

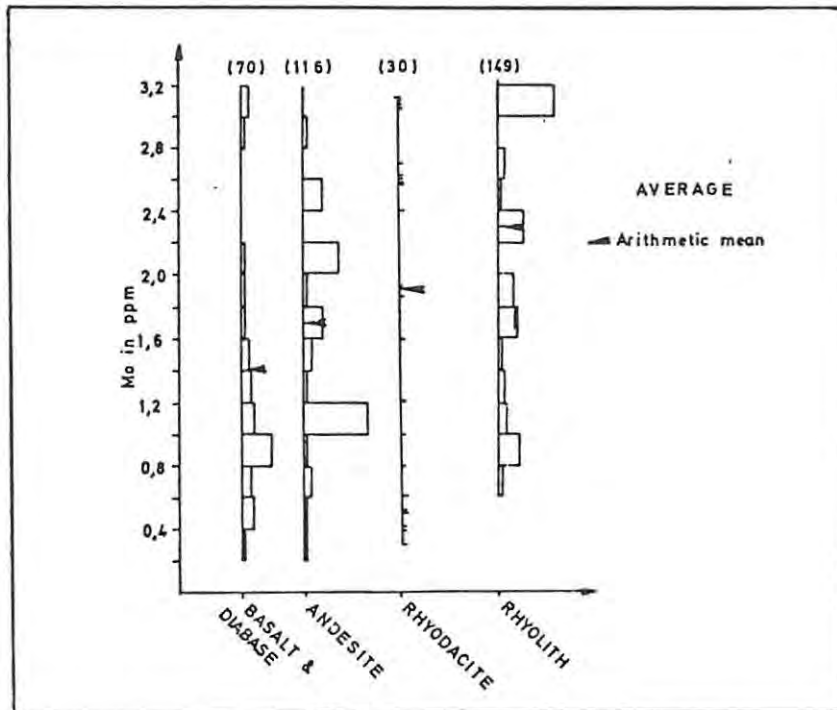


Figure 2.3 Mo - Content in different extrusive rocks (Uzkut, 1974)

Clarke of the lithosphere

1,85 ppm

The greatest concentrations of Mo are to be found in biotite, hornblende and accessory minerals. However, their contribution to the total Mo content is minor, due to the low percentages in rocks. Thus, on average, biotite contributes 19,3% amphibole, 9%, and accessory minerals, 11,4% of the total Mo in rocks. Feldspars store more than 50% of the total Mo.

The Mo content recorded in intrusive and extrusive rocks increases with alkalis and SiO_2 (Figure 2.2).

Figures 2.3 and 2.4 show a relative "depression" in the Mo content of intrusive rocks with respect to extrusives of equivalent chemical composition. Both curves intersect in the area of granite - rhyolite and begin a tendency toward rapid enrichment in granites, which could represent the pre-mineralization phases.

In spite of the relatively high Mo contents of alkaline rocks, the ore deposits are not associated with these lithological types.

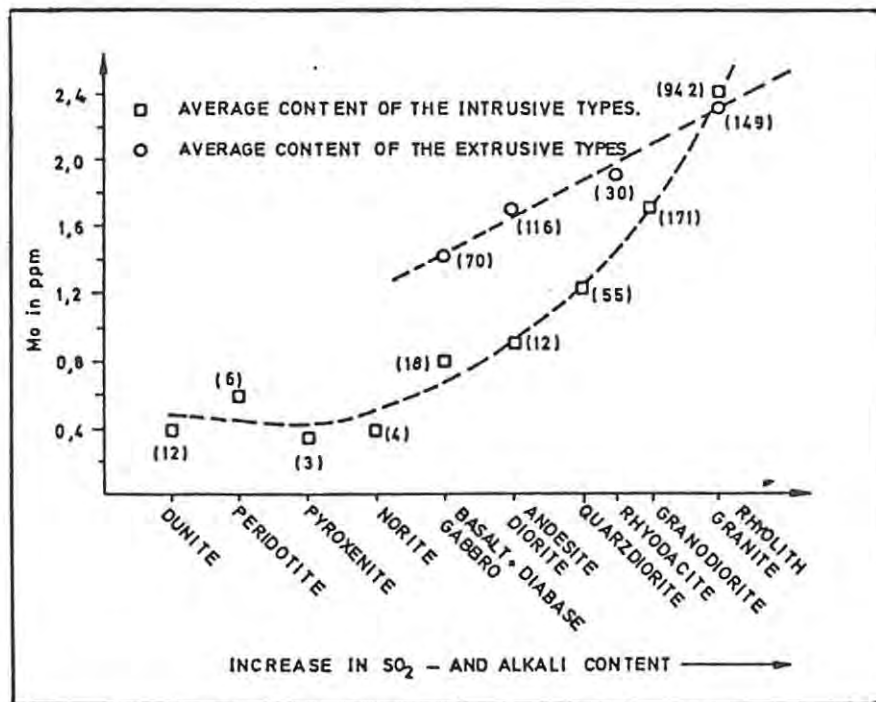


Figure 2.4 Mo - Content in different intrusive and extrusive igneous rocks (Uzkut, 1974)

2.7 Molybdenum in the Endogenic and Exogenic Cycles

2.7.1 Endogenic cycle

It is considered that the presence of Mo in the magmatic stage is feasible as a sulphide, or rather, as Mo^{4+} associated with silicated polymerized structures. However, in the pneumatolytic phase, Mo would be found mainly connected with halogens in the form of volatile halides. Increasing H_2SO_4 in the hydrothermal phase, results in the hydrolysis of the halides. The transport of the Mo in this phase is only possible in the form of the polysulphides or as thiomolybdate in an alkaline medium and as a complex ion in the form MoO_2^{+2} in an acid medium, which precipitates with decreasing pH.

Uzkut (1974), describes the behaviour of Mo during the crystallization process. He considers the case of an intrusive emplaced at a depth of between 3 and 8 km, a mean pH of 7, and a temperature of 1200°C to 900°C , in a reducing medium. Uzkut (1974), described the evolution of the Mo concentration from the early stage, main crystallization stage, pegmatitic stage, pneumatolytic to hydrothermal stage, where temperature (373°C) decreases and H_2O becomes dominant. A more detailed description will be given in chapter 6.0.

2.7.2 Exogenic cycle

pH and Eh values are of special importance. The stable forms of Mo with regard to the variability of both pH and Eh is given in figure 2.5.

In general, Mo is one of the most mobile elements in the exogenic environment due to the solubility of its oxygenated complexes with valence +6. In the process of oxidation Mo is present as an oxy-sulphide that is formed on the surface of the mineral, with mixed products of Mo^{6+} and Mo^{5+} .

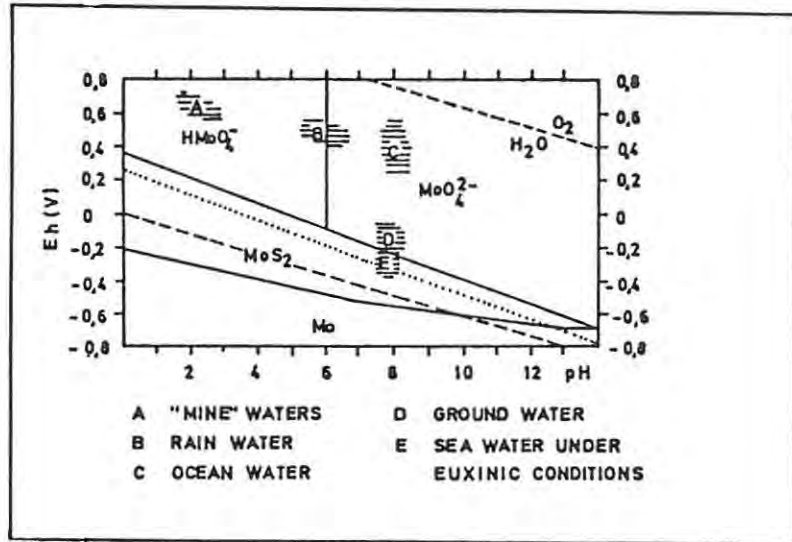


Figure 2.5 Eh-pH diagram of the system Mo-S-H₂O for $a_{\text{Mo}} = 10^{-4}$ and standard conditions (25°C, 1 Atm) From Letovsky et al., 1969; and Tischendorf et al., 1968. In Uzkut, 1974.

Part of the Mo remains also with valence $+4$. In the second stage, the oxidation process would be completed, followed by the formation of anion complexes such as MoO_4^{2-} . The entire process may be represented by: $\text{MoS}_2 + 12 \text{H}_2\text{O} = \text{MoO}_4^{2-} + 2 \text{SO}_4^{2-} + 24\text{H}^+ + 18\text{e}^-$. The precipitation of Mo in the exogenic environments can occur as the sulphide (MoS_2) in reducing environments and as minerals originated by the reaction of MoO_4^{2-} with cation of low solubility products such as Ca^{+2} , Pb^{+2} , CO^{+2} , Bi^{+3} and Cu^{+2} in oxidizing environments. The first two form powellite and wulfenite. Mo^{+4} and MoO_4^{2-} can be observed by colloidal Fe, Mn, Al hydroxides and hydrous oxides. One of these reaction forms ferrimolybdite ($\text{Fe}_2 (\text{MoO}_4)_3 \cdot 8 \text{H}_2\text{O}$).

3.0 TYPES OF MOLYBDENUM DEPOSITS AND THEIR CLASSIFICATION

The classification of Mo deposits has evolved together with the ideas on ore genesis. In the past when veins, pegmatite, pipe and contact metamorphic deposits were considered to be important, Vandervilt (1933), suggested the following classification :

1. Pegmatite and aplite dykes.
2. Quartz veins.
3. Accessory mineral in Au and Cu deposits.

Stevenson (1940), subdivided quartz veins into :

- i) Quartz veins, and
- ii) silicified fracture zone.

The same author extended this classification by including "high temperature replacement bodies".

Creasy (1957), emphasized the economic importance of the Mo deposits and suggested a new classification which formed the basis of the present day system :

1. Deposits yielding Mo or as the chief metal.
2. Cu deposits yielding Mo as a by product.
3. Contact metamorphic tungsten deposits yielding Mo as a by product.
4. Wulfenite bearing base metal deposits.

Types under 1. and 2. are the most important in terms of resources and production.

The classification suggested by King et al.,(1973), has been taken as a more accurate classification, because it includes a greater range of Mo deposits.

According to these authors Mo deposits can be divided as follows :

1. Porphyry or disseminated including stockworks and breccia pipes in which metallic sulphides are dispersed in relatively large volumes of altered and fractured rock.
2. Metamorphic deposits, including stratabound metamorphic, and contact-metamorphic types.
3. Quartz veins.
4. Pegmatites and aplite dykes.
5. Bedded deposits in sedimentary rocks.
6. Wulfenite-bearing deposits.

3.1 Porphyry or Disseminated Deposits :

This type of deposit is the most important source of Mo and it occurs associated with calc-alkaline magmatism, as porphyry Cu-Mo and porphyry Mo. They will be discussed in more detail in chapter 5.0.

3.2 Metamorphic Deposits

3.2.1 Contact metamorphic types occur along the margins of granitic intrusives. In contact metamorphic deposits (tactites and skarns), Mo is commonly associated with scheelite, bismuthinite, or Cu sulfides in zones of silicated limestone along the margins of granitic intrusive rocks. Molybdenite also occurs alone in contact metamorphic deposits. Pine Creek mine in the United States is a good example of this type of deposit, from which Cu and W have been recovered as by-products since 1939 (Bateman, 1956).

3.2.2 As stratabound metamorphic type, occurs the molybdenite deposits of the Knaben mine in Norway. They are in quartz-rich amphibolitic gneisses of probable sedimentary origins and they are included in this category by

King et al., (1973). Urban (1974), concluded that concentrations and precipitations of metals took place in marine environments, and subsequently both, the ores and the host rock underwent the same high-grade metamorphism. The ore ranges from 0,1 to 0,2% Mo and although production from the deposit has been persistent for many years, it has been relatively small.

Pine Creek deposit, the typical contact metamorphic type Mo deposit, is described below.

This deposit was discovered in 1916 and it lies in the Bishop W district located in eastern California, United States. The ore bodies along the contact between an extensive belt of Paleozoic marble that occupies the west side of the "Pine Creek" pendant, and a quartz monzonite of Mesozoic age. The mineralized area contains both W and Mo as well defined shoots. The Mo ore shoots have been found only in the upper parts of the two main ore bodies (with 1% Mo S₂). Cut off grades of 0,4% WO₃ and 0,4% MoS₂, permitted the configuration of the shoots (Bateman, 1956). Tactite is present along most of the 910 m span of contact in the mine area. The ore bodies, which are thicker masses of tactite contain within these rich shoots of W and Mo. The contact metamorphic assemblage consists of pyroxene, garnet, quartz, calcite, idocrase and epidote (Tactite). It comprises a light coloured calc silicate rock, and quartzose rock. Figure 3.1, shows the lithology and mineralization of this deposit.

Silicified zones are present along the intrusive contact. They grade to the wall rock, which is commonly shattered and accompanied by veinlets of quartz ranging in thickness from less than 2,5cm to more than 0,30m. Most of these zones contain molybdenite, chalcopyrite and bornite. These minerals are also locally disseminated in the tactite, usually in silicified areas, although the Mo shoots are more limited in their distribution than W.

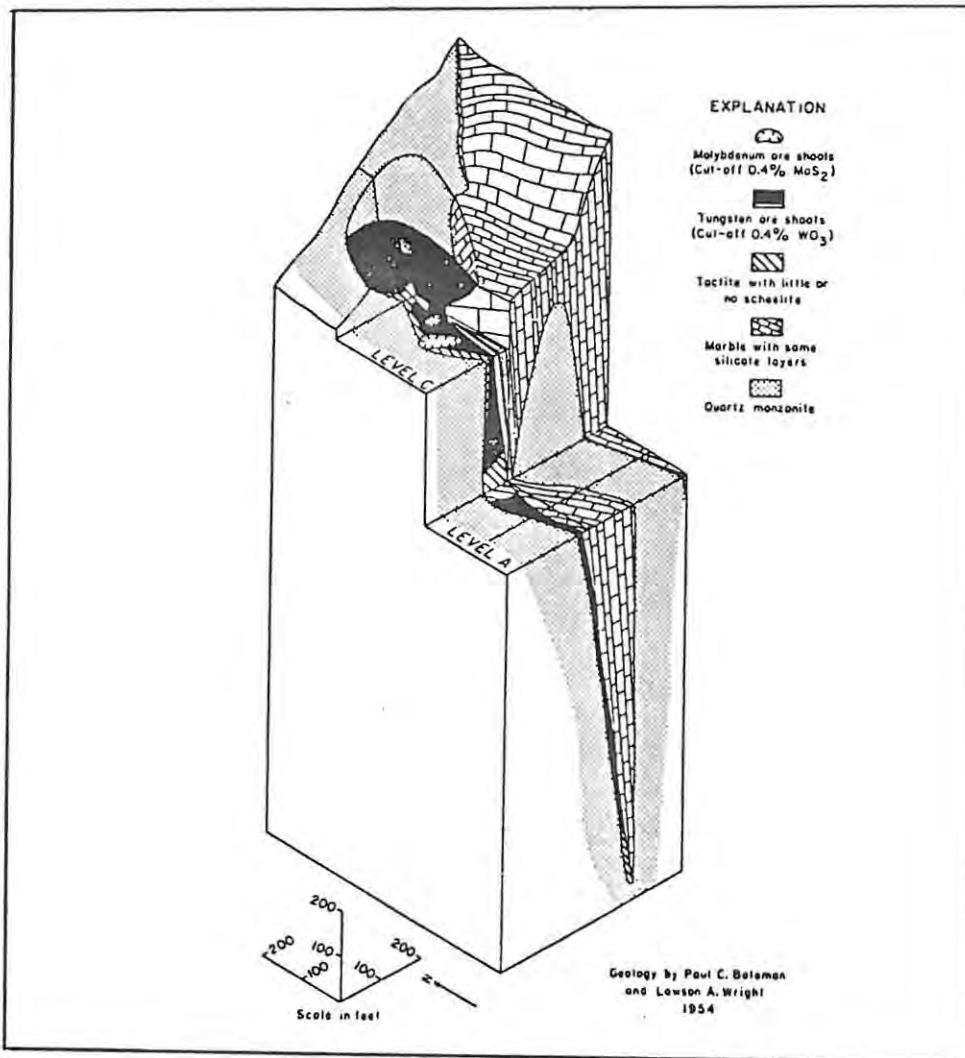


Figure 3.1 Block diagram of the South Ore Body, Pine Creek Mine - showing the tungsten and molybdenum ore shoots (Bateman, 1956)

3.3 Quartz Veins

Quartz veins containing molybdenite are widely distributed throughout the world, especially in Precambrian shields. The mineral content varies widely, pyrite and chalcopyrite are generally common and Au, Bi and W may be present. Small contents of mica and feldspar may indicate a relationship with pegmatitic deposits.

Molybdenite occurs with pyrite in a quartz gangue, often associated with chalcopyrite, fluorite and base metal sulphides, and in some places with graphite, scheelite or Be. Many Au and Ag bearing veins contain small amounts of molybdenite. Production of quartz veins deposits has been small

and exploitation is often confined to ore-rich pods. Several deposits of this type have been recognized throughout the Western Cordillera and in the Appalachian Orogen. Examples are Starr Mine in northern Washington, Cave Peak in Texas and Questa deposit.

The Questa deposit is an example of typical quartz vein type. This deposit is characterized by the presence of molybdenite in massive quartz veins, in a stockwork of discontinuous veinlets and as finely disseminated flakes in a hydrothermally altered and fractured zone. Not until the late 1950's was it discovered that the veins were associated with mineralized rocks having the characteristics and potential for a large low-grade porphyry type molybdenite ore body associated with a composite granite stock.

The quartz-molybdenite veins exploited during the earlier development period, as well as the stockwork molybdenite, lie along the contact of an intrusive body of granite and the overlying andesitic volcanic rocks. The mineralization present is rhodochrosite, fluorite and a little chalcopryite. The grade of the ore body is low, averaging only about 0,1% Mo. Figure 3.2 shows the mineral paragenesis at this deposit in which molybdenite is the earliest formed sulphide phase.

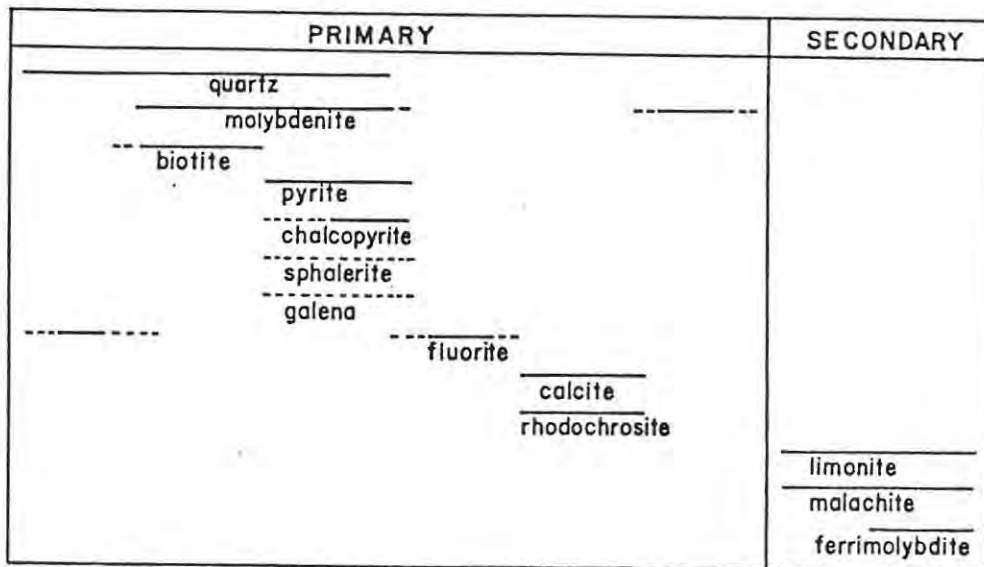


Figure 3.2 Paragenetic sequence of vein minerals of the Questa deposit (Schilling, 1956)

Limonite, malachite and ferrimolybdenite are common on the rapidly eroding areas.

3.4 Pegmatite and Aplite Dykes

Pegmatite bodies and aplite dykes contain molybdenite among many other metallic and non metallic minerals. Molybdenite is generally coarsely crystalline, occurring as rosettes and aggregates of flakes, which are erratically distributed in the host rocks. Molybdenite in aplite is normally of a finer grain size. Few deposits are of economic interest owing to the characteristically small tonnage available and the erratic distribution of molybdenite. One example is the erratically disseminated Mo at Val d'Or and Preissac deposits in eastern Quebec, Canada, where molybdenite is associated with bismuth in pegmatite bodies and greisen zones (Vokes, 1963).

The largest known Precambrian molybdenite occurrences in northern Sweden are of the aplitic type. They are associated with small plutons of intrusive character located in supracrustal belts whereas large granite areas are barren. Enrichments of molybdenite are also found in association with altered volcanic rocks and skarns. The main deposit is Munka with about 1,5 million tons of ore with 0,10% - 0,15% Mo and Bjornstjarn with more than one million tons of ore with 0,15% - 0,20% Mo (Ohlander 1985a, 1985b).

Other deposits are the Mallot property, in Washington (U.S.) and also they occur in Maine and Pennsylvania, where molybdenite occurs in quartz and pegmatite accompanied by pyrite, pyrrhotite, chalcopyrite and sphalerite.

3.5 Bedded Deposits in Sedimentary Rocks

Mo (and U,V) is concentrated in lignitic and arkosic sandstone beds, shales and phosphorites, but no economic grades have been found. Few lignitic and sandstone beds in the central - north, and central United States contain Mo grades of 0,1 - 0,2%, in deposits thick enough to be mineable (King et al, 1973). Also, Cambrian - Ordovician shales from Scandinavia show high contents of V and Mo of about 0,1% respectively (Wedepohl, 1967). The Upper Permian "Kupferschiefer" of northern Germany contain 100 - 1500 ppm Mo,

averaging about 150 ppm.

Mo bearing phases in bedded deposits include jordisite (amorphous MoS_2) ilsemannite $(\text{MoO}_2)_2 \text{MoO}_4$, U - Mo minerals such as umohoite $(\text{UO}_2 \text{MoO}_4 \cdot 2\text{H}_2\text{O})$, and iriginite, $\text{U}(\text{MoO}_4)_2 \cdot (\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and also some molybdenum - bearing iron - oxides (King, 1970).

3.6 Wulfenite-Bearing Deposits

Wulfenite occurs in oxidation zones of certain Pb - Zn deposits, associated with minerals such as vanadinite and descloizite. Wulfenite (PbMoO_4) contain only 26% Mo. The V and Mo mineralization is believed to have been introduced at a later stage. The production from these type of deposits has been small. Some examples are the Mammoth Mine (Arizona), Blinberg (Austria) and the southern Transvaal Silver Mine, in the Delmas District (South Africa).

4.0 GEOTECTONIC SETTINGS AND DISTRIBUTION

4.1 Introduction

In first approximation the Mo mineralizations can be grouped in three tectono-orogenic systems :

The Circumpacific Cenozoic Belt, the Alpine-Caucasian Cenozoic Belt and the Paleozoic Belts that surrounds the Siberian Shield (Figs. 4.1 and 4.2).

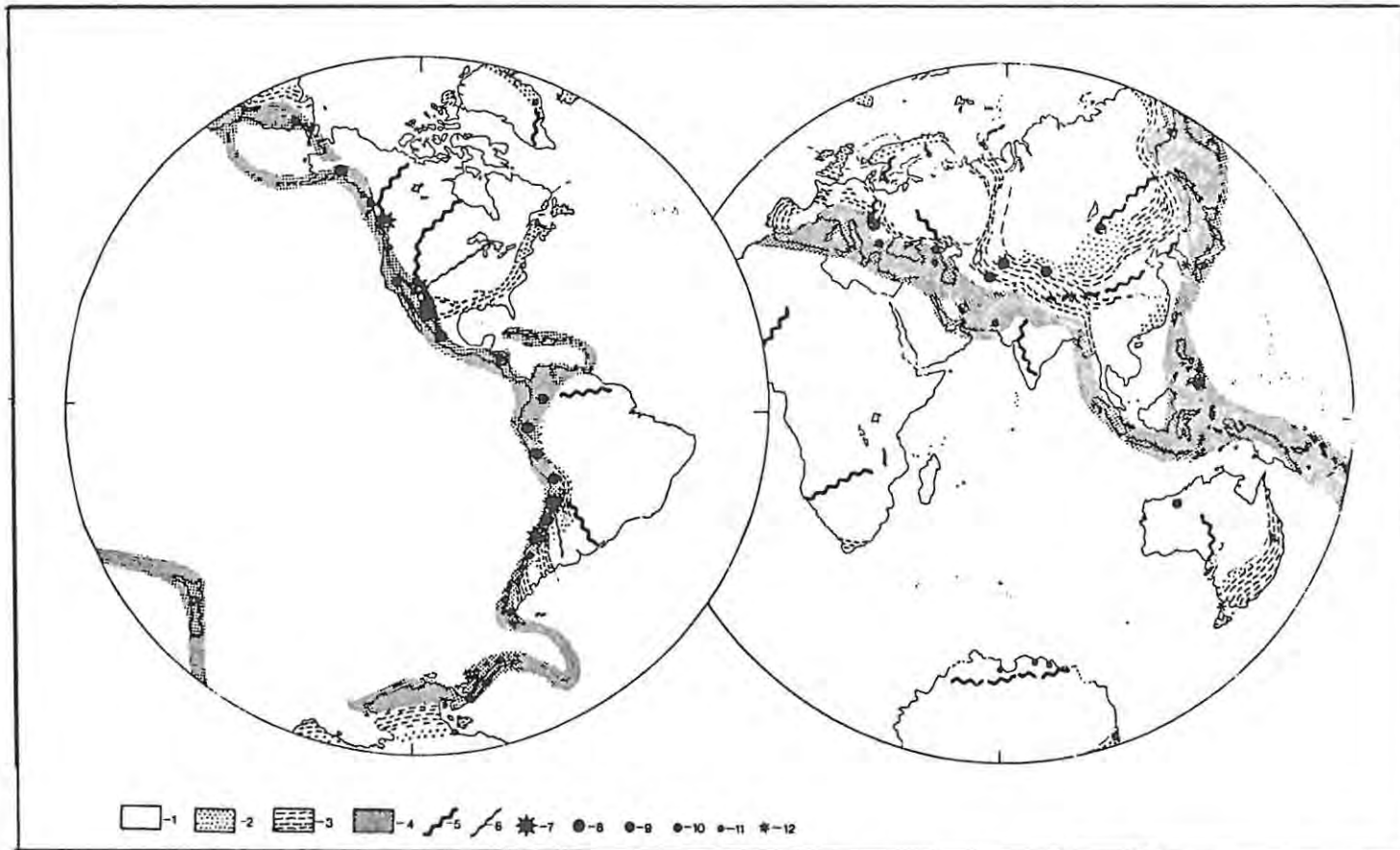


Figure 4.1 World Cu-Mo porphyry deposits related to main Phanerozoic and Precambrian orogenic belts. 1-shields; 2- Lower Palaeozoic orogenic belts (Caledonian); 3-Upper Paleozoic orogenic belts (Hercynian); 4-Cenozoic (Andean Alpine) orogenic belts; 5-Main Precambrian orogenic belts; 6-Transcontinental Silurian arc; 7-Cu-Mo porphyry deposit districts. Cu reserves 10 000 000 tons, or Mo reserves 1 000 000 tons; 8-Cu reserves: 1 000 000 - 100 000 tons; 10-Cu: 10 000 - 100 000 tons. Mo: 1 000 - 10 000; 11-Cu 10 000 tons, Mo : 1 000 tons (Sutulov, 1978)

Frutos (1978), figure 4.2, characterizes the different sectors of the orogenic belts above mentioned, through the use of a "molybdenite index"

(percentage of Mo : length of corresponding belt sectors).

The Circumpacific Orogenic Belt ends in the north (in Alaska) and in the south (Patagonian - Magallan Cordillera) with a very low index, reaching practically zero in the South West Pacific margin. There are two important sectors; in North America, generally around the Colorado Plateau and in South America (North - Central Chile).

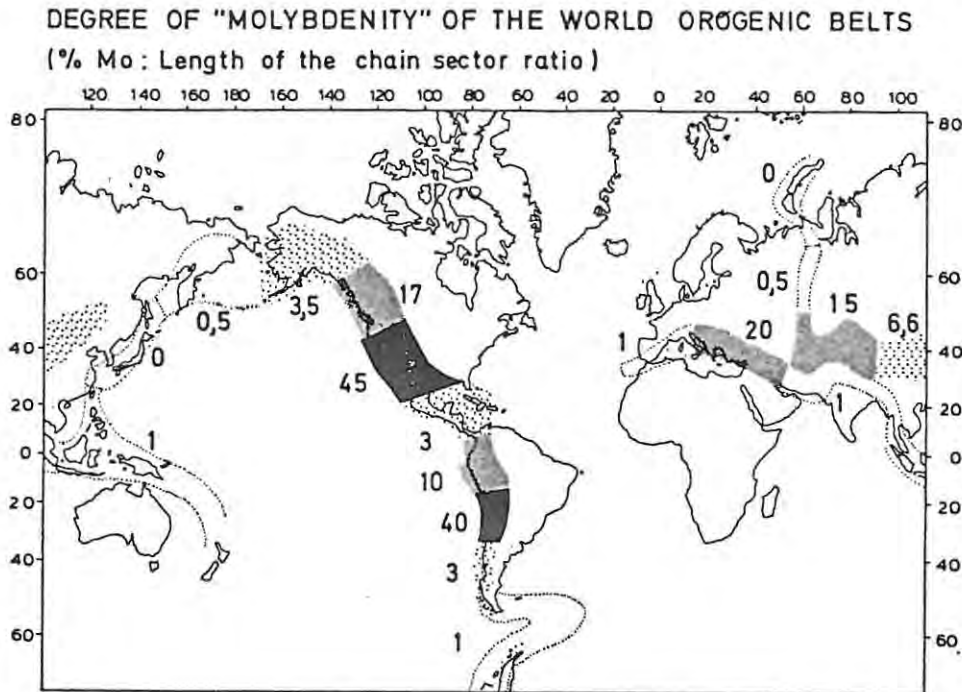


Figure 4.2 Ratio of %Mo to the length of the corresponding sector of the belt (Sutulov, 1978)

Low index values occur in Central America and in the northern part of South America. The Alpine - Caucasian Belt has a high index only in the Yugoslavian - Iranian sector and exhibits low values at either end (Spain - North Africa on the west and the Indo-Chinese Peninsula in the east). The Perisiberian Paleozoic Belt, has high values only in the Central Kazakhstan - Tienchan System - Zaysan folded systems sector. Mo deposits occur associated with geological parameters which are common to all the belts. They are :

- a. Areas having both volcanic rocks and hypabyssal granitic bodies.

- b. The distance to a corresponding subduction zone, in marginal zones of convergent plate boundaries (Mitchell and Garson, 1972; Guild 1974; Oyarzun and Frutos, 1974).
- c. The thickness of the crust, with Mo appearing preferentially in zones having thick continental crust (Ericksen, 1975).
- d. Large systems of faults crossing the orogenic belts (Nisiwaki, Ohmachi and Kobayachi, 1974; Sillitoe, 1974).

Most of the belts are Cenozoic in age and although some molybdenum deposits also occur in Paleozoic belts (Russia).

Porphyry type deposits are the most significant source of Mo, and are associated with acid magmatism, which represents the final development of an orogenic belt.

However, certain types of sedimentary rock sequences may also play a role in fixing and supplying Mo and other metals, as for example in the reducing environments of miogeosynclinal facies (organic matter etc.), which are particularly conducive to the fixing of metallic elements. It appears from isotopic studies that magmatic crustal contamination is less than previously thought. In this sense the sedimentary settings may influence or even supply the metals to the intruding magmas.

4.2 Passive Continental Margins and Interior Basins, Settings

Oil shale type sedimentary facies in the regions of Central Asia have shown high concentrations of Re and Mo (also Cu, V, Ni, Ag, Cd, Se, Bi). Holland (1979) described the similarity in enrichment factors for Ag, Cu, Ni, V and Zn relative to modern ocean waters, and suggested that the enrichment was largely due to chemical precipitation. With a few exceptions, such as the Slum shale of Cambrian age in Sweden, uraniferous black shale in the Venetian Alps, and certain Palaeozoic shale in U.S.A., total metals from bituminous shale (including Mo) is uneconomic.

Black bituminous shales in continental settings are largely pelagic and

perhaps occur most commonly in, although they are by no means restricted to, the deeper parts of passive continental shelves, the main environmental requirement being anoxic conditions at the sediment - water interface. The relationship of metalliferous black mud deposition in the sea has been discussed by Sclanger and Jenkyns (1978) and Jenkyns (1980). These workers emphasized how abundant organic material produced during flooding of epeiric and shelf seas yields oxygen - depleted waters via bacterial oxidation. In general it seems that a major marine transgression will tend to result in deposition of phosphates in suitable shallow marine areas and black metal rich muds in topographic lows, in place of hydrogenous manganese nodules and crusts which form in more oxidizing environments (Figure 4.3).

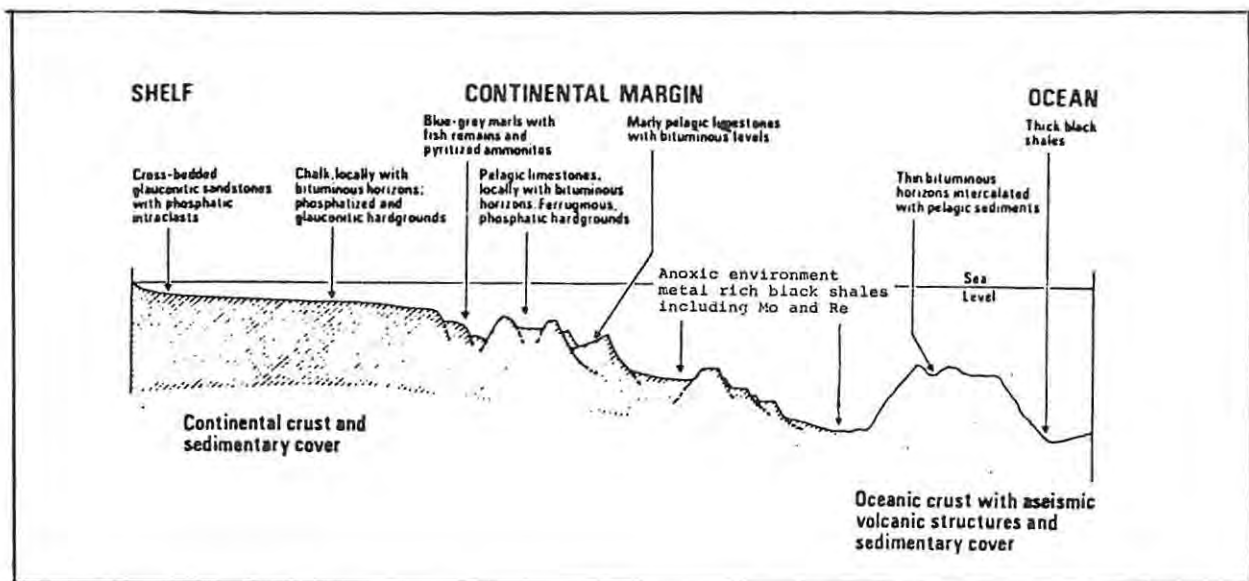


Figure 4.3 Suggested facies distribution across a continental margin of a restricted ocean during a Cretaceous oceanic anoxic event (Jenkyns, 1980).

Unconformity vein type U deposits, located beneath thick mid to late Proterozoic non marine sediments, also include Mo mineralization. These deposits have been described in intracratonic basins occurring around the margins of the Athabasca Basin in Saskatchewan (Dahlkamp, 1978) in the Alligator River Area (Northern Territory) and in the Rocky Downs (South Australia).

In both the Athabasca and Alligator River areas, lower to middle Proterozoic

metasediments overlie Archean "basement" and are in turn overlain in angular unconformity by thick relatively undeformed Proterozoic successions of terrigenous sediments. U occurs mostly beneath but within a few hundred metres of the angular unconformity, although locally also in the overlying sandstones. In the Athabasca Basin (Figure 4.4), the mineralization is commonly associated with graphitic Archean rocks. According to Langford (1978), in the Australian deposits ore mineral textures indicate open space filling, and dilatant structures such as faults and breccia zones tend to localize the ore deposits. The primary mineralization consist mainly of pitchblende, and uraninite and minor sulphides with S, As and Se commonly combined with Fe, W, Pb, Co, Ni, Bi and Mo.

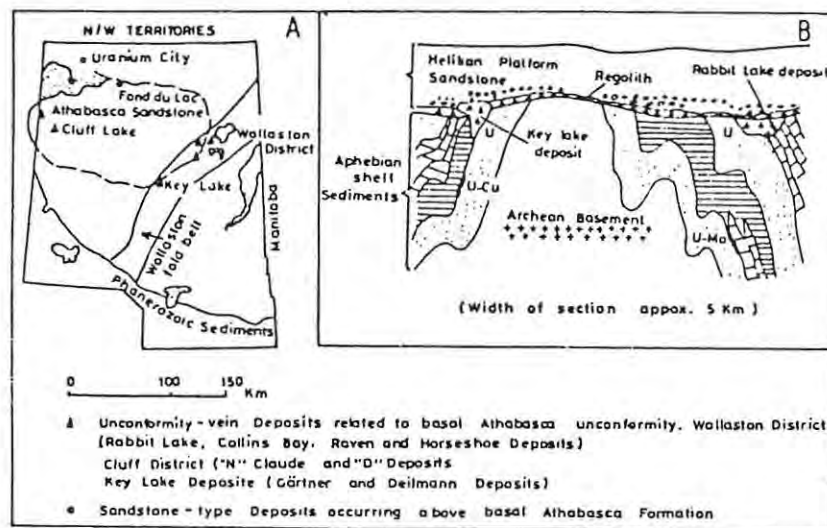


Figure 4.4 Uranium deposits in the Athabasca Sandstone and Wollaston Fold Belt, Saskatchewan (A) Location of deposits. (B) Epigenetic or secondary concentration of uranium into unconformity veins in carbonate and metapelitic rocks in Wollaston and Key Lake Districts (width of section approx. 5 km). (McMillan, 1978)

4.3 Orogenic Belts and Magmatic Arcs

These are settings in which the main districts with Mo mineralization are located. They are present in Asia, Europe and America.

4.3.1 The principal areas in Asia are located along the Caucasian Cenozoic Belt in the Circumpacific Orogen, and in the Paleozoic belts that surround the Siberian Shield in the south (Figure 4.5). The larger portion of these

deposits is situated in the U S S R and most of them are of the porphyry Cu type with associated Mo, although many of them differ somewhat from the classical porphyry model. Mesozoic and Cenozoic belts in the Alpine orogen extend into the northeastern Carpathians, where, after being interrupted by the rocks of the platform cover on the southern margin of the Russian Plate, they re-emerge in the Crimean zone, continuing into the Caucasian, where porphyry Cu deposits have been discovered. They appear to be related to deep faults on the edge of the belt, both in Caledonian and Hercynian orogenic belts which were influenced by the Alpine Orogenic event (Figure 4.5).

With regard to the distance of the paleo-Benioff Zone, Frutos (1978) distinguished two belts.

1. The Greater Caucasus, with a thicker sialic crust in which a Mo stockwork deposit contains a Cu/Mo ratio of 20:1 (Tyrny - Auz deposit)
2. The Lesser Caucasus, closer than the previous belt to the paleo-Benioff zone and in which a thinner crust occurs. Numerous Cu-Mo porphyry type deposits are found here, with a Cu/Mo ratio of 50:1.

Laznicka (1976) suggested in the Caucasus a paleo-Benioff zone dipping under an Andean type continental margin.

The circumpacific geosynclinal system includes the island arcs of the Kuriles, Sakhalin, Kamchatka, the Koryak Belt and the Okhotsk Suboceanic Median Massif. Cu-Mo porphyries have only been discovered in the Kamchatka region where they are of relatively low importance.

The volcanic arc of the Okhotsk -Chaum Region, situated on the continental margin adjacent to the circumpacific orogen, contain some stockwork-type molybdenum deposits (Figure 4.5 - district 9 and 10).

The stockwork deposits show the "classical" characteristic of Cu-Mo porphyry, associated with intrusives of granodioritic to quartz-dioritic composition, which penetrate Phanerozoic granitic batholiths. The geotectonic setting corresponds to a Benioff zone during an island arc/Andean margin transition.

Paleozoic Belts in Asia occur along the flank of the Siberian Plate in the west (Ural system), in the south west (Kazakhstan, Tren-Shan system) and in the south (Zaysan, Altai - Sayan and Mongol - Amur Folded Systems). They have Cu, Cu-Au, Cu-Mo and Mo mineralization of the disseminated porphyry type. The Cu/Mo ratio varies greatly among the different belts in relation to types of magma, degree of tectonic evolution and crustal thickness.

The Ural fold system is characterized by low concentrations of Mo. It is associated with rocks ranging from quartz diorite to gabbro type of Silurian to Devonian ages, intruded mainly into a Silurian ocean floor assemblage (basalts and spilites). The deposits are Cu stockwork type, generally superimposed on skarn-type, in a paleo-subduction zone beneath an island arc (Laznicka, 1976).

The Orogenic system of Kazakhstan (Figure 4.5 district 4), comprises the tectonic junction between the Urals and the Paleozoic belts that flank the south of the Siberian Shield. They represent the most important metallogenic district of the Asian continent. The mineralization is mainly associated with intrusive granodioritic to quartz-dioritic rocks, mostly from the Carboniferous period intruded into a Silurian Devonian ocean floor assemblage (carbonates, basalt, spilite). The deposits in general are those of the "classic" type of Cu-Mo porphyries.

The Tien-Shan system (Figure 4.5 district 5) similar in geology and general characteristics to the Kazakhstan district. The only difference is that this district is thought to be related to a paleo-Benioff zone during an island arc-Andean continental margin transition (Laznicka 1976). It represents an earlier stage in the evolution of the Orogenic system.

The Zaysan Fold system (Figure 4.5 - district 6) is of little importance, because the poor Mo mineralization, which is related more closely to a volcanic island - arc setting.

The Altai-Sayan Fold system (Figure 4.5 - district 7) has low reserves but it also has a greater proportion of molybdenum ratios $Cu/Mo = 25:1$). The Cu-Mo stockworks generally are superimposed on skarn-type deposits, and are

associated with lower Paleozoic quartz porphyries or quartz-monzonites which intruded into Upper Proterozoic to Lower Cambrian miogeosynclinal sedimentary rocks. Laznicka (1976), suggested a geotectonic setting related to a paleo-Benioff zone dipping under an Andean-type continental margin.

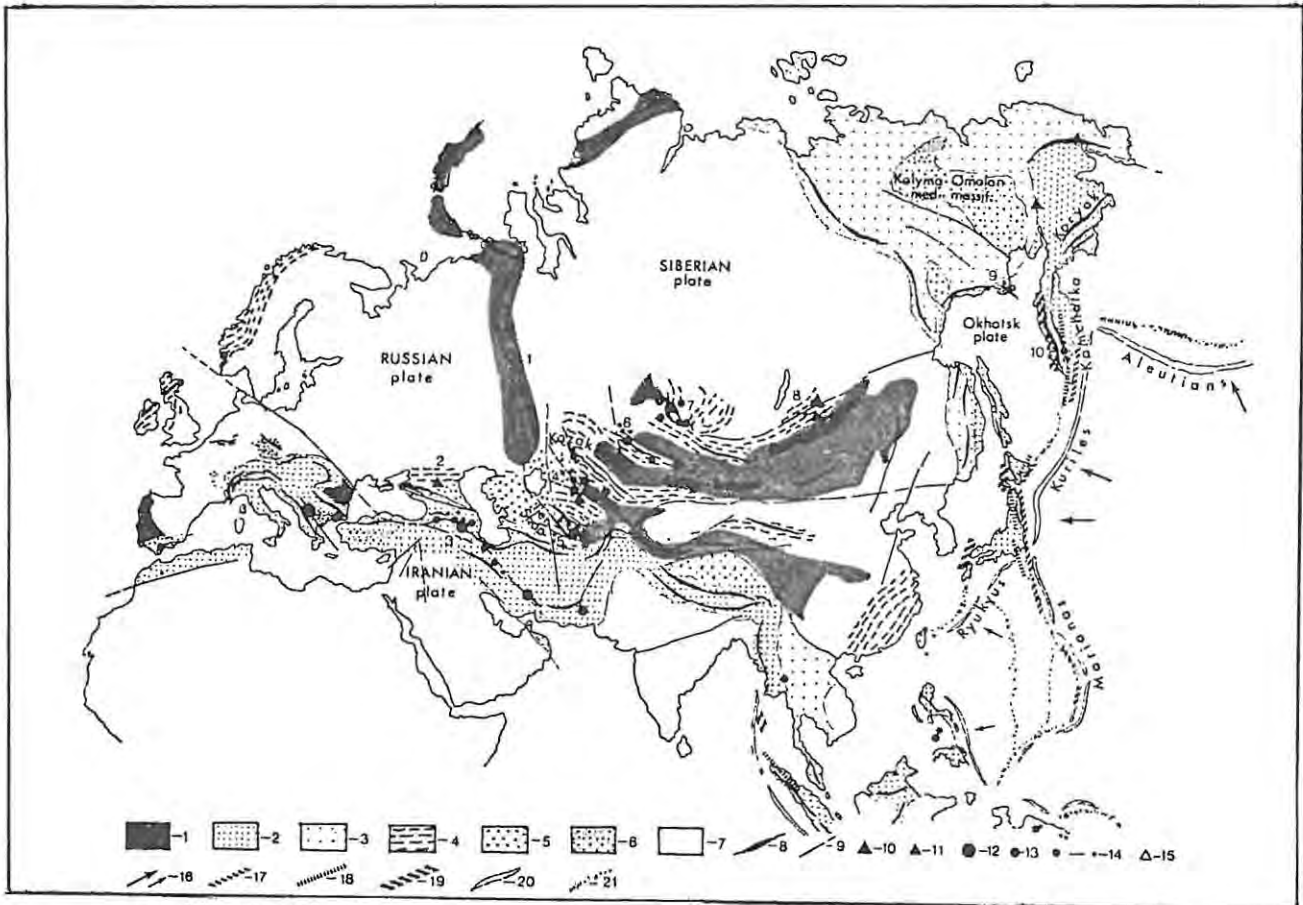


Figure 4.5 European-Asian Cu-Mo porphyries related to tectonic belts. 1 - Upper Paleozoic (Hercynian) orogenic belts; 2 - Cenozoic (Alpine) orogenic belts; 3 - Mesozoic orogenic belts; 4- Lower Paleozoic (Caledonian) orogenic belts; 5- Sedimentary cover on Paleozoic folded zones; 6- Regions at platforms involved in the Alpine Orogeny (Median Massifs); 7-Shields (cratons); 8- Main anticlinoria with Phanerozoic folded zones; 9- Deep faults; 10- Molybdenum porphyry deposits over 100 000 ton reserves of metal content; 11- Molybdenum porphyry deposits with less than 100 000 tons (metal content); 12- Cu-Mo porphyry deposits (Cu reserves 1 200 000 tons); 13- Cu-Mo porphyry deposits (Cu reserves - 500 000 - 1 000 000 tons); 14- Cu-Mo porphyry deposits (Cu reserves - 100 000 - 500 000 tons); 15- Cu-Au type porphyry deposits (Cu/Mo ratio = X000 : 1); 16- Direction of dip of Benioff zones; 17- Tholeiitic magmatism; 18- Calc-alkaline magmatism; 19- Shoshonitic magmatism; 20- Trench; 21- Island-arc (Frutos, 1978)

In the Mongol-Amur Fold System and East Transbaykal (Figure 4.5 district 8), there are important Mo occurrences. In this area mineralization is associated with acid intrusives (quartz-monzonites and quartz porphyries) of the Upper Jurassic age, intruded into a Carboniferous - Permian granitic batholith. These porphyry systems had a Cu/Mo ratio is 20:1, and are located in a geotectonic setting characterized by advanced stages in the evolution of an orogenic belt with tensional intracratonic magmatism.

4.3.2 European molybdenum occurrences

They are concentrated mainly in the Alpine Belt, with the exception of Norway where Cu-Mo porphyry mineralization is located in the extreme southeast of the Caledonian Orogenic Belt.

These types of deposits are heterogenously distributed, with high concentrations occurring in those places in which old-continental-crustal, median massifs, appear interposed within the Alpine Belt in alignments that coincide with intensive folding and fracturing. They occur in the Greater and Lesser Caucasus (above described), the Iranian Belt and in the Yugoslavian Cu-Mo Province.

In the Iranian Belt, mineralization is associated with zones of intense folding and is parallel to fractures (Figure 4.5). This metallogenic zone extends, follows the fold belt through to Pakistan.

Two important deposits are present. They are the Sar Cheshmeh in the south of Iran and the Saindak deposit in Pakistan. These deposits are associated with an Upper-Tertiary granodioritic stocks. The mineralization occurs in the early porphyry bodies peripherically intruded Tertiary volcanics (andesites) (Waterman and Hamilton, 1975).

The Yugoslavian Cu and Mo deposits are located in the southeast part of Serbia. This mineralization appears associated with granodiorites and dacites. Of Lower Tertiary age. They intrude Palaeozoic and Precambrian metamorphic rocks near to the Dinaric Fold System (Miloje, 1971). An important deposit in this belt is Machkatitza which represents a typical porphyry Mo.

4.3.3 American Mo deposits

Most important of the north American Mo deposits are located in the Cordilleran Orogen. This area exhibits a range of mineralization styles which reflect a complex tectonic development. The different types range from quartz, dioritic to granodioritic porphyry deposits rich in Au and low Mo of volcanic island arc types (Cariboo belt), through the classic Cu-Mo porphyry deposits associated with calc-alkaline magmatic series of granodioritic to quartz-monzonitic composition which correspond to a geotectonic setting transition from island arc to a state of tectonic plate converging of an Andean-type continental margin. This belt contains high values of Cu/Mo and is situated in a thick crustal zone.

In South America there are porphyry Cu-Mo type deposits, which are distributed along the Andean orogenic Belt. The Andean belt exhibits a long and complex orogenic evolution which in many sectors is superimposed on earlier orogenic events reaching back to the Precambrian.

The continental margin was evolved to the west, south west and south of the Brazilian Shield in several orogenic episodes (Precambrian, Paleozoic, and Mesozoic (Andean)), which have successively been partially or totally superposed. The geotectonic setting for all Cu-Mo deposits along the west coast of South America is related to convergent plate boundaries.

4.4 Island Arc

This type of geotectonic setting represents a good potential for Cu-Mo deposits. Here the Mo deposits are related to arc magmatism (Frutos, 1978).

Deposits associated with this geotectonic setting are found in the following:

- a. The south-western Pacific porphyry copper deposits, of the Philippine Islands, New Guinea and Bougainville.

b. The Caribbean and Central American porphyry copper deposits found mainly on the island of Jamaica, Puerto Rico, Virgin Islands, St Martin, St Barthelemy, and Hispaniola (Haiti).

The Mo mineralization of this setting will be discussed in more detail in chapter 5.0.

4.5 Intracontinental Rifting

Grabens, interpreted as extensional zones of rifting within continents, have been recognized as a major type of structural feature with associated sedimentary and volcanic fills.

Many graben or rift zones can be grouped according to their tectonic setting at the time of formation : those which developed as a "trilete" system of three rifts radiating from a crustal dome centred on a hot spot (one arm is the aulacogen that represent a rift that failed to open into oceans, Burke and Dewey, 1973), and collision-related rifts which developed following, and were related to continent-continent or continent - arc collision (Sengor et al., 1978).

Shatski (1947), described many rifts in the U S S R which are related at high angle into orogenic belts. Burke and Dewey (1973), described a large number of rifts of Proterozoic and Phanerozoic age which they considered had similar origin to the East African rift system. This type of environment in particular has important magmatic mineral deposits; few of them comprise porphyry Cu-Mo deposits.

An example is the Oslo Graben where possible porphyry-type Mo mineralization is found associated with porphyritic phase of biotite granite at several places. The occurrences of molybdenum mineralization in the Oslo Graben indicates a new environment for this Mo deposit. Porphyry Mo occur not only in magmatic arcs, and in back-arc rift setting as in the case of the mid-Cenozoic deposits of the Colorado Mineral Belt (Guild, 1978), but also

in rifts related to either hot spots or continental collision.

According to Sillitoe (1980) the world's major porphyry molybdenum ore bodies with grades of 0,15 - 0,6% Mo are occurring in rift setting.

The Oslo Graben is part of the post - Hercynian rift system which extends beneath the North Sea. The evolution of the Oslo Rift comprises initial basaltic volcanism followed by eruption of latitic porphyritic lavas with the formation of central volcanoes and cauldron subsidences. Finally, there was emplacement of composite batholiths of biotite granite, monzonite and syenitic composition. The mineralization in the Oslo Rift occurs in the central part of the large Glitrevann cauldron and it is a late, stock-shaped intrusion of aplitic biotite granite and quartz-feldspar porphyry (Geyti and Schonwandt, 1979) (Figure 4.6). Sericitic alteration, resembling that at the Climax Porphyry, is present, below which occurs a stockwork of molybdenite mineralization with K-feldspar alteration, considered to be the uppermost part of the mineralized body.

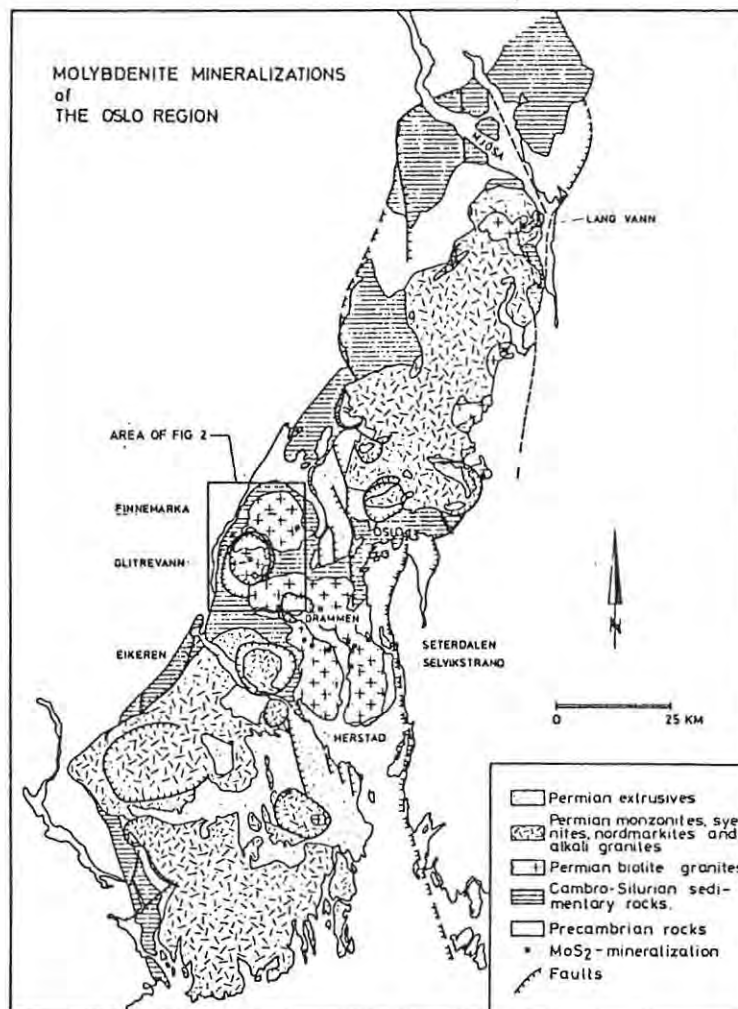


Figure 4.6 Simplified geological map of the Oslo region showing the molybdenite mineralization, most of which is granite hosted (Geyti and Schonwandt, 1979)

The Keweenaw Rift is another example where this type of mineralization is present. Four disseminated Cu-Mo porphyry-type in the Batchawana area of Ontario within the Keweenaw Rift (Figure 4.7), are similar to Cu-Mo porphyry deposits in Western American Cordilleran belts; in style mineralization with high tonnage - low grade disseminations, hydrothermal alteration and association with highly altered felsic porphyries and breccia pipes (Norman, 1978). Mitchell and Garson (1981), described similar fluid inclusion, morphology and depth, and temperature of mineralization, to those of Cordilleran porphyry deposits. Stable isotope measurements indicate that the initial mineralization resulted from typical porphyry-type magmatic hydrothermal activity.

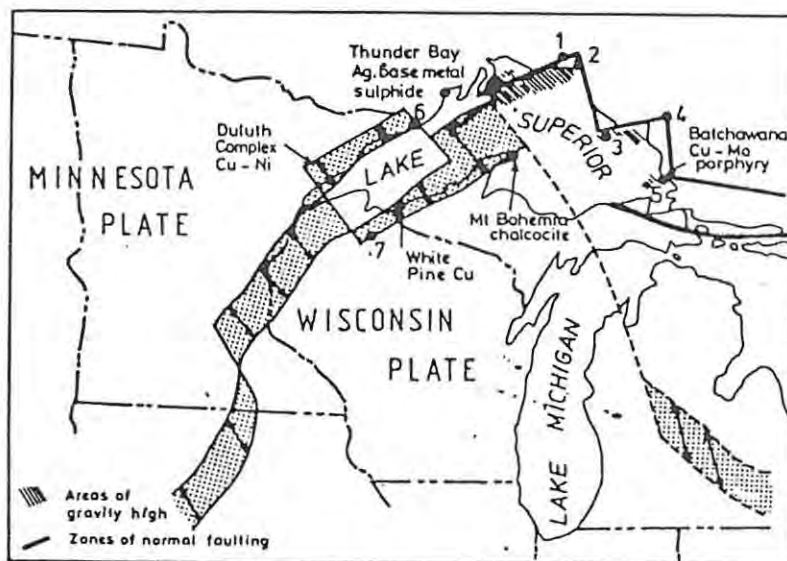


Figure 4.7 Mineralization associated with postulated zones of Keweenaw rifting in the Lake Superior area, Canada (Norman, 1978). Alkalic complexes and regions of extensive felsic magmatism apparently related to intersections of transform faulting and rifting are: 1, Prairie Lake; 2, Coldwell; 3, Michipicoten Island; 4, Fireside River; 5, Batchawana area; 6, Hoveland; 7, Mellon.

4.6 Collision Related Settings

This type of geotectonic setting is characterized by thrusting towards the foreland with magmatic arc rocks on the overriding plate, which may be tectonically juxtaposed with the other rocks. Suture zones are lines of

oceanic crust rocks, which mark a collision boundary between the continental and oceanic crust (Dewey and Bird, 1970).

One of these zones is the lower Himalayas of western Nepal where primary deposits of Sn, Ta, Nb including Mo and W have been described, from greisenized fine-grained leucocratic granite and pegmatites forming a north-dipping sheet within a thrust sheet or klippen. In the central Nepal, also has been described mineralization from the Palung Granite (Talalov, 1977).

The stratabound ore deposits in ophiolites (oceanic floor) of Italy and Austria are developed in this setting, and they may have small quantities of Mo. Mineralized zones occur within finely-banded green schists which are overlain by calcareous mica schist with thin intercalations of black phyllites and quartzites (Zuffardi, 1977). An example of this mineralization is Kies ore body which consists of 0,5 to 2m of quartzite containing pyrite, chalcopyrite, sphalerite, and Au, Mo and Pb.

5.0 MOLYBDENUM ASSOCIATED WITH PORPHYRY TYPE DEPOSITS AT CONVERGENT PLATES BOUNDARIES

5.1 Introduction

Most of the world's Cu production is derived from porphyry deposits. They occur within high sulphur anomalies of the crust, which contain significant quantities of Cu, Au, Mo and also include Ag, Pb, Zn, Bo, P and other metals.

Although each ore deposit displays particular features they also have common characteristics, such as high sulphur and sulphates contents, high S/Cu ratios, association with dykes and calcalkaline stocks, low depth of emplacement and mineralization associated with late stage events of volcanic and intrusive activity. At the continental and global scales they appear to be restricted in space and time.

Mo and Au are the most important by-products of these ore deposits. The ratio Cu/Mo varies between 10/1 and 100/1. Recent studies show a variation of the Mo content according to the geotectonic situation of the ore deposit. Mo is more abundant in deposits which are emplaced into a thick continental crust.

As mentioned in the previous chapter the most significant disseminated porphyry deposits are associated with three main belts, situated around the Circumpacific and in the Alpine mediterranean areas.

Convergent plate boundaries constitute the most favourable setting for the emplacement of porphyry deposits.

5.2 Subduction Related Environments : Andean type and Island Arc type Cu-Mo Deposits

5.2.1 Andean type

The Cu/Mo deposits of this type comprise those that are genetically related to subduction zones where oceanic and continental crust are involved. This

geotectonic environment, represents an advanced stage in the orogenic evolution and it is associated with calc-alkaline volcanism, and with intrusive rocks of intermediate composition (granodiorite-quartz monzonite).

Examples of the Andean porphyry Cu/Mo deposits, are : Cerro Colorado in Central America, and Chaucha, Morocochoa Cuajone, Chuquicamata, El Salvador, El Teniente and Rio Blanco in South America. Figure 5.1 shows the distribution of the porphyry copper deposits containing economically recoverable Mo.

According to the theory of plate tectonics, these belts have been recognized as forming at the convergent margins of crustal plates (Sacks et al., 1968; Dewey and Bird, 1970). The correlation with plate subduction is most appealing in the Western Pacific and the Andes, where relatively young deposits (less than 45 million years old) are found in tectonic volcanic belts presently at active plate margins.

The porphyries are related to hypabysal parental magmas, intruded into thick continental crust. In general the intrusive rocks are feldspar rich, and have a F content higher than those in the Philippines and Southwest Pacific island arcs.

Gustafson (1978), suggested that CO_2 , SO_2 and Cl, as well as H_2O are major components of the magmas derived from deep sources. They are thought to result from inhomogeneities in the source region and variations in the degree of partial melting. These magmas form reservoirs with metal concentration in cupola structures. If the magma contains sufficient S and metals, it may form a porphyry Cu/Mo deposit (Figure 5.2).

The Mo mineralization constitute one of the main by-product of the porphyries in the Andean type. Their grades range from 0,1% to 0,010% Mo, with an average value of 0,03% Mo (Fuster, 1983). The Au contents are lower than those in deposits of island arc-type.

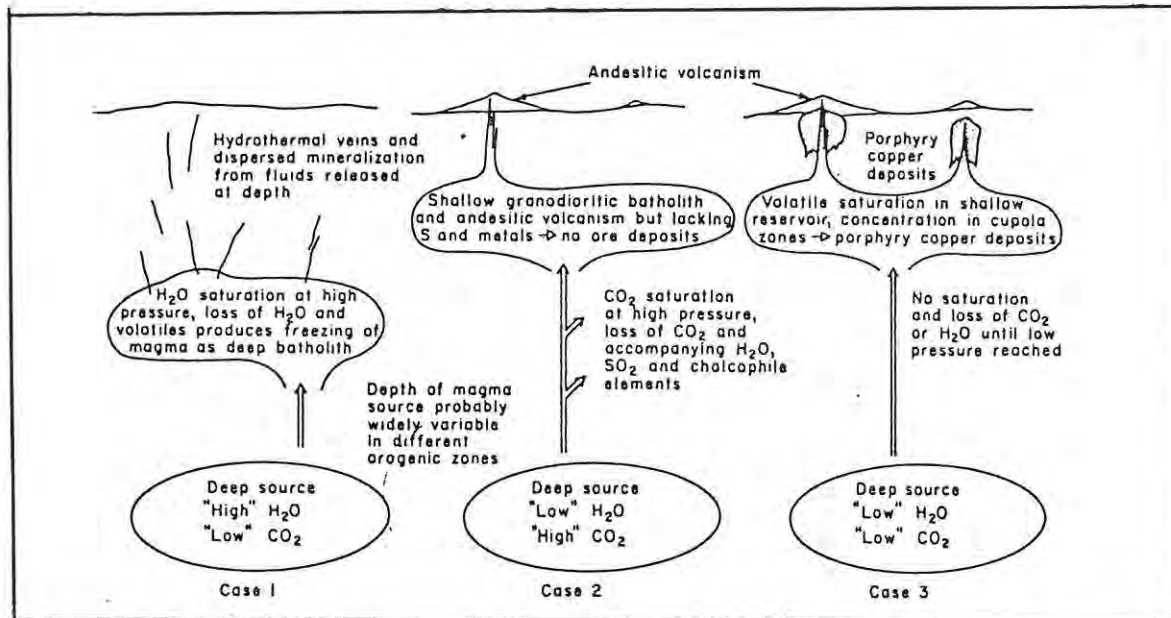


Figure 5.2 Schematic model of the effect of initial H₂O and CO₂ contents of melts formed in a deep source on the volatile evolution as they rise through the crust, and on their ability to reach shallow reservoirs with sufficient metals and sulphur to form porphyry copper deposits (Gustafson, 1978)

Chilean Porphyries

Most of the known Chilean Mo resources are located in porphyry Cu deposits. Mo concentrates are produced as by-product since 1939 (from El Teniente Mine). Chile has exceptionally promising conditions for molybdenum production because of the large resources accumulated in the porphyry Cu deposits. Table 5.1 summarizes the Mo resources in this country.

Table 5.1 Molybdenum reserves and resources at Chilean Porphyry Copper Molybdenum Deposits (Ambrus, 1978a)

	KNOWN RESERVES			POSSIBLE & PROBABLE		
	10 ⁶ M.T.	% Mo	M.T.Mo x 1000	10 ⁶ M.T.	% Mo	M.T.Mo x 1000
CERRO COLORADO	80	0.02?	16	40	0.02?	8?
COPAQUIRE				100	0.07?	70?
QUEBRADA BLANCA	100	0.015	15	200	0.015?	30?
EL ABRA	680	0.01	68	500	0.01?	50?
CHUQUICAMATA	265	0.12	318	8,800	0.01?	880?
	1,535	0.014	215			
EL SALVADOR	410	0.025	102	50	0.02?	10?
POTRERILLOS	40?	0.02?	8	20	0.02?	4?
ANDACOLLO	300	0.015	45			
LOS PELAMBRES	430	0.035	150	?		
DISPUTADA	350	0.02?	70	300	0.02?	60?
RIO BLANCO	130	0.027	35	150	0.03?	45?
(ANDINA)						
EL TENIENTE	4,000	0.022	880	1,500	0.01?	150?

Tectonic setting and magmatism

The Chilean porphyries are located in the western margin of South America in the subduction zone above the Benioff Zone.

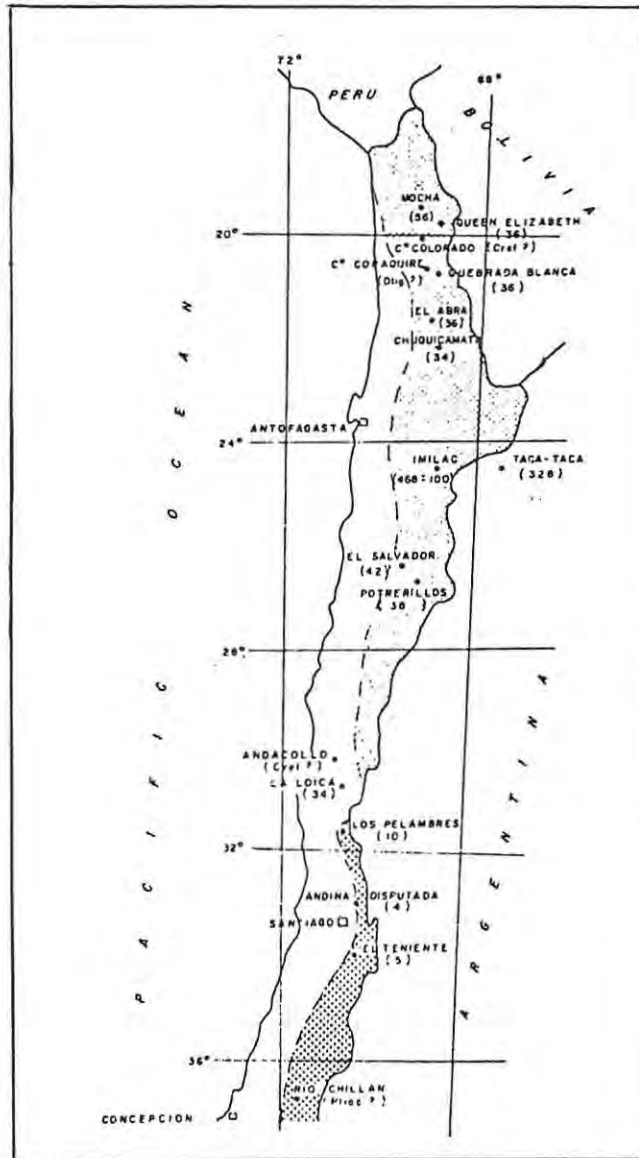


Figure 5.3 Extent of Upper-Tertiary volcanism (after Ruiz et al., 1965) related to ages of porphyry deposits (Quirt et al, 1971)

The emplacement of these mineralized porphyries can be generalized as a subvolcanic magmatic development of a metal rich magma, where residual fluids mix with meteoric waters during the late stages of cooling. The

early stages of the development of porphyry systems are controlled by the characteristics and complexity of the intrusion, the nature of the host rocks and the depth of emplacement. Intrusive events are represented by multiple phases of emplacement. It is granodioritic at Chuquicamata, Copaquire, El Salvador, Rio-Blanco-Disputada and El Teniente.

These porphyries are related to Upper - Mesozoic and Cenozoic calc-alkaline magmatic activity, which extends along most of the Andean range. They are present in a continuous belt of granodioritic intrusions, andesitic-lavas and related rocks (Figure 5.3). The sialic crust underlying Chilean porphyry Cu deposits is thinner than under western North American porphyries. The calc-alkaline magmas tend to have initial $Sr^{87/86}$ ratios of between 0,703 and 0,706 (Ambrus, 1978a), whereas the continental porphyries of the North American belt, have initial $Sr^{87/86}$ ratios ranging from 0,705 to 0,710 (Kesler et al., 1975).

Most of the Chilean deposits range in age between 34 and 42 m.y. in the North and less than 10 m.y. in the South (from latitude $30^{\circ}S$) (Figure 5.3).

Alteration and Mineralization

The classical model of alteration - mineralization, of Lowell and Guilbert (1970) and Rose (1970), can be roughly applied to most of the Chilean porphyry deposits in spite of local important differences. The gradation from K-silicate alteration into propylitized rocks without an intermediate phyllic zones is present in several deposits, for example El Abra, Chuquicamata and El Teniente. It is a common departure of Chilean deposits from the classical porphyry Cu zonal pattern.

Development of phyllic alteration in various stages is present at several deposits. It is characterized by an abundant precipitation of quartz in the open structures available to the circulation of solutions.

Tourmalinization is a common feature, related to the early main feldspar - destructive hydrothermal phase. At Rio Blanco - Disputada deposit (Figure 5.3), the tourmalinization is closely related to the Cu-Mo mineralization that occurs in breccia pipes.

Argillic alteration is characteristic of low temperature and low pressure.

It is common but not always present in the Chilean deposits probably because it can be easily removed by erosion since it is found in the highest levels of porphyry systems.

The Mo hypogene mineralization be formed during an early hydrothermal stage (Ambrus and Soto, 1974), when meteoric waters first erupted into the cooling magma (Gustafson and Hunt, 1975). The only two ore deposits where the Mo seems to be formed in later hydrothermal stages are Poterillos (March, 1933) and the Rio Blanco Mine (Urqueta, 1969).

Alteration and mineralization of some Chilean porphyries are summarized below.

Chuquicamata is characterized by large and intensive sericitic alteration with high Mo content in relatively small volumes of rocks. Its initial Mo content was high, but the porosity, permeability and hydrous conditions of the original magma were not ideal for the creation of a homogeneous Mo distribution. The central part of this porphyry are rich in this element.

El Teniente ore deposit represent a good example of the relationships of Mo mineralization and alteration zones. Mo content in the intrusive and host rock rarely exceeds 0,02% and is situated in zone of K-silicate alteration.

The earliest Mo-bearing veinlets recognized are late magmatic quartz - K - feldspar - anhydrite or quartz K- feldspar veinlets without sericitic envelopes. Here molybdenite co-exists with early Cu sulphides such as bornite and chalcopyrite. These types of veins are common at El Teniente (Camus, et al., 1978), but not in El Salvador (Roeschmann, 1979) and Chuquicamata. Early hydrothermal quartz veinlets and associated structures as "blue veins" are the most common contributors to ore production. Mo contents (grade and distribution) in most of the deposits is largely related to the abundance of early hydrothermal quartz veins.

According to Ambrus (1978a), molybdenite can be remobilized and its abundance is proportional to post to late magmatic deformation, due to late intrusion or to co-genetic tectonism. An example is the central breccia pipe in El Teniente, and its marginal breccias, which have anomalous high Mo

contents, mobilized from the earlier structures. At Chuquicamata, nearly one third of the total Mo content in the pit area occurs on fractures developed during and after hydrothermal alteration. The same situation can be observed at Rio - Blanco - Disputada deposit, at Central zone of Chile.

Supergene enrichment

This zone is very important in some ore deposits as at Chuquicamata, El Teniente and El Salvador (Figure 5.3). The development of supergene enrichment on various deposits depends on the amount of pyrite available to produce low pH environment, the nature of host rock (K-feldspar and mafic rich rocks tend to neutralize supergene solutions) and the fracturing of the rocks, which can permit a deep penetration of the solution. Major Cu oxides deposits overlie the sulphide zones of several ore bodies (e.g. Chuquicamata, El Abra and Potrerillos). Incipient Mo secondary enrichment has been described at Potrerillos, where it forms a secondary Mo sulphide (Clarke and Sillitoe, 1969) as castaingite, $(\text{Cu Mo}_2 \text{S}_{5-x})$, originating from reaction of hypogene molybdenite with supergene djurleite, $\text{Cu}_{1,97}\text{S}$. At Chuquicamata, increasing Mo grades occur towards the secondary enrichment sulphide zone.

Oxidation in Chilean Cu-Mo porphyries

Mo is generally found oxidized to slightly greater depth than Cu. Its oxides are soluble only under high pH conditions. Mo is rarely found in leached zones of porphyry systems (Titley and Anthony, 1961; Bloom, 1966). When it occurs it is generally found as pentavalent and hexavalent forms derived from reaction of molybdic acid $\text{H}_2 \text{Mo O}_4$, with different cations, causing precipitation of molybdates (Bloom, 1966). Wulfenite, PbMoO_4 and Powelite, Ca Mo O_4 have been found at Potrerillos, El Teniente and Chuquicamata. Lindgrenite, $\text{Cu}_3 (\text{Mo O}_4)_2 (\text{OH})$, is a common oxidation product of Mo S_2 at Chuquicamata and it is also present at other porphyries, as partially oxidized molybdenite co-existing with copper sulphides. The most common Mo oxide in leached cappings, is ferrimolybdite $\text{Fe} (\text{Mo O}_4)_3 \cdot 8\text{H}_2\text{O}$, originated by the reaction of the Mo O_4 ion with trivalent Fe of leached rocks. Mo can be fixed in various oxides as jarosite, copper wad and chenevixite.

Comparative Potential

The Chilean ore bodies contain a comparatively high Mo tonnage, Molybdenite being the main hypogenic sulphide. Compared to the Mo content of deposits located in other geotectonic setting, Chilean deposits have generally lower grade than those of the Tethyan and Western Canada porphyry belts; they present about the same grade as the south western porphyries of the island arc settings.

El Salvador and Chuquicamata deposits

El Salvador, geology and molybdenum mineralization

This ore deposit is located in Northern Chile (Figure 5.3), in the Indio Muerto Mountains (3 344 m above sea level). The production at El Salvador Mine was started in 1959, since then 125 million tons of ore, at an average of 1,44% Cu have been mined.

Ore reserves prior to production were about 340 million tons of 1,5% Cu. Molybdenite has been recovered from the concentrates since the beginning of operations. The Mo grades in the deposit range from 0,01 to 0,04% Mo and the average in the mill head is 0,025% Mo.

Gustafson and Hunt (1975), suggested that the formation of the porphyry copper deposit at El Salvador is the culmination of Miocenic volcanic activity. Upper Cretaceous andesitic flows with associated sediments were folded and truncated by an unconformity, and were followed by the sub-volcanic and volcanic event. The first intrusive event in the district, at about 50 million years ago, was the emplacement of a series of rhyolitic domes. A second intrusive event at about 46 million years ago, resulted in emplacement of quartz rhyolite as a volcanic neck, and of quartz porphyry as an apparently contemporaneous irregular sequence of dykes and sills. The main porphyry copper event took place at about 41 million years ago, accompanying emplacement of the granodioritic porphyry complex (Figure 5.4). The oldest of the series related to mineralization is known as "X" porphyry and it appears now fringing younger intrusions and as irregular dykes branching into andesite. Its emplacement was followed by the intrusion of

the "k" and "L" porphyry complexes, and early K - silicate alteration and mineralization. The early alteration in the porphyries is characterized by the development of perthitic groundmass, quartz veinlets with k-feldspar rim, biotitization and anhydrite. Sulphide mineralization of this stage was a chalcopyrite-bornite core zone, overlain by a chalcopyrite - pyrite hood. Late latite dykes cut through the complex.

The "Transitional" alteration and mineralization, followed the consolidation of most of the "L" porphyry, and prior to the development of the main high-sulphur hydrolytic environment, an intermediate alteration was present, characterized by bounded quartz veins which contain abundant molybdenite and minor chalcopyrite and pyrite.

The late alteration and mineralization is characterized by abundant pyrite and strong quartz sericite alteration, that surround the central sulphide zones. At the outer limit, the peripheral zone grades into the older propylitic zone. A secondary enrichment zone formed the economic ore body, which is 1,5 km in diameter and up to 200m thick, and is overlain by 200 to 400m of leached material (Figure 5.4). Chalcocite and covellite are common secondary Cu sulphides.

Fuster (1983), concluded that the distribution of the main Mo mineral at El Salvador, molybdenite, is largely controlled by the abundance of veinlets related to the transitional alteration and mineralization stage. Lindgrenite, $\text{Cu}_3(\text{MoO}_4)_2(\text{OH})_2$ is the only Mo mineralogical species other than molybdenite, occurring at El Salvador. Mo is also present in jarosite and in amorphous ferrimolybdate and jarosite. Powellite $\text{Ca}(\text{Mo}, \text{W})\text{O}_4$ is locally present at deep levels of primary zone.

In late magmatic veinlets there is the polytype 2H_1 . In veinlets associated with the transition stage, 2H_1 and 3R polytypes have been recognized. The 3R polytype is related with an increasing of the Re content in molybdenite. The same author suggested a probable relation between the 3R polytype and fluid inclusion of low temperature and salinity.

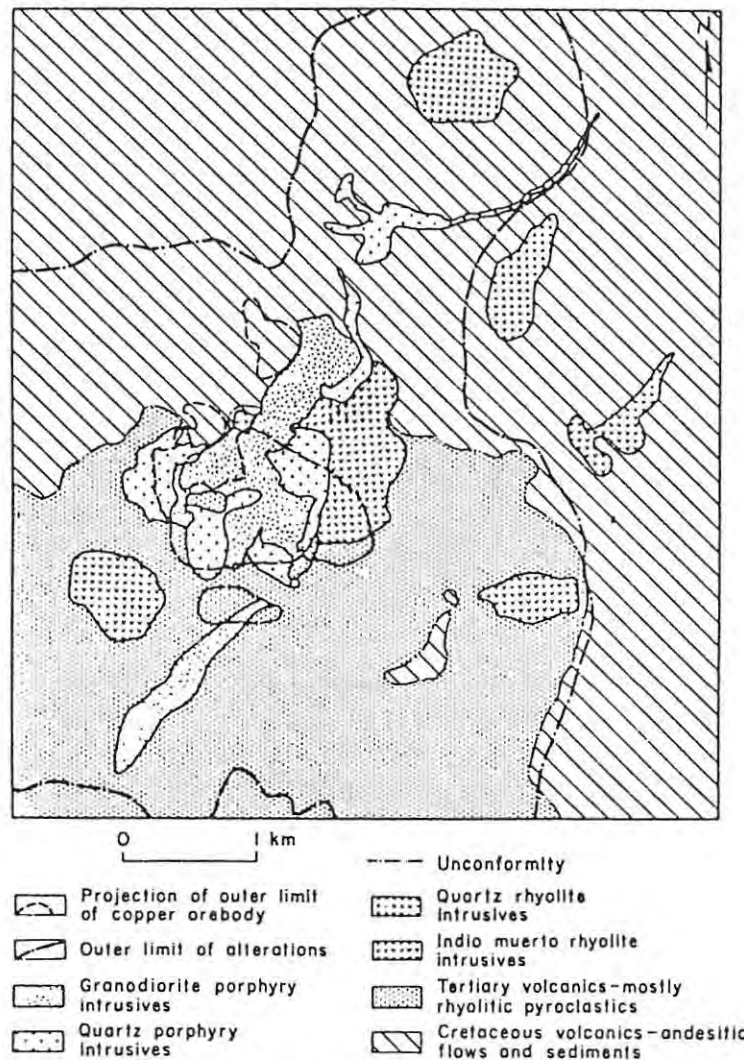


Figure 5.4 Simplified geological map of the El Salvador (Indio Muerto) district, Chile, showing distribution of principal rock types analysed in this report, the outer limit of hydrothermal alteration, and the projection of the main ore zone. (Gustafson and Hunt, 1975).

Chuquicamata, geology and Mo mineralization

This ore deposit too is located in Northern Chile, 230 km northwest of the city of Antofagasta (Figure 5.3). Important subsurface workings started around 1870, and the open pit operation was started in 1915. It is the largest copper producer as a single mine in the world. Indicated reserves, not including the Exotica ore body, are about 1,8 billion tonnes of sulphide ore with 1,12% Cu (Ambrus, 1978b).

The overall Mo content in the 1,8 billion tons known reserves of the pit

area at Chuquicamata, with grades ranging from 0,015 to 0,03% Mo. The + 0,1% Mo zone occupies a north south trending belt parallel to the West Fissure for a length of about 1 700 meters with an average width of 200 metres and a minimum depth of 300 meters.

The primary Cu-Mo mineralization is located in a 12 km long and 0.8 km average width granodioritic porphyry complex (the Chuqui porphyries), which intruded into Jurassic granodiorites (Elena Gd.), and Paleozoic metamorphosed rocks during early Oligocene age. The West Fissure is a major fault which can be recognized many kilometers north and south (Figure 5.5). Ambrus (1978b), suggests that this fault might have played an important role in the area, during and after the emplacement of the Chuqui porphyries. This fault brings into contact the ore body with Fortuna granite (Figure 5.5).

Primary mineralization started in Chuquicamata during the late magmatic stages of Chuqui porphyries intrusion, with bornite-chalcopyrite-chalcocite disseminated in the porphyry and also related to early quartz veinlets without or with alteration halos which produced potassic alteration on the host rock.

Three stages of hydrothermal mineralization are recognized in Chuquicamata. The earliest hydrothermal activity includes pyrite-molybdenite-chalcopyrite in various types of hydrothermal quartz veins. The main hydrothermal stage produced pyrite (with minor bornite, chalcopyrite, sphalerite and enargite) together with a pervasive quartz-sericite alteration which operated from the openings of the stock work. The latest mineralization occurred as veins located close to the West fissure with argillic alteration in the vein fillings and in the host rock. Pyrite-enargite, with sphalerite, galena and tennantite are recognized. Figure 5.6 show the relationships between alteration and mineralization at Chuquicamata deposit.

A very rich secondary mineralization took place in the southern portion of the ore body with the occurrence of chalcocite and covellite (Figure 5.6). This zone occupies about 3.5km in north-south direction, with an average width of 500 meters and an average thickness of 400 meters.

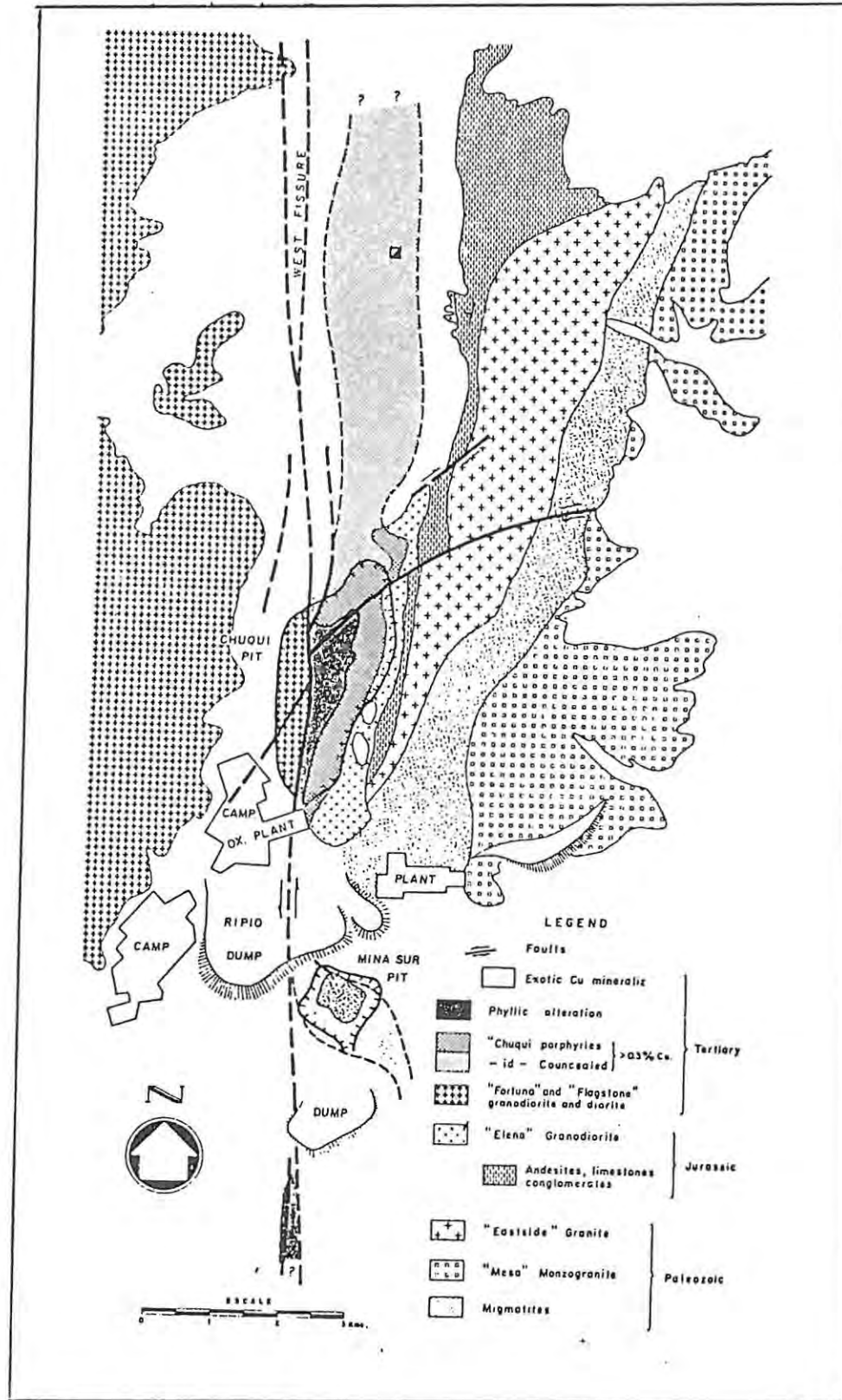


Figure 5.5 Geology of Chuquicamata Porphyry copper (Ambrus, 1978b)

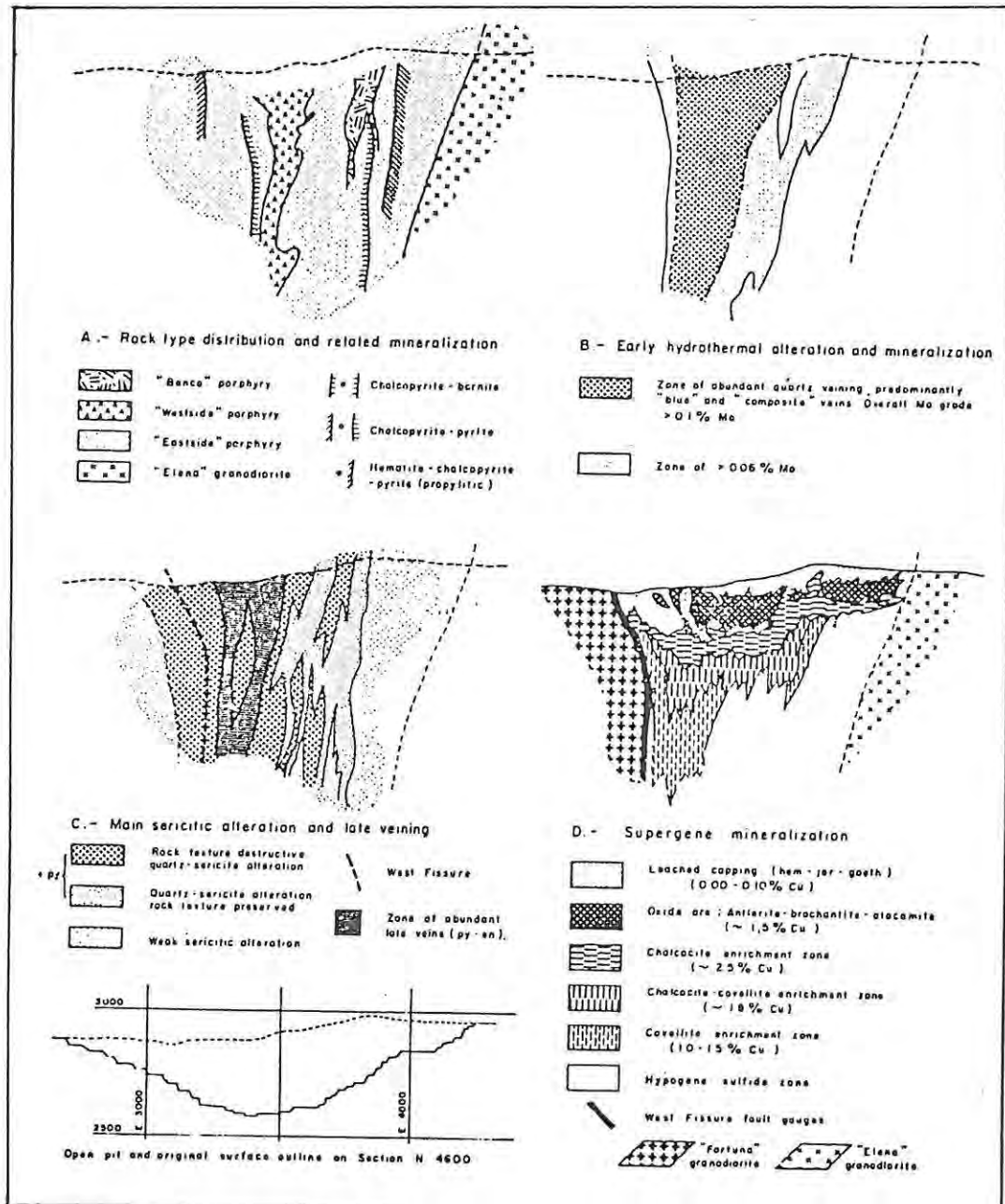


Figure 5.6 Rock type distribution, alteration and mineralization at Section N 4600, Chuquicamata, Chile (Ambrus, 1978b)

Mo mineralization at Chuquicamata is described by Ambrus and Soto (1974). They recognized three main types of early molybdenite-bearing hydrothermal quartz veins and veinlets.

a. Quartz-molybdenite veinlets, which consist of a microgranular quartz, and suture generally with sulphides. Alteration halo is not present. It is similar to the "Transitional" veins defined for El Salvador porphyry.

Molybdenite is usually present on the fringes of these veinlets, occasionally with minor amounts of chalcopyrite and pyrite.

b. "Blue veins", show a distinct bluish to greyish colour, due to molybdenite and supergene copper sulphides. Molybdenite occurs as 1 to 10 mm size individual crystals or clusters disseminated in quartz, and generally concentrated near the border of the veins. Pyrite and chalcopyrite are common. A narrow feldspar destructive halo, can be recognized around "blue veins" and fine grained molybdenite is disseminated there.

c. Composite veins, consist of major quartz veins of 0,5 to several meters in thickness and are characterized by adjacent tectonized "blue veins" and sometimes related to irregular quartz masses and pods. It presents brecciated quartz segments with coarse molybdenite in seams and fracture surfaces. Pyrite also is present.

d. Molybdenite on fracture surfaces. Nearly one third of the total Mo content in the deposit appears to be related to fracture surfaces as coarse grained, curved and elongated bunches of molybdenite crystals.

Anomalous occurrences of molybdenum have been observed in some late hydrothermal structures as pyrite-enargite veins and in pyrite quartz sericite veins.

Mo oxides occur above the top of sulphides. lindgrenite, $\text{Cu}_3(\text{Mo}_4)_2(\text{OH})$, is the most important Mo oxide and it is more abundant in zones where Cu oxides are stable, probably because the extreme acid environment of the upper levels, leach the lindgrenite to ferrimolybdite, $\text{Fe}(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$. Trace amounts of wulfenite PbMoO_4 , powellite, Ca MoO_4 , have been recognized. castaingite, $\text{Cu Mo}_2\text{S}_5$, a yellowish variety of molybdenite have been recognized near the top of enriched Cu sulphides (Ambrus, 1978b).

5.2.2 Island Arc porphyries Cu-Au and Mo deposits

Porphyry Cu or Cu/Mo and Cu/Au deposits are emplaced in island arcs, in the belt of andesitic to dacitic igneous activity above a Benioff Zone (Sillitoe, 1972). They occur at the summit, or around the margins, of

stocks or small plutons intruded beneath contemporaneously erupted volcanic rocks. Occurrences of Miocene and younger ore bodies at high elevation as at Mamut in Sabah and Ok Tedi in New Guinea, suggest the presence of a thick column of intruded host rock. Later uplift and erosion exposed the ore body and host rocks.

These porphyries are associated with the calc-alkaline group. Kesler et al., (1972), suggested that within this group, individual intrusive centres can exhibit modal compositional trends ranging from quartz-diorite to granodiorite.

Worth mentioning is a general characteristic of these volcanic arc disseminated porphyry deposits in their lack of economic Mo deposits (Cu/Mo ratio higher than 100/1) and the presence of gold in economically significant amounts. Figure 5.7 shows the abundance of Cu-Mo-Au in porphyries systems of Island arc setting.

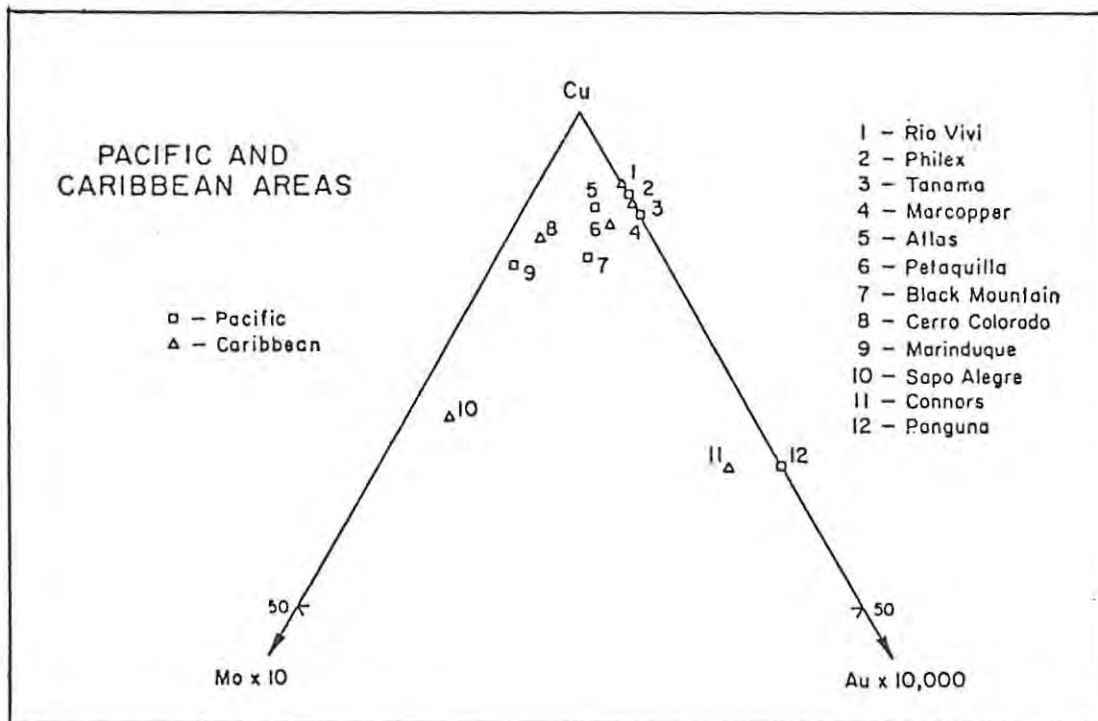


Figure 5.7 Relative abundance of copper, molybdenum and gold in porphyry copper deposits in Pacific and Caribbean island arc areas (Kesler, 1973)

In the southwestern Pacific, porphyry Cu province contains the deposits of the Philippine Islands, New Guinea and Bougainville. Despite the low Mo concentration the Philippine ore bodies contain reserves of the order of 170 000 tons. The Bougainville deposit (Panguna), with a copper grade of 0,5% contains an average of 0,009% Mo and reserves of 50 000 tons of metallic Mo.

Porphyry Cu deposits of Panama (Central America) are contained in calc-alkaline granodiorite. In contrast with other island arcs, they display a characteristic trend towards enrichment in K, because of their continental nature. They also contain higher gold, and Mo.

5.3 Continental Setting Related to Inactive Subduction Zones

Cu-Mo and Mo mineralization in North Western of North America is related to an inactive subduction environment of Mesozoic and Cenozoic age (Mitchell and Garson, 1981). Many authors argue for a regional ensialic interarc or back-arc extension during this time span (Elston, 1976; Stewart, 1978, 1980).

This comparatively relaxed stage of stress in the lithosphere is directly related to major changes in plate motion and drastic lowering of convergency rates near 40 m.y. ago (Coney, 1972), which according to Keith (1978), resulted in a rapidly increasing angle of subduction. The model in Figure 5.8 shows the relationships between magmatism, metallogeny in an arc-related rift geotectonic setting, and variations in the convergence and angle of the Benioff zone for the Colorado Mo porphyries.

Howell (1985) suggested that plate tectonic activity in western North America consists chiefly of island arc and oceanic material that have piled on to the western margin of the north American plate, throughout the past 180 m.y. He described them as "collages" or "mosaics", formed by disparate fragments (microplates) of crust swept together by the motions of the earth's great crustal plates.

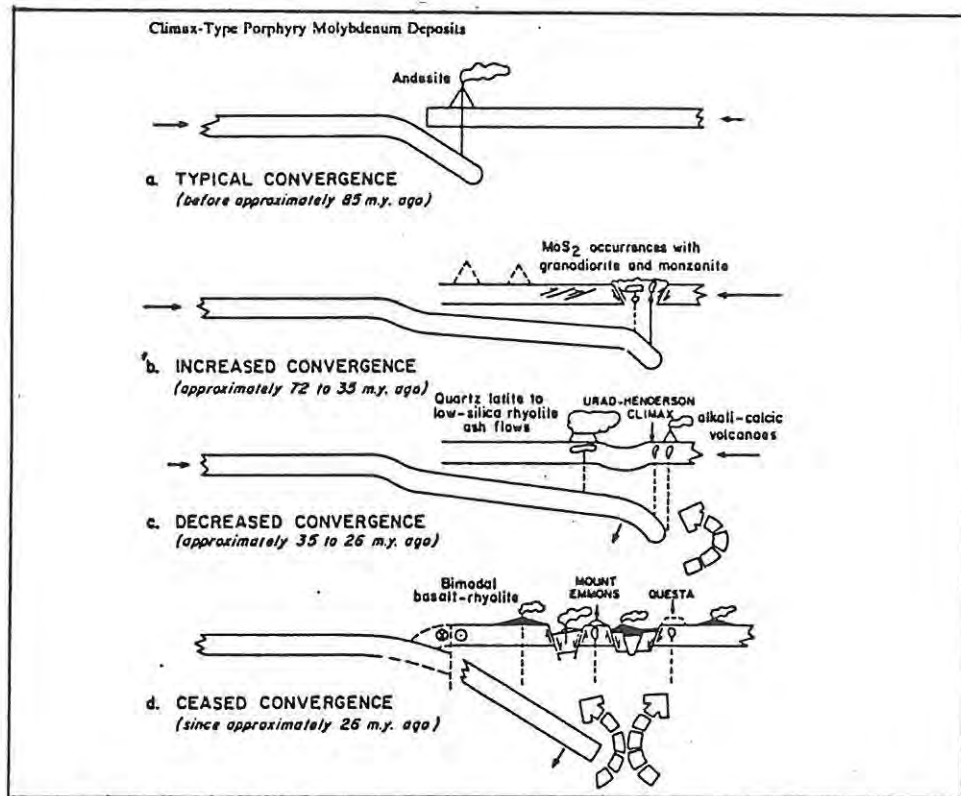


Figure 5.8 Hypothetical plate tectonic cross sections showing inferred changes in subduction, tectonism and magmatism in the Colorado Rocky Mountain region in relation to the generation of porphyry molybdenum deposits (Bookstrom, 1981). In Sawkins, 1984.

5.3.1 Porphyries Cu-Mo of western North America

As previously remarked, by-product Mo production from porphyry Cu deposits is the second major source of this element, (in the United States 34% of Mo production is from porphyry Cu-Mo deposits).

In general, North American porphyry Cu deposits are emplaced in Late-Cretaceous sediments and metasediments and are associated with Laramide (80 - 40 m.y.) quartz monzonite stocks (Figure 5.9).

The stocks are controlled by regional - scale faulting. The ore bodies have oval to pipe-like shapes, with gradational boundaries, and Mo contents average 0.015% Mo. An example is San Manuel of Kalamazoo deposit, Arizona, which has been proposed by Lowell and Guilbert (1970) as a typical porphyry deposit, in both mineralization and alteration patterns. Other porphyries are Cananea, Butte, Bingham Morenci, Ely, Ajo.

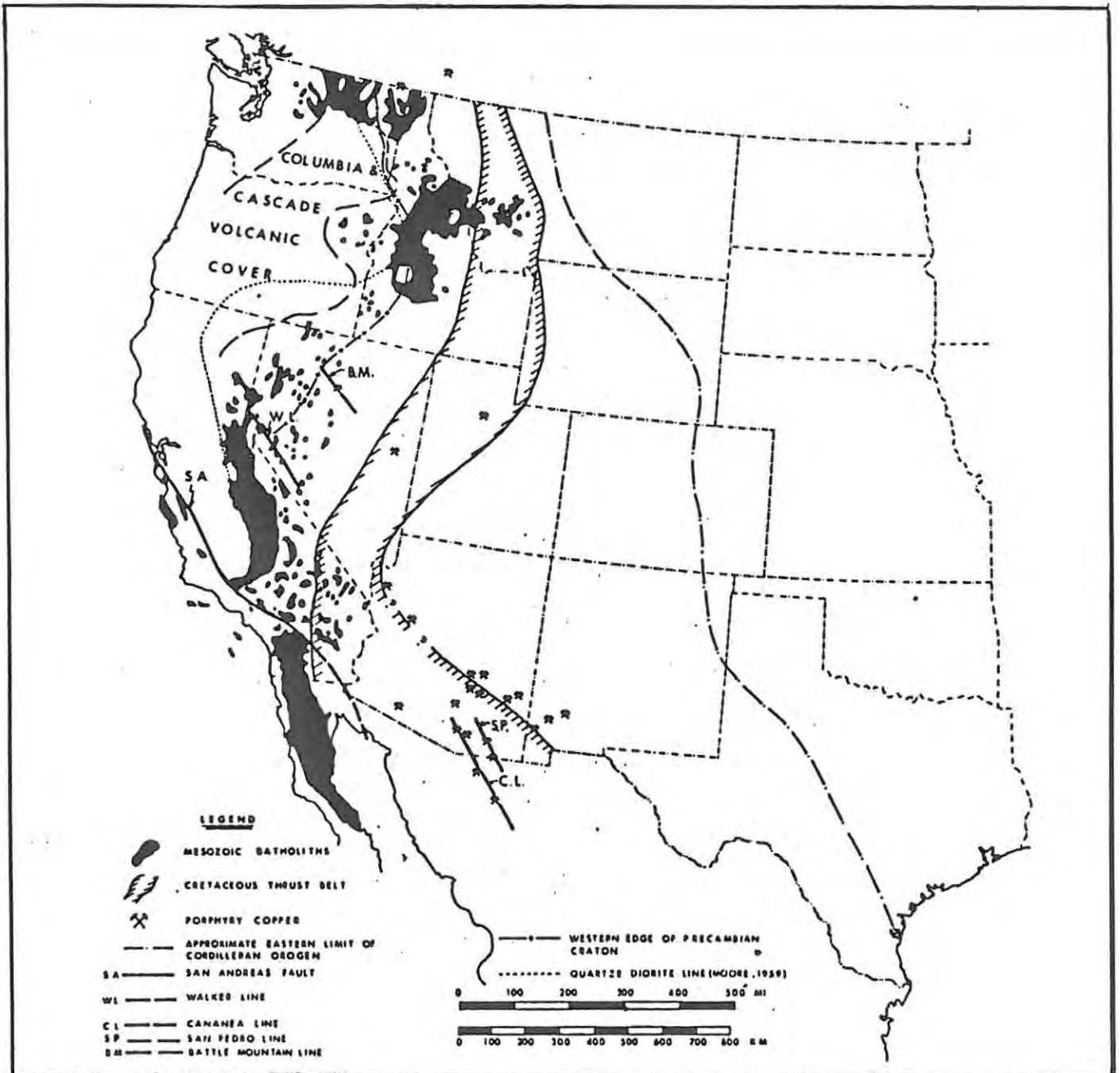


Figure 5.9 Batholiths, thrust belts, and porphyry copper belts of the southern Cordilleran orogen. Porphyry copper deposits of the southern Cordilleran Orogen tend to occur in distinct belts east of the large Mesozoic batholiths. Moore's line and the western limit of the Precambrian craton lie west of all large Lowell and Guilbert (1970) model, porphyry copper deposits now known. (Hollister, 1978)

Most major porphyry deposits in the southern Cordilleran orogen occur on regional megastructures but not all have been associated with large strike-slip faults. Bingham provides a fairly typical example of structural control of the intrusive emplacement, along a pre existing regional fault. The hypogene sulphide mineralization has a close relation with the alteration. In the potassic zone veins commonly contain quartz, orthoclase, biotite, chalcopyrite and bornite. Hypogene copper sulphide also occurs as disseminations within the potassic zone where mineral assemblages demonstrate a paragenetic simultaneity of Cu precipitation and K metasomatism (e.g. Bingham). Table 5.II shows the Cu and Mo contents of this porphyry deposit.

Table 5.II Molybdenum-bearing porphyry-type deposits of the United States (Clark, 1978)

Name & Location	Production tpd	Grade	
		% Mo	% Cu
Climax, Colorado	48,000	0.33	—
Henderson, Colorado	20,000 ¹	0.421	—
Urad, Colorado	5,000 ³	0.35	—
Questa, New Mexico	17,000	0.174	—
Bingham, Utah	108,000 ²	0.03	0.69
San Manuel, Arizona	65,000	0.015	0.69
Morenci, Arizona	60,000 ²	0.015 ³	0.83
Sierrita, Arizona	83,000	0.03	0.29
Pima, Arizona	54,000	0.017	0.56
Tyrone, New Mexico	48,000	0.012	0.89
Twin Buttes, Arizona	32,000 ²	0.03	0.60
Ray, Arizona	25,500 ²	0.015	0.98
Santa Rita, New Mexico	22,000 ²	0.008	0.90
Ely, Nevada	21,500 ³	0.016 ³	0.85 ³
Inspiration, Arizona	22,000 ²	0.007	0.71
Mission, Arizona	22,500	0.02	0.70
Mineral Park, Arizona	19,000 ²	0.03	0.42
Esperanza, Arizona	15,000 ¹	0.03	0.37
Miami, Arizona	14,000 ²	0.005	0.50
Silver Bell, Arizona	13,000 ²	0.01	0.70
Bagdad, Arizona	6,000	0.03	0.70

¹ Will climb to 30,000 tpd.

² Part of production obtained either by leaching ore or dumps.

³ Curtailed or depleted.

Porphyry Cu-Mo deposits are present in the Canadian Cordillera orogen. They give a good contribution to the production of Mo, and are distributed throughout the four western tectonic belts, reflecting the variable chemical and physical properties of related calc-alkaline batholiths, stocks and smaller plutons that range in age from Late Triassic to mid Tertiary (Figure 5.10).

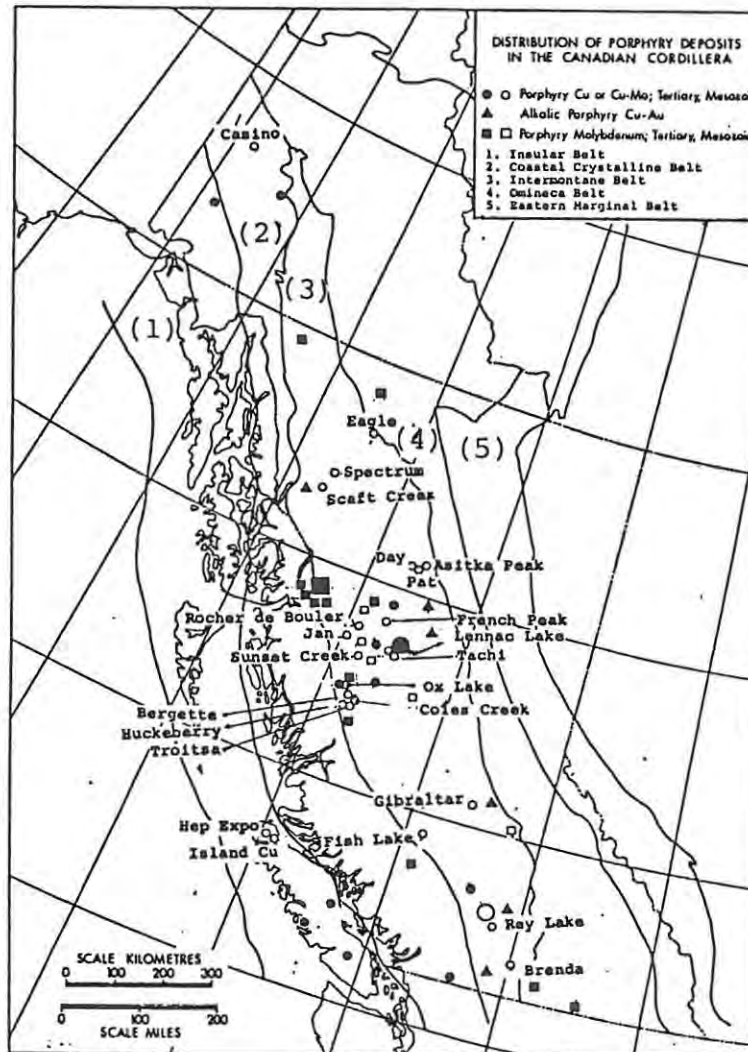


Figure 5.10 Distribution of porphyry deposits in the Canadian Cordillera (Christopher and Carter, 1976).

Hodder and Hollister (1972), have described the tectonic settings and mineral deposits of the Canadian Cordillera with reference to five district geological and physiographic belts (Figure 5.10). These are (from east to west) 1) Eastern marginal belt 2) Omineca belt, 3) Intermontane Belt 4)

Coastal Crystalline Belt and 5) Insular Belt. Field et al (1974) on the basis of age dating suggests that porphyry - type deposits of British Columbia exhibit western migration.

Three distinct types of porphyry deposits attributed to different crustal settings, occur in the North Western Cordillera orogen. (Christopher and Carter, 1976). These are Diorite porphyry type which include the following (see Figure 5.9) : Brenda, Fish Lake, Jan, Schaft Creek and Eagle deposits. The Granodiorite type includes : Rey Lake, Gibraltar, Troitsa, Huckleberry, Ox Lake, French Peak, Rocher de Bouler, Asitka Peak, Day, Pat, Spectrum, Tachi, Hep-Expo, Island Cu and Sunset Creek deposits. The Quartz Monzonitic type comprises : Coles Creek, Rey Lake, Bergette and Casino deposits.

The best concentrations of molybdenite are related to the younger phases, and commonly are best developed in the contact of the pluton with the intruded rocks.

5.3.2 Porphyry Mo deposits

These porphyries are the most significant source of Mo. They generally have Cu/Mo ratios ranging from 0,02 to 0,05. They are spatially, temporarily and genetically associated with porphyritic intrusion of quartz monzonite with high silica and alkali rich. The largest Mo tonnages are restricted to areas where this type of deposit develops in abnormally thick sialic crust.

These deposits are found in the Andes, Caucasus, Mongol - Armur, Transbaykal belts, as well as in the western Cordillera of North America where they occur in a band that extends throughout the length of British Columbia (and adjacent parts of southeast Alaska) southward through the western United States to Mexico. The latter are well documented as for example : Climax Urad, Henderson, Endako, Red Well, Mt. Emmons and others (Figure 5.11), Their age ranges from 41 m.y. (Questa) to 141 m.y. (Endako).

These deposits are characterized by molybdenite occurring alone or with quartz and/or pyrite in fractures and open spaces of stockworks and

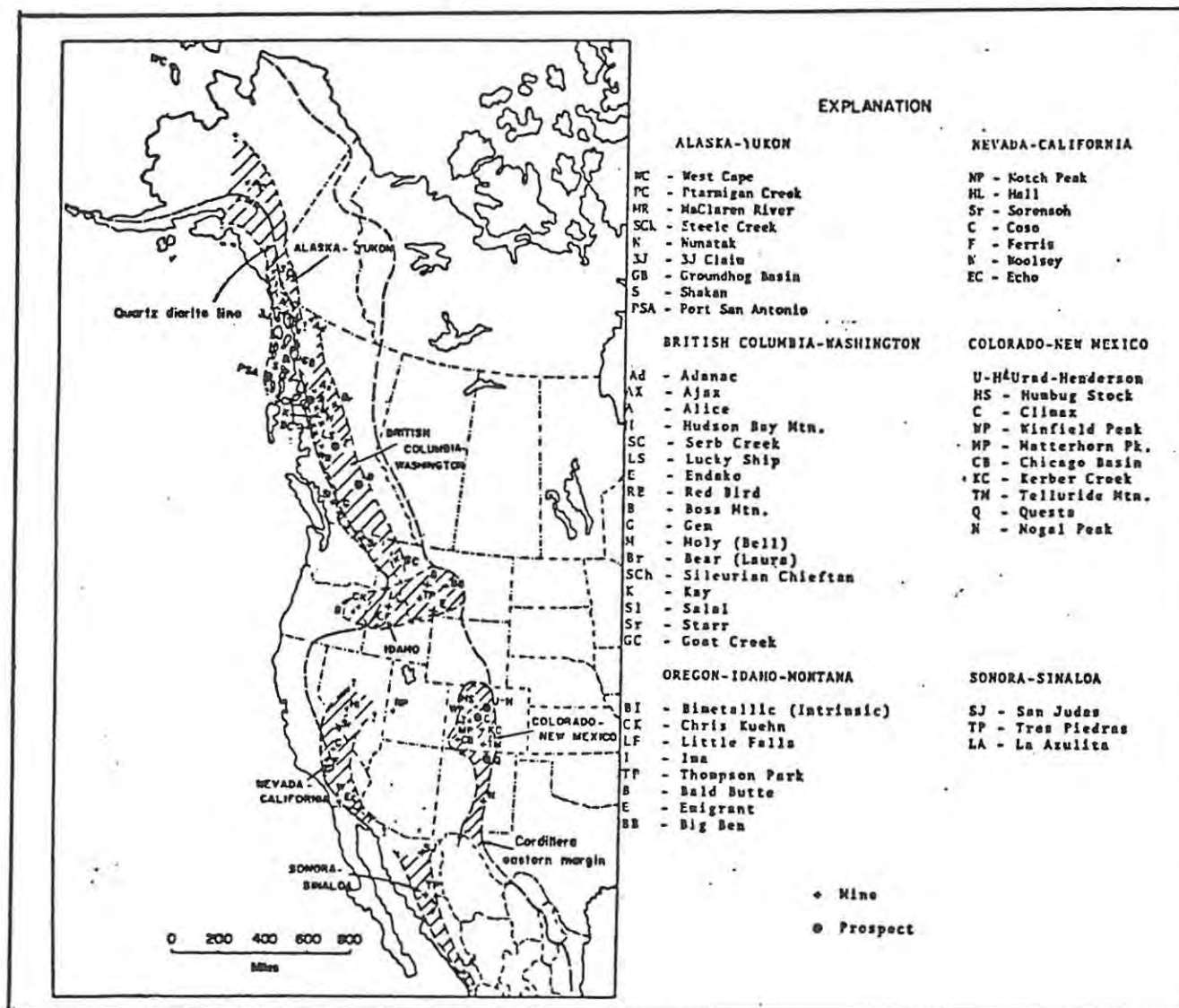


Figure 5.11 Distribution of molybdenum-bearing provinces in western Northern America, exemplified by the principal stockwork deposits, in relation to the quartz diorite line and eastern margin of the Cordillera (Clark, 1972).

breccias. The molybdenite grain size is fine, generally less than one millimetre across. Occasionally stockworks such as that exposed in Adanac (Canada) contains molybdenite crystals up to one centimetre across.

Although these porphyry Mo deposits resemble their Cu counterparts in many aspects, especially in their relation to intrusive stocks and in their association with large zones of intense hydrothermal alteration, there are some distinct differences.

The more important difference is the ratio Cu/Mo and of other metals. For example, the W to Mo ratio for porphyry Mo deposits is much greater than in most porphyry Cu deposits. The Re/Mo ratio for Mo deposits is less than one-fifth than in porphyry Cu deposits. Tin occurs sparingly and erratically in porphyry molybdenite occurrences. A high F content (fluorite and topaz) is characteristic of these deposits.

Alteration in and around the porphyry Mo deposits, shows a complex distribution, because of the multiple stages of mineralization and alteration. Both lateral and vertical zoning are present. Lowell and Guilbert (1970) who included Climax and Questa in their quartz monzonite classification, give the following alteration sequence.

- a. Quartz zone
- b. K-silicate zone : generally quartz + K-spar (orthoclase or microcline) with or without biotite.
- c. Sericitic zone : quartz + sericite + pyrite (may contain kaolinite or illite).
- d. Propylitic zone : quartz + chlorite + epidote + carbonate.

The classification of porphyry Mo deposits has had its evolution, since Clark (1972) suggested that the major porphyry molybdenite deposits of North America are of a stockwork or Climax - type model with an alteration dominated by K-feldspathization and silicification.

A. Classification

Woodcock and Hollister (1978) classified porphyry Mo deposits into two structural types : 1) stockworks and 2) Breccia. Each is further divided on the basis of the size of the associated pluton as being either a). batholithic or b). stock-type. The breccia type is believed to be a high-level variation of the stockwork type.

A detailed classification of the stockwork molybdenum deposits was suggested by Westra and Keith (1981). They classify the deposits on the basis of magma series chemistry because they are related to differentiated granitic stocks. The K_2O content in terms of 57,5% SiO_2 is estimated for the magma series which includes the parent granite. This K_2O content is called the K57,5 value. This value is used by the authors, to define different types of stockwork Mo deposits.

The F content in biotite is controlled by the HF activity in the magma and increases with higher K 57,5 values. There is an increase in the F and Sn contents, of Mo deposits associated with magma series with K57,5 values of greater than 2.5 (Table 5.III).

Table 5.III Stockwork and breccia molybdenum deposit classification (Modified from Westra and Keith, 1981). In Siems 1985.

Deposit Class	Magma Series	K _{57.5} Value	Fluorine Content	Elemental Association	Name of Deposits
Stock type	Calc-Alkaline	1.5-2.5	Low	Mo-W-Cu	Kitsault, Hall, Buckingham
Plutonic type				Mo-(Cu)-(W)	Endako, Mt. Tolman, Quartz Hill, Adanac, Thompson Creek
Transitional type	Alkali-Calcic	2.5-3.0	High	Mo-Cu-Zu-Pb-F	Questa, Mount Hope, Glacier Gulch
Climax type				Mo-F-W-Su-Zn-Ag-Pb-Cu-U	Climax, Urad-Henderson, Mt. Emmons, Pine Grove
Syenite and monzonite source	Alkalic	4.0-6.0	High	Mo-F-Sn-W	Nogal Peak-Rialto Stock, Three Rivers Stock
Granite source				Mo-F-Sn-W-(Bi)-(As)	Mount Pleasant, Cave Peak, Malmbjerg, Bordvika

Empsall (1982) however, considers this classification as unsatisfactory, due

to the scarcity of data from most of the mines, and because of the different tectonic environment of some deposits.

A two fold subdivision for porphyry Mo system is proposed by White et al., (1981), based on the composition of their cogenetic intrusion. The two subdivisions are : Climax type, for their association with intrusions of high silica, alkali-rich granite similar to those of the Climax mine, and Quartz-Monzonite type, for their association with quartz monzonite intrusions. The distribution of deposits and comparison between the two types of porphyry Mo is given in tables 5.IV and 5.V.

Table 5.IV Porphyry Molybdenum Deposits (White et al., 1981)

Climax (granite) type	Quartz monzonite type
Colorado	British Columbia
Climax	Endako
Henderson	Boss Mountain
Urzd	Kitsault (Lime Creek)
Mount Emmons	Yorke-Hardy (Glacier Gulch)
Redwell Basin	Adanac ²
New Mexico	Ajax (Dak River)
Questa	Trout Lake
Utah	Yukon
Pine Grove ¹	Boswell River (Tintina Silver)
Montana	Alaska
Big Ben ¹	Quartz Hill ² (Wilson Arm)
Greenland	Washington
Erzberg ¹	Mount Tolman
	Idaho
	White Cloud
	Thompson Creek
	Cumo
	Montana
	Cannivan
	Nevada
	Nevada Moly
	Buckingham
	Pine Nut
	Texas
	Cave Peak
	Sonora, Mexico
	Creston (Opodepe)

Table 5.V Comparison of Types of Porphyry Molybdenum Deposits (White et al., 1981)

Characteristics	Climax type	Quartz monzonite type
Cogenetic rock type	Granite porphyry	Quartz monzonite porphyry
Intrusive phases	Multiple intrusions of granite	Composite intrusions of diorite to quartz monzonite
Intrusive type	Stock	Stock or batholith
Orebody type	Stockwork	Stockwork
Orebody shape	Inverted cup	Inverted cup, tabular
Ore grade, average % MoS ₅	0.30 to 0.45	0.10 to 0.20
Orebody tonnage	50 to 1,000 million tons	50 to 1,000 million tons
Disseminated MoS ₅	Rare	Rare
Age	Middle to late Tertiary	Mesozoic and Tertiary
Fluorine minerals	Fluorite, topaz	Fluorite
Bismuth minerals	Sulfosalts	Sulfosalts
Tungsten minerals	Wolframite (huebnerite)	Scheelite
Tin minerals	Cassiterite, stannite	Rare
Copper minerals	Rare chalcopyrite	Minor chalcopyrite
Silicification	High silica core	No high silica
Greisenization	Greisen common	No greisen
Ore zone Cu:Mo ratio	1:100 to 1:50	1:30 to 1:1

¹ There is some uncertainty as to how closely Pine Grove, Big Ben, and Erzberg fit the Climax-type classification

² Adanac (White et al., 1976) and Quartz Hill (Hudson et al., 1979) are associated with alkali granite, not quartz monzonite intrusions, but otherwise they are more similar to the quartz monzonite-type than to the Climax-type deposits

B. Climax Type, Urad-Anderson deposit

Ore deposits and igneous phases

Climax-type, Mo deposits show common geological features with the Climax mine, which has been the largest single producer of Mo. Wallace et al., (1968) concluded that it formed during several mineralizing episodes associated with successive intrusions of silicic-alkalic rhyolite and granite porphyry related. This type of deposit is developed in Colorado and New Mexico and possibly also in Montana, Utah (table 5.IV). The Climax-type ore deposits in Western United States are elliptical in plan and arcuate, concave downwards in section. They are generally centred on the apex of a plug-shaped intrusion, with a diameter of 0,5 to 1,5 km and a known vertical extent of 2 km or more. These plugs are thought to be cupolas extending above high level silicic plutons with batholithic dimensions (Figure 5.12) (Mudschler et al, 1981).

Granite porphyry plugs have a metaluminous and peraluminous alkali granite composition, with high Si and K. Compared to low-Ca granites, the porphyry plugs granites usually show enrichment in the following elements : Be, Cl, Cs, F, Li, Mo, Nb, Rb, Sn, Ta, Th, U, W, and Y (Mutschler et al, 1981). Ca, Sr, Ba and Ti often are depleted. This pattern of enrichment is similar to that reported for Sn specialized granites (Tischendorf, 1977).

Host Rocks

Stocks and their related molybdenite mineralization generally intrude rocks of arid to intermediate composition. The large Henderson-Urad and Climax ore bodies intrude the Idaho Springs Formation (sericite schist) and the Silver Plume Granite, which are part of the Precambrian Basement Complex. At Questa, the stock complex penetrates Precambrian rocks. Some occurrences of Climax type in British Columbia are intruding jurassic greywackes, argillites, and tuffaceous beds (e.g. the Alice Arm deposit) (Woodstock and Hollister, 1978).

Alteration

The dominant type of alteration involves the pervasive destruction of primary rock forming minerals. Five main alteration zones are recognized. They are : 1) K-feldspar zone, 2) quartz-sericite-pyrite zone. 3) upper

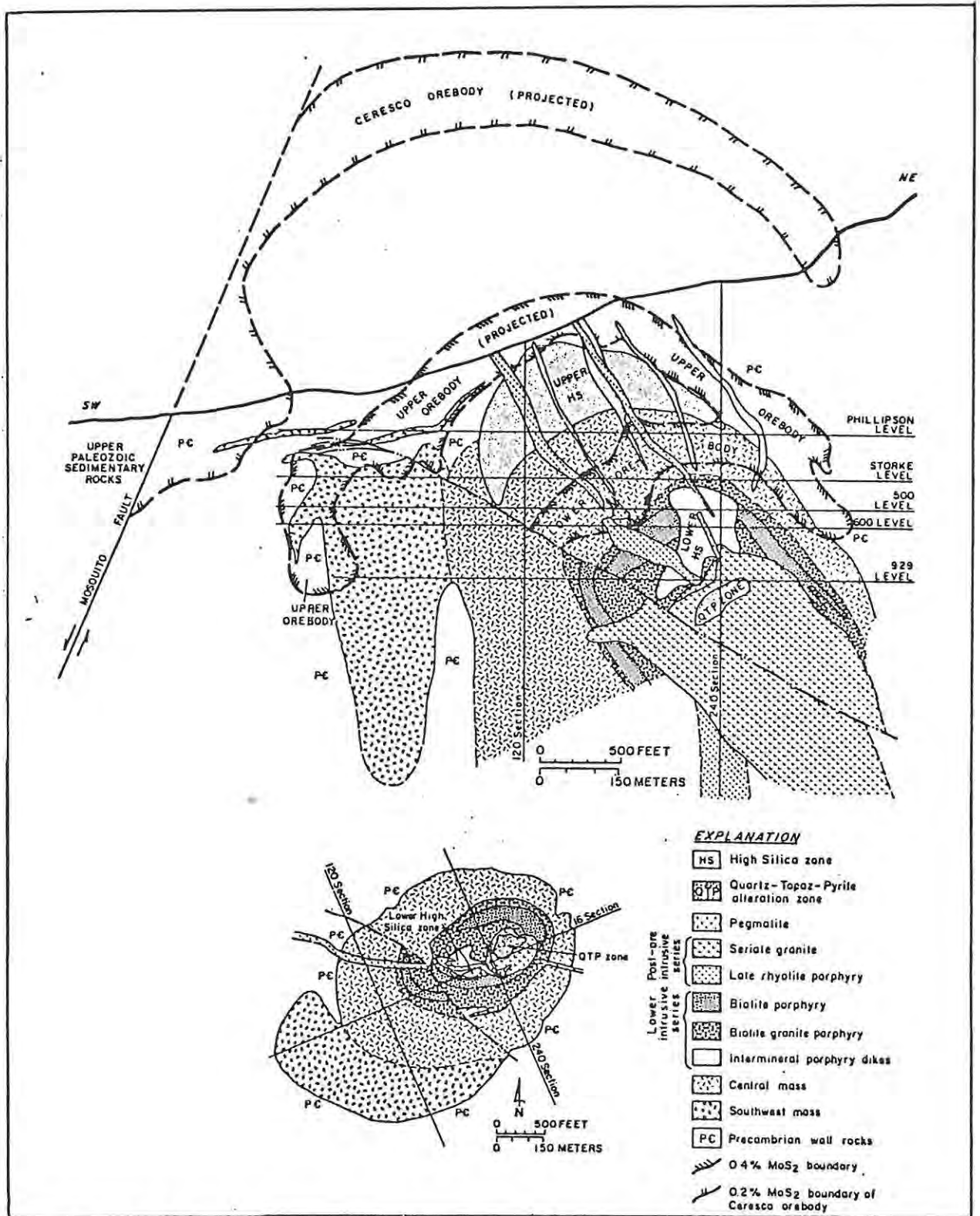


Figure 5.12 Climax section 16 showing generalized geology and ore zones. (White et al., 1981)

argillic zone, 4) lower argillic zone and propylitic zone. Minor alteration zones (silicification and greisen) overlap and cross-cut the boundaries of the major alteration zones. Silicification involves either quartz veining in the vein silica zone or nearly total silica metasomatism in the pervasive silica zone. Greisen alteration contains magnetite, topaz, garnet, quartz and muscovite.

Major rock alteration in Climax-type molybdenum deposits are similar to that associated with porphyry copper deposits. The propylitic and quartz-sericite-pyrite zones in Climax-type deposits, for example, exhibit approximately the same mineral suites and distribution (Lowell and Guilbert, 1970).

Meyer and Henley (1967) suggested that this similarity gives a like model of origin for porphyry Mo, in which also would be involved KH ion concentration.

The major differences between porphyry Mo (Climax-type) and porphyry Cu alteration (such as the intense silicification, relative abundance of F, and as at Henderson Mine, paucity of biotite) may be a function of the more advanced degree of differentiation of the magmatic - hydrothermal system related to the Mo deposit.

Mineralization

In Climax type deposits more than 90 percent of the molybdenite is in thin (less than 3 mm thick) moderately to steeply dipping, quartz-molybdenite veinlets, that form the stockwork. Molybdenite is most commonly concentrated along veinlet walls (Plate 5a, and 5b) but also occurs in discontinuous layers within quartz veins, or as dissemination throughout the vein quartz. Minor molybdenite also occurs as coatings on fractures and as oxide minerals are significantly soluble. Thus in an oxidizing pyrite-rich

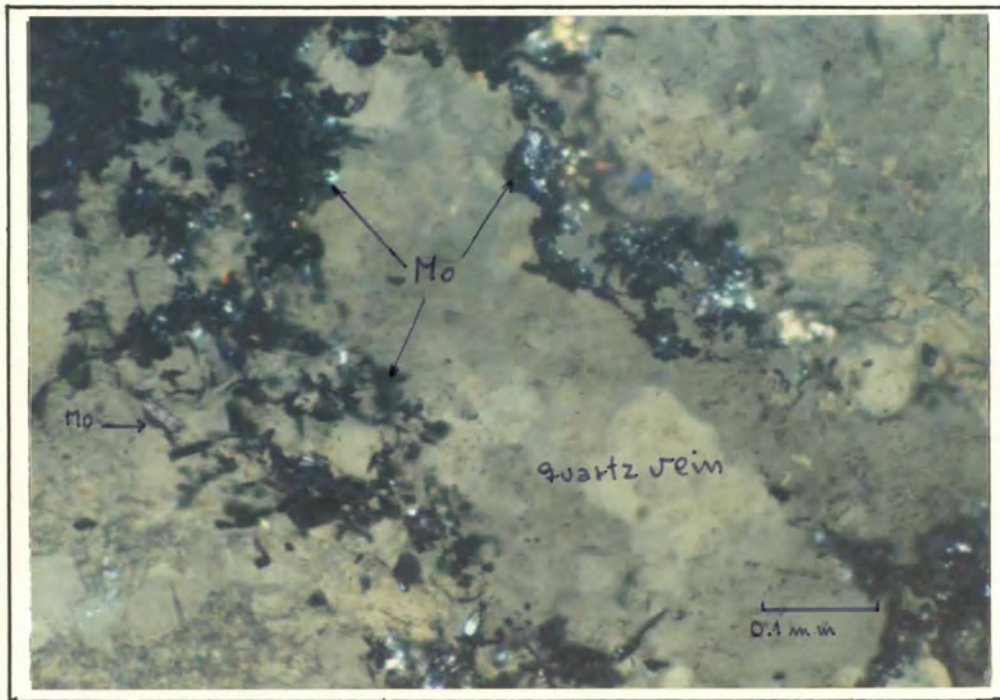


Plate 5a. Concentration of molybdenite (Mo) along veinlet walls, in the Urad-Henderson stockwork.

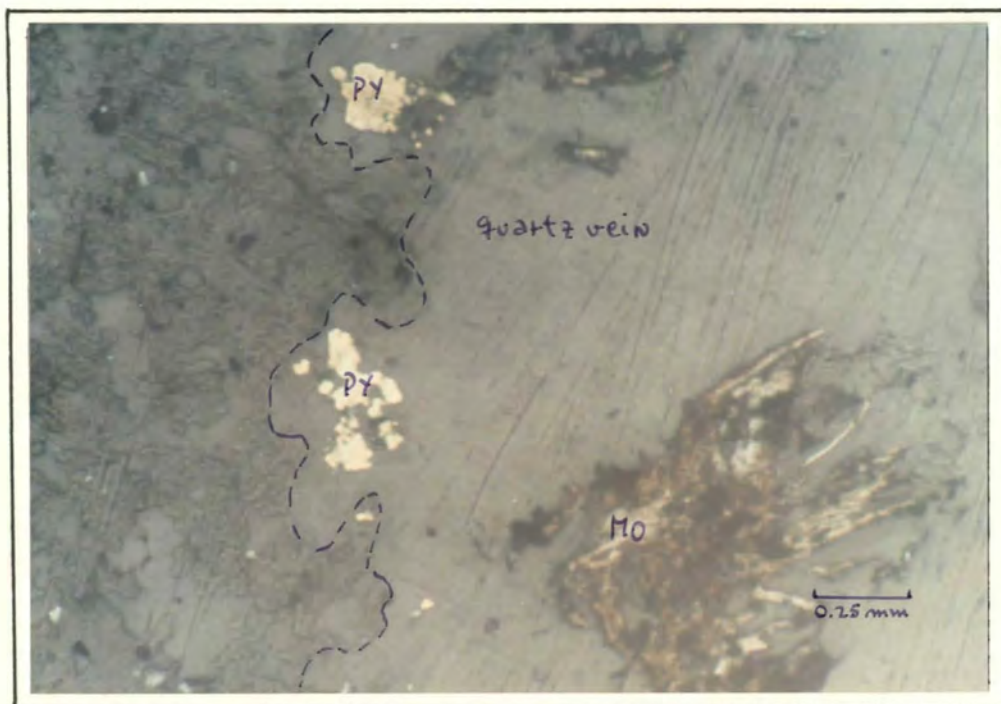


Plate 5b. Molybdenite (Mo) and pyrite (py) along the margin of mineralized veins at Bruthen stockwork Mo prospect. Victoria, Australia (Pirajno, F., 1980 unpublished data).

disseminated crystals in aplites, pegmatites, breccias and porphyries. Although most stockwork veinlets dip steeply, veins of a less abundant gently dipping set may reach 0,9 m and contain clots and rosettes of molybdenite. Evidences of dilation and cross-cutting of older veins by younger ones, indicate recurrent fracturing and movement during the mineralization.

In dilation veins, molybdenite commonly is more abundant along the vein walls in contact with K-feldspar, than in vein walls cutting quartz. Most mineralized veins contain the 2H molybdenite polytype which is the most common, although minor amounts of 3R polytype also occur. The 2H polytype is associated with quartz-pyrite, local topaz and huebnerite, and open veins containing varying amounts of K-feldspar, biotite, sericite and fluorite and rodocrosite, sphalerite, galena and rarely chalcopyrite. The paragenetic sequence is, from oldest to youngest, barren quartz, quartz-molybdenite in stockwork veinlets, quartz-molybdenite in gently dipping veins, quartz-pyrite, and fluorite-rhodochrosite. The early barren quartz sometimes is not present (Climax deposit).

Zoning is important in many of the Climax type deposits. A pyrite halo is a common characteristic and it is included by many authors as part of the quartz-sericite-pyrite alteration. Molybdenite is largely within the potassic alteration zone, whereas the pyrite halo commonly extends well beyond that into the propylitic zone.

Supergene enrichment

The behaviour of Mo in the supergene environment depends on the pH of the environment. Below pH 5 Mo is relatively insoluble, above pH 6 Mo and its

deposit, the pH is generally too low for much of the molybdenum to leach. Where the rainfall is high, an increase in pH above 5 may occur, to produce some leaching and oxidation of molybdenite. However, it may be completely flushed out of the fractured rock near the surface.

B.1 Urad-Henderson Mo deposit

The Urad and Henderson constitutes one of the largest Mo deposits in the world. They occur within the Colorado Mineral Belt, about 50 km from Climax which is a zone 25 - 100 km wide containing numerous quartz porphyry stocks of Mesozoic (Laramide) and Tertiary ages. This belt trends northeast across the Rocky Mountain of Colorado (Figure 5.10). The ore reserves at the beginning (1964) were 300 million tonnes at 0,49% MoS₂.

Regional Geology

The Urad and Henderson stockwork molybdenite ore bodies at Red Mountain are related to a rhyolitic subvolcanic centre of Oligocene age referred to as the Red Mountain Complex. The two ore bodies are well separated in space and are specifically related to different intrusive rocks of the Complex (Figure 5.13). The Urad ore body was formed first and at shallow depth. The Henderson formed deeper within the Complex and is the larger of the two.

This late Oligocene intrusive complex intruded a batholith of Precambrian (Silver Plume Granite), approximately 3 km west of the north-northeasterly Berthoud Pass Fault. This fault is a Precambrian age fault that has been reactivated in Tertiary time (Tweto and Sims, 1963).

The Red Mountain Complex comprises 15 stages and sub stages of igneous activity. All the rocks are chemically and mineralogically similar (Plate 5c). Clastic and fragmented textures are common at the surface, porphyries predominate at intermediate depths, and granitic rocks are present at the greatest depths. The major lithologic subdivisions of the Complex in order of emplacement are the Tungsten Slide, East Knob and Square Quartz Porphyry. The latter is the youngest predating the Urad Ore body and is considered to be the source of the Urad deposit.

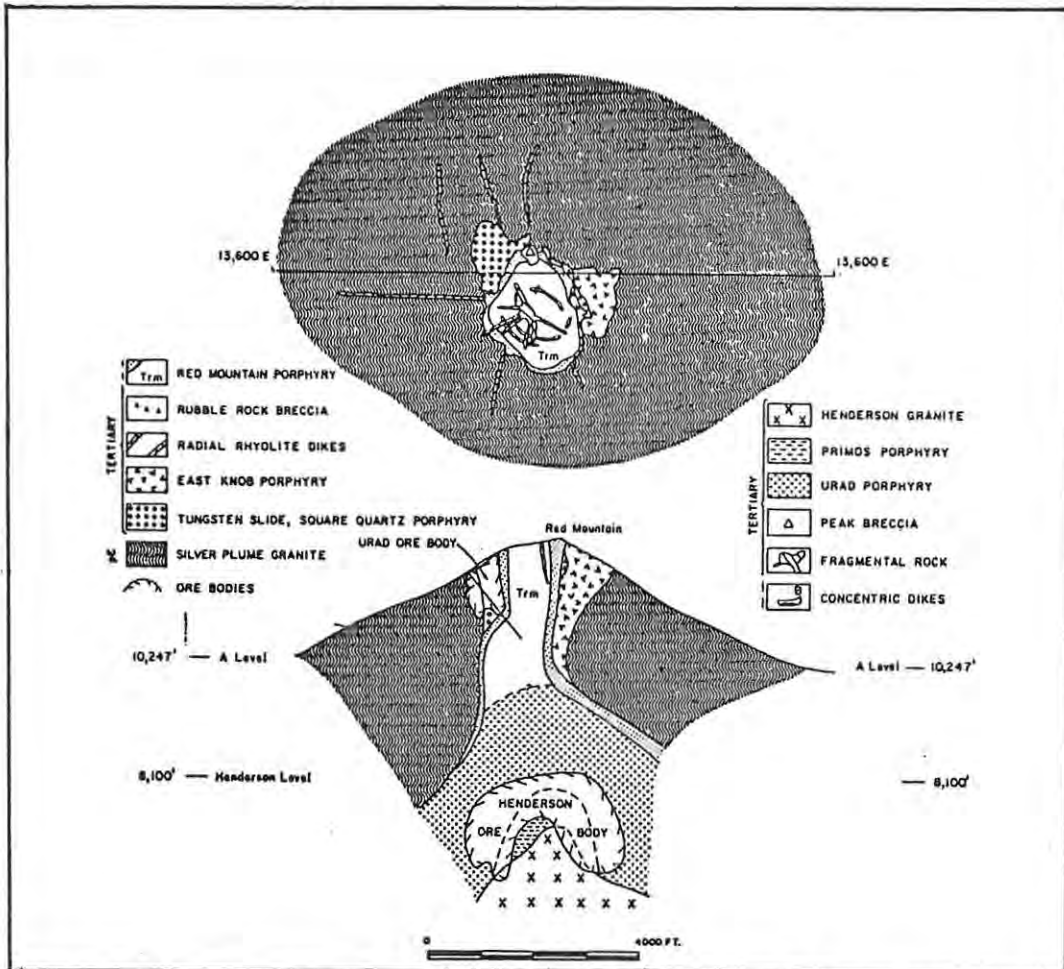


Figure 5.13 Geological sketch of the Urad and Henderson Ore Bodies, Colorado (Wallace et al., 1978)

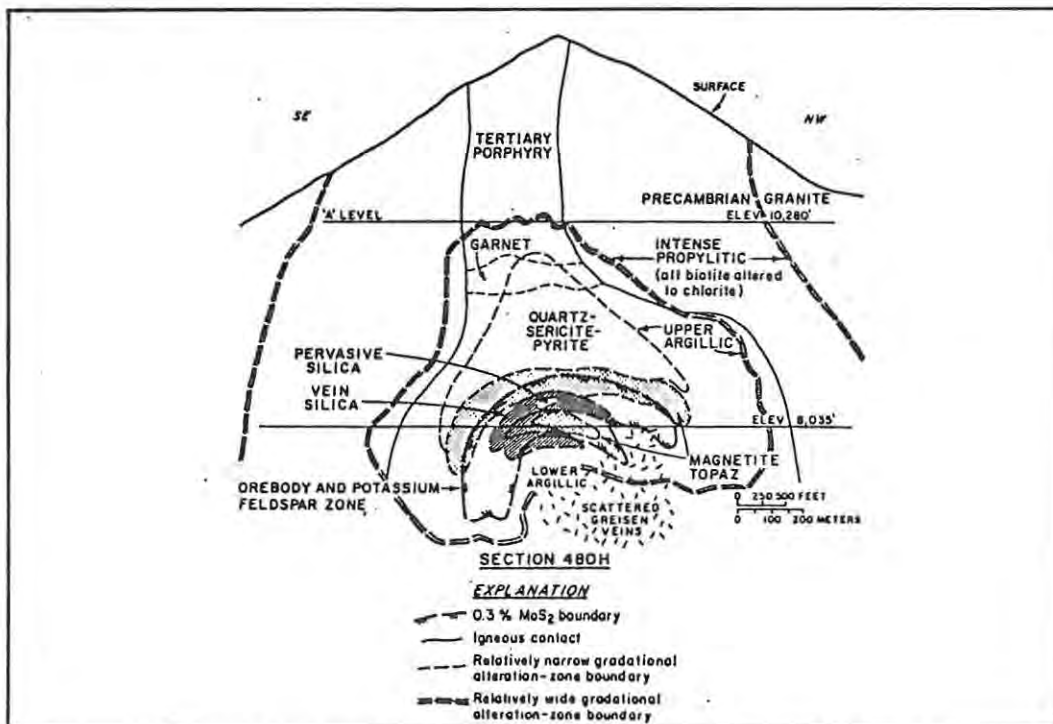


Figure 5.14 Henderson alteration zones (White et al., 1978)

Ore bodies

Mineralization was localized in arcuate fractures referred to as the main fissure system. About half the ore body is in the Red Mountain Complex, the remainder in silver Plume Granite host rock within the Precambrian age. The Urad ore body contained approximately 13 million tonnes, averaging 0,38% MoS_2 with a 0,20% MoS_2 cut off. Based on the cut off value, its arcuate shape is quite regular, because of the control by the main fissures (Hollister, 1978).

The highest grades in the Urad ore body occur in the hanging wall of some fault structures. Much of the molybdenite was precipitated as coatings on the walls of tight fractures in some places forming compound veins as much as 10cm wide. Some of the molybdenite is accompanied by quartz, pyrite, fluorite and sericite. In general the Urad mineralization contrasts sharply with that at Climax, where most molybdenite is finely intergrown within the quartz veinlets of the stockwork.

The Henderson ore body contains 300 million tons of averaging about 0,49% MoS_2 . The ore body is located over the Primos porphyry, and partially within the underlying Henderson granite (Plate 5d). The molybdenite occurs in a stockwork with much of it as discrete molybdenite or in various combinations with quartz, pyrite, and fluorite. In addition some molybdenite is disseminated in the Henderson granite. Some late stage of this sulphide occurs in the quartz fluorite-pyrite veins that are bordered by greisen alteration within the lower part of the ore body.

Alteration and mineralization

Mackenzie (1970), described a poorly developed zonation of hydrothermal alteration within the Urad mineralized area. It includes a central potassic zone (mainly K-feldspar) surrounded successively by a narrow silicified zone, a quartz-topaz zone, an asymmetrical quartz-sericite-pyrite (phyllic) zone, and an outer argillic halo. The potassic zone lies in the south eastern part of the ore body within the 0,3% MoS_2 limit, containing most of molybdenite mineralization.

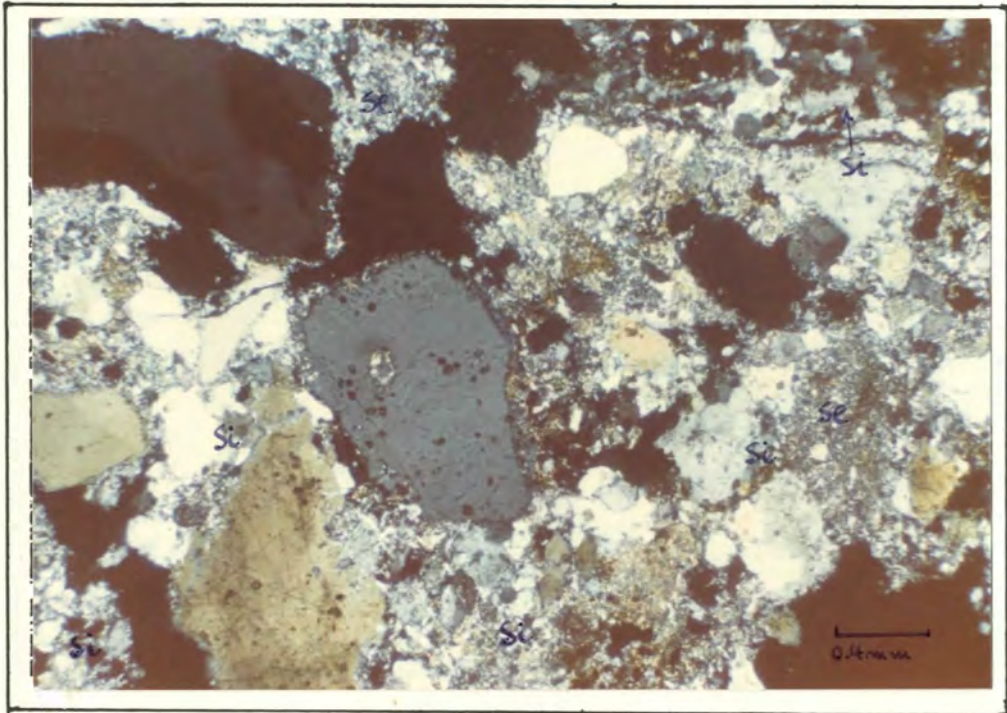


Plate 5c. Red Mountain porphyry with silicification (Si) and minor sericite (se). Urad-Henderson Porphyry Mo deposit. Qtz : Quartz; KF : K-feldspar.

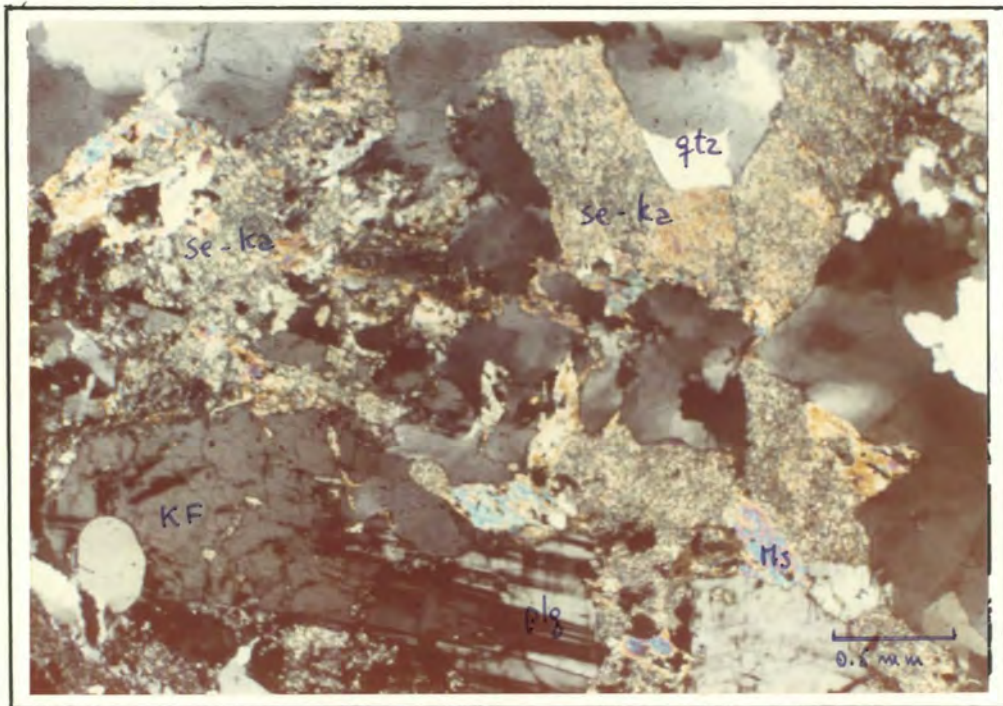


Plate 5d. Henderson granite displaying sericitic alteration (se) and minor Kaolinite (Ka). Urad-Henderson porphyry Mo deposit. Kf : k-feldspar; Qtz : Quartz; Plg : Plagioclase Ms : muscovite.

In the Henderson ore body eight alteration zones have been recognized (Raute et al., 1976). From the ore body outwards, they are : K-feldspar, quartz, magnetite-topaz, quartz-sericite-pyrite, garnet (spessartine), argillic, and propylitic zones (Figure 5.14). Late hydrothermal alteration associated with Henderson granite developed a lower argillic zone overlapping the base of the Henderson Ore Body and the greisen zone. Rock alteration patterns (sericite and silicification) are shown in the plate 5c and 5d.

C. Quartz-Monzonite type Endako deposit

Igneous phases and ore deposits

Deposits of the Quartz Monzonite type are associated with small composite stocks or late phases of batholiths. A few deposits are related to simple single phase stocks. Quartz latite porphyry commonly occurs at chilled margins, but quartz monzonite porphyry is more prevalent in these systems. Differentiation trends beginning with diorite or quartz diorite and progressing to granodiorite and finally to quartz monzonite are common in the intrusive suite (White et al., 1981).

The most important Mo deposits of this type occur within the Intermontane Belt of Central British Columbia, and minor occur in the adjacent Plutonic Complex and Omineca Crystalline Belt, and in the Insular Belt, all of them in Canada (Figure 5.15). Also occurs in southwestern North America (Figures 5.11, table 5IV).

The ore deposits comprise elongate stockwork of quartz-molybdenite veins developed within the intrusive phases. An example is the mineralized quartz monzonite at Endako, which is discussed in more detail later. Other examples are briefly described below.

The Alice arms deposits occur in a number of Mo-bearing granitic stocks (Alice Arms Intrusions) emplaced in sedimentary rocks near the northern part of the Coast Plutonic Complex (Figure 5.11). The Boss Mountain Mo deposit in British Columbia occurs within rocks of the composite Takomkane batholith near a genetically related Cretaceous quartz monzonite rock (Figure 5.11).

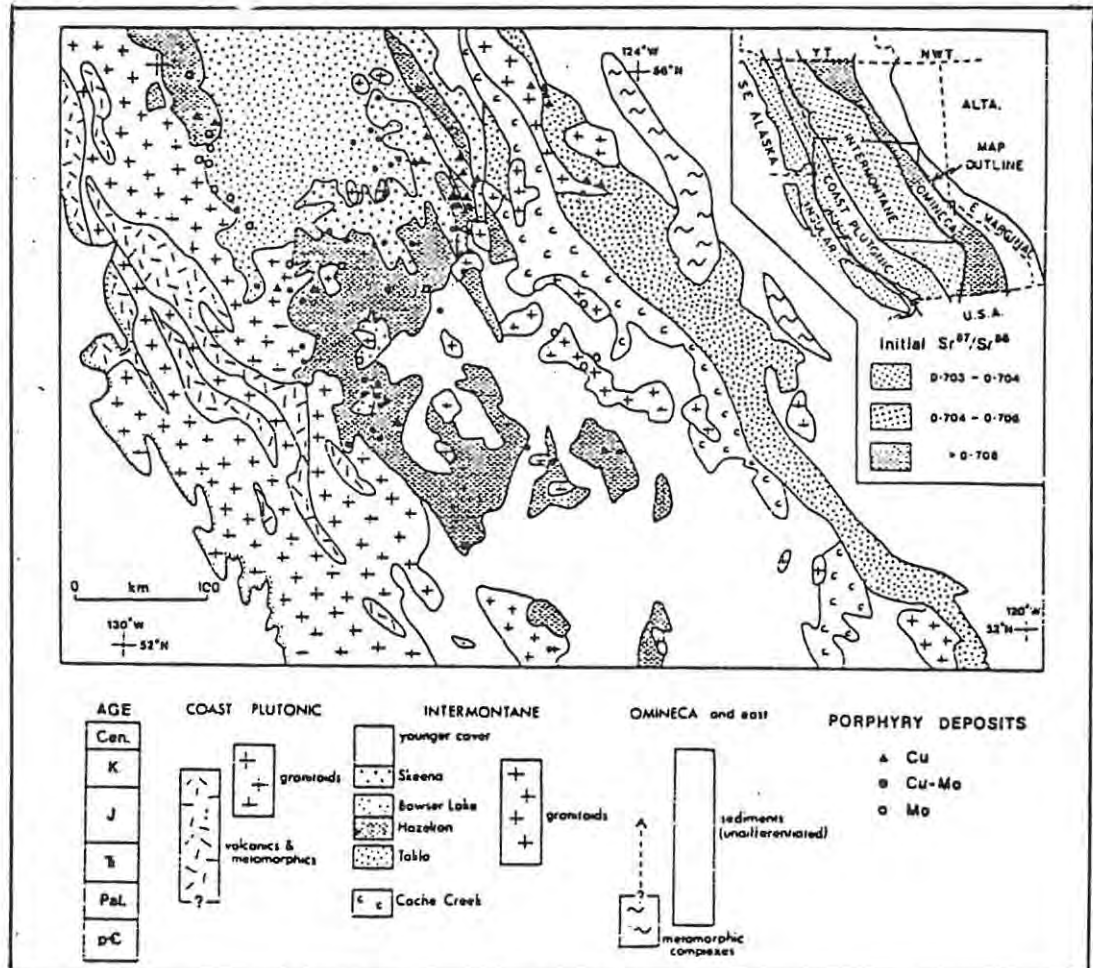


Figure 5.15 Geologic map of central British Columbia, showing stratigraphic units, major intrusions, and the distribution of porphyry deposits (Griffiths and Godwin, 1983)

The Mo mineralization is spatially and genetically related to dykes of rhyolite porphyry, rhyolite and quartz latite porphyry, and breccia phases. Other porphyry Mo of quartz monzonitic type are the Glacier Gulch and Adanac, which also display similar spatial relationship as the deposits above mentioned.

Alteration and mineralization

In the Quartz monzonite type, K-feldspar is closely related in time and space to Mo mineralization. Sericitic and argillic alteration are present in mineralized areas of Endako, Boss Mountain, Adanac, Glacier Gulch.

Propylitization occurs in the outer parts of many deposits.

These Mo deposits have a paragenetic sequence that begins with an early barren stage, through a main Mo stage and a late stage which is very weakly mineralized with increasing base-metal sulphides (Soregaroli and Sutherland Brown, 1976) (Table 5.VI).

Table 5.VI Stages of Mineralization of deposits in North Western Canada (Soregaroli and Sutherland Brown, 1976).

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
Endako.....	qz, py, mo, (mt)	qz, py (cp, mt)	qz, mo, py (cp, mt)	qz, py	qz, cal, sp	
Adanac.....	qz, mo, py	qz, mo	mo	sp, gn, asp		
Boss Mtn.....	qz, py	qz, py (mo)	qz, mo, py	(a) qz, mo, py/ (b) qz, py, cp, bi, (sc, mt, gn, sp)	qz, mo, py	
Glacier Gulch.....	qz	qz, mo, py, mt (cp, sc)	qz, mo, mt (cp, sc)	qz, mo, py, mt (cp, sc)	qz, car, py, sp, gn, (cp)	
BC Moly.....	mo	qz, mo, py	qz, mo, py	qz, mo	qz, py, gn, sp (mo)	
Roundy.....	(mo) (dissem. in dyke)	qz, mo, py stockwork		(preliminary observations)		
Bell Moly.....	qz	qz, mo (py)	qz, mo (py)	qz, car, py gn, sp		
Ajax.....	qz, po	qz, mo	qz, mo	qz, py, gn sp, cp		
Red Bird.....	qz	qz, mo (py)	qz, mo (py)	qz, mo (py)	qz	py (mo)
Lucky Ship.....	mo	qz, mo, py				

Parentheses designate minor constituents

Mo mineralization is largely fracture-controlled. Stockworks, breccia pipes, multiple vein system and disseminations are common in some deposits. Scheelite is a common accessory mineral of quartz monzonite-type systems. A few deposits associated with Quartz Monzonite stocks, contain stockworks with scheelite-molybdenite mineralization in both, the intrusive and the host rock (for example, the Logtung deposit at Logjam Creek, Yukon territory, Canada). Other deposits in the U.S.S.R., and in Nevada consist of a stockwork with scheelite and traces of molybdenite (White et al, 1981).

C.1 Endako Mo Deposit

The Endako Mo deposit is located 160 km west of Prince George (Figure 5.11) of central British Columbia. It is one of the largest Mo producers. In the mid 70's production was about 24 000 tonnes per day at an average ore grade of 0,15% Mo. Calculated reserves at a cut off grade of 0,08% Mo are estimated at 200 million tonnes with an average grade of 0,14% Mo.

Regional Geology

The Endako molybdenite deposit occurs in the Topley Intrusions, which are considered to be of late Jurassic age. They are intruded into late Paleozoic and early Mesozoic sedimentary and volcanic rock. The regional structural grain is northwesterly (Figure 5.15).

The Topley intrusion comprises a composite batholith consisting of granite quartz monzonite, granodiorite, quartz diorite, diorite and gabbro. The Endako deposit is centrally situated within the batholith in the Endako quartz monzonite rock unit. The emplacement of the Topley intrusions was probably influenced by and related to regional tectonic events which occurred during Jurassic times.

Local Geology

The distribution of rock types, major structures and location of the ore deposit are shown in figure 5.16.

The Topley Intrusions, which intrude the Taklu Group, consist of 5 distinct rock types in the mine area. They are: Casey alaskite, Francois granite (138 M.a., K/Ar), Glenaman granite, Endako quartz Monzonite (142 m.a. K/Ar), and Wheeler quartz monzonite, of uncertain age.

Ore body

The Mo deposit occurs wholly within the Endako Quartz Monzonite. The ore body consists of a series of en-echelon easterly trending ore bands within complementary east-northeast and northeast sets. These are orientated to

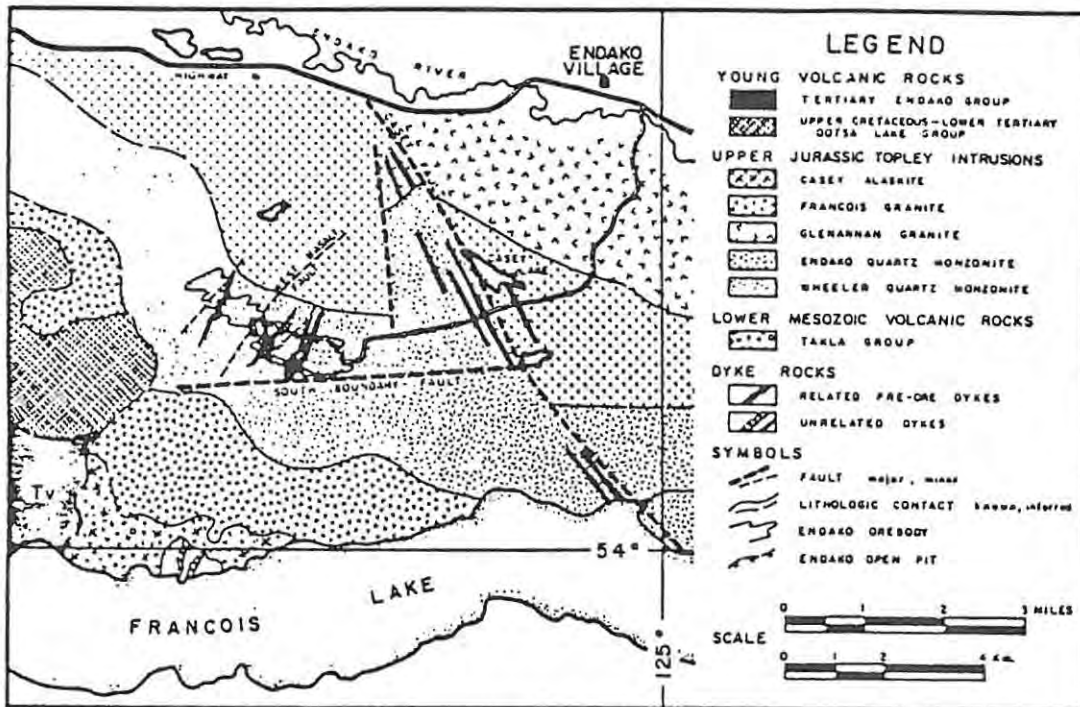


Figure 5.16 Geology of the Endako area. The Endako ore deposit is in the Endako Quartz Monzonite rock unit (Kimura et al., 1976)

form an elongated ore zone in a northwesterly direction. The zone is 3,36m wide x 370m long. The West Basalt fault offsets the western part of the ore deposits by 150 m, in a northerly direction, and divides the ore body into two domains.

The Endako quartz monzonite in the mine area is intruded by a series of pre-mineral and post-mineral dykes. Cross cutting and contact relationships have established the following age relationships.

Premineral :

quartz feldspar porphyry - youngest

porphyritic granite

andesite

aplite - oldest

Post mineral : basalt and porphyritic basalt dykes have been intruded into major faults.

Alteration and Mineralization

Three distinct hydrothermal alteration phases are recognized within the Endako ore zone.

1. K-feldspar envelopes on veins and fractures.
2. quartz - sericite - pyrite envelopes on veins.
3. pervasive kaolinization of Endako Quartz monzonite.

The K-feldspar alteration is related to the major content of molybdenite. Sericitic alteration is related to quartz-magnetite veins, and with quartz-pyrite veins in the pyrite zone.

There is no correlation between intensity of pervasive kaolinization and vein mineralogy. However within the stockwork the most common alteration type would lie between weak and moderate kaolinization (Kimura et al, 1976) (Figure 5.17).

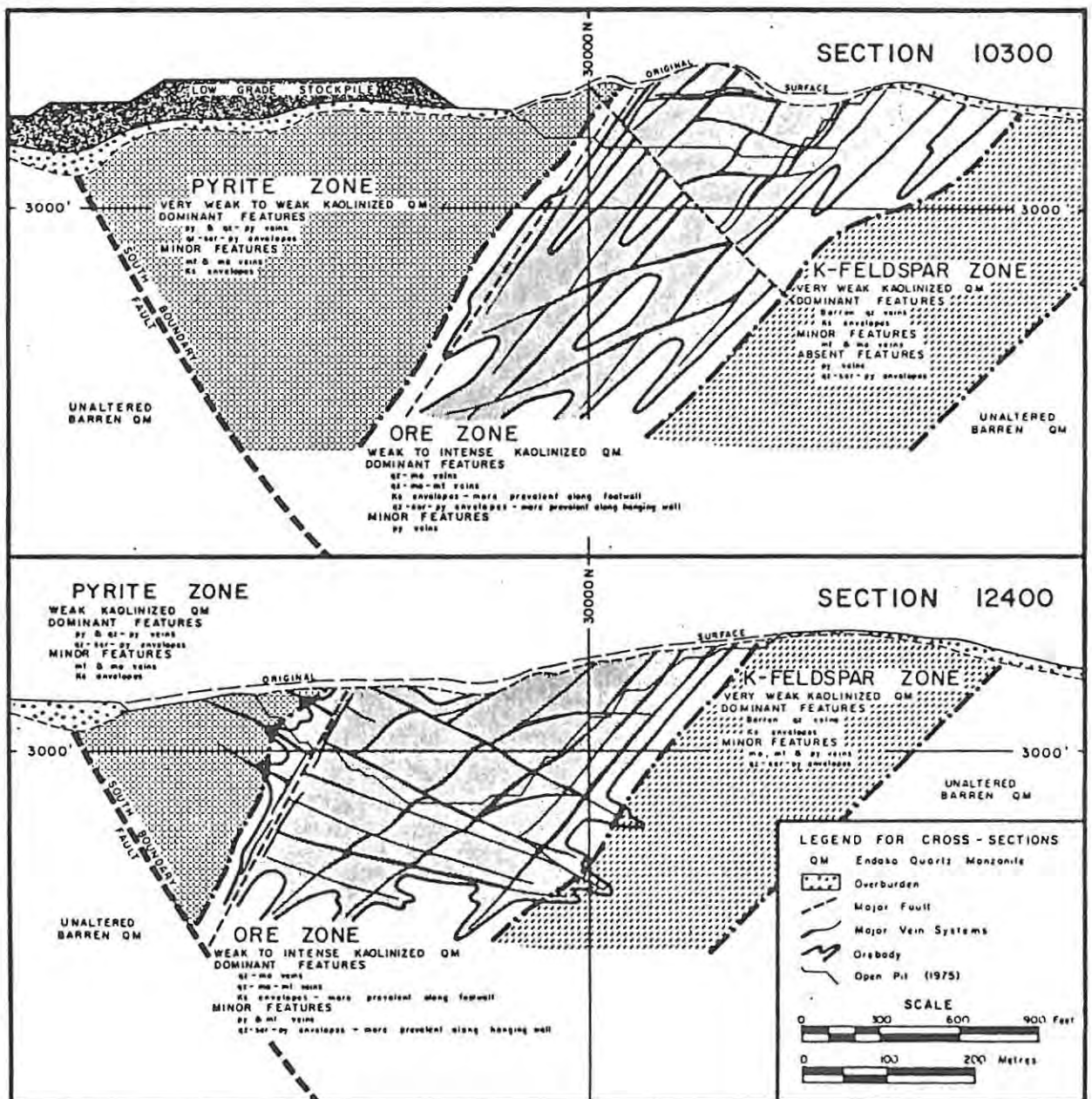


Figure 5.17 Geological cross sections of Endako ore deposit showing major structures, the ore zone and a generalized distribution of hydrothermal alteration phases (Kimura et al., 1976)

The more abundant mineral in the primary ore are : molybdenite, pyrite and magnetite + chalcopyrite - barite, bismuthinite, scheelite and specularite. The paragenesis is shown in table 5.VI. All minerals ultimately associated with quartz veins occur in two types of vein : a) large quartz-molybdenite veins and b) fine fracture fillings and veinlets in the form of stockwork. The former consists of subparallel veins of 0,15 to 1m wide, with a complementary set of molybdenite as thin (1-6mm) closely spaced laminae. The stockwork system is randomly orientated and they are located adjacent to, and surrounding the major veins.

Oxidation

An oxidation zone occurs at depths from 1,5 to 20 m over the ore body. The zone appears to have deeper penetration along major fault zones. Ferrimolybdate and limonite are the chief secondary minerals. None of the Mo oxide minerals are economically recovered. Oxidation has not appreciably affected the layer and more compact quartz-molybdenite veins. Kimura et al., (1976) recognized that molybdenite in the majority of the finer veinlets within the oxide zone, has been converted into secondary Mo minerals.

5.3.3 An unusual occurrence of porphyry Mo in New Zealand

Porphyry - Mo deposits occur in the west Nelson-Westland Province, New Zealand. They are associated with the Rangitata (Cretaceous) phase of the Karamea Batholith, and together with greisen W deposits (Tuhua phase, Paleozoic) they form a Mo-W metallogenic province (Pirajno, 1985).

The characteristics of the two types of deposits, suggest a subduction and collision related setting for the Porphyry Mo and greisen W, respectively. These deposits would have been formed in a continental environment (Tuhua ensialic terrane) and subsequently accreted against an island arc, ensimatic arc terranes (Hokonui) and against graywacke dominated terrane (Torlesse) (Howell, 1980) (Figure 5.18).

The porphyry occurrences are genetically related to small discrete stock or sheet-like high-level granitic bodies, that have intruded along some pre-existing zone of structural weakness. These granitic bodies are usually derived by differentiation from a less evolved parent.

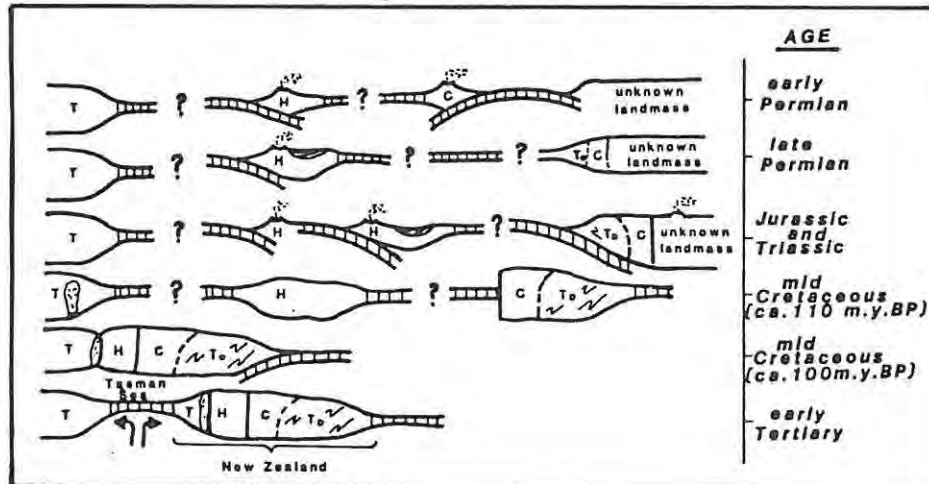


Figure 5.18 Simplified two dimensional diagram illustrating chronology of accretionary events postulated for Paleozoic and Mesozoic terranes of New Zealand. T = Tuhua ensialic terrane, H = Hokonui ensimatic arc terrane, C = Caples ensimatic arc terrane, and TO = Torlesse graywacke terrane. Because diagram is two-dimensional orientations of subduction zones are arbitrarily drawn (Howell, 1980)

The more important characteristics of this porphyry Mo occurrence, described by Scadden and Brathwaite (1980), are :

- a). Mineralization is associated with the calcalkaline granitic stocks of Cretaceous age (Rangitata phase granitoids)
- b). Molybdenite is the chief ore mineral and it occurs in quartz veins and quartz-vein stockwork, pyrite, chalcopyrite, magnetite, and minor quantities of other minerals. Generally they contain bismuth and zinc. The grades range from 0,05% to less than 0,010% Mo. The tonnage potential is small and erratic.

6.0 GENETIC ASPECTS

6.1 Origins of the Fluids

Evidence from many ore deposits suggest association of these with transporting fluids and the intrusive bodies. This association is very strong in the porphyry type ore deposits, because they are localized in the highly fractured upper parts of felsic porphyry stocks and/or wallrocks. They are centred on, and exhibit a zonal relationship to, the intrusive bodies and provide evidence of contemporaneity between hydrothermal mineralization - alteration and magmatism.

The fluids involved in this process are originated from aqueous solutions during and immediately after their separation from crystallizing magmas. Isotopic evidence indicates that meteoric waters may have been involved in late-stage hydrothermal alteration and mineralization of some porphyry type deposits (Burnham 1979). Most of the porphyry Cu-Mo are intimately associated with intermediate stages of calc-alkaline igneous rocks, ranging from diorite (andesite) to granite (rhyolite). The differentiation of these types of magmas results in residual liquids that becomes more enriched in the volatiles and other constituents, including metals, that were formerly dispersed throughout the magma.

The thermodynamic properties and the role of H_2O give the base for the understanding of the behaviour of fluids related to magma generations, emplacement and crystallization. The heat source, for most of the mineralized fluids that form porphyry deposits, is the cooling magma itself.

6.2 Solubility and Transport

Mo is considered to occur in the magmatic stage as a sulphide, or rather as Mo^{4+} associated with silicated polymerized structure. But in the pneumatolytic phase, Mo would be found mainly connected with halogens in the form of volatile halides (Uzkut, 1974). The same author suggested that with increasing H_2SO_4 , when passing on to the hydrothermal phase, the halides are hydrolyzed. Consequently, its transport in this phase is only possible as polysulphides or as thiomolybdate, which are stable in an alkaline medium.

In a strongly acid medium Mo may be present as the cationic complex, MoO_2^{2+} (equivalent to the uranyl complex, UO_2^{2+}), which is destroyed upon raising the pH. Figure 6.1 shows the Eh, pH and T° conditions from magmatic to hydrothermal stage.

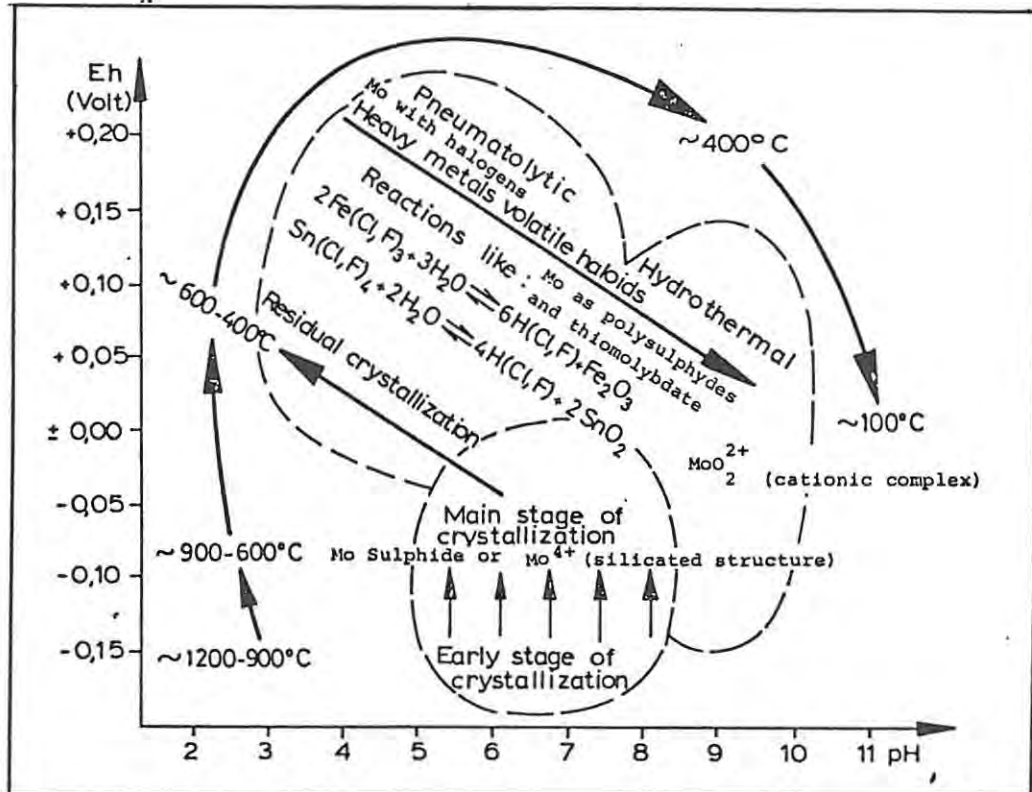


Figure 6.1 Eh, pH and T° conditions, from early crystallization to hydrothermal stage (Borchert, H. 1967) In Uzkut, 1974.

According to Westra and Keith (1981), Mo concentrated in a highly differentiated near-eutectic granitic residue may be introduced into the hydrothermal system by one or more of the following mechanisms: a) a Mo-rich vapour phase associated with a late-magmatic water saturated K-rich silicate melt (Isuk, 1976). b) Vapour transport of oxymolybdate, or halogen compounds (Scherba, 1970); and c) as molybdate, oxymolybdate, and thiomolybdate complexes in hydrothermal fluids (Smith et al., 1980).

Isuk (1976) demonstrated experimentally that the vapour phase associated with Mo-bearing water-saturated K-silicate melt, can contain high concentrations of

K, Si, and may transport Mo under weakly alkaline conditions. The same author suggests that this Mo-rich vapour phase is very important in the formation of Mo deposits.

At high temperature Mo can also be transported in the vapour phase as hydroxide and oxymolybdate species. (Yoshida et al., 1972; Krauskopf, 1957).

Thermodynamic studies and estimates of Mo complex stabilities leading Smith et al., (1980) to conclude : (a) Mo concentrations in the hydrothermal fluid may reach several thousands parts per million at 350°C and the solubility decreases drastically between 350°C and 300°C; (b) Mo is largely transported as HMoO_4^- with lesser amounts contained in H_2MoO_4 and MoO_3F^- . (c) F is not necessary for Mo transport in hydrothermal solutions.

6.3 Concentration and Deposition

It is believed that the initial Mo enrichment in alkali-calcic and alkalic magma series, may be the result of mantle enrichment above the subduction zone (Westra and Keith, 1981). However, in this Mo enriched magmas the concentration is insufficient to form a Mo deposit. Several processes may concentrate Mo in the upper regions of a magma chamber. They are magma differentiation by fractional crystallization, liquid-stage thermogravitational diffusion, volatile transfer following vapour saturation and magma convection.

Late in the crystallization sequence these magmas may generate a residual hydrous K- and SiO_2 rich fraction in which much of the Mo contained in the parent magma will be concentrated. The chemistry of calc-alkaline magmas is much less favourable for Mo concentration process.

The hydrothermal stage has temperatures below 373°C and H_2O is its dominant component. Most of the Mo mineralization in this stage occurs in between the range of 200°C - 300°C and lower. At this temperature molybdenite precipitation takes place under relatively acid conditions whereas molybdate and polyanions precipitate under neutral regimes (Wedepohl, 1978). On lowering the temperature, the ionization of HCl, HF, etc., is increased and

thus the pH is lowered. This low pH causes the precipitation of both silica and Mo (as MoS_2), which explains the normal association between them.

The capacity of Mo and S for forming soluble hexavalent oxygenated complexes in the presence of small quantities of H_2S (10^{-7}M), allows the simultaneous hydrothermal transport of both. Their subsequent reduction leads to the precipitation of MoS_2 and also UO_2 , frequently associated with volcanic formations of acid character (Tugarinov et al., 1973). This mineral assemblage also has been recognized in Chilean vetiform Cu deposits in Tocopilla (Klohn, 1961).

The late magmatic and early and potassic hydrothermal stages of porphyry systems, contain most of the molybdenite precipitation. It decreases towards more advanced magmatic and hydrothermal stages (Fig. 6.2).

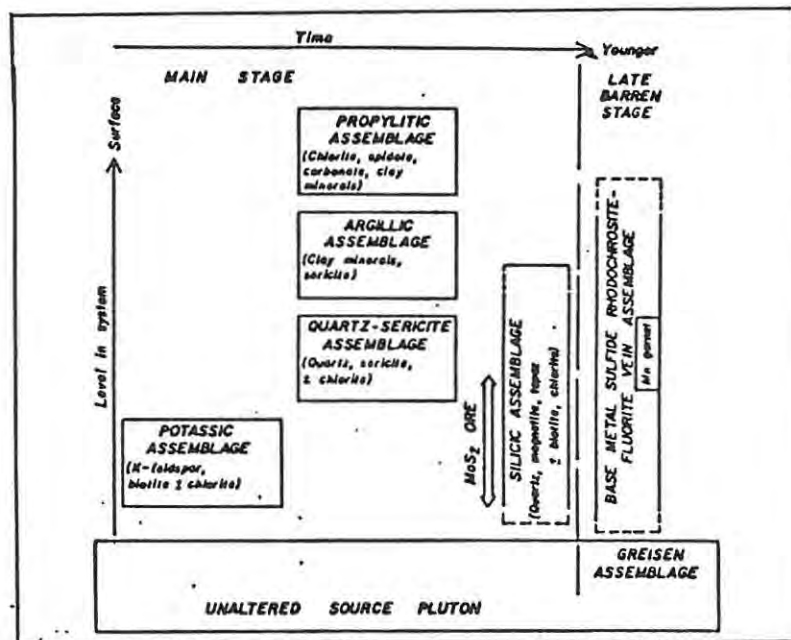


Figure 6.2 Diagrammatic representation of alteration in a granite molybdenite system. Clay minerals include kaolinite, dickite, montmorillonite, and pyrophyllite (Wallace and others, 1978).

6.4 Relationships between Magmatism, Subduction and Molybdenum Deposits

There is a close spatial and temporal relationship between plate subduction, arc magmatism and the genesis of porphyry copper and porphyry Mo deposits

(Figs 6.3 and 6.4). It is recognized at the Pacific margin of South America and northwestern North America. Keith (1978) suggested the dominant influence of arc magma chemistry and subduction angle on the genesis of Mo ore deposits.

Westra and Keith (1981), suggested that the close correlation between the K_2O content of the magma series and the depth of the Benioff Zone may reflect partial melting of subducted oceanic lithosphere. Magma generation would depend on the thermal regime in and above the slab, the mineralogical composition of the subducted material and the water released during dehydration. K, F, and minor amounts of H_2O may be carried in phlogopite to depths in excess of 250km (Fyfe and McBirney, 1975). The former authors also proposed that the chemical differences, between source plutons and hydrothermal systems in the two categories, indirectly reflect the phlogopite stability field in the subducted slab, and the overlying mantle wedge (Figure 6.3). They also proposed that Mo contained in all stockwork deposit types is of subcrustal origin.

Porphyry systems - including Climax and Quartz monzonite types of deposit are associated with calc-alkaline magmatism derived by partial fusion of subducted oceanic lithosphere (Sillitoe, 1972), at depths ranging from 120 to 240 km. The melt will undergo some modification on its way to the surface, but Cu and Mo may be largely derived from the subducted slab (Sillitoe, 1972) (Figure 6.4).

6.5 Ore Genesis of Climax type Molybdenum deposits

The Climax-type Mo deposits, are the result of multiple stages of enrichment process which started in the mantle. Partial melting of an enriched upper mantle produced alkali-calcic and alkalic magmas enriched in incompatible elements and volatiles. Differentiation and influence of deep crustal material may result in the formation of a F rich, high silica, and K-rich granitic melt.

At Henderson, boiling took place at the end of Mo concentration process. Boiling of the magmatic hydrothermal fluid in these deposits produced an acid vapour phase enriched in HF, H_2S , and CO_2 and high HF/HCl ratio (Berzina and

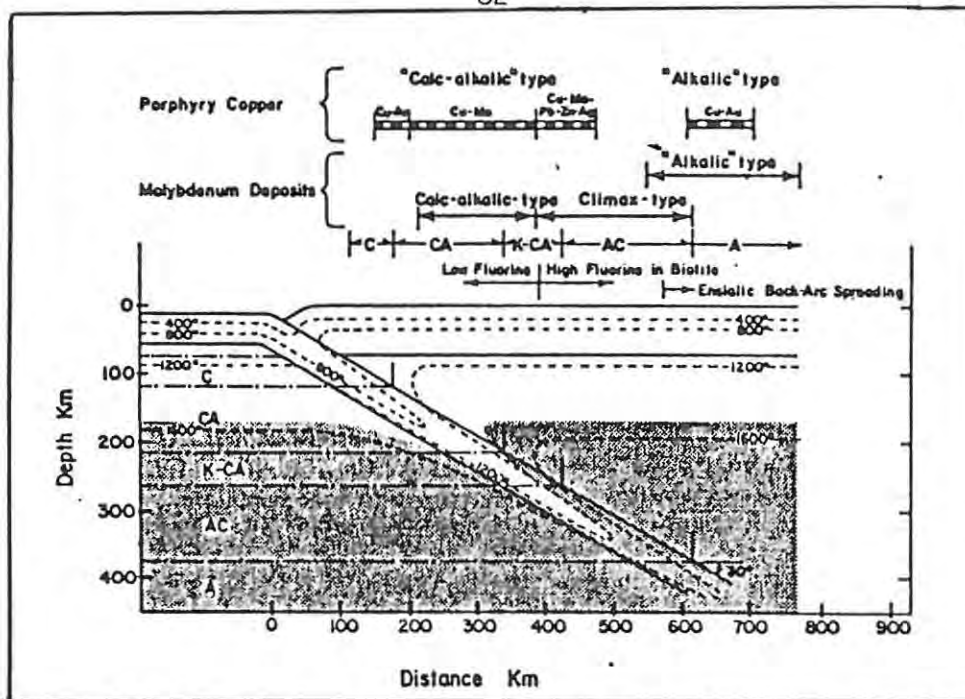


Figure 6.3 Schematic representation of the relationship between stockwork molybdenum deposits, porphyry copper deposits, and arc magma chemistry in a convergent plate margin setting. Shaded area outlines zone in which phlogopite is no longer stable. Note that the stability limit of phlogopite in the mantle is strongly dependent on the thermal configuration one adopts (Westra and Keith, 1981).

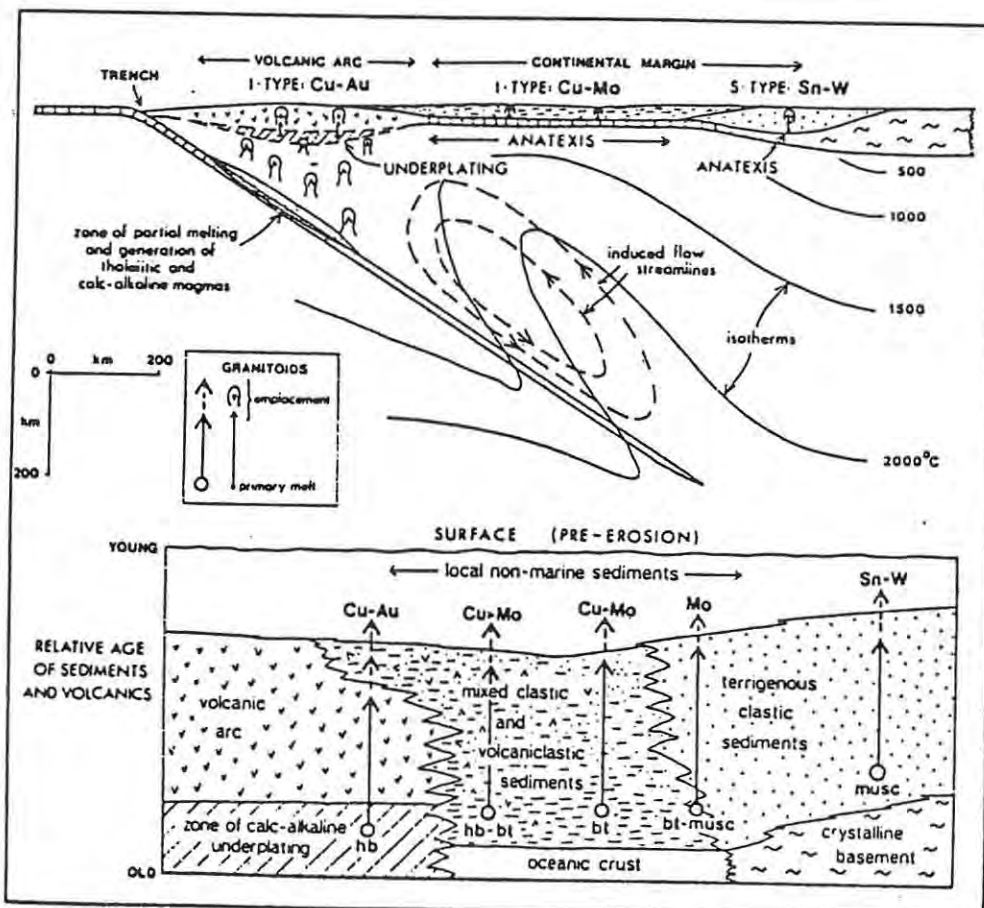


Figure 6.4 Summary of possible and probable sources of granitic magmas associated with porphyry deposits. Upper: cross section (approximately to scale, crust exaggerated vertically) of a "typical" subduction zone. Lower: schematic diagram showing a variety of parent rocks and sites of emplacement of magmas, with hydrous minerals in the source rocks shown thus: hornblende, hb; biotite, bt; muscovite, musc; also associated primary mineralization (Griffiths and Godwin 1983).

Sotnikov, 1977). The zone of boiling contains high silica, and replacement of K-feldspar by fluorite and/or topaz. Extensive mixing of magmatic and meteoric hydrothermal fluids took place in the quartz-sericite-pyrite and argillic zones (Hall et al., 1974). The importance of meteoric waters to the formation of the molybdenite ore shell appears minor. Base metal and manganese anomalies, could form by mixing of meteoric waters with Pb, Zn, Ag and Mn. Reaction of the fluids with the wall rock and dilution of vapour condensate, result in an increasing of K^+/H^+ ratio reflected in an inner kaolinite zone, and an outer montmorillonite zone, outside the quartz-sericite-pyrite zone (eg. Climax Deposit). Following maximum expansion of the magmatic hydrothermal fluid domain, the temperature and pressure tend to decrease, causing the precipitation of late base metals quartz-fluorite veins at 200^o to 300^oC, mainly in the core of the system (Hall et al., 1974). This sequence of events may be repeated several times, resulting in overlapping or spatially separated pulses of molybdenite mineralization, each cogenetic with a separate event of magma crystallization (Climax and Urad-Henderson, Wallace et al., 1968, 1978). The high water solubility in the melt, its low solidus temperature, and its low crystal/melt ratio, favour crystallization of only a small volume of water-saturated melts without interfering with magma convection at depth. Liquid state thermogravitational diffusion will rapidly re-establish trace element gradients in the magma column and, following water saturation at the top of the column, a new phase of stockwork fracturing and hydrothermal activity may occur (Westra and Keith, 1981).

The release of hydrothermal fluids with high Mo concentrations into a hydrothermal system with very sharp thermal gradients, results in the complete removal of Mo from the fluids within a relatively small rock volume that is represented by the ore deposit.

6.6 Ore Genesis of Quartz-Monzonite type Molybdenum Deposits

This type of deposit is characterized for its close association with calc-alkaline and high K-calc-alkalic arc magmas (Figure 6.3). Parent magmas are low in F, Mo and, incompatible elements, with water not more than 1,5% (Maaloe and Wyllie, 1975).

Granodiorite and quartz monzonite intruded the host rocks and by fractional

crystallization may have produced a highly differentiated silicic granite melt, low in mafics and enriched in volatiles, K and Mo. To form a stock type Mo deposit, this separated differentiation has to intrude the host rocks between 3 km of the surface. Following vapour saturation of the magma column, explosive pressure release and the formation of a zone of stockwork fracturing signals the start of a complex magmatic - hydrothermal convective system. According to Westra and Keith (1981), Mo released from the magma was probably concentrated in a K-rich hydrothermal fluid at near-magmatic temperature, above the water saturated surface in a convecting water undersaturated magma column. Due to the low initial Mo concentration in the parent magma, and the ineffective concentration mechanism, the final molybdenite grade in the hydrothermal system, will rarely exceed 0,25% MoS₂.

According to Westra and Keith (1981), a plutonic Mo stock work deposit would be formed when the granitic differentiate is trapped within or in the cupola of the batholith containing Mo and volatiles. Wall rock permeability may be increased by stockwork fracturing or tectonic causes (Endako deposit). As discussed in the previous section, molybdenite precipitates as a result of the gently cooling and a decreasing of the pH. Subsequently the molybdenite is dispersed in a very large rock volume and grades tend to be low (0,10 - 0,15% MoS₂).

7.0 EXPLORATION CRITERIA

7.1 General

The exploration for new Mo deposits remains active as demand for this metal continues to be strong. In particular, large tonnage porphyry - type deposits continue to be of interest.

As mentioned in the previous chapters, the more important Mo occurrences are hosted in porphyry systems. They display distinctive geological patterns, including geotectonic setting, magmatism, alteration and mineralization. Therefore, most concepts of exploration for porphyry Cu, are also valid for this purpose. Figure 7.1 shows the general patterns for Cu and Mo exploration in porphyry systems.

New techniques for the exploration of porphyry systems have been developed as a result of studies and research throughout the last 20 years. Computers are playing an important role in the improvement of quality and interpretation of remote sensing, geochemical and geophysical data.

7.2 Geotectonic Setting and Type of Magmatism: Guidelines

Following the advent of plate tectonic concepts, in the 1970's the first attempts were made to relate mineralization to plate boundaries. Numerous papers have been concerned largely with porphyry copper deposits and hence with subduction related magmatic arcs in which they occur. According to the geographic, tectonic distribution, and plate tectonic models, it is possible to recognise that magmatic compressive arcs and back arc extensional settings, are the areas where Mo deposits occur persistently. The former with Cu-Mo and the latter mainly Mo or with associated Sn, W.

Active, and inactive, subduction zones (south and Central America and western of North America respectively) are good targets for the exploration of Mo deposits. In Europe and Asia it is of great importance to be able to fossil subduction environments and rifts related to back arc extensional settings.

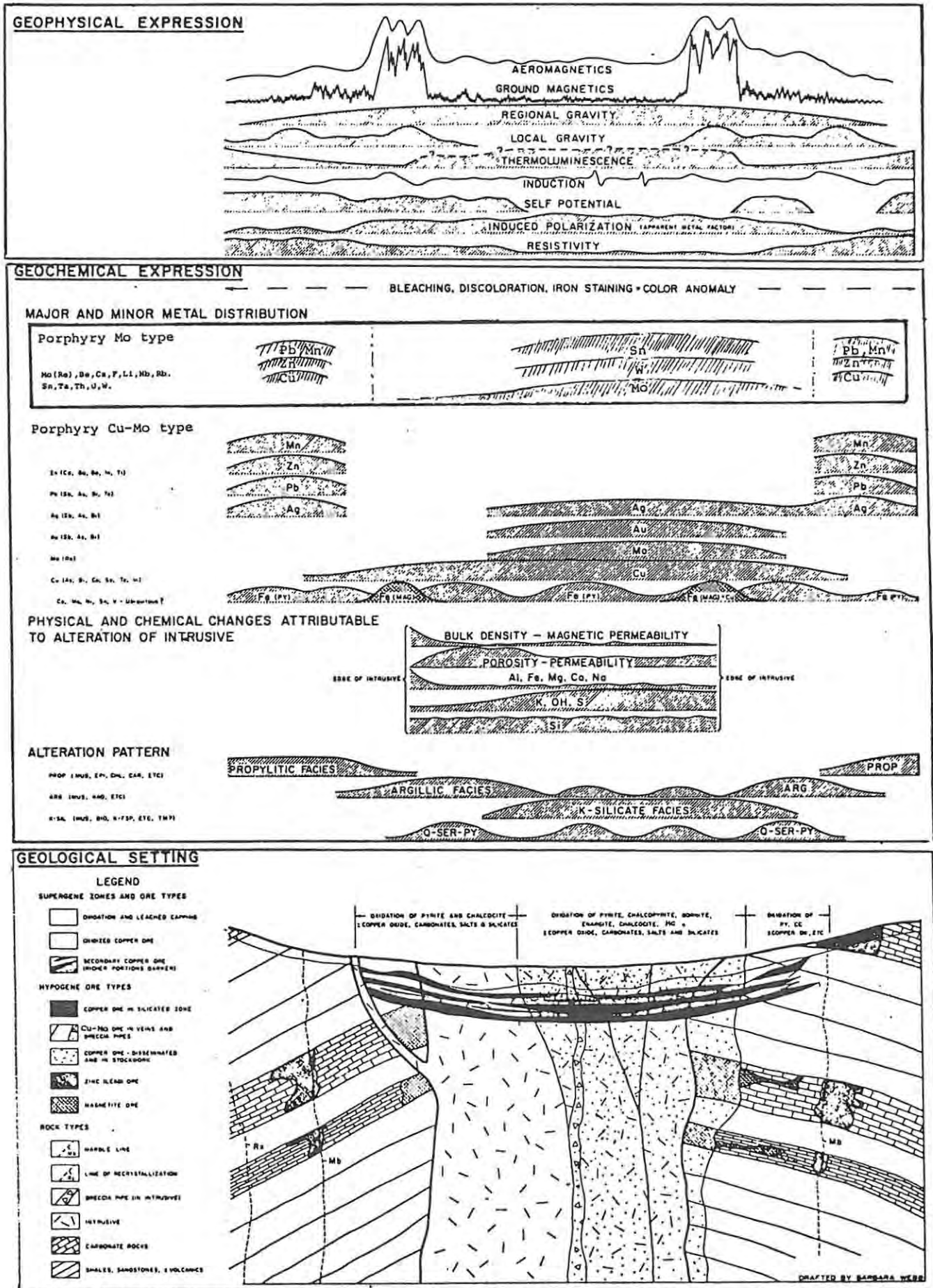


Figure 7.1 General geological patterns of porphyry Cu-Mo as guidelines for porphyry Mo exploration (adapted from Jerume, 1966).

Calc-alkaline to alkaline magmas (I-S and S type) related to anatectic processes at deepest levels above the Benioff zone, represent potential hosts for the Mo, mineralization (Figs 6.3 and 6.4).

7.3 Geochemical Criteria

The exploration for Mo is facilitated by its physical properties as well as its geochemical characteristics. The exogenous differential mobility between Cu and Mo are useful in porphyry Cu geological prospecting (Hansbult, 1967). Eh-pH diagrams show how the mobility of Cu becomes accentuated under acid conditions while that of Mo increases in alkaline media. The greater portion of Cu migrate from strongly acid soils (due to pyrite oxidation), while Mo may remain whether it be due to its lesser mobility under acid conditions or due to its fixation by iron oxide.

In the case of drainage waters, which in semi-arid regions are usually alkaline, Cu has a very low mobility, while the reverse situation is true for Mo. Therefore it is easier to detect anomalous concentrations of Mo. Coope (1973), concluded that the use of Mo as a tracer for Cu is practical even in districts in which Cu is not associated with economically significant concentrations of Mo.

Mo also has mobility during post-magmatic stages, associated with silicification in hydrothermal alteration zones (Oyarzun, 1978), hence rock sampling is a useful tool for Mo exploration, together with drainage and soil sampling. Geobotanic and biochemical prospecting have been applied with modest success, largely due to difficulties in the collection of samples and the interpretation of the data.

Mutschler and Wright (1981), suggested that computer assisted analysis of major element data displayed as normative albite, orthoclase, quartz and molecular Al_2O_3 , K_2O and $FeO+MgO+MnO$, can characterize potassic, quartz-sericite, argillic, and silicic alteration assemblages, and lead to areas of high exploration potential and to the evaluation of the probable depth of the mineralization. Minor elements concentrated in Mo-bearing granites include Be, Cs, F, Li, Nb, Rb, Sn, Ta, Th, U and W.

7.4 Geophysical Criteria

In the world wide search for porphyry Cu and Cu-Mo, magnetics and induced polarization have been used most extensively. Some geophysical approaches used in combination with geology and geochemistry may yield results suggestive of this type of deposit.

The resistivity response in hydrothermally altered zones shows a decreasing resistance or increasing conductance, toward the primary ore body, which is due to the major concentration of sulphides.

Although the induced polarization measurements do not distinguish the type of sulphide, they do suggest the percentage of conducting sulphides in the ore bodies. The response may help to indicate a possible correlation of the higher apparent metal factor with the primary sulphide zone. When a porphyry deposit is surveyed by induced polarization methods, results can be confused by salt-bearing ground water or other nonsulphide conducting material. The trend of the self-potential response follows a major negative potential centre over the oxidized zones of the porphyry systems. Self-potential anomalies are produced by electrochemical reactions at shallow depths, and they may occur under such a variety of conditions that they are not definitive by themselves, unless of especially large size.

The induction method is not normally regarded as applicable in porphyries exploration, but could be useful in detecting satellite bodies (Pima deposit, Arizona; Jerome, 1966) or in high concentrations of sulphides in stockwork type ore deposit from distances of not more than 100m. The response is represented by the broad deflections of the values.

Although gravity methods have no wide applicability in the exploration for porphyries systems, at the regional scale, airborne gravity surveys can detect zones of negative anomalies in response to greatest alteration in intrusive rocks with decreased bulk density and increased porosity.

For the Western of United States several authors (King et al., 1970; Woodcock and Hollister, 1978) have stressed an apparent relationship between

thick sialic crust, pronounced gravity lows and large high grade Mo deposits (Figure 7.2).

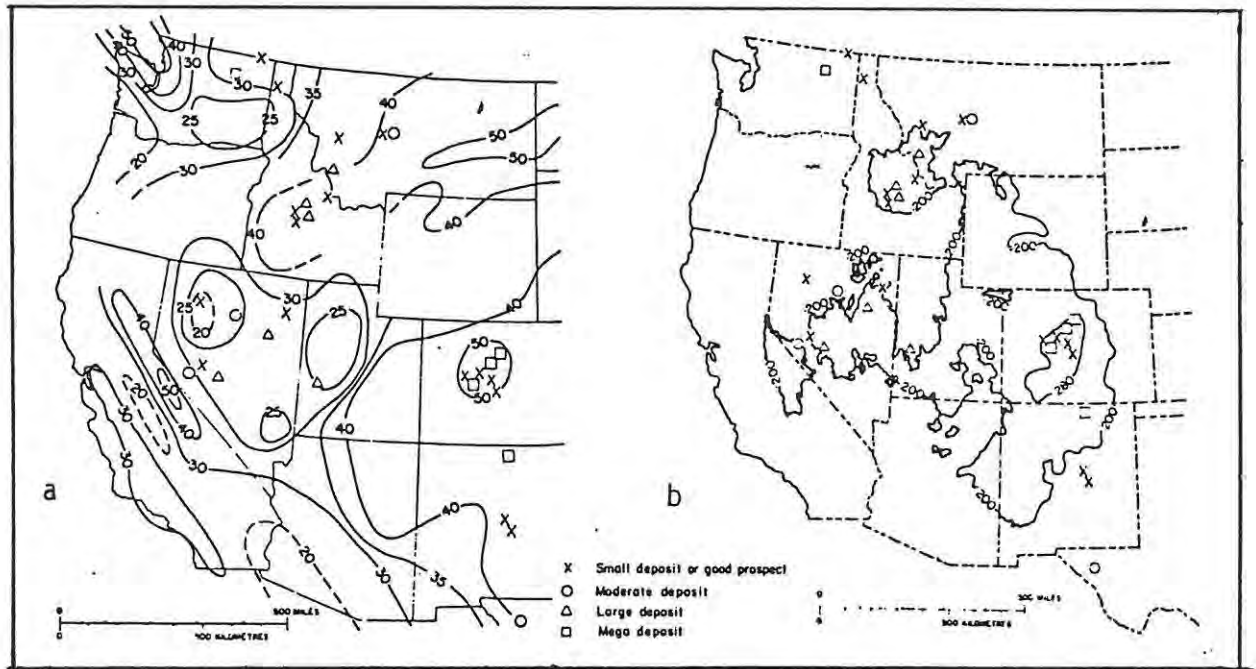


Figure 7.2 Relationships between thick sialic crust (a) and pronounced gravity lows and high grade Mo deposits (b) in the Western United States (Smith, 1978; Eaton et al., 1978 and Woodcock and Hollister, 1978).

Porphyry Cu/Mo systems are characterized by a magnetic low in the centre, and magnetic highs at the margins, due to magnetite concentration there. Airborne magnetometer surveys however are not very successful in locating this magnetic signature because they are usually carried out at too high a speed. Helicopter-borne magnetometer can compensate for the airborne and ground gravimetric surveys. To look for magnetic anomalies associated with mineralized porphyries requires good geologic control to eliminate, or explain, the many other relatively low or high values not related to the mineralization.

7.5 Aerial Photography and Remote Sensing

Hydrothermal alteration, oxidation, leached zones, lineaments and structures are geological features that are readily recognized with these methods. In

Landsat imagery the alteration zones of porphyry Cu-Mo deposits, show a strong tonal and textural contrast, with yellow-white colours and strong reflectivity. In Landsat imagery the regional structures that are normally related with porphyry deposits are identified as lineaments. Tidy (1984) described interesting examples of the relationships between megalineaments and Chilean Cu-Mo porphyries.

8.0 CONCLUSIONS

Throughout this dissertation it has become apparent that there are a great variety of Mo deposits, of which however the more important ones are those of porphyry affinities in terms of general geological features, tonnage, grade and hence economic viability.

An interesting conclusion that can be drawn is that a careful analysis of the geological evidence, and geotectonic settings can lead to good exploration targets for this type of deposit.

The concentration of Mo in porphyry systems is indicative of areas where there has been significant thickening of the lithosphere, crustal melting, magmatic differentiation and anatexis processes. These occur in environments related to ensialic orogeny at convergent plate boundaries.

Distinctive geochemical signatures characterize the type of magmatism involved in the genetic processes of Mo and Cu-Mo deposits. Mo contents increase proportionally towards alkaline phases, represented by I-S and S type granitoids.

The more frequent economic manifestations of molybdenite mineralization are related to stockwork and breccias, which are associated with strong K-alteration.

It is concluded that detailed studies of magmatic phases in conjunction with the careful application of exploration techniques, can provide good results for Cu-Mo and Mo prospecting.

Precambrian, Paleozoic and principally the Mesozoic orogenic belts, all have a good potential for economic Mo deposits. In the latter, the Andean and Cordilleran orogenic belts present the more promising targets.

ACKNOWLEDGEMENTS

I would like to record my sincere appreciation for the much valued assistance and suggestions of Professor Franco Pirajno in the initiation and preparation of this dissertation, and for his constant stimulation throughout the year. Professor Roger E. Jacob is thanked for his help and corrections of my seminars.

Philip Ash, Volker Petzel and Clyde Mallinson also are thanked for their companionship, help and moral support during the year.

Luis Olcay and Ricardo Rojas of El Salvador Copper Mine (Codelco - Chile) and Jozsef Ambrus of Geoestudios Ltda Chile., are thanked for supplying information for this dissertation so promptly. My thanks to Margaret Tierney and Gerda Bezuidenhout for their patience with my typing.

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