

Porphyry Molybdenum Deposits : A Literature Review

Won Choon Park*

Abstract: This paper is a literature review on the following subjects: 1) relationships between porphyry molybdenum and copper systems; 2) hydrothermal environments of molybdenite depositions; 3) genetic significance of molybdenite polyforms; and 4) trace element patterns in molybdenite useful as an exploration guide.

The geologic similarities between porphyry molybdenum (e. g. Climax) and porphyry copper (e. g. Bingham) systems exist, and similar techniques can be applied for exploring deposits of either type. Several features suggest that tungsten and tin may form porphyry-like systems (i. e. low grade, large tonnage). The clustering of porphyry-like systems in geophysically distinctive batholithic provinces is well documented and provides larger targets for reconnaissance exploration. Geochemical studies suggest that uranium should often occur in close proximity to molybdenum ores in igneous as well as sedimentary environments.

Introduction

Molybdenum production has increased about one million pounds in 1925⁽¹⁷²⁾ to an estimated 200 million pounds by 1980 (Table 1).⁽²¹⁴⁾ Between 1964 and 1968, production increased by 85% and at least ten new mines contributed to the increase.⁽¹⁷²⁾ Since the mid-1960s, by-product molybdenite from porphyry copper deposits has represented an increasing fraction of total production (about 40% by 1980), and this trend is expected to continue.⁽²²⁾ These changes have made the world Mo market more competitive.⁽²²⁾ Molybdenum demand closely parallels the cyclic fluctuations of the steel industry which accounts for 85% the total U.S. consumption.⁽²¹⁴⁾ Since 1974, molybdenum demand exceeded supply and at the same time price has increased more than quadruple from \$ 2/lb to \$ 9/lb by 1980. As a result, exploration and development work for new properties are intensified.

Estimated world reserves⁽¹⁰⁴⁾ in identified prospects exceed 30 million tons of molybdenum;

over 50% of this reserve is located in the United States. Hypothetical resources are estimated to exceed one billion tons, of which slightly less than 50% is projected for the United States. The U.S. is a net exporter of molybdenum (over 50% of the total production is exported⁽²¹⁴⁾).

Geology

Six major deposit types have been identified as molybdenum sources⁽¹⁰⁴⁾: 1) stockwork Mo (Climax type); 2) porphyry Cu-Mo; 3) complex (endogenic or vein-type) Mo-W-Sn; 4) Mo-W skarns; 5) pegmatites; and 6) bedded sedimentary deposits. The first two types constitute the bulk of economically attractive Mo resources (it is estimated that they account for 95% of the world's production⁽¹⁰⁴⁾; about 70% of the free world production, in 1969, was from Climax-type deposits⁽³⁷⁾). Complex, vein-type deposits (Panasqueira, Portugal^(91,164) have relatively small production capacity, while the last three deposit types are less attractive due to variable grade, small size, and beneficiation problems.⁽¹⁰⁴⁾ In the stockwork Mo deposits, molybdenum is often the only element recovered,⁽³⁷⁾ although tungsten, tin,

* Occidental Research Corp. Irvine, California 92714, USA

Table 1: Polyethylene Production and Consumption; Data in lbs x 10³ [Data from (214) unless noted]

	USA		Consumption	Canada		Chile	Peru	USSR(e)	Others	Total	% U.S.
	Production	Exports		Production Only	Imports						
	lbs x 10 ³ %										
1960	69,237	30,245	44,784	(e) 1,000(22)	(e) 4,000(22)	<1,000(22)	NA	(e) 2,000(22)	89,100	76.6	
1965	77,372	24,095	66,112	(e) 10,000(22)	(e) 8,000(22)	<1,000(22)	15,000(202)	(e) 3,000(22)	98,531	78.5	
1970	111,352	55,736	76,101	33,772	12,589	1,338	17,000	5,388	181,429	61.4	
1971	109,592	45,284	66,399	28,663	13,935	1,782	17,600	5,492	171,064	64.1	
1972	112,138	45,362	62,560	24,493	13,045	1,712	18,100	4,930	174,418	64.3	
1973	119,859	73,958	82,477	27,450	12,974	1,592	18,700	4,577	181,152	64.0	
1974	112,011	78,660	91,706	(e) 32,500	(e) 10,000	(e) 2,000	NA	NA	(e) 160,500	(e) 69.8	
1975(e)	105,564	63,908	91,934	NA	NA	NA	NA	NA	NA	NA	
References (lbs x 10 ⁶) [Data from (108)]											
Identified	3.5 x 10 ⁴										
Hypothetical	10 ⁶										
Percent By-Product											
Production											
1966 [Data: (202)]	31			5.6	100	100	34	8 x 10 ³	27	31	55.6
1972	27			-	100	100	-	? 10 ⁶	< 10 ⁵	41	45.5

(e) indicates estimated values

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and potentially uranium can be produced as by-products⁽¹⁸⁾. Molybdenum is the primary by-product of most porphyry copper mines, and several (Sierrita, Az., and Brenda, B. C.) are economic only because of the associated Mo credit. In complex deposits and skarns, molybdenum, tungsten⁽¹⁰⁴⁾, or tin may play the dominant role, and Pb, Zn, Ag, Bi and As are frequent by-products.⁽¹⁴⁰⁾ Bedded sedimentary deposits are usually associated with roll-type uranium ores; because the ore-grade Mo is somewhat separate from the uranium ores in space⁽¹⁰⁴⁾ it is usually not recovered.

Geologic evidence does not indicate that the first three deposit types are genetically distinct. In fact, the first five types can all be regarded as components of a single, highly complex deposit type, in which Climax-type deposits and porphyry coppers are essentially end-members of the same type. The end-member concept is difficult to demonstrate, since continuous values of Cu-Mo ratios do not seem to exist (Table 2 and Fig. 1), and critical data are missing for most deposits. Variation of Cu/Mo within deposits is as great as the variation reported between deposits (Fig. 2). The correlation of reported Cu and Mo values is not statistically significant. Additionally, the

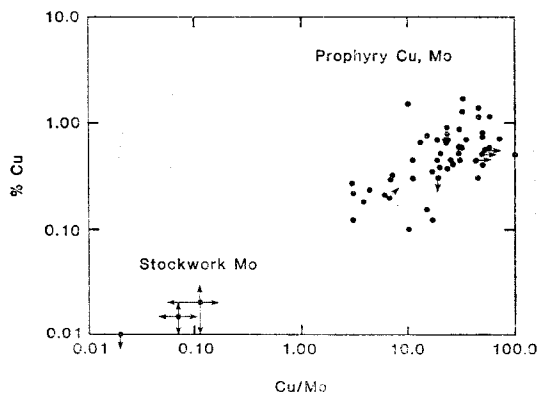


Fig. 1 Scatter diagram from Table 2. Porphyry copper and stockwork molybdenum form distinct populations.

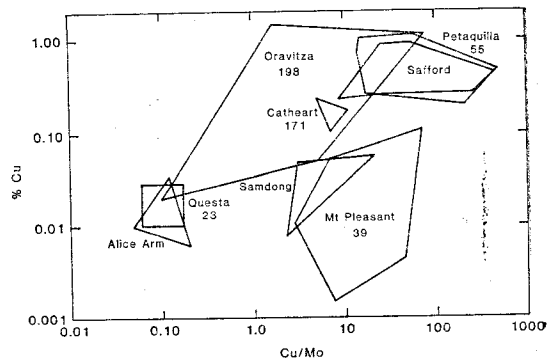
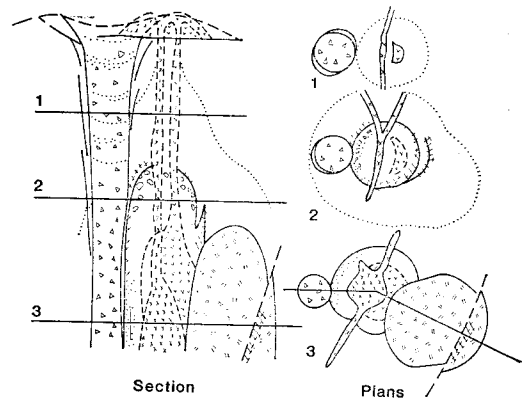


Fig. 2 Variation of Cu/Mo wt. ratio with wt. % Cu within several selected deposits. Numbers indicate references for data.

Mo content of Cu porphyries appears to vary systematically with rock type, geologic environment, and paragenetic sequence, suggesting that fundamental chemical controls are operative in the concentration of Cu and Mo in porphyritic



LEGEND

- Mineralized Stockwork
- EARLY PHASES
 - Pre-mineral Phase
 - Phase Synchronous with Mineralization?
 - Early Post Mineral Phase
- LATER PHASES
 - Diatreme
 - Late Intrusive Phase
- Biotite Line

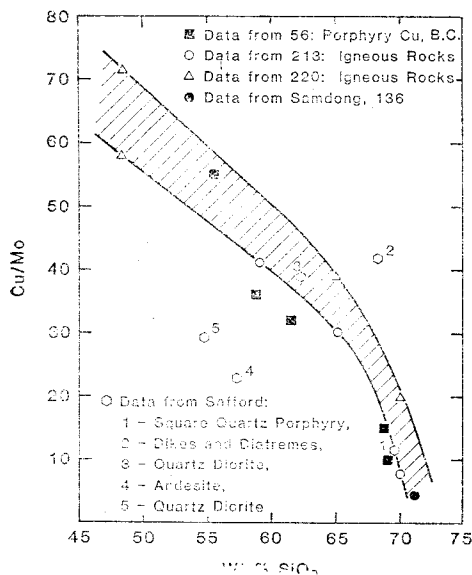
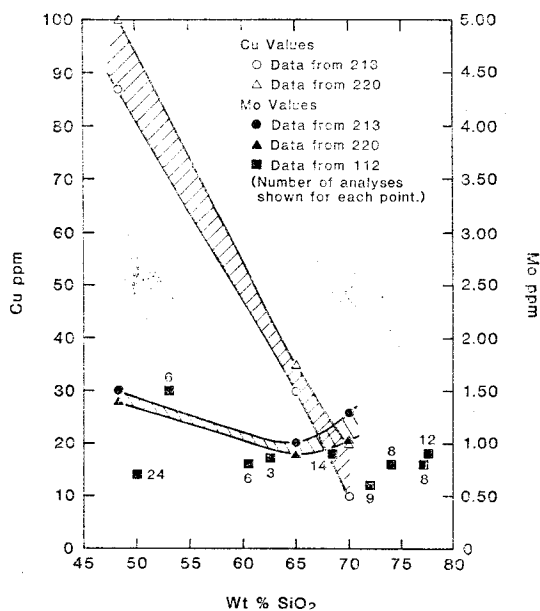
Fig. 3 Schematic vertical and plan sections of a hypothetical porphyry-stockwork deposit showing multiple intrusive phases.

Table 3. Classification of porphyry/stockwork deposits (199)

Type	Description	Examples
I. Simple:	Small cylindrical intrusive Alteration and mineralization annular	Ajax (Mo) Berg (Cu,Mo) Newman (Cu) Red Bird (Mo)
II. Elaborate:	a) Non-concentric, multiple intrusion	Alice (Mo) Glacier Gulch (Mo) Granisle (Cu) Lucky Ship (Mo)
	b) Dike swarm	Satface (Cu,Mo) Morrison (Cu) Serb (Mo)
	c) Breccia pipe	Boss Mtn. (Mo) Gam (Mo)
	d) Irregular intrusion	Eg Onion (Cu,Mo)
III. Complex:	Multiple intrusion, dike swarms, breccias and faulting all important. Significant alteration.	Ethlehem (Cu) Cariboo Bell (Cu) Copper Mtn. (Cu) Ingerbelle (Cu) Iron Mask (Cu) Lornex (Cu,Mo) Lorraine (Cu) Stikine (Cu)
IV. Plutonic:	In granitoid plutonic rocks, associated with porphyries; along conjugate and parallel fractures.	Srenda (Cu,Mo) Endako (Mo)

intrusives. Vein, skarn, and pegmatite deposits can form in a generalized porphyry system in response to varying T and P conditions, permeability variations, and host rock inhomogeneities.

Sutherland-Brown has proposed a generalized porphyry classification in recognition of these variables (Table 3)⁽¹⁹⁹⁾. The deposits range from simple to complex, with larger, complex deposits

**Fig. 4** Variation of Cu/Mo ratio with SiO₂ content in igneous rocks.**Fig. 5** Variation of Cu and Mo with SiO₂ content in igneous rocks.

showing multiple mineralization cycles. As Fig. 3 shows, Sutherland-Brown recognizes that the apparent level of complexity of a stockwork system is intimately related to both the depth of its formation and the degree of its present exposure⁽¹⁹⁹⁾.

Stockwork Mo deposits are persistently associated with highly silicic, somewhat alkaline porphyries^(37, 104). The complexing (?) of molybdenum by silica⁽¹⁵⁶⁾ may account for this. Though some researchers have indicated that Mo is enriched in silica-rich rocks⁽¹⁸⁶⁾, the majority of available analyses show no relationship between Mo and Si (or Mo and K₂O+Na₂O)⁽¹¹²⁾. The sympathetic variation of the Cu/Mo ratio with SiO₂ in porphyry deposits (Fig. 4) is due to a sharp drop in the Cu content of silica-rich rocks (Fig. 5)⁽²¹³⁾.

The host rocks of the stockwork Mo deposits are highly variable⁽³⁷⁾, including metamorphic⁽²²²⁾ and sedimentary^(107, 179) rocks as well as comagmatic^(23, 123) and unrelated⁽¹⁹¹⁾ igneous rocks. Most stockwork deposits are associated with intersections of large-scale fractures⁽³⁷⁾ which sug-

est that persistent, pre-ore crustal weaknesses localized the ore-forming intrusions^(104, 134). The clustering of molybdenum-bearing deposits, their location in batholithic provinces or regional gravity and magnetic lows⁽¹⁰⁴⁾, the variety and volume of cogenetic igneous rocks related to them⁽²³⁾, and calculated fluid/rock ratios for known ore bodies^(5, 222) suggest that most deposits are associated with batholithic intrusions at depth. Domal fracturing has been recognized at Climax⁽²²²⁾, Hudson Bay Mtn.^(39, 88), and Questa^(23, 149), and may be related to deep-seated batholithic intrusions.

The cyclic pulsation of ore formation in the Mo stockworks has been ascribed to periodic pressure build up and subsequent release by fracturing^(23, 191, 222). Highly variable depths of formation can be inferred for stockwork deposits. Urad is associated with a volcanic center and probably formed within 2,000 ft. of the present surface⁽¹²³⁾, while Climax is estimated to have formed at about 10,000 ft.⁽⁷³⁾. The similarity of the upper zones of some stockwork molybdenum deposits to active volcanic centers in striking^(48, 138, 229, 231). Known stockwork Mo deposits are variable in age⁽³⁷⁾, although the larger deposits are relatively young (Climax is 30mybp⁽²²²⁾, Questa is 22mybp⁽¹¹⁶⁾). Deposits of all ages are known worldwide^(6, 37, 79).

Metal zoning in the stockwork Mo deposits is limited to possibly four distinct zones (discussion here is based on (123) and (222)). The core zone, located mostly inside the causative intrusive, is generally Mo-poor ($< .05\%$ MoS₂), but contains relatively higher proportions of Pb, Zn, Mn, and Cu (50–300 ppm). This polymetallic assemblage is usually paragenetically the latest sulfide vein stage; it may be anomalously located due to structural controls. Polymetallic veins are found in the core at Climax⁽²²²⁾, Henderson⁽¹²³⁾, Alice Arm, and Questa⁽²³⁾, though their distribution is erratic. The molybdenum ore shell (annular and/or arcua-

te; average grade varies from 0.15% MoS₂ at Endako⁽¹⁰³⁾ to 0.49% MoS₂ Henderson⁽¹²³⁾, while cut-off grade varies from 0.08% MoS₂ at Endako⁽¹⁰³⁾ to 0.25% MoS₂ at Henderson⁽¹²³⁾) may overlap the upper and outer contacts of the causative intrusion, but also may be as much as 400'–500' above it (the Ceresco orebody at Climax); it is generally free of other recoverable metals. The limits of the ore zone can be quite sharp⁽²⁰⁾ and are generally determined by the limits of stockwork fracturing^(23, 103, 190). Pre-ore faults have acted as significant controls for mineralization at Questa⁽²³⁾, Urad⁽¹²³⁾, Boss Mtn.⁽¹⁹¹⁾, Hudson Bay Mtn.⁽⁸⁸⁾, and Alice Arm, producing large, high-grade (+5% MoS₂ at Questa) veins. These veins are traceable for hundreds of feet and often cut virtually barren rock, thus distorting the Mo ore zone.

A pyrite halo is located outside and above the ore zone, although its inside edge may overlap the orebody. Pyrite is the most abundant sulfide in the stockwork Mo deposits⁽³⁷⁾; pyrite-molybdenite ratios range between 5 and 10 in the Climax and Henderson ore zones, and may reach 100 in the pyrite halo. A low grade tungsten-tin-uranium zone [.03% WO₃, .005% SnO₃, and 1.5 ppm U₃O₈ at Climax⁽¹⁸⁾; $< .05\%$ WO₃ at Henderson⁽¹²³⁾] is at least partly coincident with the pyrite halo, and partly overlaps the outside edge of the ore zone.

Tungsten is present mostly as huebnerite, although some scheelite has been reported⁽³⁹⁾. Cassiterite is the source of tin, and brannerite and uraninite provide the uranium values. Tungsten and tin may be somewhat separately zoned, with tin slightly farther from the intrusion, although "telescoping" of these zones into the Mo ore is also observed [Questa and Sorsk⁽¹¹⁹⁾].

The tungsten zone sometimes shows internal zonation from huebnerite (MnWO₄) near the intrusion to ferberite (FeWO₄) farther out⁽⁷⁸⁾. A base-metal sulfide zone is often recognized outside

the pyrite halo, sometimes appearing almost regional in scale (Questa)⁽²³⁾. Numerous elements (Cu, Pb, Zn, As, Au, Ag, Bi, Sb, Mn) appear concentrated in this zone, with Cu and As being broadly distributed.

A Zn–Au association is toward the intrusion, while a Pb–Ag zone is slightly more distant from it at Hudson Bay Mtn.⁽⁸⁸⁾; at Compaccha⁽⁷⁸⁾, Pb and Zn occur together, with an exterior Sb halo. The peripheral base-metal zone, because it is often structurally controlled, is poorly zoned; at Questa, Cu, Pb and Zn form no distinctive zonal pattern, while As seems to be concentrated in the periphery of mineralization. The mineralized sequence may cover up to 7000' vertically [Hudson Bay Mtn.⁽⁸⁸⁾ and possibly Henderson–Urad⁽¹²³⁾].

The paragenesis of the major minerals of the Mo stockworks is complex, involving up to eight episodes of vein formation⁽¹⁹¹⁾. Generally (discussion follows),⁽³⁷⁾ biotite, magnetite, K-feldspar and barren quartz are contemporaneous with or earlier than molybdenite, which is usually the earliest sulfide. Up to ten pulses of molybdenite deposition have been recorded in banded quartz molybdenite veins⁽¹⁰³⁾. Composite veins, reflecting solution flow at different times, have been recognized at Climax⁽²²²⁾ and Questa⁽²³⁾.

Tungsten and tin mineralization and the base metal sulfides are mostly later than molybdenite, although pre-molybdenite chalcopyrite is reported at Hudson Bay Mtn.⁽⁸⁸⁾. Topaz, fluorite, and carbonates are mostly post-ore. Fluorite appears contemporaneous with molybdenite at Questa, and Mo grade varies strongly with whole-rock F content. Some post-carbonate pyrite veining at Hudson Bay Mtn.⁽⁸⁸⁾ suggests that pyrite is a relatively late mineral in the Mo stockworks. Carbonate-zeolite veining is reported as the last hydrothermal event in several deposits^(148,191).

On a larger scale, the metal ratios in the intrusive phases change during multiple intrusion. At Climax, the Mo–W ratio decrease with time⁽²²²⁾,

as does the Mo–base metals ratio⁽²²²⁾. The Kolyvan massif, a four-phase, differentiated granitic intrusion in the Siberian SSR carried base-metal sulfides in the first phase, Mo–W in the second, Mo–W–Sn–Bi–Ag–Au (“rare metals”?) in the third, and anomalously high Ta–Nb in the fourth⁽¹⁴⁶⁾. The late stage concentration of Ta–Nb in intrusives associated with Mo–W–Sn mineralization has also been reported elsewhere^(20,28,39), may indicate the affinity of the intrusions with the Ta–Nb rich alkaline rocks, and may be useful as an exploration tool.

Alteration of host rocks and Mo-bearing intrusions is generally conformable^(45,123) with Hemley and Jones’ work⁽⁷⁴⁾ on hydrogen metasomatism. The most complex alteration patterns are developed at Climax and Henderson, and have up to seven recognizable zones (Fig. 6⁽¹²³⁾). The potassic alteration zone is most intimately associated with ore^(123,222), except at Endako^(45,103). Some potas-

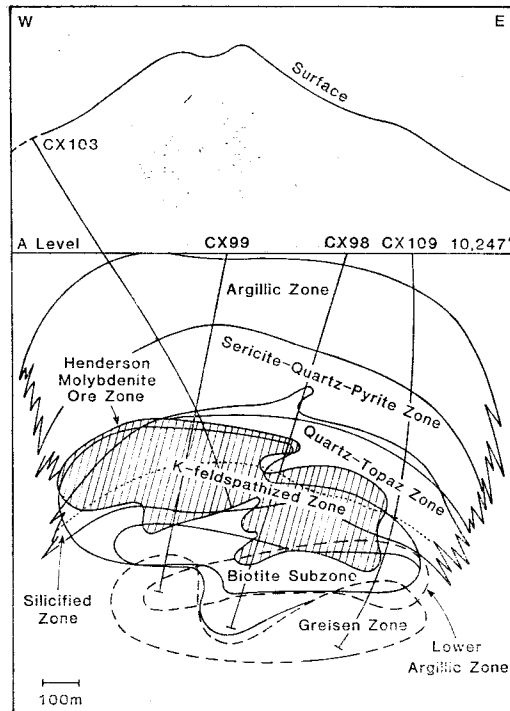


Fig. 6 The relationship of alteration zones to the ore at Henderson⁽¹²³⁾

ssic alteration may be a post-ore feature responsible for partial redistribution of Mo values⁽¹²⁷⁾; whether this is due to multiple intrusion is not clear. Silicification may also disperse preexisting molybdenite mineralization—only partly as a consequence of multiple intrusion⁽²²²⁾.

Host rock control of alteration assemblages is pronounced. While biotite is rare in the altered rhyolitic rocks at Urad-Henderson⁽¹²³⁾, the ore host andesite at Questa is strongly biotitized⁽²³⁾, and the causative aplite intrusive is biotite-poor and K-feldspar rich⁽²³⁾. At Boss Mtn., magnesium- and iron-rich assemblages (garnet-hornblende, biotite, chlorite-talc) are developed in pre-ore granodiorite⁽¹⁹¹⁾. A similar mafic assemblage (amphibole-biotite-chlorite-magnetite) predates ore at Hudson Bay Mtn.⁽⁸⁸⁾, and chloritization appears to be the earliest alteration at Alice Arm⁽²⁵⁾. Alterations are highly variable and are often telescoped.

The alteration halos at Henderson and Climax suggest and approximately isothermal environment with little outward migration of alteration zones⁽¹²³⁾, contrary to the process defined at Butte by Sales and Meyer⁽¹⁶⁶⁾. There is evidence that inward encroachment of alteration zones occurred during cooling⁽¹²³⁾.

Few fluid inclusion studies have been done on the stockwork Mo deposits. The work of Hall, Friedman, and Nash⁽⁷³⁾ at Climax indicates that Mo stockworks are relatively low temperature (325–375°C) deposits, with some inclusions from the pyrite-tungsten halo homogenizing as low as 200°C. The salinity of the trapped fluids ranges from 0.7‰ to 43‰ NaCl equivalent (only 3‰ had salinities over 35‰). The inclusion salinities at Climax appear to be zoned, with the most saline fluids being associated with the oldest ore zone. Carbon dioxide is present in about 2% of the inclusions examined, reflecting the relatively prominent role of carbonates at Climax. Analysis of the inclusion fluids did not indicate a systematic

change of Na/K with salinity or homogenization temperature.

Isotope data are similarly scarce for the stockwork Mo deposits. At Climax⁽⁷³⁾, oxygen and hydrogen isotope data can be interpreted to show a) that the isotopic composition of fluids shifted with time under approximately isothermal conditions (this is consistent with a model involving convective-circulation of ore forming fluids, with progressive mixing of early magmatic and later meteoric waters); b) that quartz was in isotopic equilibrium with fluids of the causative intrusion; and c) that reequilibration and isotopic exchange at lower temperature affected the feldspars. Isotope data for Climax corroborate the genetic interpretations based on examination of fluid inclusions. Sulfur isotope data are limited⁽²¹¹⁾ but indicate a magmatic source for the sulfur in some deposits. Strontium isotope ratios at Questa⁽¹¹⁶⁾ do not differ from those of other western U.S. volcanics.

Stockwork Mo deposits may show leached cappings and oxidation zones, some of which extend to depths over 400 ft⁽²²²⁾. Oxidized ores rarely constitute more than 30% of the total⁽¹²⁹⁾ and are now economically beneficiated only at Endako⁽¹⁰³⁾, though Climax had operated a hydrometallurgical oxide treatment plant⁽¹¹⁵⁾. Studies of several deposits indicate that molybdenum loss from the deposits during oxidation is partly climatically controlled⁽¹⁴⁵⁾, and is generally insignificant^(23, 129, 222). At Brenda, up to 50% of the initial Mo may have been lost due to leaching⁽¹⁹⁰⁾. Enrichment is negligible⁽¹²⁹⁾.

The essential similarity of stockwork molybdenum and porphyry copper deposits is obvious. The differences that are observed should be readily interpreted in terms of the geochemical behavior of molybdenum and copper (the latter is distinctly more chalcophile), the lower crustal abundance of molybdenum, and the characteristics of their major ore minerals.

The most important potential difference is the persistent association of Mo deposits with intrusions that seem to be more siliceous and alkali-rich than the causative intrusions of the porphyry coppers (Intrusions of Mo deposits are reported more silica-rich than those of W deposits also^(80,81)). To what extent this difference is real can not be determined from the literature. The causative intrusions at Safford, Bingham, and OK Tedi at least, are almost as siliceous (70% SiO₂) as those at Climax, Henderson, and Questa (72–75% SiO₂). The difference of alkali-content (8% K₂O+Na₂O at Safford; 10% K₂O+Na₂O at Questa) in the causative intrusions may be more significant.

The descriptions of most porphyry copper deposits indicate the presence of quartz-feldspar porphyries or quartz-porphyries, but only few of these make critical evaluations, based on zoning patterns and similar data, of what the causative intrusive is. Until reliable analytical data on the composition of the causative intrusions become available, the preferential association of Mo deposits with siliceous, alkali-rich intrusions must remain a speculative generalization, despite experimental demonstration of the close relationship between Mo and Si in hydrothermal systems.

The tectonic setting of these deposit types may be related to the composition of the causative intrusions. Igneous rocks, in the western United States, at least, show a zonation of eastward increasing silica and alkali content. This is thought to correlate with the subduction history of the western edge of the continent^{(120)*}. Clark⁽³⁷⁾ suggests that the Colorado–New Mexico molybdenum province lies east of the porphyry copper “belt” on the west edge of the Colorado Plateau (recent exploration may show that porphyry coppers occur in the Colorado mineral belt, as well). This would imply a more siliceous and alkali-rich intrusive association in the Mo province, determined by fundamental tectonic controls.

The distinction between the composition of

causative(?) intrusions in island arc and continental margin environments has been demonstrated^(93,94,95), but stockwork Mo deposits also form in island arc environments.^(168,178) The relative scarcity of Cu–Mo deposits (as opposed to Cu–Au) in island arc environments^{(93,94,95)**} suggests that some control of Mo concentration restricts most Mo-rich deposits to intra-continental localities, in association with siliceous and alkali-rich intrusions.

Magmatic differentiation produces silica- and alkali-rich residue. The careful documentation of multiple intrusion and mineralization for the Mo stockworks has underscored the significance of these late differentiates as ore-bearing intrusions. Though multiple cogenetic intrusions are recognized at most porphyry coppers, the presence of repeated mineralization episodes has been conclusively shown only at El Salvador⁽⁷¹⁾. This suggests that the physical conditions (depth of emplacement, extent of fracturing), tectonic environment, and chemical parameters (amount of fluid and mineralizers in the causative intrusions) that permitted repeated, cyclic, or pulse-like mineralization of the stockwork Mo deposits may differ from those of the porphyry coppers. The porphyry coppers typically contain less fluorite, topaz, and carbonates than the stockwork Mo deposits, though Compaccha⁽⁷⁸⁾, Alice Arm⁽²²⁷⁾, and Questa contain little fluorite and topaz. The presence of mineralizers which dramatically affect Mo mobility in igneous rocks^(72,97,177) may

* Apparently, the data is not as concise as Lipman et al.⁽¹²⁰⁾ have presented it, and correlations of alkali content with depth to the Benioff zone are not very accurate for igneous rocks of equivalent age. The demonstrated scatter and unreliability of K–Ar age determinations further complicates these interpretations.

** These data, also, are equivocal; the variation seems due to the comparatively high Au-content of island arc porphyries rather than a relatively low Mo content. Additionally, significant deposits conflict with this interpretation—Bingham is in a continental environment, and is relatively Au-rich.

represent a significant genetic difference between the deposits. Similarly, the temperature of formation ($> 400^{\circ}\text{C}$ for the Cu porphyries⁽¹⁶⁰⁾, $\sim 350^{\circ}\text{C}$ for the Mo stockworks⁽⁷³⁾) of the deposits may be significantly different. The data in the literature are insufficient to gauge the impact of these differences on the episodic character of mineralization in the Mo stockworks.

There seems to be no distinction between the size of porphyry copper and molybdenum deposits. Kesler^(93, 94) has suggested that, among the Cu porphyries, the Cu-Mo deposits (continental margins) are larger than the Cu-Au deposits (island arcs). His suggestions are based on limited data and need corroboration. From the degree of differentiation exhibited by Mo systems, and from the required concentration factor of about 1000 (from 1.5 ppm to 1500 ppm), the association of Mo deposits with larger intrusive masses might be inferred.

The metal zoning of stockwork Mo deposits seems to differ from that of the copper porphyries. The differences are at least in part due to variations in metal abundances—tungsten and tin though present, are generally rare in porphyry copper systems, and thus can hardly be defined in a zonal pattern. Both deposit types have a “barren” core zone, a pyrite halo, and a Pb-Zn halo. The distribution of Cu in the Mo stockworks needs additional documentation, while the supposed central location of Mo⁽⁵⁶⁾ in porphyry coppers may not be real. The data in the literature are not conclusive in this regard.

The paragenesis of the major minerals varies only slightly between the deposit types, and this variation, also, is partly a function of metal abundance. Molybdenite is usually the earliest sulfide in the stockwork Mo deposits, while chalcopyrite sometimes can be quite late⁽²²²⁾. In the porphyry coppers, there may exist a weak, early-molybdenite stage, prior to chalcopyrite formation, but the bulk of the molybdenite is post-chalcopy-

rite. This is consistent with the different temperatures of formation of the deposit types, and with the relative concentration of metals in late-circulating solutions. Both deposit types have extensive barren quartz stockworks.

The factors governing the alteration sequence in the two deposit types are identical. The Mo stockworks seem to have more complicated and variable alterations, equivalents of which are present but poorly developed in Cu-porphyries. Supergene alterations seem to be more pronounced in the Cu porphyries. The character of the alteration may differ in the deposits—the pervasive alteration of the Mo stockworks appears not to be an outward-encroaching vein halo effect, and vein halos are rare in most Mo deposits (present and significant at Alice Arm, however). In the porphyry coppers, vein halos are often pronounced, and pervasive alterations seem to be related to the extension of the vein halos.

Many porphyry Cu deposits have extensive oxidation zones and are characterized by economically significant enrichment blankets. In this respect, they differ from the Mo stockworks. Molybdenite is not as readily oxidized, and mineralogically is not readily enriched. But even with enrichment, the porphyry coppers rarely achieve the level of concentration, compared to average igneous rocks, that Mo stockworks exhibit. Unfortunately little or no information is available on the distribution and characteristics of sub-economic Mo stockworks.

Molybdenum: Geochemistry in Hydrothermal Systems

Molybdenum occurs naturally as sulfide and oxide (molybdate) phases. Molybdenite is the primary ore mineral from which molybdenum is recovered, and appears to be the only one stable in hydrothermal, sulfide-forming systems. Several impure^(58, 157, 184) and structural variants of molybdenite^(203, 225) are known, and a

variety of other ill-defined sulfides [MoS_3 ^(35, 159), Mo_2S_3 ⁽¹⁹²⁾, CuMo_2S_3 ⁽⁷⁰⁾ and $\text{CuMo}_2\text{S}_{5-x}$ ⁽³⁶⁾] have been encountered in hydrothermal experiments. Molybdenum oxides and molybdates are mostly supergene products; many U–Mo compounds have been identified in roll-type uranium deposits^(64, 187).

Conditions of molybdenite formation in natural systems are poorly understood. From hydrothermal experiments, these conclusions are indicated:

- a) Mo transport in hydrothermal solutions occurs⁽⁵⁵⁾ dominantly as $(\text{MoO}_4)^{2-}$; thiomolybdate and oxythiomolybdate solutions ($\text{MoS}_{4-x}\text{O}_x^{2-}$) are capable of transporting co-existing Mo and S in alkaline hydrothermal environments⁽²⁾,
- b) Mo can be transported both as Mo^{+4} and Mo^{+6} , the latter form predominating in more neutral, oxygen-rich environments⁽²⁾,
- c) in aqueous H_2S solutions, Mo can be carried as colloidal $\text{MoS}_3 \cdot n\text{H}_2\text{O}$; this suspension is stable to 200°C without NaCl, and to 250°C in the presence of NaCl,⁽²⁰⁶⁾
- d) coprecipitation of MoS_2 by silica, in H_2S saturated solutions, is indicated between pH 4–8, at temperatures between 20–200°C, and with variable Mo and Si concentrations⁽¹⁵⁶⁾.

Rekharskii et al.⁽¹⁵⁶⁾ indicate there is no molybdenite precipitation from H_2S saturated solutions lacking silica in the pH range 4–8, but Tereshina and Feodot'ev⁽²⁰⁷⁾ observed molybdenite formation under these conditions. Few experiments have been done at higher temperatures ($>3000^\circ\text{C}$), or under more realistic conditions ($[\text{Mo}] = 10\text{--}1000$ ppm, low $[\text{H}_2\text{S}]$). It is likely that $250^\circ\text{C} \leq T \leq 730^\circ\text{C}$ (Fe–Mo–S liquid phase appears)⁽¹¹⁰⁾, pH 4–8, and some silica and NaCl are necessary for molybdenite formation in natural hydrothermal systems. No constraints on f_{S_2} can be imposed from the data presently available.

By comparison, observations of Yoshida et al.⁽²³¹⁾ show that Mo oxides are sublimated ($T \geq 400^\circ\text{C}$) from fumarolic gases containing 0.3–0.7

mg Mo/l. Molybdenite is formed in cooler ($\sim 200^\circ\text{C}$) fumarolic environments by subsequent reaction of the oxide with fumarolic H_2S . The gases transport Mo as a hydroxide or an oxyhalide at $T \geq 550^\circ\text{C}$. Vapor transport of Mo under experimental conditions is interpreted to be geologically important above 250°C ⁽⁹⁶⁾.

Among the molybdates, the powellite (CaMoO_4)–scheelite (CaWO_4)⁽⁸⁰⁾ series can be of significance in the genetic interpretation of hydrothermal deposits. Powellite and/or scheelite are found in several porphyry Cu systems (Butte and Safford being examples). Coexisting hypogene powellite–molybdenite pairs may help define the local f_{O_2} and f_{S_2} conditions prevailing in hydrothermal systems, if T and pH can be independently determined. Scheelite and molybdenite have widely overlapping stability fields⁽⁸⁰⁾. The separation of W and Mo in different deposits and within deposits is due to the difference in the stabilities of the sulfides.⁽²¹⁵⁾

The persistent U–Mo association reflects the similarity of U and Mo geochemistry^(177, 212). U–Mo complexing occurs over a wide range of pH ($\sim 2.5\text{--}11$)⁽¹⁵⁵⁾; the U–Mo complexes break down near pH 2.0, releasing U and Mo independently into solution. The complexes are stable to several g/l concentrations, with temperatures 200–250°C, and are not affected by the presence of chlorides, sulfates, and carbonates. The precipitation of U and Mo in the presence of H_2S is strongly pH dependent. Stockwork sulfide deposits associated with silicic, alkali-rich, porphyritic intrusives often contain associated Mo and U values, both of which may be economically recoverable^(18, 228). This makes stockwork Mo deposits attractive for U exploration.

Oxidation of molybdenite has an extensive Russian literature, well reviewed by Pokalov and Orlov⁽¹⁴³⁾. Molybdenite oxidation is strongly dependent on $[\text{H}_2\text{SO}_4]$ from oxidation of associated pyrite. A galvanic interaction between pyrite

and molybdenite passivates molybdenite while accelerating pyrite oxidation⁽⁷⁶⁾. Thus, the apparent refractory character of molybdenite in leached cappings is in part due to the overwhelming abundance of pyrite. Retention of molybdenum in solution requires $\text{pH} < 3.2$ (ferrimolybdate forms at $\text{pH} > 3.2$ ^(23,167)) subject to some variation by Eh; powellite forms if calcium is available⁽¹⁴³⁾. At $\text{pH} \geq 4.7$ ⁽¹⁴³⁾, ferrimolybdate is hydrolyzed to produce goethite (FeOOH), which coprecipitates molybdenum oxides. Goethite has been found to contain up to 2.7% Mo, and jarosite may contain up to 1.75% Mo⁽²³⁾. Oxidation thus easily leads to dispersion of primary Mo values. Dispersion (Mo loss) in leached cappings is three times as rapid in arid climates as it is in cold, humid climates⁽¹⁴³⁾. The prominence of iron sulfates and oxides in leached cappings of porphyry type Cu-deposits helps to fix Mo in the cappings, making reconstruction of primary Mo grades from surface assay data attractive, especially in cold, humid climates. The thermodynamic stability of secondary molybdenum minerals make molybdenum enrichment unlikely, although slight increases in Mo grade toward the bottom of oxidation zones is sometimes observed.

Molybdenite: Polytypes and Their Genetic Significance

Dickinson and Pauling⁽⁴²⁾ first examined the crystal structure of molybdenite and found it to be hexagonal, with space group $\text{P6}_3/\text{mmc}-\text{D}_{6h}^4$, and $a=3.16\text{\AA}$, $c=12.29\text{\AA}$. Examination of synthetic MoS_2 for quality control led to the discovery of a rhombohedral polytype by Bell and Herfert; ⁽¹³⁾ Jellinek et al.⁽⁸⁶⁾ showed this to belong to space group $\text{R3m}-\text{C}_{3v}^5$, with $a=3.17\text{\AA}$ and $c=18.38\text{\AA}$. Later studies showed that as many as 112 polytypes with fewer than seven layers may exist⁽²²⁵⁾; of these, six polytypes are most likely to occur (2H_1 , 2H_2 , 2H_3 , 3R , 3T , and 6R)^(203,225,237), and to be distinguishable by x-ray te-

chniques.

Naturally occurring polytypes have been identified 2H ⁽²³⁰⁾, 2H_1 , and 3R . An orthorhombic (β - MoS_2) molybdenite has also been reported⁽⁵⁰⁾, but not confirmed. The polytypes differ in their x-ray diffraction patterns (the 3R has doublets in place of the 103 and 105 reflections of 2H molybdenite⁽²¹⁰⁾; reflectivity (2H had higher reflectivity; at 546nm, 2H is 45%, 3R is 37%⁽³³⁾); microhardness (2H is harder; VHN_{15} is 20–76 kg/mm² for 2H and 10–35 kg/mm² for 3R ⁽³³⁾); and possibly composition (3R is 1–5% metal rich compared to 2H ⁽³³⁾).

The genetic significance of polytype variation is not completely clear. Initial studies showed iron⁽¹⁹⁾ or rhenium^(50,62) impurities may be responsible for the formation of the lower symmetry 3R polytype. This has been questioned,^(10,101) but there is evidence that $\text{Re} > 1.2\%$ stabilizes the 3R structure⁽²³⁵⁾. The more frequent occurrence of 3R MoS in medium and low-temperature environments^(10,102) suggests that the 3R polytype has limited thermal stability⁽³³⁾. Temperature-dependent MoS formation shows this postulated sequence^(2,102): amorphous MoS_2 (20–300°C, pH 6–7) → colloform MoS_2 (200–300°C) → 3R MoS_2 (350–900°C) → 2H_1 MoS_2 (600–1300°C). The occurrence of 3R MoS in pegmatites⁽³¹⁾, the experimental thermal stability of the 3R structure (up to 2000°C)⁽³¹⁾, and the regular, submicroscopic intergrowth of 2H_1 and 3R molybdenites⁽⁴³⁾ indicate that temperature is not the only control, as proposed by several authors^(4,10,101,102). The rate of cooling, suggested as a control by Chukhrov et al.⁽³¹⁾, has been discounted⁽¹⁰²⁾. Pressure does not affect the 3R – 2H_1 transformation^(31,102). The most cogent interpretation^(33,159,235), based on experimental and field evidence, proposes a thermodynamic control by sulfur fugacity. Experimental data⁽³³⁾ show 3R stability below $500^\circ\text{C} \pm 100^\circ\text{C}$ (metastability? above 500°C) at sulfur fugacities $\leq 10^{-5}$ atm. 3R becomes

unstable when fs_2 is sufficient to stabilize pyrite with respect to pyrrhotite.

A fairly consistent association of the 3R polytype with porphyry copper deposits has been observed^(7,62). Unfortunately, the location of the samples examined has not been adequately reported, but the implication is that sulfur fugacity in the porphyry coppers is fairly low. Determination of molybdenite polytype character in different zones of porphyry copper deposits can help to define the variations in sulfur fugacity that prevailed during ore formation (Sulfur isotope and fluid inclusion geothermometry can identify zones where the temperature restriction of $\leq 500^\circ\text{C}$ is met.). Since pyrite is the most important Fe-S phase in the porphyries and pyrrhotite is virtually absent, it is likely that metastability of the 3R polytype at high fs_2 will make interpretation of the polytype distribution data difficult.

Trace Elements in Molybdenite and Molybdenum and Re/Os Isotopes

Over a dozen trace elements have been identified in molybdenites from a variety of localities. Some of the trace constituents are expected to be present as lattice substitutions for Mo^(50,205) (Re, Os) and S(Se, Te?), while others (Cu, Fe, Pb, and U) may be due to physical admixtures⁽¹⁵⁷⁾ in the impure molybdenite varieties femolite and jordisite. The presence of discrete, submicron-sized inclusions of ReS_2 and MoSe_2 in some molybdenites has not been discounted. Most trace element concentrations are below 500 ppm, although Re up to 1.88%⁽⁵⁰⁾ has been reported, and some molybdenites contain 0.9% Bi⁽¹²²⁾.

The trace element of primary interest is Re, because Re/Os ratios can be used to date molybdenite, Re zoning in some deposits can be used

as an exploration tool, and Re may occur in economically recoverable quantities in some molybdenite. Dating techniques based on Re/Os ratios⁽⁷⁵⁾ are not applicable to relatively young porphyry deposits; the decay time of the ^{187}Os daughter (half-life $4.3 + 0.5 \times 10^{10}\text{yr}$)⁽¹⁸³⁾ limits reliable Re/Os dating to Precambrian ($>1 \pm 10^9$ yrbp) molybdenite, although Russian workers have successfully dated Paleozoic deposits⁽¹⁸³⁾.

Re zoning is evident in several deposits⁽⁶⁵⁾, including some porphyry systems. The concentration of Re in molybdenite increases as temperature of formation decreases^(65,122,142,236), providing a zonation related to thermal gradients. Combined with other data (fluid inclusion or sulfur isotope thermometry), or independently, if sufficient analyses are available, Re concentration can thus define a vector toward the center of mineralization. It also has the potential of defining the size of a system by defining the magnitude of thermal gradients as a function of distance. The absolute level of Re concentration is determined by factors other than temperature, mostly related to the initial concentration of Re in the host intrusive⁽⁸⁾. Re seems relatively enriched in molybdenites from porphyry coppers^(141,158,202). Re analyses are somewhat involved, and much of the information to be gained from the study of Re distribution can be more readily obtained from other sources. Re concentrations also vary with deposit type (Table 4).

Data on other trace elements are sketchy and seem to offer no incentives for further study.

Preliminary studies of molybdenum isotope distributions in molybdenite and wulfenite showed no deviations exceeding 0.7 permil (at 95% confidence) from natural abundance ratios (195, 204).

Table 4: Trace Elements in Molybdenites (in ppm) [Data from (122) unless specified]

	Re	Se	Te	Bi
Cu-Mo Porphyry	91-2840(65) 720(66)	120-800(57); 127-664 364(57); 335	2-180(57) 33	
Skarns	1300(198) 444	150		110-2500
Q-Mo veins	150-1930			
Mo Stockwork	7-129(65) to 1.88%(50) 53(5)	134-142(90)	<150(100)	
Greisens	5-40(100)	20-86(100)		
Q-Mo-sericite	17-750 163	100-290(100)		
Q-Mo-chalcopyrite	to 1.38% (50) 540	230-600(100)		
Complex Mo-W-Sn	3-7(208)	99-238(208)	35-125	937
Skarns	4-910; 26-428(65) 111; 153(65)	60	55	280-8900 3500
Q-kspar-biotite		45	125	260-2160 1210
Q-Mo veins	0.6-56	30-75 61	35-125 65	50-1350 350
Granitoid host	0.1			
Kupferschiefer	<10-30(208)			
Pegmatites	4-800; 28-131(65) 71(65)	62		
Syenitic Intrusives	<1(65)			
Average, All Types	144(85)			

	Re Distribution in Paragenetically Related Molybdenites (in ppm)			
	Complex Mo-W-Sn(?) Kazakhstan(236)	Mo-Stockwork Alice(65)	Mo-Stockwork Questa(65)	Complex Mo-W Tyrny-Auz
Early (High T)	1-5.6	36	42	280 385
Late (Low T)	220-390 320	129	113	321 139

몰리브덴 반암광상 : 문헌해설

朴 源 春

요약 : 본논문은 다음과 같은 사실에 대하여 문헌적으로 검토해본 것이다.

(1) 합동 반암계와 합몰리브덴 반암계의 상호관계 ; (2) 몰리브테나이트 침전의 열수환경 ; (3) 몰리브테나이트의 다형의 성인적 중요성 ; (4) 탐사지시자로서 유용한 몰리브테나이트 내의 미량원소의 양상.

합몰리브덴 반암계 (예 : Climax)와 합동반암계 (예 : Blinham) 사이에는 지질학적인 유사성이 있으며, 두 유형의 광상탐사에도 비슷한 기술이 적용된다. 몇가지 특징은 증석과 주석도 반암계와 유사한 시스템 (즉, 저풍위, 대량)으로 형성될 수 있음을 지시해 준다. 지구물리학적으 뚜렷이 구별되는 저반지역에서의 일련의 반암계가 잘 설명되고 있으며, 이들은 예비탐사를 위한 중요한 목표지점이다. 지화학적 연구로 우라늄은 퇴적환경에서 뿐만 아니라 화성환경에서 종종 몰리브덴 광석과 밀접한 연관성을 가지고 산출된다는 것을 제시해 준다.

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Table 2: Reported Grade and Cu/Mo Ratio of Porphyry and Stockwork Deposits

Cu-Mo Porphyries

	Cu(wt.%)		Mo(wt.%)	Cu/Mo
	Supergene	Hypogene		
<u>United States [Data of (121), unless marked]</u>				
Bagdad, Az.	.76	.5	±.025	20
Bingham, Ut.	.75	.75	.05	15
Catheart, Me.		.108-.243(171)(.21)	.016-.048(171)(.037)	4.8-10.1 (6.04)
Chino, N.M.	.97	±.15	.01(202)	15
Ely, Nev.	.90	±.10	.01(202)	10
Esperanza, Az.	.51	± 0.3	.028	11
Inspiration, Az.	±.90	.15-1.20 (.4)	.007	21-171 (50)
Miami, Az.	.50(202)	-	.005(202)	100
Mineral Park, Az.	.5	0.1-0.15 (.12)	.04	2.5-3.75 (3.0)
Mission-Pima, Az.	.8	.8	.013-.02(202) (.016)	40-61 (50)
Morenci, Az.	.88	0.1-0.15 (.12)	.007	14.3-21.4 (17)
Nogal Peak, N.M.	-	0.22(37)	.05-0.18(37) (.11)	1.2-4.4 (3.0)
Ray, Az.	.80	0.1-0.8 (.3)	.01(202)	10-80 (45)
Safford (Kennecott), Az.*	-	0.45	.02-.03 (.025)	15-23 (19)
San Manuel, Az.	±.75	±.75	.015	50
Sierrita, Az.**	.32(202)	-	.045(202)	7.1
Silver Bell, Az.	.75	0.3-0.4 (.35)	.02(202)	15-20 (17)
<u>Canada [Data of (56) unless marked]</u>				
Batchawana, Ont.	-	.23(16)	.054(16)	4.26
Bell, B.C.	-	.51	<.01	>51
Bethlehem, B.C.	1.14	.52	.017	30.6
Brenda, B.C.	-	.183	.049	3.73
Dorothy, B.C.	-	>.20(24)	.03(24)	>6.67
Caspé, W.B.	1.17(202)	-	.02(202)	58.5
Gibraltar, B.C.	-	.37	.016	23.1
Granisle, B.C.	-	.44	<.01	>44
Highmont, B.C.	-	.287(14)	.042(14)	6.83
		.273(14)	.093(14)	2.94
Ingerbelle, B.C.	-	.53	<.01?	>53
Island Copper, B.C.	-	.52	.029	17.9
Liard Copper, B.C.	-	.40	.036	11.1
Lornex, B.C.	-	.43	.014	30.7
Mount Pleasant, N.B. +	-	.0002-.11(39)	.0001-.10(39)	.21-68.8
<u>South America [Data of (77) unless marked]</u>				
Chaucha, Ecu.	-	.7	.03	23
Chuquicamata, Chile	± 1.7(121)	1.3	.04	32
Co Blanco, Chile	-	1.38	.03	46
Cuajone, Peru	-	.7	.03	23
El Salvador, Chile	± 1.5(121)	.9	.04	23
El Teniente, Chile	2.25(121)	1.7	.05	34
La Alumbreira, Arg.	-	.4	.04	10
La Caridad, Mex.	.75(165)	<.3(165)	.01-.04(165) (.025)	7.5-30(18)
Los Pelambres, Chile	-	.8(181)	.035(181)	23
Michiquillay, Peru	-	.6	.02	30
Morococha, Peru	-	.7	.02	35
Paramillos, Arg.	-	.38	.02	19
Petaquilla, Panama	.59(55)	(?~.35)(55)	.016(55)	36.9
Queloveco, Peru	-	.6	.03	20
Toquepala, Peru	0.9(121)	.7	.04	18

Others [Data of (202) unless marked]				
Atmalyk, USSR	.72	-	.01	72
Atlas, Philippines	-	.4-.5 (.45)	.04(.01-.16)	10-12.5
Balkhash, USSR	.58	-	.01	58
Bozschekul, USSR	.60	-	.02	30
Kadzharan, USSR	1.50	-	.15	10
Medet, Bulgaria	.35	-	.02	17
Ok Tedi, PNG	-	.6-.7 (.65)	.05	12-14(12)
Rosen, Bulgaria	1.15	-	.025	46
Sar Cheshmeh, Iran	2.00(223)	.895(223)	.03(223)	30
Sipalay, Philippines	.7	-	.04	18
Tanama, Puerto Rico	-	.4-.5 (.45)	.01-.05 (.03)	8-50(24)
<u>Models:</u>				
Lowell and Guilbert(121)	-	.45	.015	30
DeGeoffroy and Wignall(40)	-	.67	.029	23
<u>Summary of Above Data (Does not include model data)</u>				
Range	.32-2.25	<0.10-1.7	.005-.18	1.2-171
Lower Quartile	<.6	<.3	<.016	<11
Upper Quartile	>1.15	>.7	>.04	>44
Median	.76	.52	.028	20
Mean	.93	.53	.031	27.1
Standard Deviation	.47	.33	.025	18.9
95% Confidence Interval (Mean)	.75-1.11	.43-.63	.024-.038	22.0-32.2
<u>Thermal Waters and Associated Rocks [Data of (105) in ppm]</u>				
Taupo, N.Z.	-	.018	.036	.5
Wairakei, N.Z.	-	.012	.060	.2
unaltered rocks	-	<80	6.5	<12.3
altered rocks	-	<85	10-192	.44-8.5
<u>Stockwork Mo Deposits [Data of (37), unless marked]</u>				
Alice, B.C.		.01-.02	.21	.05-.09
Big Ben, Mont.			0.19-0.26	
Boss Mtn, B.C.			.25	
Climax, Colo.		.005	.33	.02
Compaccha, Peru(78)			>.2	
Endako, B.C.			.15	
Hall, Nev.			0.28-0.35(129)	
Henderson, Colo.			.42	
Hudson Bay Mtn., B.C.			±.2	
Machkatica, Yugo.(81)			>.1	
Questa, N.M.		.01-.03	.18	.06-.17
Samdong, Korea(136)		.01-.03	0.05-0.15	2.5-10.5
<u>In Igneous Rocks (ppm)(196)</u>				
Ore Grade		70	1.5	46.7
Concentration Factor		5000	1500	3.3
		70	1000	.093

[Where ranges of values are given, number in parenthesis (on line) was used in calculations.]

* Data are those used for economic projections. The average Cu/Mo may be as high as 27.5.

** Data for Sierrita, Az. are more accurately 0.35 Cu (hypogene), 0.036 Mo, 9.72 Cu/Mo.

+ Not included in calculations.