Polytypism in molybdenite (II): relationships between polytypism, ore deposition/alteration stages and rhenium contents

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Abstract

Detailed analysis of samples from 34 porphyry copper, porphyry molybdenum, and copper skarn deposits indicates that the generally rare 3R polytype of molybdenite is common in these deposits and its occurrence is related to rhenium abundance and mineralization stage. Both rhenium content and 3R abundance increase with time during the primary stages of mineralization, as the molybdenite deposition changes from veinlets associated with K-silicate alteration to veinlets with no associated alteration. Late hydrolytic alteration, associated with pyrite–quartz veins in porphyry systems and hydrous silicate–calcite–sulfide deposition in associated skarns, results in reworking of earlier-deposited molybdenite, leaching of rhenium, and recrystallization of the metastable 3R polytype to the stable $2H_1$ polytype. Supergene alteration also results in rhenium leaching, but kinetic barriers impede recrystallization to the $2H_1$ polytype. A model is suggested to account for this behavior, based on different solubilities of rhenium and molybdenum as a function of K^+/Na^+ and pH changes in the hydrothermal solutions.

Introduction

Part I (Newberry, 1979) showed that there is a general relationship between 3R abundance and impurity contents of molybdenites. Lack of a truly quantitative relationship, however, is caused by significant intra-deposit variations, associated with different alteration and mineralization stages, particularly in the multi-stage porphyry copper/molybdenum deposits. In particular, since it has been shown that the 3R polytype (the phase which is kinetically favored at high impurity contents) is metastable with respect to recrystallization to the $2H_1$ polytype, it is likely that some late-stage processes will be capable of catalyzing the conversion from 3R to $2H_1$. Such partial conversions could, in fact, be responsible for much of the confusion in the literature concerning polytype abundance, impurity content, and environments of deposition. Thus, the polytype abundance data presented in Part I are further analyzed to suggest relations between mineralization stages, rhenium contents, and polytype abundances in porphyry copper, porphyry molybdenum, and copper skarn deposits.

Results

Table 1 presents mineralization features, 3R contents, and Re concentrations for the porphyry copper and copper skarn samples studied in Part I (Newberry, 1979). The vein classification scheme used here, (A,B,D), based on Gustafson and Hunt (1975), is summarized in Table 2. Table 1 suggests that 3R-rich molybdenites are associated with certain vein and alteration types. Figure 1 is a histogram which shows that B-type veinlets are associated with 3R molybdenite, whereas A-veinlets, D-veins, and sericitically-altered veins are associated with $2H_1$ molybdenites.[1] The data in Table 1 also indicate that molybdenite associated with prograde calc-silicate minerals (garnet and pyroxene) in skarn samples is 3R, whereas molybdenite associated with retrograde alteration (*e.g.* vein calcite) is $2H_1$. Several high 3R samples are extensively supergene altered, a fact which suggests that supergene alteration (weathering) has had little effect on polytype stability.

In a similar manner, the polytypism of molybde-

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[1] It should be noted that the assignment of vein types is difficult and complicated by the abundance of transitional types. However, while ambiguities in vein types prevent a rigid classification scheme and thus a quantitative analysis of the data, the ambiguities do not significantly affect the qualitative conclusions drawn in this paper. The reader may find additional information on the samples and justification for their classification in Newberry (1978).

Table 1. Alteration/mineralization characteristics, 3R abundances, and Re contents of the porphyry copper and copper skarn samples

Sample number	Locale	Occurrence	Vein mineralogy[1]	Vein type[2]	Extent of supergene alteration[3]	Pervasive alteration & extent[3]		Re content[4]	3R content
9950	Bingham, Ut.	vein	$Qz_{50}Mo_{40}Py_{10}$	B	2	none	--	.1%	95%
9951	Bingham, Ut.	vein	$Mo_{70}Qz_{30}$	B	1	uncertain	--		70%
9941	Bingham, Ut.	vein	$Qz_{80}(Cc_{10})Py_5Mo_5$	B	4	none	--		60%
9952	Bingham, Ut.	vein	$Qz_{50}Mo_{50}$	B	4	potassic	5	.05%	20%
B-1	Bingham, Ut.	vein	$Qz_{90}Cp_5Bn_4Mo_1$	A-B	4	potassic	5		20%
9937	Bingham, Ut.	vein	$Qz_{80}Mo_{15}Cp_5$	B	4	potassic	5		30%
5059	Ely, Nv.	vein	$Qz_{90}Mo_7Cp_3$	B?	1	uncertain	--	.25%	95%
5060	Ely, Nv.	vein	$Qz_{90}Mo_8Cp_2$	B	1	uncertain	--	.20%	80%
5076	Ely, Nv.	vein	$Qz_{50}Mo_{40}Cp_{10}$	B	5	none	--	.05%	20%
5083g	Ely, Nv.	vein	$Qz_{60}Mo_{30}Cp_{10}$	B'	1	sericitic	4	bdl	0%
SM-9	San Manuel, Az.	vein	$Qz_{70}Mo_{25}Cp_5$	A-B	2	none	--	bdl	90%
SM-10	San Manuel, Az.	vein	$Qz_{40}Mo_{60}$	B	2	none	--	.2%	95%
3977	San Manuel, Az.	vein	$Qz_{70}Mo_{20}Py_8Cp_2$	B	1	potassic	3		40%
45206a	San Manuel, Az.	vein	$Qz_{90}Mo_5Cp_5$	B'	0	sericitic	5	bdl	0%
SM-6a	San Manuel, Az.	vein	$Py_{40}Mo_{40}Qz_{20}$	D	2	potassic	2	.05%	0%
AgB-13	Silver Bell, Az.	vein	$Mo_{40}Qz_{30}Cp_{30}$	B'	0	sericitic	5	bdl	0%
AgB-11	Silver Bell, Az.	vein	$Py_{40}Mo_{40}Qz_{20}$	D	4	uncertain	--	bdl	0%
LDMSB-15	Silver Bell, Az.	vein	$Py_{70}Mo_{20}Qz_{10}$	D	2	potassic	3		0%
AgB-1	Silver Bell, Az.	vein	$Qz_{80}Mo_{15}Cp_5$	A	1	propylitic	4	bdl	0%
AgB-2	Silver Bell, Az.	vein	$Qz_{50}Mo_{45}Cp_2Py_3$	A	1	sericitic	3		0%
AgB-4	Silver Bell, Az.	vein	Mo_{100}	A-B	2	potassic	3		5%
AgB-16	Silver Bell, Az.	fracture	Mo_{100}	-	2	gar/pyx	5		0%
17581	Silver Bell, Az.	vein	$(Cc_{40})Qz_{40}Mo_{10}Py_{10}$	D	4	sericitic	4	bdl	0%
17582	Silver Bell, Az.	vein	$Py_{40}Qz_{40}Mo_{10}(Cc_{10})$	D	3	uncertain	--		0%
17575	Silver Bell, Az.	fracture	Mo_{100}	-	1	serpentine	5		0%
AgB-9	Silver Bell, Az.	vein	$Mo_{60}Qz_{30}Ca_5Cp_5$	?	1	gar/pyx	5		0%
AgB-7	Silver Bell, Az.	vein	$Qz_{80}Mo_{18}Cp_2$	B	2	uncertain	--	.06%	40%
AgB-6	Silver Bell, Az.	vein	$Qz_{50}Mo_{45}Cp_2Py_3$	B	1	potassic	2		60%
RC-Ox-2	Silver Bell, Az.	vein	$Py_{40}Qz_{55}Mo_5$	D-B	1	none	--		30%
17576	Silver Bell, Az.	vein	$Mo_{60}Qz_{35}Py_5$	D	1	propylitic	2	.03%	0%
17574	Silver Bell, Az.	vein	$(Cc_{60})Qz_{30}Py_5Mo_5$	D	4	potassic	1	bdl	0%
SR-111	Santa Rita, N.M.	vein	$Qz_{80}Mo_{20}$	B	5	uncertain	--	bdl	90%
SR-108	Santa Rita, N.M.	vein	$Qz_{90}Mo_{10}$	B	5	potassic	2	.05%	60%
10969a	Santa Rita, N.M.	vein	$Mo_{90}Qz_{10}$	B'	5	sericitic	5		0%
10969b	Santa Rita, N.M.	vein	$Mo_{80}Qz_{20}$	D	4	potassic	1	bdl	0%
LDMS-8	Sierrita, Az.	vein	$Qz_{80}Mo_{15}Cp_2Py_3$	A	0	potassic	3	bdl	0%
LDMS-4	Sierrita, Az.	vein	$Gyp_{80}Qz_{15}Mo_1Py_2Cp_2$	A	0	potassic	4		0%
MTES-4	Sierrita, Az.	vein	$Ksp_{80}Qz_{10}Mo_{10}$	A	0	propylitic	4		0%
JHDS-4	Sierrita, Az.	fracture	Mo_{100}	-	0	propylitic	3		0%
JMSS-1	Sierrita, Az.	vein	$Qz_{50}Cp_{10}Py_{10}Mo_{30}$	A	0	potassic	3	bdl	0%
JMSS-5	Sierrita, Az.	vein	$Qz_{80}Cp_9Py_9Mo_2$	A	0	potassic	4		0%
JMSS-2	Sierrita, Az.	vein	$Gyp_{70}Qz_{20}Py_3Cp_3Mo_4$	A	0	potassic	3		0%
3902	Miami, Az.	vein	$Qz_{70}Mo_{30}$	A	4	potassic	1	bdl	0%
3905	Miami, Az.	vein	$Qz_{80}(Cc_{18})Mo_2$	D	4	uncertain	--		0%
16920	Bagdad, Az.	vein	$Py_{50}Qz_{45}Mo_5$	D	3	uncertain	--		0%
Mo-17	Morenci, Az.	vein	$Mo_{60}Qz_{40}$	D	5	uncertain	--		0%
AJO-2	Ajo, Az.	fracture	Mo_{100}	-	0	sericitic	2		0%
JMSA2c	Ajo, Az.	vein	$Qz_{95}Py_4Mo_1$	D	0	uncertain	--		0%

Table 1. (continued)

Sample number	Locale	Occurrence	Vein mineralogy[1]	Vein type[2]	Extent of supergene alteration[3]	Pervasive alteration & extent[3]		Re content	3R content
43575	Mission, Az.	vein	$Qz_{90}Mo_9Cp_1$	A-B	1	potassic	5		10%
28506	Braden, Chile	vein	$Qz_{60}Mo_{35}Cp_5$	B	2	none	--	.10%	50%
28502	Braden, Chile	vein	$Qz_{60}Mo_{39}(Cup_1)$	B	5	potassic	3		20%
28530	Braden, Chile	vein	$Qz_{60}Cp_{30}Mo_{10}$	B	1	tourmaline	4		10%
28532	Braden, Chile	vein	$Gyp_{70}(Cc_{20})Py_5Mo_5$	D	3	potassic	3		0%
LDME-1	Esperanza, Az.	vein	$Qz_{70}Mo_{15}Cp_7Py_8$	A	1	potassic	3		0%
DCDE-1	Esperanza, Az.	vein	$Qz_{70}Mo_{15}Cp_{15}$	A	0	potassic	3	bdl	0%
JMSE-1	Esperanza, Az.	vein	$Qz_{70}Mo_{15}Py_{10}Cp_5$	A	0	potassic	3		0%
JMSE-2a	Esperanza, Az.	vein	$Qz_{50}Mo_{25}Py_{20}Cp_5$	A-B	1	propylitic	4	bdl	0%
RTCA-1a	Esperanza, Az.	vein	$Qz_{50}Mo_{40}Cp_{10}$	A	0	potassic	5		0%
LDME-3	Esperanza, Az.	vein	$Ksp_{70}Mo_{15}Cp_{15}$	A	0	propylitic	4		0%
RTCE-2a	Esperanza, Az.	vein	$Qz_{60}Mo_{40}$	A	1	potassic	3		0%
RTCE-2b	Esperanza, Az.	vein	$Qz_{80}Mo_{10}Cp_{10}$	B	0	potassic	3		10%
RTCE-2b'	Esperanza, Az.	vein	$Qz_{80}Mo_{15}Cp_5$	B'	0	sericitic	5		0%
30302	Esperanza, Az.	vein	$Mo_{90}Qz_{10}$	D	0	sericitic	5	bdl	0%
30303	Esperanza, Az.	fracture	Mo_{100}	-	5	sericitic	5		0%
4708	Inspiration, Az.	vein	$Qz_{70}Py_{29}Mo_1$	D	1	uncertain	--		0%
2650	Butte, Mt.	vein	$Qz_{95}Mo_5$	A	3	potassic	4	bdl	0%
BUT3AR	Butte, Mt.	vein	$Qz_{95}Mo_5$	A	3	potassic	3		0%
27642	Moracocha, Peru	vein	$Qz_{60}Py_{40}Mo_5Cp_5$	B?	0	uncertain	--	.07%	50%
28306	Morococha, Peru	vein	$Qz_{80}Py_{10}Cp_8Mo_2$	B	0	potassic	5		30%
Ith-5	Ithaca Peak, Az.	vein	$Qz_{70}Mo_{30}$	D	4	uncertain	--		0%
Ith-3	Ithaca Peak, Az.	vein	$Qz_{80}Tq_{10}Py_8Mo_2$	D?	5	uncertain	--	bdl	0%
Ith-2	Ithaca Peak, Az.	vein	$Qz_{90}Mo_{10}$	B'	5	sericitic	5		0%
Ith-1	Ithaca Peak, Az.	vein	$Qz_{60}Py_{45}Mo_4(Cc_1)$	D	3	uncertain	--		0%
20561	Marble Bay, B.C.	disseminated	Mo-Cp-Pyx	-	0	pyroxene	5		95%
20558	Marble Bay, B.C.	disseminated	Mo-Cp-Pyx	-	1	pyroxene	5	.07%	50%
4579	Marble Peak, Az.	vein	Mo_{100}	-	1	gar/pyx	5		50%
4517	Marble Peak, Az.	vein	$Mo_{60}Qz_{40}$	?	1	uncertain	--		10%
4516	Marble Peak, Az.	fracture	Mo_{100}	-	3	garnet	5		0%
14933a	Johnson Camp, Az.	disseminated	Mo-Gar-Pyx	-	1	gar/pyx	5	.08%	50%
14976	Johnson Camp, Az.	disseminated	Mo-Pyx	-	1	pyroxene	5		20%
11933b	Johnson Camp, Az.	vein	$Ca_{80}Py_{10}Mo_{10}$	?	1	gar/pyx	5		0%

[1]Mineral abbreviations: Ca=calcite, Cc=chalcocite, Cp=chalcopyrite, Cup=cuprite, Gar=garnet, Gyp=gypsum, Ksp=k-feldspar, Mo=molybdenite, Py=pyrite, Pyx=pyroxene, Qz=quartz, Tq=turquoise; ( ) indicates a supergene mineral; [2]based on the classification scheme of Gustafson and Hunt (1975), two vein types indicates a transitional vein, ' indicates a vein affected by sericitic alteration; [3]qualitative intensity scale: 0=fresh, 5=totally altered; [4]semi-quantitative microprobe analysis by the author, bdl=below detection limit (approximately 300 ppm).

nites from porphyry molybdenum deposits depends on the stage of mineralization, as indicated in Table 3. Of the 21 samples examined from Climax, Colorado, only those associated with silicification or very weak alteration contain 3R molybdenites, whereas those associated with the earlier mineralization stages (characterized by potassic alteration) and the last stage (characterized by high pyrite and abundant sericitic alteration) contained only $2H_1$. At Urad–Henderson MacKenzie (1970) found 3R molybdenites associated with late-stage greisen-type altera-

tion at the bottom of the Henderson orebody, rather than with K-silicate alteration or sericitic alteration in the main portions of the orebody.

Discussion

Rhenium content and mineralization stage in porphyry copper deposits

Most occurrences of 3R molybdenite, as indicated earlier, are associated with high levels of rhenium. Although little is known about the geochemistry of

Table 2. Porphyry copper vein classification scheme

Parameter	"A" veinlets	"B" veinlets	"D" veins
Mineral assemblage	quartz-k-feldspar-sulfide± anhydrite; 50 - 95% quartz; no vein symmetry, no open space in veins	quartz-sulfide±anhydrite; coarse-grained quartz, frequently cox-comb, open space filling; vein symmetry common	sulfide±quartz±anhydrite;frequently banded anhydrite-sulfide textures; generally low quartz: sulfide
Alteration halo	k-feldspar generally developed around veins	characterized by lack of an alteration halo	sericite replacement of biotite/ feldspars around veins
Structural style	randomly oriented, discontinuous, segmented, whispy; 1 - 25 mm wide	regular and continuous; 5 - 50 mm wide; generally flat-walled	continuous, but locally irregular; 1-100 mm wide
Sulfide assemblage & texture	disseminated chalcopyrite± bornite±molybdenite; pyrite rare	chalcopyrite±molybdenite±pyrite; coarse grained, frequently banded	pyrite±bornite±chalcopyrite± enargite, etc.; minor molybden-ite; sulfides often "gobby" in low-quartz veins
Paragenesis & zoning	early; generally limited to the porphyry stock	intermediate; generally abundant at stock margins and in surrounding wall rocks	very late, cross-cuts all zones; structurally controlled

rhenium, experimental evidence indicates that rhenium oxides are more volatile than the corresponding molybdenum oxides (Morris and Short, 1969), and that rhenium can be preferentially leached from molybdenites at moderate temperatures (Morachevskii and Nechaeva, 1960).

Figure 2 is a plot of molybdenum grade *vs.* average rhenium contents of molybdenites from several porphyry deposits. The hyperbolic shape of the graph indicates that the actual grade of rhenium in the deposits does not change considerably from deposit to deposit, despite a 20-fold variation in molybdenum grades. In other words, it appears that the transport and deposition of rhenium occurs by a mechanism different from that of molybdenum. Furthermore, the transport and deposition mechanisms may change with time: deposits characterized by A-veinlet deposition (*e.g.* Butte, Chuqui, Sierrita) are high-grade molybdenum/low-ppm rhenium, whereas those characterized by B-veinlet deposition (*e.g.* Ely, Ray, San Manuel) are low-grade molybdenum/high-ppm rhenium.

Although no studies directly connect the rhenium contents of molybdenite with veinlet type in porphyry copper deposits, Giles and Schilling (1972) made a detailed study of the spatial distribution of rhenium in molybdenite at Bingham, Utah, and observed that the rhenium contents of molybdenite are lower in the central stock area than in the surrounding host rocks. This observation, combined with the fact that A-veinlets in porphyry systems tend to be limited to the central stock, whereas B-veinlets penetrate through the surrounding wall rocks (Einaudi, personal communication, 1978), strongly suggests a spatial correlation between high rhenium and B-veinlet associated molybdenites. Giles and Schilling's (1972) study of Questa, New Mexico, and Lime Creek, British Columbia, indicated that the rhenium content of molybdenite increases from early "pegmatitic" veinlets (A-type) to the late "thick, banded, through-going quartz–MoS₂ veins" (B-type).

The limited data of Table 1 indicate that low-rhenium molybdenites are found in A-veinlets and high-rhenium molybdenites are found in B-veinlets. Figure 3 is a plot of the mean rhenium contents of
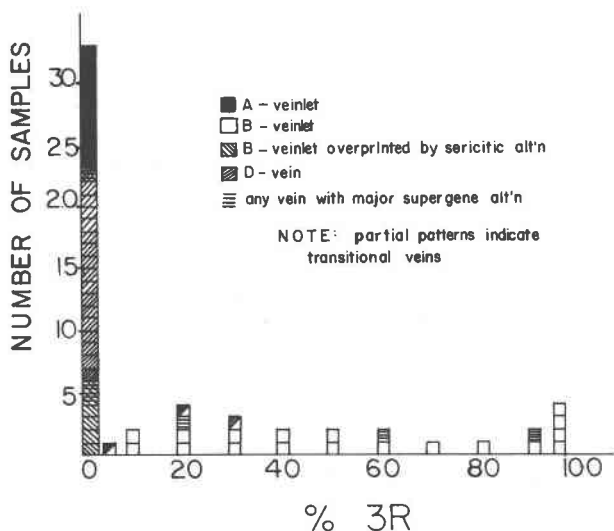

Fig. 1. Histogram of 3R contents of the porphyry copper samples, showing alteration and mineralization styles of the samples. Note that 3R is found only in B-type veinlets.

Table 3. Alteration, mineralization, and polytype characteristics of the Climax, Colorado samples

Sample number	Host rock	Orebody	Associated alteration	3R content
12589	SW Mass, Climax Porphyry	upper	potassic	0%
44753	SW Mass, Climax Porphyry	upper	potassic	0%
44762	Idaho Springs formation	upper	potassic	0%
44741	Idaho Springs formation	upper	potassic	0%
CX-4	Silver Plume granite	upper	potassic	0%
44752	Central Mass, Climax Porphyry	lower	potassic	0%
44755	Central Mass, Climax Porphyry	lower	potassic	0%
44755a	Central Mass, Climax Porphyry	lower	potassic	0%
44754	Central Mass, Climax Porphyry	lower	potassic	0%
44750	Central Mass, Climax Porphyry	lower	potassic	0%
CX-11	Central Mass, Climax Porphyry	lower	potassic	0%
PMCX-3	Central Mass, Climax Porphyry	lower	sericitic	0%
PMCX-1	Central Mass, Climax Porphyry	lower	silicic	40%
CX-12	Central Mass, Climax Porphyry	lower	silicic	0%
CX-13	Intra-mineral Rhyolite Porph	lower	none	5%
44760	Intra-mineral Rhyolite Porph	lower	none	10%
CX-9	Climax Porphyritic Granite	"barren"	sericitic	0%
44756	Climax Porphyritic Granite	"barren"	sericitic	0%
44756a	Climax Porphyritic Granite	"barren"	sericitic	0%
CX-15	Climax Porphyritic Granite	"barren"	sericitic	0%
CX-16	Climax Porphyritic Granite	"barren"	sericitic	0%

Fig. 2. Plot of molybdenum grade *vs.* rhenium content of molybdenites for several porphyry deposits. Mo grades are taken from Sutulov (1976); rhenium contents from Table 6 of Newberry (1979).

molybdenites from several deposits *vs.* the mineralization style of the molybdenites. The latter is based on personal observations and an interpretation of the literature (*e.g.* Lynch, 1966, reports that at Esperanza "Molybdenite veins from this location usually show a thin selvage of potash feldspar"). Figure 3 confirms that, in general, deposits characterized by A-veinlet associated molybdenite are low in rhenium, whereas those characterized by B-veinlet associated molybdenite are higher in rhenium. D-veins generally show low rhenium contents.

The data of Table 1 and Figure 1 indicate that hypogene sericitic alteration of B-veinlet molybdenite results in recrystallization to the $2H_1$ polytype. Supergene alteration (weathering), however, does not affect the 3R polytype, as several supergene altered samples contained significant 3R contents. The metastability of 3R in the weathering environment is also indicated by Neuerburg *et al.*'s (1974) discovery of a mixed $3R + 2H_1$ molybdenite grain in a stream sediment sample from the Montezuma district of Colorado. Supergene leaching of rhenium from such grains, however, as expected from the experiments of Morachevskii and Nechaeva (1960), would result in a low-rhenium 3R molybdenite.

Rhenium content and alteration style in porphyry copper deposits

Within the porphyry copper group correlations can be made between vein/alteration types, rhenium content, and 3R abundance. These observations can be understood by considering the geochemical
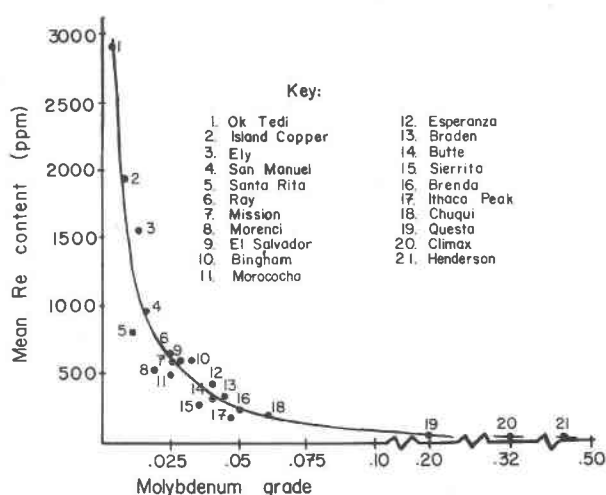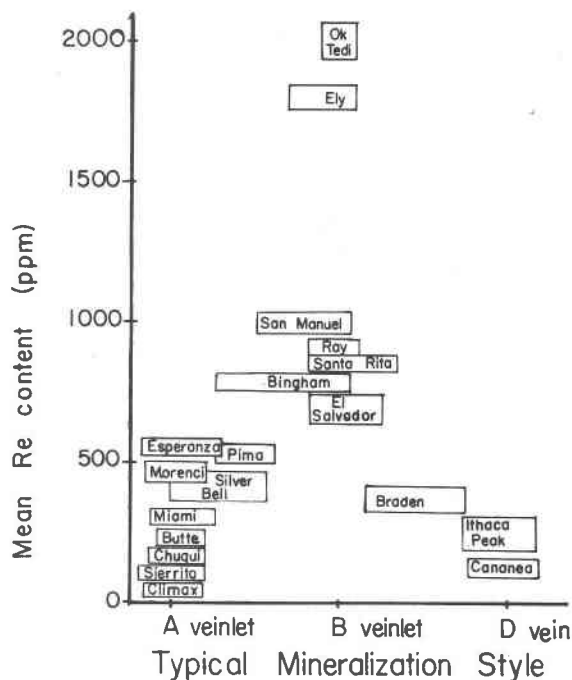

Fig. 3. Plot of mineralization style of molybdenite *vs.* average rhenium content of molybdenites for several porphyry deposits. Mineralization styles interpreted from Titley and Hicks (1966); rhenium contents from Table 6 of Newberry (1979). The position and extent of the box surrounding a deposit name is a qualitative indication of the extent that molybdenite in the deposit is associated with A,B,D or transitional veins. Because of the geometry of D-vein deposition, alteration of A-veinlets by D-veins is uncommon.
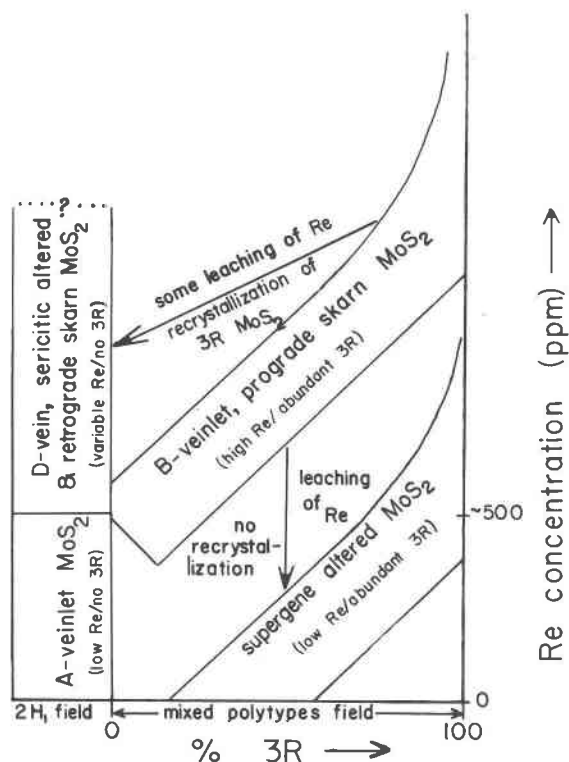
Fig. 4. Diagrammatic representation of 3R/Re relations in porphyry and skarn deposits during the various stages of molybdenite deposition and alteration.

changes taking place in the fluids during alteration and molybdenite deposition.

Molybdenite deposited in A-type veinlets is associated with intense potassic alteration—*i.e.* conversion of hornblende to biotite, conversion of plagioclase to K-feldspar, and in some cases deposition of secondary K-feldspar. This process locally decreases the K^+/Na^+ ratio of the depositing fluid. Isuk (1976) has demonstrated experimentally that MoS_2 solubility is significantly greater in the $K_2Si_2O_5$–SiO_2–H_2O system than in the sodic analogue or the non-alkali system. This suggests that molybdenite is deposited in A-veinlets due to a drop in the K^+/Na^+ ratio of the altering fluids. There is no evidence to indicate that rhenium should be similarly less soluble under decreasing K^+/Na^+ conditions (as pointed out earlier, Re is probably deposited by a different mechanism than is Mo), and thus molybdenites associated with A-veinlets are low in rhenium. Such low-rhenium molybdenites are of the $2H_1$ polytype, as indicated in Part I of this series. The absence of molybdenite deposited during this stage in several deposits is probably due to an insufficiency of molybdenum in the hydrothermal system.

B-veinlets, on the other hand, have no associated alteration; thus molybdenite deposition in these veins occurs through some other mechanism, perhaps a decrease in temperature. Hydrothermal solutions are now frequently higher in Re/Mo due to precipitation of low-rhenium molybdenite during A-veinlet formation. In many cases molybdenum appears to be exhausted in the porphyry system by the time this stage occurs; in others molybdenum is not sufficiently concentrated to be deposited until this stage. Rhenium is precipitated with molybdenum by the new deposition mechanism during B-veinlet formation; the rhenium content of the molybdenite appears to be largely an inverse function of the amount of molybdenite deposited (*i.e.* the more molybdenite deposited, the lower its rhenium content). This stage, on the whole, is characterized by high rhenium/abundant 3R molybdenites. Bingham is a transitional deposit, characterized by early A-veinlet associated low rhenium $2H_1$ molybdenites, and later B-veinlet associated high rhenium/abundant 3R molybdenites.

D-veins, with their attendant hypogene hydrolytic alteration, indicate the presence of low pH fluids; such fluids are known to be capable of leaching rhenium from molybdenite (Vlasov, 1966, p. 607–633). The temperatures at this stage are also sufficiently high (*ca.* 350°C) for recrystallization of the rhenium-depleted molybdenite. Sample RTC-E2b illustrates this process: molybdenite from an early B-veinlet, 9 cm from a cross-cutting D-vein, contains approximately 10% 3R. Where the D-vein crosses the B-veinlet, recrystallization of the molybdenite in the B-veinlet has occurred and the molybdenite is 100% $2H_1$. Similarly, those molybdenites from Ithaca Peak, San Manuel, and Silver Bell which are associated with abundant hypogene sericite contain the pure $2H_1$ polytype and are low in rhenium. Clark (1970) also has shown that recrystallization of 3R molybdenite gives rise to $2H_1$ molybdenite at Panasqueira, Portugal.

Copper-bearing skarns show analogous features: 3R molybdenite is associated with prograde calc-silicate minerals, and $2H_1$ is associated with later calcite–quartz–amphibole retrograde veins. In porphyry molybdenum deposits the vast majority of the molybdenite is $2H_1$, contains minor rhenium (0.01–100 ppm) and is associated with K-silicate alteration (MacKenzie, 1970). 3R molybdenite, where found, is associated with late-stage deposition, has higher rhenium contents (Giles and Schilling, 1972), and is not associated with either K-silicate or hydrolytic alteration (MacKenzie, 1970).

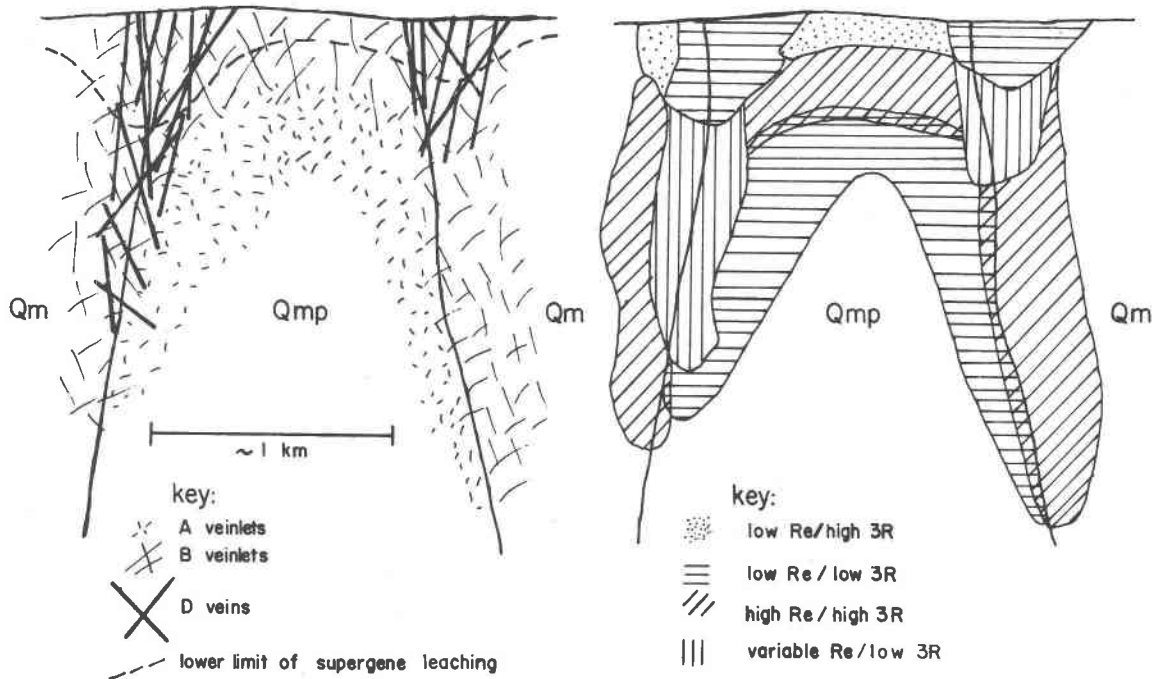Supergene alteration processes which occur under

Fig. 5. Spatial distributions of 3R/Re relationships for a hypothetical porphyry copper deposit cross-section. Fig. 5a is a hypothetical configuration of vein and alteration types, and Fig. 5b is the spatial distribution of 3R/Re relationships derived from the configuration of 5a.

conditions of low pH do not cause a 3R to $2H_1$ conversion, because insufficient kinetic energy is available at these low temperatures to cause recrystallization. Thus, weathered 3R molybdenites might or might not be rhenium-rich, depending on the effectiveness of rhenium leaching. In weathered samples, therefore, present rhenium contents are not indicative of the original rhenium content and thus of the original 3R content.

Figure 4 summarizes the relations between mineralization/alteration stages, rhenium contents, and 3R abundances. Note particularly how late hydrolytic and supergene alteration affect the early close relationship between rhenium content and 3R abundance. D-vein-associated hydrolytic alteration causes recrystallization to $2H_1$ and incomplete rhenium leaching, whereas weathering causes leaching of rhenium but no recrystallization.

Figure 5 indicates the distribution of various 3R/Re combinations for a hypothetical porphyry copper cross-section. Figure 5a is a hypothetical configuration of vein and alteration types; Figure 5b shows the distribution of the various 3R/Re relationships that result from the configuration of 5a. It is clear that the degree of correlation between 3R abundance and Re content at a given deposit depends rather critically on the depths of weathering and exposure and the

abundance of hydrolytic alteration. Thus, by sampling several deposits one would expect to see conflicting 3R/Re relationships unless one understood the context of one's samples.

Perhaps the conflicting data of earlier workers can be resolved in light of Figure 5. For example, Sutulov (1976) indicates that "molybdenites found at greater depths contain more rhenium than those at the surface" (weathering of B-veinlet molybdenite?), whereas Badalov *et al.* (1971) suggest that 3R is confined to shallower depths than $2H_1$ (B-veinlet *vs.* A-veinlet deposition?). Similarly, Chukhrov *et al.* (1968) note differences in polytypism of molybdenites from veins with greisen envelopes *vs.* those without alteration envelopes, which they ascribe to differences in rates of cooling, but might instead be caused by differences in alteration/mineralization style.

Conclusions

Analysis of approximately 130 porphyry copper/molybdenum and copper skarn deposit samples indicates that relationships between 3R molybdenite abundance and rhenium content can be explained by the effects of initial rhenium contents, recrystallization, and rhenium leaching. Porphyry copper, porphyry molybdenum, and copper skarn deposits

show an increase in 3R abundance with time during the primary stages of molybdenite deposition. This corresponds to the transition from A-veinlet deposition to B-veinlet deposition and is correlated with increasing rhenium content in molybdenite. Early stages are followed by an overprint of rhenium leaching and recrystallization of 3R to $2H_1$ during D-vein deposition and hydrothermal remobilization. Finally, leaching of rhenium without recrystallization of 3R to $2H_1$ takes place during weathering. Thus, the geochemistry of rhenium and polytypism of molybdenite are strongly tied into the geochemistry of hydrothermal and supergene alteration. Similar detailed mineralogical and geochemical analysis of other molybdenum deposit types could lead to a better understanding of the origins of the 3R polytype in greisens, pegmatites, and quartz veins.

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