

## Polytypism in molybdenite (I): a non-equilibrium impurity-induced phenomenon

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### Abstract

Molybdenite is known to occur in either of two structures: the common 2H<sub>1</sub> polytype and the rare 3R polytype. Most previous work has suggested that 3R forms in low sulfur fugacity environments and is sulfur-deficient relative to 2H<sub>1</sub>. A thorough review of the literature on molybdenite, however, suggests that the occurrence of 3R molybdenite in nature is not related to sulfur fugacities or temperatures of formation, but rather to impurity content. X-ray diffraction analysis of 184 specimens of molybdenite indicates (1) there is a semi-quantitative relationship between the mean 3R abundance and the mean impurity content of molybdenites from a given deposit and (2) the 3R abundance is independent of the sulfidation states of the associated sulfides. Microprobe studies indicate that there are no significant major-element differences between 3R and 2H<sub>1</sub> molybdenite in the samples studied.

A synthesis of the experimental stability studies of molybdenite polytypes suggests that 3R grows by a screw-dislocation mechanism and is unstable with respect to 2H<sub>1</sub>, but does not readily convert due to kinetic barriers. Growth by screw dislocations in nature most frequently occurs due to internal strains generated by high impurity contents in the growing crystals. Rhenium, tin, titanium, bismuth, iron, and tungsten are the most common impurities found in 3R molybdenite, and their role in the mineralization process with respect to formation of 3R molybdenite is discussed for several deposit types.

### Introduction

The structure of molybdenite (MoS<sub>2</sub>) is based on stacking of planar close-packed S-Mo-S layers. Although such layers could be stacked in a variety of ways, only two stacking sequences have been observed in natural and synthetic molybdenites. Because both minerals consist of structurally identical MoS<sub>2</sub> layers and differ only in the length of *c*, they are polytypes. The most common polytype in nature is hexagonal (2H<sub>1</sub>, space group *P6<sub>3</sub>/mmc*), consisting of two layers per unit cell. The less common natural polytype is rhombohedral (3R, space group *R3m*), consisting of three layers per unit cell (Fig. 1).

The origins and controls of polytypism are not well understood, although most studies of the SiC, ZnS, and CdI<sub>2</sub> systems have indicated that the phenomenon in these systems is related to dislocation/growth processes and differences in energies of different stacking sequences (e.g. Trigunayat, 1971). In the case of molybdenite much controversy exists concerning the origins of polytypism. Some authors sug-

gest that the two polytypes are stoichiometrically dissimilar (Clark, 1970), whereas others believe that the trace-element contents differ (e.g. Somina, 1966). Still others postulate differences in pressures of formation (Badalov *et al.*, 1971), temperatures of formation (Arutyunyan *et al.*, 1966), or cooling rate during formation (Chukhrov *et al.*, 1968).

Frondel and Wickman (1970) have shown that 3R molybdenite is present in a variety of ore deposits and is not restricted to "exotic" low *f*(S<sub>2</sub>) environments as suggested by Clark (1970). However, Clark's (1970) conclusion that 3R is 1 to 5 weight percent sulfur-deficient relative to 2H<sub>1</sub> has been accepted by several authors (e.g. Hasan, 1971; Craig and Scott, 1974). If, indeed, 3R molybdenite is an indicator of low sulfidation states, its rarity in nature suggests that molybdenite deposition occurs under relatively high sulfur fugacity conditions. This hypothesis has significant implications for molybdenite ore deposition, e.g., it suggests transport by high sulfide mechanisms.

This investigation is based on a study of 184 mo-

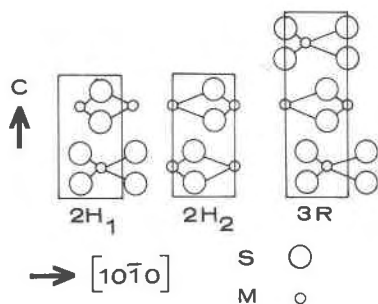


Fig. 1. Structures of some  $MS_2$  polytypes projected onto (1120), modified from Takeuchi and Nowacki (1963).

lybdenite-bearing hand specimens to determine polytype content, vein mineralogy, alteration, major- and trace-element content, and environment of deposition, in order to better understand the causes of polytypism in molybdenite. Part I is a study of what causes original formation of the 3R polytype; it leads up to a hypothesis explaining the relation between trace-element and 3R content. Part II examines the details of a particular system (Re/3R in the porphyry environment) and discusses the geochemical circumstances under which 3R is preserved and/or destroyed by post-depositional alteration.

### Review of past work

#### *Polytypism and sulfidation states*

Little information is available in the literature on the major-element compositions of  $2H_1$  and 3R molybdenite. Available analyses, however, show that no systematic correlation exists between sulfur contents and 3R abundances. Moreover, these data show no indication that the  $2H_1$  polytype is 1 to 5 percent richer in sulfur than the 3R polytype. Both polytypes have been reported with compositions ranging from 39.9% S (Seebach, 1926) to 40.4% S (Zelikman *et al.*, 1961) (Fig. 2). Detailed tabulations of these and other molybdenite data may be found in Newberry (1978).

If natural polytype occurrences are a function of sulfidation state of the environment, as has been suggested by several studies, then there should be some correlation between 3R/ $2H_1$  occurrences and the sulfidation states of the associated minerals. Literature data suggest, however, that there is no such correlation. 3R molybdenite has been found associated with sulfidation states ranging from high—native sulfur (Znamenskiy, 1969)—through intermediate—chalcopyrite + bornite + pyrite (Hasan, 1971)—to low—bismuth + pyrrhotite (Petruk, 1964). Similarly,  $2H_1$

is found in a variety of environments. Indeed,  $2H_1$  and 3R polytypes are commonly mixed within a single specimen, as shown by single-crystal experiments (Drits and Chukhrov, 1971). Similarly, grain size is not related to polytype abundance, contrary to the suggestion of Wildervanck and Jellinek (1964), as indicated by a review of the literature.

#### *Polytype abundance and impurity content*

Several studies, starting with Somina (1966), have suggested that 3R molybdenites characteristically contain high impurity contents. Rhenium is the most common impurity element, ranging in concentration from less than 1 ppm to greater than 5000 ppm. No detailed study of impurity contents and polytypism in the same samples has been undertaken, but the general trend of the literature is that high rhenium contents can be correlated with high 3R contents (*e.g.* Ayres, 1974). High contents of other trace elements, such as Ti, Bi, W, and Fe are also correlatable with the presence of the 3R polytype (Table 1). In contrast,  $2H_1$  polytypes are relatively pure (Chukhrov *et al.*, 1968).

#### *Synthesis studies*

Published experimental data show that (1) both polytypes can be synthesized (Bell and Herfert, 1957), (2) 3R converts to  $2H_1$  when heated for long periods at temperatures in excess of 500°C (Wildervanck and Jellinek, 1964), (3) the time necessary for complete conversion increases drastically as temperature falls (Clark, 1970), (4) 3R converts to  $2H_1$  faster and more completely in the presence of sulfur gas (Zelikman *et al.*, 1969), and (5) 3R converts to  $2H_1$  only by recrystallization (Zelikman *et al.*, 1969).

Experimental synthesis of molybdenite by reaction of molybdenum metal with sulfur vapor or liquid generally results in a mixture of the 3R and  $2H_1$  polytypes (Dukhovskoi *et al.*, 1976). In one experiment two  $MoS_2$  layers were formed: a  $2H_1$  layer next to the molybdenum metal and a mixed 3R +  $2H_1$  layer next to the sulfur (Zelikman *et al.*, 1976). These results are

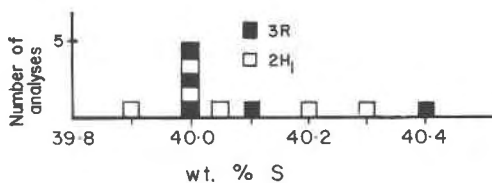


Fig. 2. Histogram of molybdenite chemical analyses taken from the literature.

inconsistent with the theory that 3R forms in comparatively sulfur-poor environments. Rather, as Zelikman *et al.* (1976) point out, there are differences in the growth mechanisms of molybdenite formed at the metal- and sulfur-interfaces.

Similarly, molybdenite formed by reaction between MoO<sub>2</sub> and sulfur is 2H<sub>1</sub>, whereas in the presence of an alkali-carbonate flux 3R forms. Again, there are differences in growth mechanisms between the two experiments, rather than differences in sulfur activities. Elwell and Neale (1971) have shown that fluxes generally cause crystal growth by a screw-dislocation mechanism.

Finally, the addition of an impurity (in particular Re) in synthetic molybdenite affects the 3R to 2H<sub>1</sub> conversion reaction. 3R molybdenite containing 0.05 to 3% Re converts more slowly than pure 3R molybdenite, and 3R containing more than 3% Re has not been observed to convert at all, even at temperatures of 1100°C (Zelikman *et al.*, 1969).

In summary, experimental work suggests that 3R is unstable with respect to 2H<sub>1</sub> under geologically reasonable *P-T* conditions, but that there are kinetic barriers to establishment of equilibrium once a given polytype has formed. This implies that polytype formation depends more on growth processes than on equilibrium processes. A survey of the literature also indicates a possible correlation between the polytype and trace-element content, and a lack of correlation between 3R content and sulfur fugacity or temperature of formation. A lack of hard data supporting any one cause of 3R formation, a lack of a mechanism for explaining the formation of 3R, and a lack of data on the post-crystallization behavior of 3R prompted this detailed study of polytypism in molybdenite.

### Experimental details

The polytype content of 184 molybdenite samples was determined by X-ray diffraction techniques, following the methods of Frondel and Wickman (1970). Polytype abundances were determined by comparing intensities of the (100), (101), (102), (103), (006), and (105) peaks of 2H<sub>1</sub> and the (101), (012), (104), (015), (009), and (107) peaks of 3R to the theoretical mixtures of 2H<sub>1</sub> and 3R calculated by Wickman and Smith (1970).

All diffractometer experiments were carried out using Ni-filtered CuK $\alpha$  radiation, a scan speed of 1/8° 2 $\theta$ /minute, and a scan range of 26 to 53° 2 $\theta$ . Quartz was added to all samples as an internal standard.

Table 1. Impurity contents of some 3R molybdenites from the literature

Location	Impurity	Reference*
Binnental, Switz.	0.7% W	1
Kurile Island, USSR	ca. 500 ppm Fe	2
East Siberia, USSR	2% Ti; 300 ppm Nb, V	3
Panasqueira, Portugal	150 ppm Fe; "some" W	4
Armenia, USSR	1.88% Re	5
synthetic	0.16% Ti	6
Con Mine, Yellowknife, Can.	ca. 500 ppm Fe	7

\*References: (1) Graessner (1964); (2) Znamenskiy *et al.* (1970); (3) Somina (1966); (4) Clark (1965); (5) Paramazyan and Khurehudyun (1963); (6) Bell and Herfert (1957); (7) Boyle (1968)

Five molybdenite-bearing samples representing different deposit types were trimmed to 0.5-cm pieces, mounted in epoxy, polished, and carbon-coated. Qualitative wavelength scans of the five samples on an ARL-EMX-SM microprobe indicated that only Mo, S, and Re were present in quantities greater than the 0.05% limit of detection. The samples were qualitatively analyzed for Mo and Re. Overlap of the Mo *L* $\alpha$  and S *K* $\alpha$  peaks prohibited analysis of sulfur; the Mo *L* $\beta$  peak was employed for Mo analysis. Pure metals were employed as standards. The following analytical conditions were used: output voltage, 15 kV; emission current, 50 mA; sample current, 0.03 mA; count time, 10 sec. Results were corrected for background and drift and expressed as k-ratios (ratio of sample to standard counts).

Six samples of 2H<sub>1</sub> molybdenite from the Climax Mine, Colorado, were cut to 0.05 × 0.5 × 0.5 cm pieces and heated to 700°C in a stream of pure hydrogen gas for 1 to 36 hours by H. Wise and P. Wentrack of SRI International. As shown by Aoshima and Wise (1974), this procedure results in the formation of sulfur-deficient molybdenite. All samples were analyzed for 3R content.

### Results

#### *Polytype abundance*

Polytype abundance for molybdenite from each deposit is presented in Table 2, with rhenium contents taken from the literature. Although there is a wide range of both 3R abundances and rhenium contents within a given deposit, in general the 3R polytype occurs in rhenium-rich molybdenite deposits. Mean values of %3R and ppm Re are plotted in Figure 3, which shows a linear correlation between rhenium content and 3R abundance for several deposits.

This correlation might only indicate that rhenium

Table 2. Molybdenite polytype abundances with literature rhenium data

Location	Deposit number	Number of samples analyzed	3R content (%)	Rhenium content (ppm)	Rhenium reference*	Location	Deposit number	Number of samples analyzed	3R content (%)	Rhenium content (ppm)	Rhenium reference*
I. Porphyry Copper and related copper deposits											
Ely, Nevada	1	4	0-95	1200-2800	1,2,8	San Manuel, Az.	2	5	0-95	700-1200	1
Bingham, Utah	3	6	0-90	130-2000	1	Santa Rita, N.M.	4	5	0-90	200-1100	1
Silver Bell, Az.	5	18	0-60	340-620	1	Esperanza, Az.	6	14	0-10	90-800	1
Morococha, Peru	7	2	0-50	490	1	El Teniente, Chile	8	4	0-50	380-420	1,3
Commonwealth, Az.	9	2	0-10	360	2	Cananea, Mexico	10	10	0-10	120-420	2,3,8
Pima, Az.	11	1	10	600	1	Morenci, Az.	12	1	0	260-610	1
Miami, Az.	13	2	0	260-610	1	Bagdad, Az.	14	1	0	220	2
Ithica Peak, Az.	15	5	0	240-300	1	Sierrita, Az.	16	6	0	120	1
Butte, Mont.	17	10	0	240	1	Chuquicamata, Chile	18	1	0	200-280	1,3,5
Copper Creek, Az.	19	2	0	40-100	2	Inspiracion, Az.	1	1	0		
Ajo, Az.	4	4	0			Yagi, Sonora, Mexico	5	5	0		
II. Porphyry Molybdenum deposits											
Climax, Colo.	20	28	0	11-80	1,2,4	Johnson Camp, Az.	2	20-50			
(Upper Orebodies)		4	0-40			Larap, Philippines	6	6	0-10		
(Lower Orebody)		8	0	38-120	1,4,8	Marble Peak, Az.	4	4	0-50		
Questá, New Mexico	21	8	0			Marble Bay, B.C.	22	3	30-90	750	8
Mt. Hope, Nevada	3	3	0			Deva, Romania	23	2	0-50	760	6
Mt. Emmons, Colo.	2	2	0			Mission, Az.	1	1	10		
III. Copper-Molybdenum-bearing skarns											
IV. Tungsten-Molybdenum-bearing skarns											
Brownstone Mine, Ca.	24	3	0	177-428	1,8	V. Pegmatites/Quartz veins/Greifers					
Pine Creek, Calif.	25	6	0	35-178	1	Honshu, Japan	27	1	0	0.1-22	4
Getchell, Nev.	26	1	0	26-34	1	Yamasa Mine, Japan	28	2	0	110-200	4
Sandong, Korea	1	1	0			Bora, NSW, Austr.	29	1	0	8.7	7
Nevada-Mass. Mine, Nev.	2	2	0			Plumas, Calif.	30	1	0	90-131	1
						Alum Gulch, Nev.	1	1	0		
Garnet Hill, Calif.	3	3	0			Neihart, Mont.	1	1	0		
Alpine Mine, Calif.	2	2	0			Corma, Calif.	1	1	0		
Westwood, B.C., Canada	1	1	0			Clayton, Idaho	1	1	0		
Ward Creek, Montana	1	1	0			Antler Creek, Nev.	1	1	0		
Little Bidr. Crk., Id.	1	1	0			Taylorville, Calif.	1	1	0		
Colorado Gulch, Mont.	1	1	0			Lost River, Alaska	1	1	60		

\*References: (1) Giles and Schilling (1972); (2) Vlasov (1966); (3) Shtulov (1976); (4) Terada (1971); (5) Ambrose and Soto (1974); Petruian and Steelact (1964); (7) Morgan et al. (1968); (8) this study

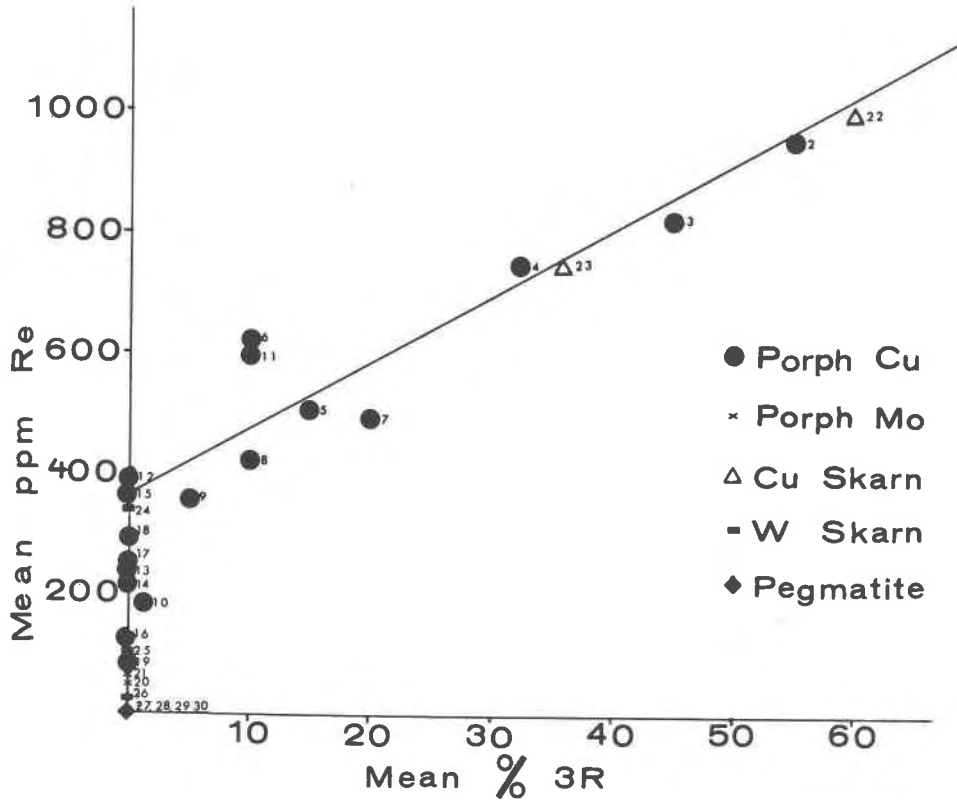


Fig. 3. Mean 3R abundance vs. mean rhenium content for molybdenites from deposits listed in Table 2.

concentration and 3R formation fortuitously occur under similar conditions. However, within a group of similar deposits (*e.g.* porphyry copper deposits), those with high-rhenium molybdenites also tend to show greater 3R abundance than those with low-rhenium molybdenites. There is no evidence indicating that the Sierrita deposit, for example, formed under significantly different  $T$ - $f(S_2)$  conditions than the San Manuel deposit, yet San Manuel has high rhenium contents and high 3R abundances, whereas Sierrita has low rhenium and no 3R.

There are also no indications of a correlation between low sulfidation state and 3R abundance in the samples studied. Table 3 lists coexisting sulfide assemblages for selected samples, covering a variety of 3R abundances; the lack of correlation with sulfidation state is readily apparent.

#### Compositional variations

Table 4 shows the 3R content and concentration of rhenium and molybdenum in five molybdenite samples. As Table 4 indicates, there is no significant variation in molybdenum content for the five samples,

but there is a significant difference in rhenium content. These results again indicate that impurity content, rather than sulfur/molybdenum stoichiometry, is the determining factor in polytype abundance.

#### Annealing experiments

Six samples of  $2H_1$  molybdenite were held at  $700^\circ\text{C}$  in a sulfur-deficient atmosphere for 1–36 hours. None of the samples showed any sign of conversion to 3R. Quenching from  $700^\circ\text{C}$  prevented recrystallization back to  $2H_1$ , had any 3R formed, and the presence of a sulfur-deficient atmosphere would have allowed the transition from  $2H_1$  to 3R to occur if the low  $f(S_2)$  made  $2H_1$  unstable with respect to 3R. These experiments, therefore, indicate that 3R/ $2H_1$  stability is not a function of sulfur fugacity.

In summary, the analytical results indicate that 3R molybdenite (1) is not uncommon in several geologic environments, (2) is not a product of the sulfur fugacity of the depositional environment nor of stoichiometry, but (3) is related to the amount of impurity present in the molybdenite. Finally, 3R cannot be produced by recrystallization in a sulfur-deficient atmosphere.

Table 3. Typical molybdenite mineral associations, polytype contents, deposit types, and relative sulfidation states

Sample #	Location	Assemblage <sup>1</sup>	Deposit type	Polytype	Sulfidation State
26801	Bora, NSW, Australia	Q <sub>90</sub> Mo <sub>7</sub> Tour <sub>3</sub>	Pegmatite	2H <sub>1</sub>	---
10884	Alum Gulch, Nevada	Q <sub>90</sub> Mo <sub>5</sub> Marc <sub>5</sub>	Quartz vein	2H <sub>1</sub>	intermediate
N7604	Alpine Mine, Calif.	Py <sub>40</sub> Mo <sub>40</sub> Sch <sub>20</sub>	Tungsten skarn	2H <sub>1</sub>	low
Bm48	Brownstone Mine, Calif.	Mo-Cp-Py (dissem)	Tungsten skarn	2H <sub>1</sub>	intermediate
20561	Marble Bay, B.C.	Mo <sub>60</sub> Pyx <sub>48</sub> Py <sub>1</sub> Cp <sub>1</sub>	Cu-Mo skarn	95% 3R	intermediate
DDH-9-618	Larap, Philippines	Py <sub>40</sub> Mt <sub>45</sub> Mo <sub>5</sub>	Cu-Fe-Mo skarn	10% 3R	intermediate
SM-9	San Manuel, Az.	Q <sub>60</sub> Mo <sub>20</sub> Cp <sub>18</sub> Py <sub>2</sub>	Porphyry Copper	95% 3R	intermediate
JMS-S-1	Sierrita, Az.	Q <sub>60</sub> Mo <sub>30</sub> Cp <sub>8</sub> Py <sub>2</sub>	Porphyry Copper	2H <sub>1</sub>	intermediate
Ith-2	Ithica Peak, Az.	Q <sub>40</sub> Cc <sub>40</sub> Py <sub>15</sub> Mo <sub>5</sub> <sup>2</sup>	Porphyry Copper	2H <sub>1</sub>	intermediate
CX-2	Climax, Colo.	Q <sub>40</sub> Wolf <sub>20</sub> Mo <sub>20</sub> Py <sub>20</sub>	Porphyry Molybdenum	2H <sub>1</sub>	intermediate

<sup>1</sup>Mineral abbreviations: Co=chalcocite, Cp=chalcopyrite, Marc=marcasite, Mo=molybdenite, Mt=magnetite, Py=pyrite, Pyx=pyroxene, Q=quartz, Sch=scheelite, Tour=tourmaline, Wolf=wolframite.

<sup>2</sup>Cc is supergene in this sample.

## Discussion

Any discussion of polytypism in molybdenite must account for three observed facts: (1) 3R is unstable relative to 2H<sub>1</sub>; (2) despite this instability, 3R is commonly formed in nature; and (3) it is kinetically difficult to convert from 3R to 2H<sub>1</sub>. These facts are best discussed in light of the crystal chemistry of molybdenite.

### Structure-energetic reasons for polytypism

Examination of the geometry of the 3R and 2H<sub>1</sub> polytypes indicates that Mo ions in a given S-Mo-S layer can either be (1) directly above and below S ions in immediately adjacent layers, or (2) slightly offset. Bonding between layers should be stronger in case (1) where Mo ions are closest to adjacent-layer S

ions. The 2H<sub>1</sub> polytype is of configuration (1), while several theoretical polytypes not observed in nature or the laboratory have configuration (2). The 3R polytype has an intermediate geometry, in which a given Mo ion has an adjacent-layer S ion either directly above or directly below it, but not both. These configurations are illustrated in Figure 1.

Weaker layer-layer bonding in 3R than in 2H<sub>1</sub>, as indicated by layer geometries and Vickers hardnesses, makes 3R less stable than 2H<sub>1</sub>. The exciton spectra of molybdenites also indicates that the 2H<sub>1</sub> polytype is energetically stable relative to 3R (Wilson and Yoffe, 1969).

### Polytypism and growth mechanisms

There are strong indications that occurrence of the 3R polytype is not caused by an equilibrium mechanism, but rather by a growth phenomenon with a lack of subsequent re-equilibration. Zelikman *et al.* (1976) noted that there were differences in the growth mechanisms of 3R and 2H<sub>1</sub> molybdenite, but were unable to quantify these differences. However, by considering the differences in orientations of successive layers in MoS<sub>2</sub>, Jellinek (1963) concluded that 3R molybdenite would form by screw dislocation growth, whereas 2H<sub>1</sub> could not form by such a mechanism. In laboratory syntheses, molybdenite grown in an alkali-carbonate flux (a flux causes growth by addition onto screw dislocations, according to Elwell

Table 4. Electron microprobe analyses of selected molybdenite samples

Sample number	Location	# points analyzed	K <sub>Mo</sub> <sup>*</sup> X 10 <sup>2</sup>	K <sub>Re</sub> X 10 <sup>4</sup>	%3R
5059	Ely, Nevada	8	54.9 ± 0.3	2500 ± 500	95
20121	Cananea, Mexico	6	55.0 ± 0.3	not detected	0
20558	Marble Bay, B.C.	8	54.8 ± 0.3	750 ± 300	50
42034	Questa, N.M.	6	54.8 ± 0.3	not detected	0
N7604	Alpine Mine, Calif.	5	54.9 ± 0.3	not detected	0

\*K = (counts for sample/counts for metal standard) = concentration

Table 5. Structural and chemical parameters for  $MS_n$  layer compounds

Compound	M-S Coordination	Structure	M-S Bond Length ( $\text{\AA}$ )	Metal Electronegativity	Formal charge on metal
$MoS_2$	trigonal prismatic	layer	2.42	1.8	4+
$WS_2$	trigonal prismatic	layer	2.41	1.7	4+
$ReS_2$	distorted octahedral	layer	2.28 - 2.56	1.9	4+
$TiS_2$	octahedral	layer	2.43	1.5	4+
$SnS_2$	octahedral	layer	2.52	1.8	4+
$Bi_2S_3$	square prismatic	layered ribbons	2.56 - 3.05	1.9	3+

\*Data from Hulliger (1976) and Pauling (1960).

and Neale, 1971) is 3R, whereas molybdenite grown from melt without the flux is 2H<sub>1</sub> (Rode and Lebedev, 1961). Agarwal and Joseph (1974) used a sodium peroxide/potassium nitrate etch to show that screw dislocations were at the centers of growth spirals in synthetic 3R molybdenite; they were unable to confirm these results for natural 2H<sub>1</sub> molybdenite. Hulliger (1968) indicated that there were differences in the dislocation networks of the 3R and 2H<sub>1</sub> polytypes of molybdenite.

#### Polytypism and impurity content

The factors which give rise to screw dislocations in molybdenite will cause the formation of the 3R polytype. In the absence of strong mechanical stresses, the most likely cause is compositional impurity. In nature variations in impurity content are due to factors such as: (1) abundance of the impurity elements (e.g., Re, W, Sn) in the hydrothermal system, (2) availability of impurities with the correct oxidation/sulfidation states, and (3) sufficient insolubility of the impurity elements at the time of molybdenite deposition.

These factors can be illustrated for the elements Sn, Ti, Bi, W, and Re. All these elements form  $MS_n$  layer sulfides and are of approximately the correct size to fit into the molybdenite structure. Chemical and structural parameters are listed in Table 5 for these elements; the data indicate that none possesses the perfect size, charge, and/or electronegativity to fit into molybdenite without some strain. The amount of strain depends on the misfit of the element: a given amount of tungsten, for example, causes a good deal less strain than an equal amount of tin. Thus the level of impurity necessary to cause

sufficient strain for the formation of significant numbers of screw dislocations also depends on the element considered—there is no one set level of impurities above which 3R molybdenite is formed. Whatever these levels are, however, there are environments that will give rise to a concentration of each impurity in molybdenite, and these are frequently associated with the occurrence of 3R molybdenite.

3R molybdenite is associated with tin-bearing greisens at Lost River, Alaska; Altenberg, Saxony (Fron del and Wickman, 1970); Cinovec, Bohemia (Fron del and Wickman, 1970); and Rooiberg, South Africa (Mandarino and Gait, 1970). Semiquantitative spectral analysis of Cinovec molybdenite indicates the presence of several hundred ppm Sn (Kvacek and Trdlicka, 1970). At the Panasqueira, Portugal, tin-greisen early molybdenites are 3R, but those which have been recrystallized are 2H<sub>1</sub>.

Similarly, titanium-bearing molybdenites from high-titanium deposits have been reported. At Mont St. Hilaire, Quebec, 3R molybdenite is associated with the rare titanium minerals leucosphenite, narsarsukite, and ramsayite (Chao *et al.*, 1967). Molybdenite from a rare-metal-bearing carbonatite in East Siberia contains 2.00% Ti, 0.03% Nb, and 0.01% Zr (Somina, 1966).

Bismuth and bismuthinite are also associated with 3R molybdenite: at Whipstick, Kingsgate, and King Island, Australia (Ayres, 1974); the Pax Mine, Ontario, Canada (Mandarino and Gait, 1970), and Mt. Pleasant, New Brunswick, Canada (Petruk, 1964). At Mount Pleasant, molybdenite containing bismuth inclusions in greisen is 3R whereas molybdenite in sphalerite veins is 2H<sub>1</sub> (Petruk, 1964).



Most tungsten associated with molybdenite is in the tungstate form: wolframite and/or scheelite. This molybdenite is inevitably  $2H_1$ , unless there are high levels of other impurities. Molybdenite from Binnental, Switzerland, however, which is associated with several high-sulfur sulfosalts, contains 0.7% W and is 3R (Graeser, 1964). As Hsu (1977) has shown, tungstenite is stable only under very low  $f(O_2)$ /very high  $f(S_2)$  conditions. The general scarcity of tungsten in molybdenite, despite similar radii, electronegativities, etc., is due to this fact, and thus molybdenite from tungsten deposits rarely is 3R.

We have already seen that porphyry copper deposits are commonly associated with high rhenium levels and abundant 3R molybdenite. Due to the multi-stage nature of the porphyry copper system, however, in which temperature, pH, and other geochemical variables undergo significant changes with time, one cannot automatically assume that all such deposits are associated with abundant rhenium and 3R molybdenite. The second paper in this series on polytypism in molybdenite will deal with the particular characteristics of the porphyry copper system as it relates to changes in the rhenium content of molybdenite and appearance/persistence of the 3R polytype.

#### *Polytypism and recrystallization*

The importance of high-temperature recrystallization as a mechanism for conversion from 3R to  $2H_1$  molybdenite cannot be overstated. This mechanism is necessary because the S-Mo-S layers must be rotated as well as translated to convert one polytype to the other. The process of moving layers requires energy because there is significant bonding between layers. Further, the strongly-repelling S ions of adjacent layers are forced to come in close contact when layers are moved. Thus, the process of polytype interconversion requires far more energy than the simple displacive mechanisms characteristic of many polytypic conversions. The difficulty of 3R to  $2H_1$  conversion is further illustrated by the results of intercalation reactions, in which alkali-metal ions are chemically inserted between adjacent  $MoS_2$  layers. Somoano *et al.* (1973) observed that the intercalation of Rb or Cs ions into molybdenite at 70°C does not affect the symmetry—*i.e.* 3R remains 3R and  $2H_1$  remains  $2H_1$ —although the interlayer separation increases by more than 100%.

Thus, unless energy is available for the recrystallization process, 3R will be metastably maintained. The presence of impurities in molybdenite will also

hinder recrystallization, as pointed out earlier. Recrystallization *can* occur, however, and thus the presence of high levels of impurities does not *guarantee* the presence of 3R. What has been demonstrated in this paper is that the general trend to recrystallization is sufficiently hindered that a 3R/impurity relationship can be established. Part II of this series deals with the recrystallization process and how it affects 3R/impurity relationships.

#### Conclusions

Results of polytype determinations of 184 molybdenite-bearing specimens, trace- and major-element analyses of selected samples, detailed hand-specimen examination, and thorough literature review strongly suggest that the formation of 3R molybdenite in nature results from non-equilibrium growth processes, which in general are impurity-related. No correlation exists between the 3R polytype and sulfur fugacity of formation or stoichiometry of the molybdenite as seen from depositional environments, local sulfide assemblages, and major-element analyses. Strong evidence suggests that molybdenite samples containing more than about 500 ppm impurities contain some of the 3R polytype.

A geometrical treatment of bonding in molybdenum sulfide indicates that the 3R polytype is unstable relative to the  $2H_1$  polytype and that there are energetic barriers to interconversion. However, the structure of 3R makes it the kinetically favored phase when molybdenite crystals grow by a screw-dislocation mechanism. Such growth in nature can be caused by strains induced by high impurity contents in the growing crystals; in particular, the elements Re, Ti, Sn, Bi, W, and Fe occur in anomalous amounts in 3R molybdenite. As different natural hydrothermal systems will tend to concentrate different impurity elements in different ways, no generalizations can be made about the specific environments of deposition of 3R molybdenite.

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