

## Rhenium behavior in molybdenite in hypogene and near-surface environments: Implications for Re-Os geochronometry

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**Abstract**—Rhenium is concentrated mainly in molybdenite ( $\text{MoS}_2$ ) and occurs as a major cation in only a few rare minerals. This affinity makes molybdenite an ideal mineral for Re-Os geochronometry, but research on the behavior of Re in molybdenite is limited. Infrared microscope, XRD, back-scattered electron (BSE), and microprobe techniques have been used in this study to document Re behavior in molybdenite affected by hypogene and near-surface processes. In the hypogene environment, both 3R and 2H molybdenite can experience Re loss during hydrothermal alteration, which also causes increased infrared transparency (IR). Alteration at temperatures as low as  $\sim 150^\circ\text{C}$  can cause Re loss in the presence of advecting fluids, and will affect Re-Os dating if it occurs long after primary mineralization. Re loss in 3R and 2H molybdenite under supergene conditions does not increase IR transparency. Rhenium is not incorporated into supergene ferrimolybdate, but is enriched in K-Al-silicate intergrowths which may be illite(?). These minute intergrowths are present in several samples and would not be detected in a simple optical examination. In the supergene environment elemental Os is stable, whereas Re is not. Rhenium in molybdenite may be removed by supergene fluids after some has decayed to  $^{187}\text{Os}$ , causing erroneously old ages, or it may be adsorbed into the illite intergrowths, creating ages which are too young. In the weathering environment, Proterozoic molybdenites have altered to Re-enriched powellite, which can be detected using back-scattered electron imagery. Combined microprobe, XRD, BSE, and infrared microscopy can be successfully used to detect alteration in molybdenite prior to dating. These techniques are non-destructive and should be performed before any molybdenite is dated by the Re-Os system.

### INTRODUCTION

MOLYBDENITE ( $\text{MoS}_2$ ) IS THE MAJOR source of Re, and as a dominant cation Re occurs in only a few rare minerals (SARP et al., 1981; EKSTRÖM and HÅLENIUS, 1982; VOLBORTH, 1985; MITCHELL et al., 1989; GABELMAN, 1990; TARKIAN et al., 1991). In spite of this affinity, past studies have produced limited and sometimes contradictory results regarding the distribution of Re in molybdenite (RILEY, 1967; MORGAN et al., 1968; GILES and SCHILLING, 1972; NEWBERRY, 1979a,b; FILIMONOVA et al., 1984; ISHIHARA, 1988). Molybdenite is a hexagonal disulfide mineral with  $\text{Mo}^{+4}$  octahedrally coordinated by  $\text{S}^{-2}$ . Six-fold coordination in molybdenite is distorted to a prismatic rather than octahedral form, and continuous Mo-S layers stack one above another in simple sequence (WILSON and YOFFE, 1969). The two polytypes, 2H and 3R, differ in the manner of stacking in the c unit cell direction, in which c for 3R is  $1.5 \cdot (c)$  for 2H (Fig. 1). The 3R polytype is less common and is believed to form by screw dislocation, caused by the substitution of ions with ionic radii nearly similar to Mo (ZELIKMAN et al., 1969; NEWBERRY, 1979a; WATANABE and SOEDA, 1981; FILIMONOVA et al., 1984). NEWBERRY (1979a,b) found a positive correlation between polytype abundance and Re concentration in molybdenites. In 3R-Re space, he divided molybdenites into four regions representing crystallization and alteration environments (Fig. 2a). Region 1 represents low-Re 2H molybdenites crystallized in veins dominated by K-feldspar and quartz and with K-feldspar alteration selvages (A-veinlets). Region 2 represents high-Re 2H molybdenites crystallized with quartz in veins dominated by sulfides and

sericitic selvages (D-veins). Region 3 contains mixed polytype molybdenite with high Re associated with prograde skarns and quartz-dominant veins without alteration selvages (B-veins). NEWBERRY (1979b) also proposed that recrystallization of high 3R molybdenite to 2H molybdenite could occur at high temperatures with some loss of Re, as indicated by the left-pointing arrow in Fig. 2a. This process may not be tenable, based on results presented in this study. The fourth region contains molybdenites altered by supergene fluids which can remove Re without altering polytype structure (Fig. 2a). In this study, samples from porphyry deposits are dominantly quartz-molybdenite veins with no alteration selvages except when otherwise noted.

The potential application of molybdenite as a geochronometer in the Re-Os isotopic system has been recognized for nearly forty years, but dating attempts have been sporadic and produced mixed results (Fig. 3; HERR and MERZ, 1955, 1958; HIRT et al., 1963; LUCK and ALLÈGRE, 1982; LUCK et al., 1983; ISHIHARA et al., 1989). Rhenium loss rather than Os addition may account for the poor results, and if it is possible to document postcrystallization loss of Re in molybdenite, then samples suitable for dating can be selected. This study is an attempt to document the behavior of Re in molybdenite by applying microprobe, BSE, XRD, and infrared microscope techniques to molybdenite samples from a variety of geologically well-constrained settings. The samples are from base metal porphyry deposits, pegmatites, and skarns which have been exposed to processes active in hypogene, supergene, and weathering environments. These processes produce discernable effects in molybdenite, which can be detected prior to dating by the Re-Os method. All data collected

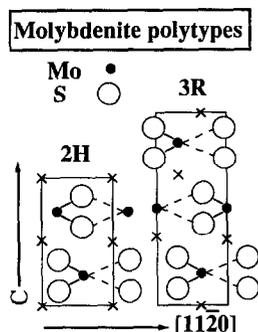


FIG. 1. Crystal structure of molybdenite polytypes 2H and 3R (after WILSON and YOFFE, 1969).

during this study are compiled in Table 1, and a summary of locations and results is listed in the Appendix.

#### ANALYTICAL TECHNIQUES

##### Polytype Abundance

Polytype abundance was determined by X-ray diffraction (XRD) using the technique of FRONDEL and WICKMAN (1970). Molybdenite was scraped from samples to produce a powder of flakes  $\sim 0.2$  mm in diameter. To avoid orientation of the molybdenite, the powder was sprinkled onto double-stick cellophane tape attached to a  $50 \times 50 \times 4$  mm glass slide. The powders were scanned on a Siemens D-500 X-ray diffractometer using  $\text{CuK}\alpha$  radiation. Scans were from  $25$ – $60^\circ 2\theta$  at a rate of  $1^\circ 2\theta \text{ min}^{-1}$  and count rate of  $10^3 \text{ sec}^{-1}$ . Theoretical modeling of WICKMAN and SMITH (1970) allowed FRONDEL and WICKMAN (1970) to demonstrate that naturally occurring polytypes of molybdenite have distinct XRD patterns with respect to  $2\theta$ . In mixed polytype molybdenite, the relative heights of the major 3R and 2H peaks are a function of the dominant polytype present (FRONDEL and WICKMAN, 1970). Using this relation and the XRD patterns of molybdenites reported by FRONDEL and WICKMAN (1970), polytype compositions for the molybdenites of this study are determined and reported as percentage of 3R present (%3R) in Table 1.

##### Rhenium Concentration by Microprobe

Molybdenite flakes were selected from the XRD slides and remounted so that smooth cleavage surfaces were face up on the mount and parallel to the mount surface. The molybdenites were C-coated and analyzed on a Cameca SX-50 electron microprobe. Del Norte troilite was used for S, and metal foil for Mo, W, and Re standards. Matrix effects were corrected using ZAF. Counting times for Mo and S were 10 seconds with 10 seconds background counting. Molybdenum was analyzed on a PET crystal using the  $L\alpha$  line, with backgrounds adjusted to avoid interferences from S  $K\alpha$  lines. Sulfur was analyzed on PET using the  $K\alpha$  line with backgrounds adjusted to avoid interference from Mo  $L\alpha$  lines. Rhenium was measured on TIAP using the  $M\alpha$  line. Rhenium and tungsten counting times were 30 sec with 30 sec background counting time. This ensured a lower detection limit of 0.01 wt% for Re, with  $0.01 \text{ wt}\% 2\sigma$ . An average of five grains from each sample were analyzed, and the average for each sample is reported in Table 1. Tungsten concentrations were below detection limits in most cases and are not reported. Our measured Re concentrations in some cases are higher than previously reported for molybdenites from the same locality (FLEISCHER, 1959, 1960; GILES and SCHILLING, 1972; KOSKI, 1981) and plot above the primary crystallization fields of NEWBERRY (1979b; Fig. 2b). To confirm that the measured Re concentrations are real and not an artifact of mounting or analytical methods, high and low Re molybdenite samples were mounted in epoxy on glass slides and carefully polished. Identical points were analyzed on microprobes located at the universities of Arizona and Cape Town using different standards. Mea-

sured Re values from the two probes are virtually indistinguishable. However, the random points selected in both molybdenites do show greater within-sample variations than can be accounted for by counting statistics. In this study, an average of five random points is taken to represent the average Re concentration of a molybdenite. Results suggest that Re estimated in this manner is generally comparable to concentrations determined by isotope dilution. The standard deviation reported for samples in Table 1 reflects the real variation of Re in molybdenite and is not based on counting statistics.

##### Infrared Transparency

The same molybdenite flakes analyzed on the microprobe were examined for infrared transparency (IR) using a Research Devices model F infrared microscope with a wavelength range from  $0.8$ – $1.2 \mu\text{m}$  (CAMPBELL et al., 1984). The band gap for molybdenite indicates that it should be near-opaque to infrared light and have variable IR transparency (SHUEY, 1975; CAMPBELL et al., 1984). Samples were examined to determine if the variable transparency is related to heterogeneous Re distribution, as the IR transparency of many minerals is apparently dependent on trace element concentrations (CAMPBELL, 1991). IR transparency is qualitatively rated on a scale from 1 to 4, with transparent IR = 1 and opaque IR = 4 (Fig. 3a–d). IR is sensitive to sample thickness, and results are based on grains with an approximate thickness of 0.2 mm. Individual molybdenite grains are also variable in transparency, and so the IR transparency of each grain in the sample is averaged. For each sample, the IR transparencies of

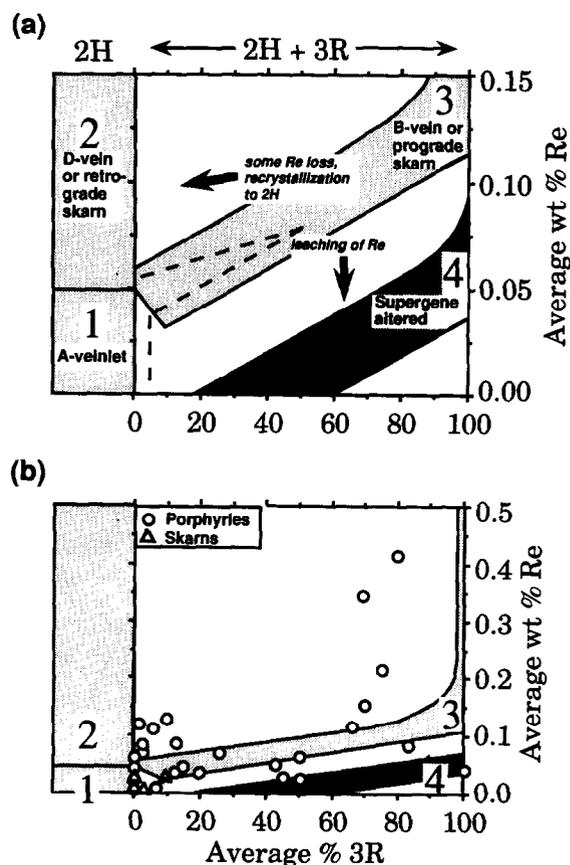


FIG. 2. (a) Polytype abundance vs. Re diagram of NEWBERRY (1979b), showing the three regions of molybdenite crystallization (light stipple), and alteration (dark stipple). Alteration processes are indicated in italics with direction of change indicated by arrows. See text for details. Dashed line encloses region of original database of NEWBERRY (1979b). (b) The same regions in (a), now compressed along the vertical axis to account for the higher Re content in molybdenites of this study.

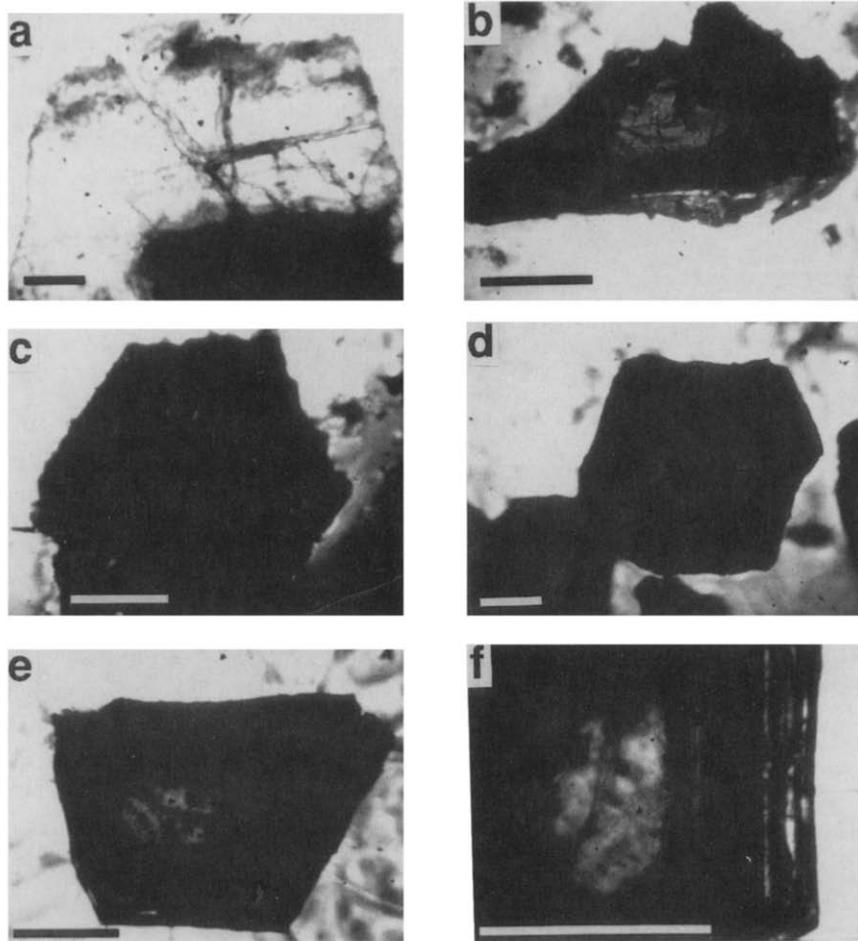


FIG. 3. Infrared microscopy images of molybdenites showing range in transparency and zoning. (a) 29GRVB, Gravelotte, South Africa, IR = 1; (b) 98LL, Lorelei, South Africa, IR = 2; (c) 81KAL, San Manuel, Arizona, IR = 3; (d) 5CACC, Copper Creek Arizona, IR = 4; (e) 78MAR, Maria, Mexico, IR = 3 with apparent zoning along crystal edge. (f) close-up of edge in (e). Scale bars are 0.25 mm.

all grains measured are averaged, and this value is listed in Table 1. Infrared banding in one sample (78MAR; Fig. 3e,f) showed no correspondence with Re concentration. Increased IR transparency does seem to correlate with alteration of molybdenite, however, as is presented in the following section.

#### Rhenium and Osmium Concentrations by ICP-MS

Rhenium and osmium concentrations in selected molybdenites were determined using isotope dilution. The samples were treated by alkaline fusion with distillation of Os after the technique of MORGAN and WALKER (1989). The Os distillate and an aliquot of the Re-bearing residual solution were analyzed on a TS-Sola ICP-MS. Analytical uncertainty on the instrument is much better than 1%.  $^{185}\text{Re}$ -enriched metal was used as a Re spike. Natural Os served for the Os spike because analysis of unspiked molybdenites indicated that only  $^{187}\text{Os}$  is present.

#### HYPOGENE ENVIRONMENTS: MOLYBDENITE FORMATION AND ALTERATION

In the hypogene environment sulfide minerals are precipitated and concentrated by circulating solutions associated with a thermal event, usually an intrusion, at depths of 1–10 km (LINDGREN, 1933; TITLEY, 1982). Alteration of the

intrusion occurs in concert with sulfide mineralization, which in porphyry deposits produces mineral assemblages specific to certain  $P$ - $T$ - $x$  conditions. Potassic alteration (orthoclase + biotite + quartz) is usually associated with molybdenite + chalcopyrite mineralization and occurs near the center of the intrusive stock. Phyllic/argillic alteration (sericite + biotite + clays) occurs peripheral to potassic alteration, but can overprint potassic alteration. Propylitic alteration (chlorite + epidote + calcite) is peripheral to phyllic/argillic alteration and represents the waning stages of alteration in a porphyry system (TITLEY, 1982). These alteration assemblages form over a temperature range of  $T \approx 500$ – $150^\circ\text{C}$ , which in this study is considered high-temperature alteration. The type and timing of fluid interaction with the molybdenites in the hypogene environment is based on the association of these alteration assemblages with our samples.

#### Porphyry Base Metal Deposits

##### *Copper Creek, Arizona, USA*

Molybdenites from porphyry base-metal deposits are plotted in Fig. 4 in the regions for molybdenites from similar

Table 1. Average composition, polytype, and infrared transparency values for molybdenites of this study. Element values are in weight percent, with standard deviation listed. Polytype abundance reported in percentage of 3R polytype. See Appendix 1 for location and sample descriptions.

Sample	Mo	S	Re	Total	%3R	IR	Sample	Mo	S	Re	Total	%3R	IR
<b>PORPHYRY DEPOSITS</b>													
<b>American Eagle, AZ</b>													
60CCAEA	60.2	0.67	40.8	0.33	0.08	0.04	101.1	83	3.3				
60CCAEB	59.0	0.57	40.2	0.62	0.35	0.35	99.6	69	4.0				
<b>Ajo, AZ</b>													
54AJ03	59.2	0.40	40.1	0.96	0.07	0.06	99.4	50	2.0				
<b>Bagdad, AZ</b>													
34BAGI	59.9	0.12	40.8	0.13	0.05	0.01	100.8	0	4.0				
34BAGE	59.9	0.30	40.5	0.57	0.04	0.05	100.4	13	3.1				
<b>Bingham, UT</b>													
30QMA23	60.0	0.60	40.3	0.27	0.07	0.05	100.4	25	3.9				
56B	59.6	0.85	40.2	0.45	0.04	0.03	99.8	0	4.0				
57B	60.1	0.80	39.9	0.86	0.04	0.03	100.0	0	3.8				
<b>Christmas, AZ</b>													
8XMAS	59.7	0.75	40.1	0.61	0.21	0.13	100.0	75	2.0				
<b>Copper Creek, AZ</b>													
1CACC	59.1	0.13	40.8	0.28	0.12	0.07	100.0	66	4.0				
6CCJG	59.5	0.30	40.0	0.35	0.42	0.18	99.9	80	3.5				
5CACC	59.7	0.82	40.4	0.52	0.15	0.15	100.3	70	4.0				
<b>Diamond Joe, AZ</b>													
7DJLV	59.3	0.83	40.6	0.19	0.02	0.01	99.9	0	4.0				
<b>Ely, NV</b>													
66ELYS	59.0	0.70	40.3	0.47	0.10	0.02	99.4	7	2.5				
<b>Henderson, CO</b>													
50HNBK	59.0	1.48	41.0	0.24	0.01	0.01	100.0	7	4.0				
75HEN	60.0	0.39	40.7	0.15	0.01	0.01	100.7	0	3.5				
<b>Lorelei, Namibia</b>													
98LL	59.5	0.55	40.6	0.20	0.04	0.03	100.1	100	2.9				
<b>Maria, Mexico</b>													
48MARF	59.6	0.99	40.2	0.30	0.04	0.05	99.8	0	3.5				
55MARI	59.5	0.59	40.8	0.72	0.01	0.01	100.3	0	3.5				
55MARE	59.3	0.90	40.2	0.73	0.05	0.10	99.6	0	3.4				
78MAR	59.1	0.52	40.8	0.44	0.02	0.01	99.9	0	3.5				
<b>Mineral Park, AZ</b>													
127MP8	60.1	0.72	39.6	0.28	0.01	0.01	99.9	0	2.6				
2MPJL	59.2	0.41	40.7	0.47	0.02	0.02	99.9	0	3.0				
<b>Morenci, AZ</b>													
88MOR	59.5	0.68	40.5	0.77	0.01	0.01	100.0	6	3.6				
89MOR	59.9	0.36	40.7	0.18	0.03	0.00	100.6	0	3.0				
91MOR	59.6	0.82	40.5	0.59	0.06	0.05	100.2	0	3.3				
94MOR	59.7	0.11	40.4	0.38	0.41	0.38	100.5	85	3.7				
95MOR	59.4	0.58	40.3	0.77	0.06	0.05	99.8	13	3.5				
<b>Quartz, NM</b>													
115QUI	59.5	0.05	41.3	0.15	0.02	0.01	100.8	0	3.0				
<b>PORPHYRY DEPOSITS</b>													
<b>Ray, AZ</b>													
128RY4	59.7	0.40	39.7	0.36	0.06	0.04	99.5	43	3.0				
<b>San Manuel, AZ</b>													
81KAL	59.4	0.38	40.7	0.52	0.08	0.02	100.2	2	3.0				
84KAL	59.7	1.16	40.6	0.21	0.03	0.02	100.3	0	2.5				
99SAN	58.9	0.28	40.4	0.42	0.12	0.15	99.4	2	3.0				
100SAN	59.5	0.06	40.5	0.32	0.07	0.04	100.1	2	3.0				
<b>Santa Rita, NM</b>													
3CHN1	59.7	0.31	40.1	0.51	0.11	0.10	99.9	6	3.9				
4CHN3	58.9	0.85	40.0	0.49	0.05	0.04	99.0	15	2.5				
<b>Sierrita, AZ</b>													
130SIE	59.5	0.67	40.1	0.16	0.02	0.01	99.6	50	3.3				
<b>Silver Bell, AZ</b>													
32SBI	59.5	0.69	40.2	0.40	0.13	0.02	99.8	10	4.0				
43SBT	59.6	2.54	41.2	0.59	0.00	0.00	100.8	0	4.5				
45SBT	59.5	0.68	40.1	0.54	0.04	0.03	99.6	20	4.0				
47SBH	59.4	0.62	39.9	0.27	0.02	0.02	99.3	0	4.0				
<b>Squaw Peak, AZ</b>													
129SP3	59.6	0.35	39.6	0.31	0.02	0.01	99.2	45	2.3				
<b>SKARNS</b>													
<b>Gold, Acres, NV</b>													
35GAIP	59.7	0.70	40.4	0.25	0.02	0.01	100.1	0	2.8				
<b>Mission, AZ</b>													
97MIS	60.6	0.35	39.5	1.65	0.04	0.01	100.1	0	4.0				
<b>San Martin, Mexico</b>													
61PKM	59.0	0.96	40.1	0.39	0.01	0.01	99.1	0	4.0				
<b>Silver Bell, AZ</b>													
36SBCJ	59.2	0.44	40.2	0.36	0.03	0.02	99.4	11	4.0				
<b>Star, NV</b>													
72STM	59.5	0.47	40.7	0.39	0.00	0.00	100.2	5	3.5				
73STM	58.8	0.18	40.5	0.74	0.01	0.01	99.3	0	4.0				
<b>PEGMATITES</b>													
<b>Gravelotte, South Africa</b>													
29GRVAI	59.3	0.14	40.8	0.16	0.03	0.02	100.1	0	3.0				
29GRVAE	60.2	0.09	40.2	0.48	0.02	0.02	100.4	0	3.0				
29GRVB	59.6	0.54	40.5	0.07	0.00	0.00	100.1	0	2.0				
<b>Xamchab, South Africa</b>													
28XAMI	59.5	0.41	40.0	0.25	0.14	0.06	99.6	-	2.0				
28XAME	60.2	0.60	40.2	0.33	0.16	0.04	100.6	-	2.0				
37XAME	59.6	0.46	40.4	0.39	0.07	0.04	100.0	44	2.0				
37XAMI	60.3	0.88	40.2	0.12	0.18	0.07	100.7	35	4.0				

- = not determined

deposits defined by NEWBERRY (1979b). The best constrained 3R molybdenites from a primary environment are from the Copper Creek deposit, a shallowly emplaced base metal porphyry associated with a short-lived pulse of hydrothermal alteration (Fig. 4a; GUTHRIE and MOORE, 1978; J. D. Guthrie, pers. commun., 1991). Molybdenites from breccia pipes at Copper Creek are believed to represent primary crystallization molybdenites which have experienced neither subsequent high-temperature nor supergene alteration. Infrared transparency is  $>3.5$  in all cases, and both Re content and 3R correlate positively (Table 1; Figs. 3d,4a). In some large individual crystals Re-rich zones were detected. X-ray imaging of a single crystal 6 mm in diameter revealed a 0.15 mm<sup>2</sup> area with an average of 0.49 wt% Re vs. 0.32 wt% for the region surrounding it (Fig. 5a,b). The Re-enhanced region is small relative to the whole crystal, comprising only 0.53% of the total surface area scanned.

#### American Eagle, Arizona, USA

The hypogene core of the porphyry system at Copper Creek is 800 m below the surface in the American Eagle Basin (J. D. Guthrie, pers. commun., 1990). Two aggregates of

molybdenite in separate quartz veins about 8 cm apart have high average 3R values of 69% and 83%, but for the latter, Re content is much lower at 0.08 vs. 0.35 wt% (Table 1; Fig. 4a). The Re-depleted aggregate also has calcite in the vein and intergrown with the molybdenite. Calcite in porphyry deposits is usually associated with propylitic alteration, which postdates molybdenite mineralization. The high-Re aggregate has IR = 4.0 vs. IR = 3.3 in the Re-depleted aggregate. It is possible that the molybdenite which is Re-depleted may have been accessed by late-stage hydrothermal fluids which removed Re and increased IR transparency, without affecting polytype structure. Rhenium appears to have been incorporated or absorbed into the calcite intergrowths, with 5.45 wt% Re present.

#### Christmas and Ajo, Arizona, USA

Evidence for high-temperature alteration of molybdenite is indicated for samples from the Christmas and Ajo deposits, which were also collected from the hypogene cores of their respective porphyry systems. The Ajo and Christmas samples fall in the high 3R, high-Re trend (Fig. 4a), but have IR = 2 (Figs. 4a,6a-c). Geological evidence suggests that later,

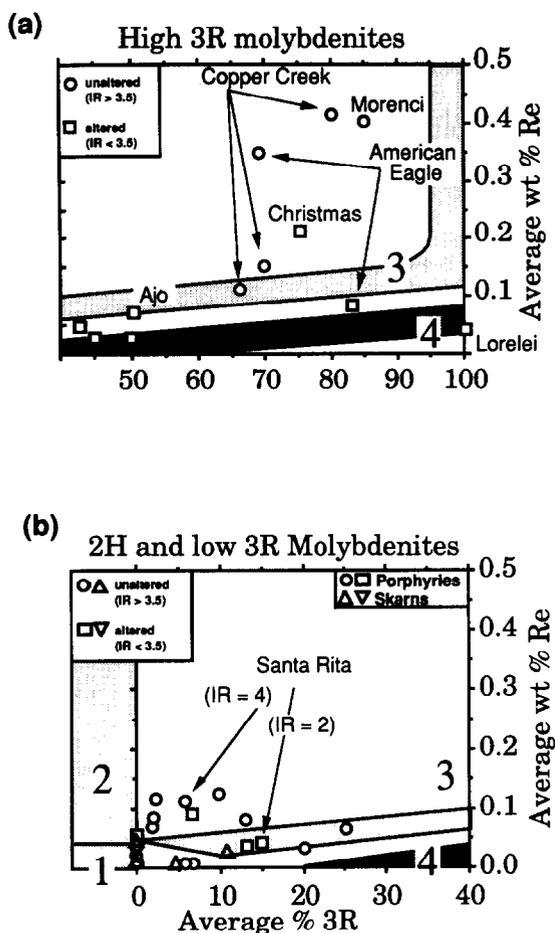


FIG. 4. Polytype abundance vs. Re content, divided into (a) high 3R and (b) low 3R or 2H groups. Shaded areas are the same as in Fig. 2.

high-temperature events have affected the molybdenites. Basic dikes are present in the pit at Christmas and are 25.5 Ma old (MCKEE and KOSKI, 1981; KOSKI and COOK, 1982), in contrast to the 62 Ma old stock which is responsible for mineralization (CREASEY and KISTLER, 1962). At the Ajo mine, the 63 Ma mineralizing stock was intruded by a granite stock 21 Ma ago (HAGSTRUM et al., 1987). The molybdenite at Ajo is from the northwestern margin of the older stock, which has been affected by temperatures in excess of 300°C, as indicated by reset K-Ar ages and paleomagnetic orientations (HAGSTRUM et al., 1987). It is possible that fluids associated with these later high  $T$  events at Christmas and Ajo have caused Re loss and increased IR transparency, without significantly modifying polytype.

#### *Santa Rita, New Mexico, USA*

High-temperature alteration is also proposed for 2H molybdenite from Santa Rita. Stockwork molybdenite + chalcopyrite mineralization associated with potassic alteration has in some areas been overprinted by later phyllic/argillic alteration (NIELSEN, 1968). Two molybdenite + quartz veins were sampled from the potassically altered center of the deposit, with one bearing the phyllic/argillic overprint. The

molybdenites are roughly identical in polytype abundance, but differ by a factor of 2 in Re content (Fig. 4b). The samples are about 250 m apart and differ only by the presence of the phyllic/argillic overprint in the low-Re sample. This sample also has a lower IR transparency (IR = 2 vs. 4; Fig. 6e,f), which suggests that the later high-temperature fluids which produced the overprint may have also removed Re and increased transparency.

#### *Bagdad, Arizona, USA*

Mineralization at Bagdad is associated with a quartz-monzonite intrusion into Proterozoic granite and metasediments, with molybdenite + chalcopyrite + quartz veins up to 8 cm in thickness (MEDHI, 1978; J. Hawley, pers. comm., 1991). In a molybdenite + quartz vein 25 mm thick from the hypogene zone of the deposit, 3R polytype is higher at the edge of the vein (13% vs. 0% 3R), but Re values are lower (0.04 vs. 0.05 wt% Re; Table 1; Appendix). A lower Re content for the higher 3R edge suggests that Re loss has occurred. Back-scattered electron (BSE) imagery of molybdenite from the edge of the vein revealed dark regions which have K, Al, and Si as major components detected in an energy dispersive spectra, and contain up to 0.14 wt% Re. The K-Al silicate mineral is possibly illite, analogous to illite intergrown with molybdenite at Questa, New Mexico, USA (CARPENTER, 1968). IR is also lower at the edge of the vein (IR = 3.1 vs. 4). The sample is from an area dominated by pervasive potassic alteration, but minor phyllic alteration may have developed cryptically along pre-existing vein structures. It is possible that Re loss was coupled with selective phyllic alteration at Bagdad, increasing transparency along the edge of the molybdenite vein. The illite(?) may also have formed at this time, as a product of alteration of muscovite or orthoclase inclusions in molybdenite. The occurrence is significant and suggests that Re lost from molybdenite may be taken up by intergrown K-Al silicate phases during alteration.

#### **Skarns**

Carbonate and calcareous pelitic host rocks undergo dramatic alteration to Ca-Mg-Fe-Al silicate assemblages in proximity to intrusions (EINAUDI and BURT, 1982). The skarn assemblages vary according to protolith, but can be separated into prograde or retrograde stages of skarn formation (NEWBERRY, 1979b). Rhenium depletion may occur in molybdenite associated with retrograde skarn development (NEWBERRY, 1979b). Five skarns were sampled in this study, and only one is associated with retrograde skarn development (Star, Table 1; Appendix). The molybdenites are largely 2H polytype, with 3R less than 11%. Molybdenites associated with Cu-Mo porphyries at Mission and Silver Bell, Arizona, USA, are higher in Re than the W-Mo skarn at Star, Nevada, USA, and the Cu-Zn-Ag skarn at San Martín, Mexico (Table 1). Higher Re in molybdenites from Cu-Mo skarns was also noted by NEWBERRY (1979b). At Gold Acres, Nevada, USA, a Cu-Mo skarn has been faulted and a later epithermal gold deposit has been superimposed on it, with fluid temperatures reaching 150–175°C (HAYS and FOO, 1991; NASH, 1972). Rhenium in the Gold Acres molybdenite is lower relative to the Mission and Silver Bell Cu-Mo skarns, and IR is signif-

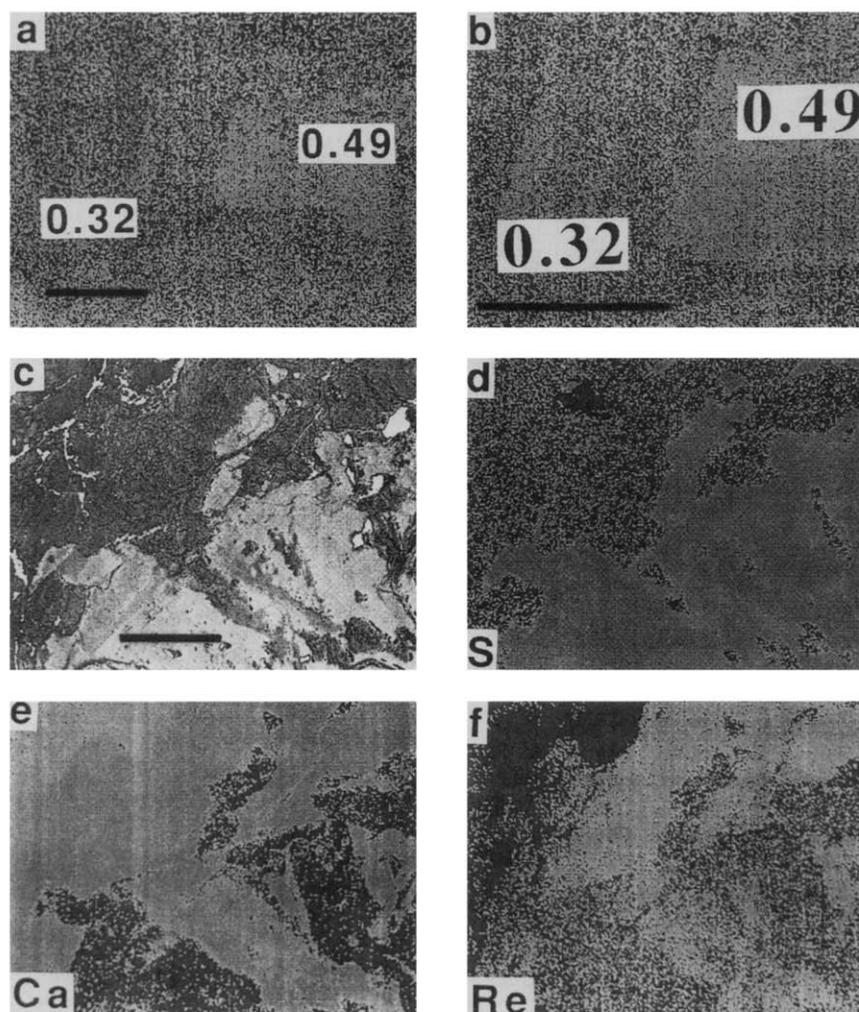


FIG. 5. (a,b) 6CCJG. Microprobe element map of 80% 3R molybdenite from Copper Creek showing high-Re zone (0.49 wt% Re) surrounded by molybdenite containing only 0.32 wt% Re. Higher Re indicated by a denser gray pattern. (c) 28XAM. Back-scattered electron image for molybdenite (light gray, lower right) with powellite (dark gray, upper left) alteration rim from Xamchab, South Africa. (d,e,f) Microprobe element maps of S, Ca, and Re concentration for same image as in (c). Dense gray areas indicate higher element abundance. Scale bars are 0.25 mm.

icantly lower (2.8 vs. 4; Fig. 6d; Table 1). The fluids which produced the epithermal gold deposit may have altered the molybdenite, lowering Re and increasing transparency.

#### NEAR-SURFACE ENVIRONMENTS AND MOLYBDENITE ALTERATION

##### The Supergene Zone

In sulfide-bearing rocks the near-surface environment consists of a coupled zone of dissolution in the weathering zone, and of precipitation in the supergene zone. In the supergene zone, sulfides oxidized during weathering release mobile components which percolate downward to form new minerals under ambient *P-T* but oxygen-poor conditions, usually near the water table (EMMONS, 1933; TITLEY, 1982; SATO, 1992). Molybdenite associated with supergene Cu-minerals was considered supergene molybdenite by NEWBERRY (1979a,b); this criteria was applied to samples from Silver Bell and Morenci, Arizona, USA.

##### Silver Bell, Arizona, USA

At Silver Bell, molybdenite was collected from the open pit in the supergene zone, and a single drill core provided samples from the transitional and hypogene zones (Fig. 7a). The transitional zone is defined by molybdenite plus both hypogene chalcopyrite and supergene chalcocite, and in the other zones either chalcocite or chalcopyrite dominates, as shown in Fig. 7a. All samples are in a monzonite stock (73–69 Ma; LIPMAN and SAWYER, 1985). A plot of Re concentration vs. depth for the molybdenites shows some apparent loss of Re from the supergene to transitional zone of the deposit. The 20% 3R molybdenite at ~100 m depth in the transitional zone should have more Re than the 10% 3R sample from 25 m, but is lower by a factor of three (0.04 vs. 0.13 wt% Re; Fig. 7a). For the 2H molybdenites, Re content is slightly lower in the transitional zone relative to the hypogene zone (Fig. 7a). There are also K-Al silicate patches in molybdenite, with Re increasing from 0.15 wt% in the

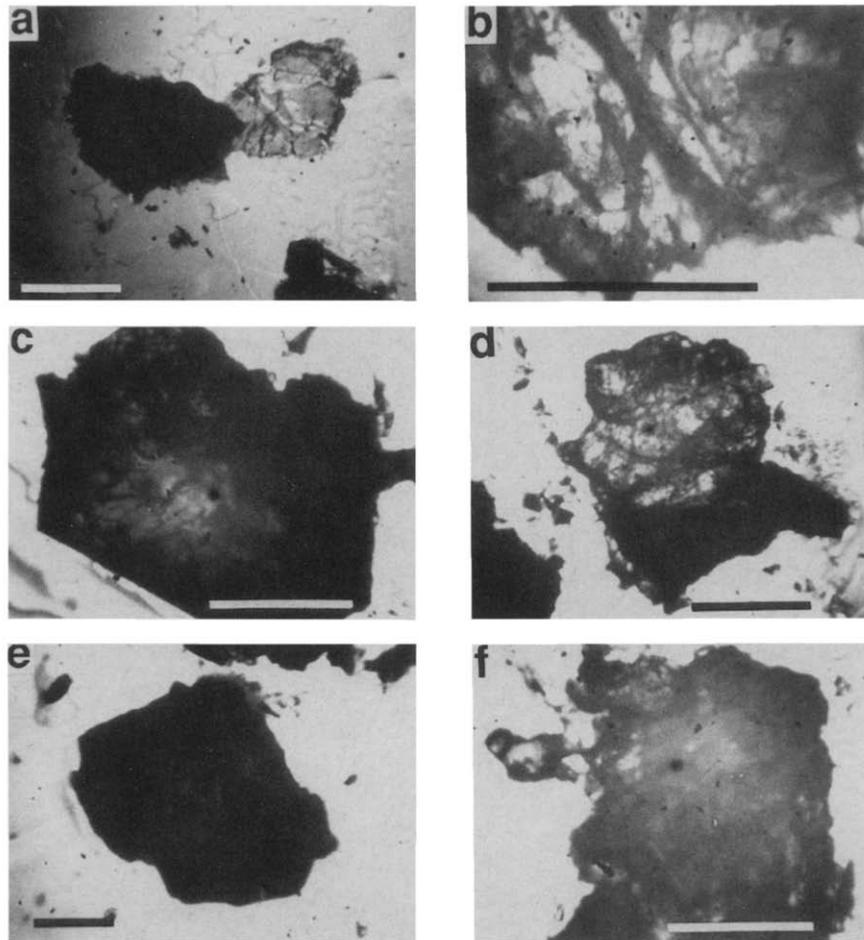


FIG. 6. Infrared microscopy images of molybdenites possibly altered by high-temperature fluids. (a,b) 8XMAS1, Christmas, Arizona, showing (a) IR = 1 and (b) IR = 2; (c) 54AJ03, Ajo, Arizona, IR = 2; (d) 35GAIP, Gold Acres, Nevada, IR = 2; (e) 3CHN1, Santa Rita, New Mexico, molybdenite from potassic zone with IR = 3.5; and (f) 4CHN3, from phyllically overprinted vein with IR = 2. Scale bars are 0.25 mm.

hypogene zone to 0.50 wt% in the transitional zone. This suggests that in the transitional zone, Re has been locally remobilized from molybdenite into the K-Al silicate intergrowths. K-Al silicates are absent in the 10% 3R molybdenite from the pit, suggesting that the phase never developed, or has been removed by supergene fluids. Significantly, IR for all samples is 4 regardless of location (Fig. 7a). The observations suggest that Re loss due to low-temperature supergene processes has occurred, but did not increase IR transparency.

#### *Morenci, Arizona, USA*

Molybdenite-quartz veins from the supergene and hypogene zones of mineralized Precambrian granite and two early Tertiary monzonite porphyry stocks were sampled. In the Precambrian granite, supergene molybdenite is higher in 3R but lower in Re relative to molybdenite from the hypogene zone (0.01 vs. 0.03 wt% Re; Fig. 7b). In the 58 Ma quartz monzonite stock, supergene molybdenite with 13% 3R is only slightly higher in Re than hypogene 2H molybdenite (0.08 vs. 0.06 wt% Re). Both cases suggest possible depletion of Re in the supergene samples. Molybdenite from the supergene

zone of the younger quartz monzonite porphyry is 85% 3R with 0.41 wt% Re (Figs. 4a,7b). In this sample, the molybdenite is completely surrounded by secondary chalcocite. A few Re-enriched K-Al silicate intergrowths in this sample suggest some alteration, but IR is unaffected (IR = 3.7). IR is less than 3.6 in the other samples and is in fact lower for molybdenites in the hypogene zone (Fig. 7b). As at Silver Bell, the results suggest that in the supergene zone, Re loss has occurred, but is not associated with increased IR transparency.

#### *Questa, New Mexico, USA*

At Questa, New Mexico, USA, much of the Mo is in the form of the supergene mineral ferrimolybdate ( $\text{Fe}_2(\text{MoO}_4)_3 \cdot n\text{H}_2\text{O}$ ; CARPENTER, 1968). High Fe/Mo ratios favor the formation of ferrimolybdate (TITLEY, 1963), and the abundance of pyrite at Questa provided Fe for widespread development of this supergene mineral (CARPENTER, 1968). Element mapping and analysis of 2H molybdenite with a ferrimolybdate and illite rim show that the ferrimolybdate contains no Re vs. 0.02 wt% Re in the molybdenite (Fig. 8;

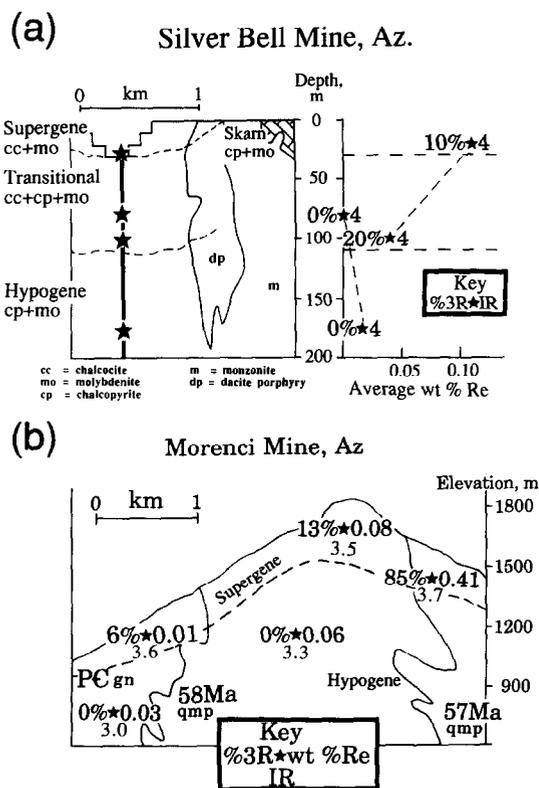


FIG. 7. (a) Schematic cross-section of monzonite, dacite porphyry, and skarn relationships at Silver Bell Mine with approximate boundaries for the supergene, transitional, and hypogene zones. Geology is after RICHARD and COURTRIGHT (1966), and zones are defined by base metal sulfide assemblages as indicated. Stars indicate sample locations from the pit and drill hole, and Re content with depth is shown on the right. IR and 3R values also listed as indicated in the key. (b) Schematic cross-section at Morenci showing hypogene mineralization and supergene enrichment in Precambrian granite (gn) and quartz monzonite stocks (qmp). Sample locations are stars, with 3R, Re content, and IR values as indicated in the key.

Tables 1,2). The absence of Re in supergene ferrimolybdenite has been observed elsewhere (MORACHEVSKII and NECHAEVA, 1960). Rhenium enhancement does occur in a K-Al silicate phase similar to that observed at Bagdad, Silver Bell, and Morenci, USA, which is revealed by element mapping (Fig. 8). Molybdenite at Questa described as "sooty" has been shown to be intimately mixed with illite (CARPENTER, 1968). It is assumed that the K-Al silicate phase in this sample is also illite. Rhenium content in the illite is an order of magnitude greater than in the molybdenite (0.21 wt% Re).

### Weathering Zone

Hypogene sulfides exposed to the weathering zone interact with oxidizing fluids which alter the minerals, and the components are either removed (to the supergene zone as in the previous case) or precipitate alteration products in situ from the primary phases (EMMONS, 1933). Rhenium loss from molybdenite in a non-advective weathering environment may be a subtle effect most detectable at the crystal edges. Large molybdenites from two Precambrian pegmatites and a Cu-

Mo porphyry were examined to evaluate Re loss from weathering.

### Gravelotte, South Africa

The albitite pegmatite at Gravelotte is at the contact between Archean tonalitic gneiss and talc-chlorite-biotite schists in the Murchison greenstone of northeastern South Africa. Molybdenite at this locality is associated with native bismuth, scheelite, and emerald (ROBB and ROBB, 1986). A single muscovite age of 2040 Ma from a pegmatite 35 km southeast of Gravelotte may or may not reflect the emplacement age of the Mo-bearing pegmatites (JAMIESON and SCHREINER, 1957; ROBB and ROBB, 1986). No significant weathering or enrichment zones exist at the mine. Two molybdenites 20–30 mm in diameter were large enough for average Re and polytype to be determined from the center and edge of the crystals. The samples are 2H, and the Re-depleted rim for one molybdenite is within uncertainty of the analyses (Fig. 9). Both the edge and interior have IR = 3, suggesting Re loss from some earlier high-temperature event. A second 2H molybdenite which contains no Re has an even lower IR value (IR = 2; Fig. 3a).

### Xamchab, South Africa

The pegmatites at Xamchab are in the Vioolsdrif leucogranite of  $1730 \pm 20$  Ma (REID, 1979) and contain molybdenite with scheelite and base metal sulfides (BOWLES, 1988). Molybdenite from this locality was dated by HERR and MERZ (1958), and gives an age of 1275 Ma ( $\lambda = 1.64 \cdot 10^{-11}$ ; LINDNER et al., 1989). The Vioolsdrif batholith is within the Namaqua mobile belt, which experienced metamorphism at 1100–1000 Ma, expressed by greenschist metamorphism in the region of Xamchab (REID, 1982; D. L. Reid, pers. commun., 1991). The core and rim of one slightly altered molybdenite 30 mm in diameter shows a large difference in both polytype and Re content from center to edge (Fig. 9). The edge is 44% 3R but has less Re than the 35% 3R center (0.07 vs. 0.18 wt% Re; Table 1). The molybdenite may have crystallized with a higher polytype and Re-rich edge which has since lost Re. The edge of the sample is significantly more transparent, with IR = 2 vs. 4 for the center. It is possible that some Re loss occurred during the 1100–1000 Ma metamorphic event, as well as from weathering. BSE and element mapping indicate that Re-enriched powellite ( $\text{Ca}(\text{Mo},\text{Re})\text{O}_4$ ) is present as an alteration product with 2.46–3.00 wt%  $\text{ReO}_3$  (Table 2). The boundaries between the molybdenite and powellite are fairly sharp, suggesting that high 3R, high-Re zones may have been selectively altered. A second molybdenite heavily rimmed by powellite also shows Re enrichment in the powellite (Fig. 5c–f). Probe traverses across the boundary between the powellite and molybdenite even in this heavily altered sample indicate that Re enhancement occurs within tens of microns (Fig. 10a,b). Rhenium loss from weathering is not diffuse from the center of the molybdenite to the molybdenite-powellite boundary; instead, specific high-Re zones or rims are preferentially altered. The molybdenite has IR = 2, which is a value expected for a high 3R molybdenite which has been altered by a later high-tem-

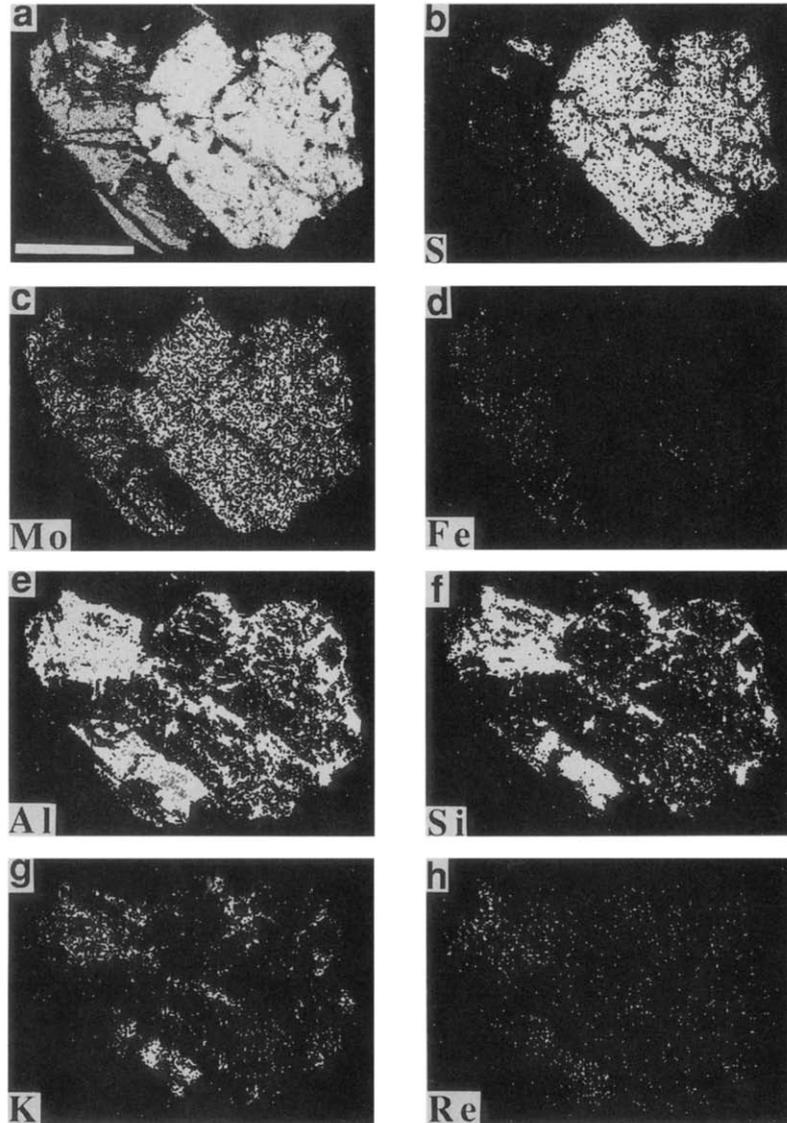


FIG. 8. (a) 115QU. Back-scattered electron image of molybdenite (white) altered to ferrimolybdenite (light gray) and illite(?) (dark gray) from Questa. Microprobe element maps for (b) S, (c) Mo, (d) Fe, (e) Al, (f) Si, (g) K, and (h) Re abundances. High concentrations indicated by white areas. Scale bar is 0.25 mm.

perature event. However, mixtures of molybdenite and powellite can increase transparency, as powellite is transparent to infrared radiation.

Table 2. Representative analyses of powellite and ferrimolybdenite alteration products of molybdenite. All values in weight percent.

	Xam-372	Xam-37	Xam-28	115Qu2
CaO	25.6	24.5	26.7	--
Fe <sub>2</sub> O <sub>3</sub>	--	--	--	25.2
MoO <sub>3</sub>	71.3	72.1	70.9	65.9
ReO <sub>3</sub>	3.00	2.46	2.77	0.00
Total	99.9	99.1	100.4	91.1*

Key: Xam-372, 37, 28, powellite in molybdenite 37XAM (Table 1); 115Qu2, ferrimolybdenite in molybdenite 115QU. -- = not determined; \*H<sub>2</sub>O content not determined.

#### *Lorelei Cu-Mo porphyry, Namibia*

The Lorelei porphyry Cu-Mo deposit in Namibia is part of the Haib volcanic group and has a primary crystallization age of 1960 Ma (REID, 1979; REID et al., 1987; VILJOEN et al., 1986). The molybdenite has been exposed to supergene alteration and the same metamorphic events as at Xamchab. It is 100% 3R, but very low in Re (0.04 wt% Re; Fig. 4a). IR is 2.9 (Fig. 3b), suggesting that early Re loss occurred during greenschist metamorphism as suggested at Xamchab, with further loss likely from supergene and weathering processes.

#### DISCUSSION

##### **Molybdenite in the Hypogene Environment**

In contrast to the prediction of NEWBERRY (1979b), high-temperature fluids appear to cause Re loss and increased

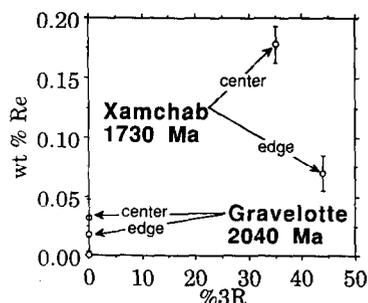


FIG. 9. Polytype-Re plot of large single molybdenite crystals from Precambrian pegmatites at Gravelotte and Xamchab, South Africa, with approximate ages for mineralization as indicated.

transparency in both 3R and 2H molybdenites without significantly changing polytype. The critical IR value is  $\sim 3.5$ ; molybdenites below this have probably experienced alteration from high-temperature fluids. In porphyry systems, fluids move largely along fractures, which are intermittently sealed off by precipitating minerals (TITLEY, 1982). Late-stage hydrothermal fluids can therefore remove Re from molybdenite in one vein, whereas molybdenite in a nearby vein may escape alteration because it is sealed. This may explain why quartz-molybdenite veins only centimeters apart from American Eagle differ greatly in IR and Re content. Similar late-stage phyllic/argillic alteration along vein edges at Bagdad produced Re-enriched K-Al silicate intergrowths in molybdenite, which are detectable only by BSE imagery. On a larger scale Re-depleted 2H molybdenite at Santa Rita occurs in late-stage phyllic/argillic alteration envelopes within the potassically altered hypogene core of the system. Molybdenite from the skarn at Gold Acres is more transparent than molybdenite from other Cu-Mo skarns and appears to have lost Re to fluids associated with later epithermal Au mineralization. These observations imply that Re loss can occur in fluids associated with phyllic/argillic to propylitic alteration, at temperatures as low as  $150^{\circ}\text{C}$ . Infrared microscopy, coupled with microprobe, BSE, and XRD analysis of molybdenites, can document Re loss from alteration associated with high-temperature thermal events.

#### Molybdenite in the Near-Surface Environment

Field and theoretical studies suggest that  $\text{MoS}_2$  should be unstable in supergene settings and that Re may be more mobile than Mo (VINOGRADOV, 1957a,b; TITLEY and ANTHONY, 1961). Some molybdenites in the supergene zone at Silver Bell and Morenci were Re-depleted relative to samples in the hypogene zone, but others appeared to be unaffected. As with the hypogene environment, supergene processes are also fracture-controlled (TITLEY, 1982), and some molybdenites may escape alteration due to restricted fluid access. This cannot explain the apparent stability of 3R molybdenite surrounded by supergene chalcocite at Morenci. At most base metal porphyry deposits, and in this study, the supergene zone is defined by the presence of chalcocite after chalcopyrite (NEWBERRY, 1979b). Theoretical studies suggest that conditions favorable for increased Cu solubility are not consanguinous with increased Mo solubility, so fluids which alter

chalcopyrite may not affect molybdenite (HANSULD, 1966). In Eh-pH space, this is supported by the observation that the lower limit of chalcocite stability just overlaps with the upper limits of  $\text{ReS}_2$  and  $\text{MoS}_2$  stability (Fig. 11a,b). Hence, fluids capable of altering chalcopyrite and precipitating chalcocite may be unreactive with molybdenite. An alternate possibility is that the metastable chalcocite + molybdenite assemblage exists because molybdenite alteration is hindered by a high activation energy barrier (SATO, 1992). High Fe/Mo ratios do produce favorable conditions for supergene alteration of molybdenite at Questa, and 2H molybdenite partially altered to ferrimolybdenite is low in Re and may have suffered some Re loss. Rhenium is not enriched in the ferrimolybdenite, but in a K-Al silicate phase. Rhenium can form insoluble rhenates in the presence of K which often absorb onto clays (BOYKO and MILLER, 1980). This observation, and the association of molybdenite with illite at Questa (CARPENTER, 1968), leads us to suspect that the K-Al-silicate phase detected at Questa, Bagdad, Morenci, and Silver Bell, USA, is illite. Molybdenites from the supergene zone are generally opaque with  $\text{IR} > 3.5$ , making infrared microscopy an ineffective means of detecting Re loss under these conditions.

In the weathering environment, a single molybdenite from Gravelotte appears to have slight Re depletion at the edge, though the difference relative to the interior of the crystal is within analytical error. Molybdenites from Gravelotte have

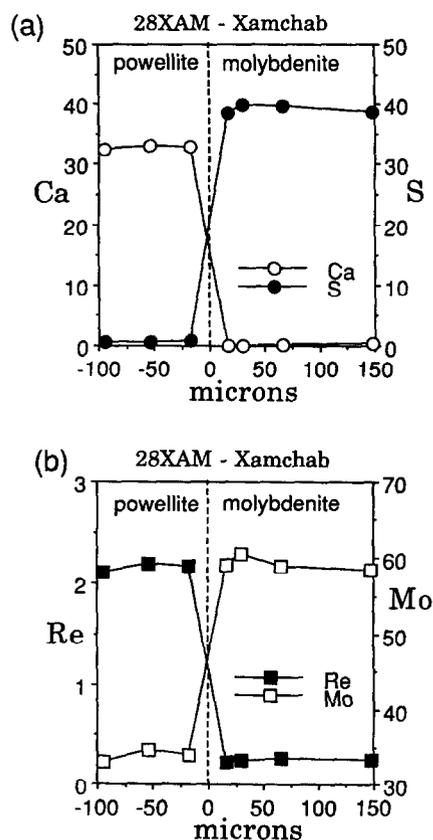


FIG. 10. 28XAM. Microprobe element traverses of (a) Ca, S, and (b) Mo, Re, across the molybdenite/powellite boundary in Fig. 5c. Note the absence of diffusion gradients. Values are in wt% of element.

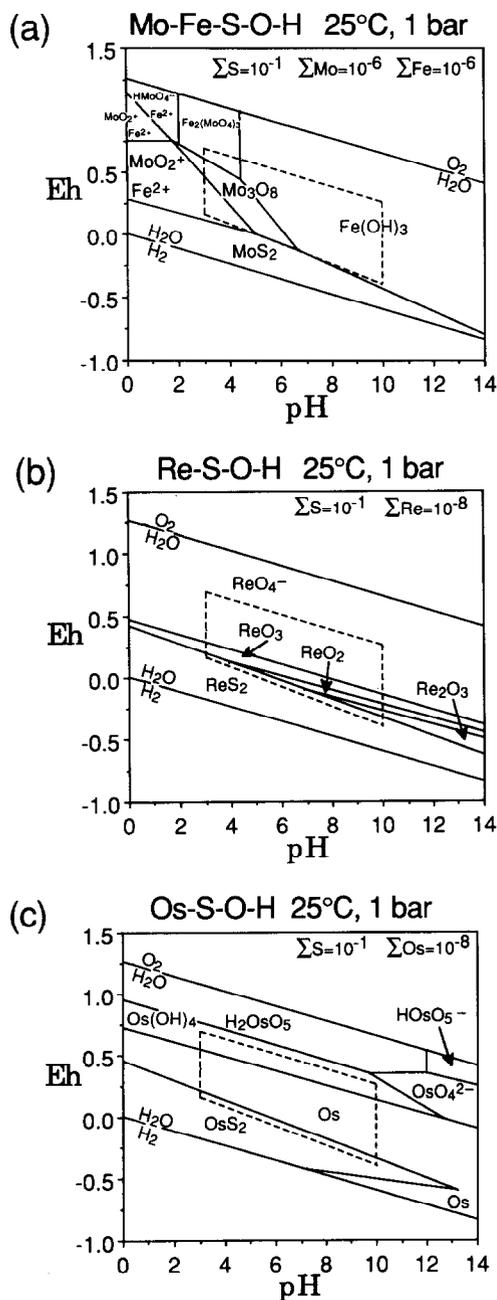


FIG. 11. Eh-pH diagram showing relationships of (a) Mo, (b) Re, and (c) Os species at 25°C and 1 bar. Data from TITLEY (1963); BROOKINS (1986, 1987). The weathering/supergene environment enclosed by the dashed line is defined using data from SATO (1960), with the lower boundary defined by the lower limit of chalcocite stability after GARRELS and CHRIST (1965;  $\Sigma Cu = 10^{-6}$ ).

IR < 3, and Re loss may be also associated with some high-temperature event. Weathering of molybdenites from Xamchab produced powellite which is Re enriched. The powellite may have preferentially formed from alteration of high 3R, Re-enriched zones in the molybdenites, as broad elemental diffusion zones between phases, are absent. The IR transparent edge of one crystal is depleted in Re relative to the interior. Fluids associated with later greenschist metamor-

phism may account for the increased transparency and Re depletion. A 100% 3R molybdenite from the Lorelei porphyry experienced the same metamorphic event and is also Re-depleted. All of these Precambrian settings have molybdenites with IR < 3.5. Since there is no correlation between Re loss and increased IR transparency in supergene environments, the increase must have occurred from some earlier thermal event. Initial Re loss likely occurred from this earlier event, with additional loss during weathering. The techniques applied here can therefore unravel the geologic history of some molybdenites prior to attempts to date them by Re-Os geochronometry.

**Implications for Re-Os Geochronometry**

*Re distribution during molybdenite crystallization*

This study has demonstrated that Re concentration is heterogeneous for molybdenites from hypogene environments. In extremely rare cases such as at Copper Creek, high-Re zones can be detected (Fig. 5a,b), but usually the variation is at the submicron scale. GILES and SCHILLING (1972) obtained microprobe analyses of a molybdenite in which Re varied from <200 ppm to several percent, with highs occurring as “spot maximums” within the molybdenite. Erratic concentrations from 0.25–4.00 wt% are also reported over a 100 μm traverse in a Re-rich molybdenite from Noril’sk (KOVALENKER et al., 1974), and microprobe analyses of molybdenite precipitates from volcanic gases also show Re variability in single crystals only tens of microns in size (BERNARD et al., 1990). This heterogeneous distribution pattern of Re in unaltered molybdenite lends support to the proposal that Re causes an increase in 3R polytype (NEWBERRY, 1979a). The difference in 3R and 2H molybdenite structure is rotation and translation of the S-Mo-S layers (Fig. 1). This means that a mixture of 2H and 3R polytypes in molybdenite is not ideal chemical substitution, but a physical mix of two minerals with significantly different mineral structures. The physical mixture is seen by the microprobe as Re-enriched zones and “spot maximums.” With respect to Re-Os geochronometry, this type of heterogeneity within a sample is not a problem as long as both polytypes in the molybdenite formed *contemporaneously*.

*Recrystallization and Re loss*

NEWBERRY (1979b) predicted that minor Re loss and recrystallization of 3R to 2H molybdenite under high-temperature conditions may form high-Re, 2H molybdenite (Fig. 2a). However, high-Re, 2H molybdenite was not encountered in this study. The difference in the ionic radius of Re<sup>+4</sup> compared to Mo<sup>+4</sup> (0.63 vs. 0.65 Å; Weunsch, 1977) leads to 3R polytype growth by screw dislocation (NEWBERRY, 1979a). Screw dislocations enhance crystal growth because ions forming the structure prefer to bond to the edge of the dislocation, rather than nucleate entirely new layers on a flat crystal surface. The smaller radii of Re<sup>+4</sup> ions relative to Mo<sup>+4</sup> form point defects about which screw dislocation growth can occur. Point defects are also the sites most prone to bond breaking in subsequent chemical reactions. Alteration will preferentially cause Re loss at these sites but may not convert 3R structure to 2H because significant energy is required to

rotate S-Mo-S layers. If sufficient energy is available, it is not likely that high-Re, 3R molybdenite will recrystallize to a high-Re, 2H polytype because Re present in solution would again be drawn to molybdenite and nucleate by screw dislocation. Only the advective removal of Re by hydrothermal fluids would allow 3R to recrystallize as 2H molybdenite. Thus, polytype transformation without Re loss (left-pointing arrow, Fig. 2a) is geochemically unreasonable. The results of this study suggest that Re loss occurs with little or no polytype transformation (downward-pointing arrow, Fig. 2a). Evaluating suitable molybdenites for dating based solely on the diagram of NEWBERRY (1979b; Fig. 2a), a possibility alluded to in previous dating attempts (LUCK and ALLÈGRE, 1982; ISHIHARA et al., 1989), is ineffective for these reasons.

#### High-temperature alteration and Re loss

Molybdenites which have experienced high-temperature alteration evidenced by geologic criteria have also shown increased transparency. Infrared microscopy may be an additional tool in evaluating Re loss for molybdenites under these conditions. Molybdenite affected by high-temperature alteration can still give a reasonable age, if the alteration is associated with the same thermal event responsible for mineralization. The Re-depleted molybdenites from American Eagle and Santa Rita may have been altered soon after crystallization and may give ages that are within error of the measurement. At the Ajo and Christmas mines, geologic evidence supports the possibility that increased transparency and Re loss in 3R molybdenite may be related to alteration from thermal events which are much later than the alteration associated with the mineralizing event, and erroneous ages may be expected from these samples. Infrared microscopy cannot distinguish when the increased transparency developed, and ages obtained on any molybdenites with IR < 3.5 may be erroneous.

#### Re loss in the supergene environment

In the supergene environment, molybdenite may experience Re loss, although it is possible that some molybdenite may be unaffected by supergene fluids. In the weathering environment, significant Re may be concentrated into secondary phases such as powellite or illite. Molybdenite in either setting would typically not be selected for dating, except in cases where no other samples are available. The most effective method of detecting molybdenite affected by weathering or supergene processes is examination using BSE imagery for the presence of zones of alteration and replacement by secondary minerals.

The most significant detriment to the successful application of molybdenite Re-Os geochronometry is the presence of Re-enriched K-Al-Si (illite?) phases in molybdenite. The illite inclusions in molybdenite from Bagdad, Questa, Morenci, and Silver Bell, USA, typically have an order of magnitude more Re relative to their molybdenite host. Illite may be identified by XRD in molybdenites which appear "sooty" (CARPENTER, 1968). The small amounts of illite in samples of this study were not detected using XRD and would be overlooked in a simple optical examination prior to dating.

The presence of this phase in a dated sample is significant, because in Eh-pH space, Re and Mo share roughly similar stability fields in the system M-S-O-H and can be complexed under supergene conditions, whereas Os is stable as an elemental species (Fig. 11c). Rhenium in molybdenite may be removed by supergene fluids after some has decayed to <sup>187</sup>Os, causing erroneously old ages, or it may be enriched in the illite intergrowths, creating ages which are too young.

#### Re-Os Molybdenite Ages

Following the evaluative techniques outlined above, Re-Os ages for selected molybdenites were determined (Table 3; Fig. 12). Molybdenites from the Copper Creek and Maria porphyries, and the Mission skarn, are unaltered and plot within uncertainty of the K-Ar ages for the mineralizing intrusions (Fig. 12b). Molybdenite from the center of the 25-mm-thick vein at Bagdad also has a Re-Os age in agreement with the stock age. In contrast, molybdenite from the vein edge is more transparent, contains Re-enriched K-Al silicates, and has a younger age. High 3R molybdenite from the supergene zone at Morenci also contains a few Re-enriched K-Al silicates, but gives an age within error of the 57-Ma stock. Rhenium in this molybdenite is five times greater than the molybdenite from the vein edge at Bagdad (2041.9 vs. 465.6 ppm; Table 3). It is likely that the intergrowths in the Morenci molybdenite are insufficient in number, or contain too little Re, to have an effect on the Re-Os age.

Molybdenite from the Gold Acres Cu-Mo skarn was clearly affected by fluids associated with later epithermal gold mineralization. The molybdenite is transparent, Re-depleted, and gives an age of 168.3 Ma vs. 99.0 Ma for the associated stock (Fig. 12a). Molybdenite from the Lorelei deposit was predicted to have lost Re from later thermal events, with further loss during weathering. The Re-Os is younger than predicted, however, which requires either Re addition or Os loss (Fig. 12a). The stability of Os in near-surface environment has been demonstrated previously (Fig. 11c). It is possible that Re-enriched weathering products similar to those observed at nearby Xamchab were also present in the Lorelei molybdenite, but escaped detection by BSE imagery. Rhenium content is similar to the altered Bagdad molybdenite (349.5 ppm), and small amounts of Re-enriched phases could significantly shift the Re-Os age toward a younger value.

Table 3. Rhenium and osmium concentrations and Re-Os ages for molybdenites, with K-Ar ages for stocks attributed to molybdenite crystallization at each location. See Appendix 1 for K-Ar age references and sample descriptions.

Sample	Location	Re, ppm	Os, ppm	Re-Os* age, Ma	K-Ar age, Ma
34BAG1	Bagdad, AZ	618.6	0.452	70.8	72.6
34BAGE	Bagdad, AZ	465.8	0.322	67.0	72.6
1CACC	Copper Creek, AZ	856.3	0.503	56.9	59.0
35GAIP	Gold Acres, NV	61.0	0.106	168.3	99.0
98LL	Lorelei, S. Africa	349.5	5.733	1570.9	1960†
48MARF	Maria, Mexico	413.8	0.245	57.4	58.0
97MIS	Mission, AZ	427.1	0.265	60.2	60.0
94MOR	Morenci, AZ	2041.9	1.175	55.8	57.0

\* $\lambda = 1.64 \cdot 10^{-6} \text{ yr}^{-1}$  (Lindner et al., 1989)

†Rb-Sr age

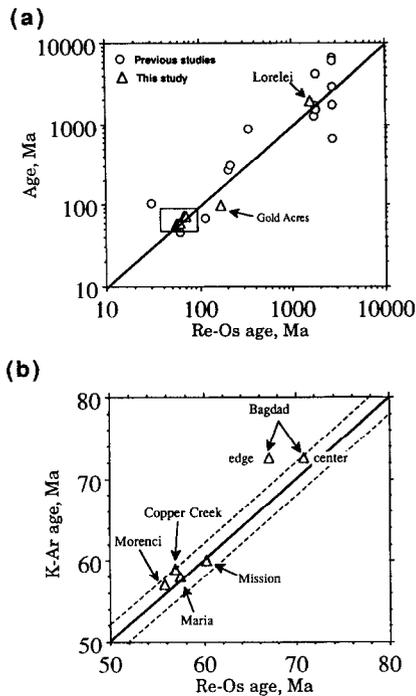


FIG. 12. Comparison of Re-Os ages for molybdenites with ages determined using other isotopic systems, or based on geological relations. (a) Re-Os age for altered molybdenite from the Gold Acres skarn and the Lorelei porphyry (log scale). Ages for the Mission skarn and the Copper Creek, Maria, and Morenci porphyries are in the boxed area. (Other data from HERR and MERZ, 1955, 1958; HIRT et al., 1963; LUCK and ALLÈGRE, 1982; ISHIHARA et al., 1989.) (b) Detail of boxed area (linear scale). Dashed line represents the average standard deviation of the K-Ar ages used for comparison.

### CONCLUSIONS

The results of this study show that Re loss in molybdenite can occur in hypogene and supergene environments. Simple optical examination is insufficient for selecting molybdenite which is suitable for dating. Polytype and Re measurements alone are also insufficient because molybdenite can experience Re loss without significant polytype shift, and will plot in the primary crystallization Re-3R regions defined by NEWBERRY (1979b; Fig. 2a). Combined microprobe, XRD, BSE, and infrared microscopy can be successfully used to detect alteration in molybdenite prior to dating. Some molybdenites that have been dated give correct or erroneous ages, and their reliability was successfully predicted prior to dating. These techniques are nondestructive and should be performed before any molybdenite is dated by the Re-Os system.

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## Appendix: Geologic setting, description of samples, and summary of results for molybdenites of this study.

LOCATION	AGE	DEPOSIT	DESCRIPTION - STATE OF MOLYBDENITE	ALTERATION	REF.
<b>American Eagle, AZ</b> 60CCAEA 60CCAEB	59 K-Ar	porphyry	Dacite core of Copper Creek system. Fracture-controlled alteration potassic to phyllic. Mineral zoning with depth is py-cp-mo-bn. Two mo-quartz veins sampled with 15 mm diameter aggregates of fine-grained mo. 60CCAEB has late-stage calcite with 5.45 wt.% Re, Re-depleted for 83% 3R; IR=3.1.	Hi T fluids have reduced IR and removed Re.	1
<b>Ajo, AZ</b> 54AJO3	63 K-Ar	porphyry	Granodiorite intrusion into PC basement and Kv. Cp-mo mineralization with potassic alteration and propylitic alteration overprint. Intruded by 21 Ma monzogranite which reset K-Ar age and paleomagnetism at contacts. Open-space vein in thermally affected zone near monzogranite has ~2 mm thick mo with solution-etched euhedral quartz. Re not low for 50% 3R, but IR=2.	High T fluids associated with 21 Ma monzogranite have reduced IR and removed Re.	2
<b>Bagdad, AZ</b> 34BAGI 34BAGE	73 K-Ar	porphyry	Quartz-monzonite intrusion into PC granite and metasediments. Mineralization cp-mo in PC and Laramide stock. 34BAGE is edge of 25 mm thick quartz-mo vein, is lower in Re for higher %3R than center (0.04 wt.% Re, 13% 3R vs 0.05 wt.% Re and 0% 3R). High Re K-silicate phase intimately intergrown with mo. IR lower in edge, 3.1 vs 4.0.	High T fluids associated with phyllic alteration reduced IR removed Re along vein edges, adsorbed Re into K-silicate intergrowths.	3 4 5
<b>Bingham, UT</b> 30GMA23 56B 57B	39 K-Ar	porphyry	Monzonite/quartz-monzonite stocks intruded Pz strata to form skarns; cp-mo-bn mineralization in stocks. Mo-quartz veins in potassic zone sampled. Two 2H mo have IR>3.8, low Re. One mo with 25% 3R is Re depleted, has slickensides in mo, IR=3.9.	2H mo unaltered; 25% 3R mo possibly altered by low T fluids moving along faults.	6
<b>Christmas, AZ</b> 8XMAS1	63-61 K-Ar	porphyry	Granodiorite composite stock intrusion into Pz carbonates and Kv. Mo-cp mineralization in stock. Basaltic dikes emplaced along faults in mine are 25 Ma. Mo-rich apophyse of stock sampled in potassic zone. Mo is Re depleted for 7.5% 3R; IR=2.	High T fluids associated with basaltic dikes have reduced IR and removed Re.	7 8
<b>Copper Creek, AZ</b> 1CACC 6CCJG 5CACC	68-52 K-Ar	porphyry	Breccia pipes in shallowly-emplaced composite stock which intrudes PC, Pz, K rocks. Short-lived alteration event. Molybdenite-quartz veins in breccias associated with dacite, as 25 mm diameter radiating crystal aggregates. Positive correlation between 3R and Re. IR=3.5.	No alteration.	1
<b>Diamond Joe, AZ</b> 7DJLV	72 K-Ar	porphyry	Concentrically zoned granodiorite to granite in core representing single magma pulse. Potassic alteration widespread but sparse mineralization, mo-cp-quartz veins. Disseminated and fracture controlled mineralization absent. Mo-quartz with low Re, 2H mo has IR=4.	No alteration.	3
<b>Ely, NV</b> 66ELY5	115-103 K-Ar	porphyry	Composite granodiorite-quartz monzonite stock intrusion into Pz strata; skarn and disseminated cp-mo veins. Numerous normal faults from Tertiary extension. Multicrystalline aggregate of euhedral mo in quartz-mo-cp vein has 0.10 wt.% Re with 7% 3R, but IR=2.5.	Some Re loss from high T fluids which reduced IR.	9
<b>Gold Acres, NV</b> 35GAIP	99 K-Ar	skarn	Granitic intrusion in Pz strata produced cp-mo skarn. Skarn split in half by reverse faulting, with epithermal Au mineralization superimposed on the shear zone. Massive mo from lower skarn unit is 2H with only 0.02 wt.% Re, and IR=2.8.	Fluids associated with Au mineralization removed Re from mo and reduced IR.	10
<b>Gravelotte, South Africa</b> 29GRVAI 29GRVAE 29GRVB	2040 K-Ar	pegmatite	Albite pegmatite in Archean tonalite and talc-chlorite-biotite schist. Weathering effects are minor. Mo-Bi-scheelite-beryl mineralization. Mo 30 mm in diameter shows no Re loss or IR difference from core (I) to rim (E). A second mo is 6 mm diameter has no Re, IR=2.	Low T weathering caused possible Re loss in mo rim. High T fluids removed Re and reduced IR in smaller mo.	11 12
<b>Henderson, CO</b> 75HEN 50HNBK	28	porphyry	75HEN is vertical quartz-mo vein cutting granite of Primos stock. 7755 foot level, mo vein 15 mm thick is 2H with low Re, IR=3.5-4.0. 50HNBK location uncertain.	None.	13
<b>Lorelei, Namibia</b> 98LL	1960 Rb-Sr	porphyry	Granodiorite intrusion into metavolcanic rocks to produce cp-mo mineralization. patch of mo ~40 mm in diameter from potassic zone, stained with malachite. 3R mo with only 0.04 wt.% Re has IR=2.9.	High T fluids removed Re and reduced IR. Weathering likely also removed Re.	14 15
<b>Maria, Mexico</b> 48MARF 55MARE 55MARI 78MAR	58 K-Ar	porphyry	Quartz-feldspar stock intrusion into granodiorite produced mo-cp pegmatite, high grade breccia of cp-py, with mo-cp-py in lower portion. Change occurs over 75 m, telescoped porphyry system. Mo from mo-cp pegmatite (78MAR, 48MARF) and breccia (55MAR). All are 2H, IR=3.5, Re low.	No alteration.	16
<b>Mineral Park, AZ</b> 2MPJL	73 K-Ar	porphyry	Stocks of diorite, quartz-monzonite intruded into PC metasediments, metavolcanics, granite, to produce cp-mo mineralization. Mo intimately intergrown with quartz. Low in 3R, Re, IR<3.0.	High T fluids may have removed Re and reduced IR.	5 17

LOCATION	AGE	DEPOSIT	DESCRIPTION - STATE OF MOLYBDENITE	ALTERTION	REF.
<b>Mission, AZ</b> 97MIS	60 K-Ar	porphyry	Quartz-monzonite intrusion in Pz strata produced py-mo-cp mineralization near contact, zoning outward to Cp only skarn-marble contact. Mo paint from near inner contact is 2H with 0.04 wt.% Re and IR=4.	No alteration.	18 19
<b>Morenci, AZ</b> 88MOR (superg.) 89MOR (hypog.) 91MOR (hypog.) 94MOR (superg.) 95MOR (hypog.)	58-57 K-Ar	porphyry	Monzonite intrusion into PC schist, granite, and Pz strata. Mineralizing pluton intruded slightly older monzonite. Mo-quartz veins hosted in supergene and hypogene zones of PC granite, 58 Ma and 57 Ma stocks. Mo from supergene zones is lower in Re for higher %3R than mo in hypogene zones. Mo in supergene of younger stock is 85% 3R, 0.41 wt.% Re, IR=3.7; contains some high Re, K-Al silicate phases. No K-Al silicates in other samples.	Low T supergene fluids removed Re from mo. IR not significantly affected by low T processes.	20 21
<b>Questa, NM</b> 115QU	23 K-Ar	porphyry	Aplite intrusion in Tv produced mo-quartz, banded mo-quartz-biotite-orthoclase, and mo veins on shears and fractures. Oxidation of mo to ferrimolybdate is common. Mo-quartz patches in aplite are partially altered to ferrimolybdate. Mo is 2H with 0.02 wt.% Re. No detectable Re in ferrimolybdate. Ilite(?) contains 0.25 wt.% Re.	Low T supergene fluids altered mo. Re loss to K-Al silicates is likely.	22
<b>Ray, AZ</b> 128RY4	80-70 K-Ar	porphyry	Twelve different intrusions from diorite to granite intruded Pz, PC rocks to produce cp-mo mineralization in sediments and PC diabase sill. Mo favors granite intrusion and quartzose metasediments. Mo-quartz vein ~15 mm thick from metasediment sampled. Re not low for 50 %3R, but IR=3.0.	High T alteration reduced IR and removed some Re.	23
<b>San Manuel, AZ</b> 81KAL 84KAL 99SAN 100SAN	69-65 K-Ar	porphyry	Quartz monzonite emplaced in 1.4 Ga granite produced cp-mo stockwork mineralization. Mo-quartz veins from Kalamazoo hypogene zone 2890' level show slickensides. 99SAN, 100SAN are mo concentrates from mill; geologically unconstrained. All have IR<3.5, but concentrate grains are smaller than 0.2 mm.	Alteration by high T or meteoric fluids along post-mineralization faults	24
<b>San Martin, Mexico</b> 61PKMM	46	skarn	Quartz-monzonite stock intruded K limestones to produce asp-bn-cp-mo, with later sp-cp-gal, lastly tetrahedrite-stibnite-py zones. Massive mo from 12th level is 2H and low Re, IR=4.	None observed, sooty texture suggests other minerals are intergrown.	25 26
<b>Santa Rita, NM</b> 3CHN1 4CHN3	63 K-Ar	porphyry	Granodiorite intrusion into Pz, Mz strata. Hypoogene cp-mo-py-bn mineralization. Potassic alteration in center of stock has sericitic-argillic overprinting in some areas. Quartz-mo vein in 4CHN3 has sericitic overprint, lower Re and IR relative to quartz-mo vein without overprint.	High T fluids associated with sericitic alteration reduced IR and removed Re.	27 28
<b>Sierrita, AZ</b> 130SIE	67-57 K-Ar	porphyry	Quartz-monzonite intrusion into into Mv and quartz monzonite produced cp-mo in veins and fractures. Mo-quartz-K feldspar vein 3 mm thick has slickensides and silicates are smeared. Low Re for 50 %3R polytype; IR=3.3.	Post-mineralization fluids associated with faulting removed Re.	29
<b>Silver Bell, AZ</b> 36SBCJ (skarn) 32SB1 (superg.) 43SBT (trans.) 45SBT (trans.) 47SBH (hypog.)	66 K-Ar	porphyry and skarn	Quartz-monzonite and dacite intrusions in Pz carbonates produced cp-mo-bn skarn, and cp-mo mineralization in the stock. Cp-mo from skarn-stock contact, mo-quartz veins in supergene zone in pit, from transitional and hypogene zones in drill core. IR is 4 for all samples, K-silicate phase is present in porphyry mo-quartz veins and is Re-rich (0.15-0.50 wt.% Re).	Low T supergene fluids removed Re from mo without affecting IR.	5 30
<b>Squaw Peak, AZ</b> 129SP3	not dated	porphyry	Cp-mo in veins occur in Laramide (?) quartz monzonite intrusion in PC granodiorite. Loose mo crystals obtained from dump. Jarosite(?) alteration on surfaces, Re low for 43 %3R, IR=2.3.	Alteration by high T and possibly supergene fluids suggested by presence of jarosite (?).	31
<b>Star W, NV</b> 72STM 73STM	37-30 K-Ar	skarn	Granodiorite intrusion in Pz rocks produced mo-scheelite-beryl skarn. Mo-cp-scheelite-tremolite-quartz rock, mo is ~2H and low Re, IR=3.5-4.	No alteration.	32
<b>Xamchab, South Africa</b> 28XAMI 28XAME 37XAMI 37XAME	1730 Rb-Sr	pegmatite	Cp-mo-scheelite mineralization in aplite with quartz-rich core intruded into leucogranite. Greenschist metamorphism at 1100-1000 Ma, dyke swarms at 720 Ma. Two mo ~30 mm in diameter from quartz-rich zone, one has patchy replacement by powellite (37XAM), the other has a powellite rim (28XAM). Edge of 37XAM is higher in 3R, but lower Re and IR. No gradual Re depletion detected from center to edge of 28XAM. Powellite is Re enriched with 2.46-3.00 wt.% Re.	High T fluids removed Re, reduced IR from rim of 37XAM. Low T weathering altered mo to powellite.	14 33

**Abbreviations:** mo = molybdenite; cp = chalcopyrite; py = pyrite; bn = bornite; gal = galena; sp = sphalerite; asp = arsenopyrite; PC = Precambrian; Pz = Paleozoic; Mv = Mesozoic volcanics; Kv = Cretaceous volcanics; Tv = Tertiary volcanics. K-Ar = potassium argon age; Rb-Sr = rubidium-strontium age.

**References:** (1) Guthrie and Moore, 1978; (2) Hagstrum et al., 1987; J. Thomas, pers. comm., 1991; (3) Lang, 1991; (4) J. Hawley, pers. comm., 1991; (5) Damon, 1970; (6) Bowman et al., 1987; (7) Koski and Cook, 1982; (8) McKee and Koski, 1981; (9) Westra, 1982; (10) Hays and Foo, 1991; (11) Jamieson and Schreiner, 1957; (12) Robb and Robb, 1980; (13) Carten, et al., 1988; R. Ganster, pers. comm., 1991; (14) Bowles, 1988; (15) Reid et al., 1987; (16) Wodzicki, 1992; (17) Lang and Eastoe, 1988; (18) Einaudi et al., 1981; (19) R. Williamson, pers. comm., 1991; (20) Langton, 1973; (21) T. Weiskopf, R. Preece, pers. comm. 1991; (22) Carpenter, 1968; (23) Phillips et al., 1974; (24) Lowell and Guilbert, 1970; (25) Shafiqullah et al., 1980; (26) Rubin and Kyle, 1988; (27) Nielsen, 1968; (28) Taylor and Frier, 1983; (29) Preece and Beane, 1982; (30) Lipman and Sawyer, 1985; (31) Roe, 1976; (32) Kistler et al., 1981; (33) Reid, 1979, 1982.