MOLYBDENITE POLYTYPES IN THEORY AND OCCURRENCE. II. SOME NATURALLY-OCCURRING POLYTYPES OF MOLYBDENITE

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108 specimens of naturally-occurring molybdenite, representing 83 localities throughout the world, were studied. About 80 percent of the specimens were the $2H_1$ polytype, three were the $3R$ polytype, and the remainder were mixtures of $2H_1$ and $3R$ in varying proportions. No new modifications of naturally-occurring molybdenite were found. Copper mineralization may play a role in the production of $3R$ and mixtures of $2H_1+3R$ polytypes, and a possible correlation between their occurrence and enrichment of rhenium is suggested.

INTRODUCTION

This study was made on 108 specimens of molybdenite from 83 localities throughout the world. This is, by no means, an exhaustive sampling of molybdenite, nor as detailed as some studies on specific geographical areas (e.g. Marmadov, 1965; Vorma et al., 1966; Khurshudyan et al., 1969), but may give a general idea of the great variety of geological occurrences of molybdenite. Some information about the geological environment was obtainable for a large percent of the localities.

THE MATERIAL

<table>
<thead>
<tr>
<th>Specimen number</th>
<th>Locality</th>
<th>Polytype, and approximate ratio of mixtures</th>
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<tbody>
<tr>
<td>A. United States</td>
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<tr>
<td>U.S.N.M. 94598</td>
<td>Copper Mt., Prince of Wales Is., Alaska</td>
<td>$2H_1$</td>
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<tr>
<td>U.S.N.M. 96611</td>
<td>Santa Niño Mine, Patagonia Mts.,</td>
<td>$2H_1$</td>
</tr>
<tr>
<td>U.S.N.M. 97491</td>
<td>Santa Cruz Co., Arizona</td>
<td>$2H_1$</td>
</tr>
</tbody>
</table>

1 Specimens came from the mineralogical collections of Harvard University and the U. S. National Museum.

1857
Molybdenite occurs here as "large bodies of fine grained massive material, as disseminated grains in quartz monzonite, and as good crystals in vein quartz with pyrite" (Galbraith, 1947). Chalcopyrite is found in massive ore (Kirkemo et al. 1965, pp. 14-16).

U.S.N.M. 97990 50 miles S.W. of Kingman, Hualpai Mts., 2H
Mojave Co., Arizona.

Many greisen-pegmatite deposits are known in this area (Wilson, 1941).

U.S.N.M. 91775 Helvetia, Pima Co., Arizona 2H+3R~9:1
Around Helvetia there are many deposits containing molybdenite, which generally is associated with chalcopyrite.

Harvard 106525 Arizona 2H
The locality designation is too indefinite; therefore, nothing can be stated with certainty about this specimen.

Harvard unnumbered Kenawyer Mine, King's River Canyon, 2H
Fresno Co., Calif.
Molybdenite occurs with chalcopyrite in quartz veins in a granite (Horton, 1916, p. 62).

Harvard 4211 Mono Lake, California 2H
This particular specimen consists of flakes of molybdenite in quartz and has been mentioned by Horton (1916, p. 59), but nothing else is known about it.

U.S.N.M. 91868 Lake Tahoe, California 2H
Contact metamorphic occurrences of molybdenite are known from this region. This specimen is probably from the Alpine Mine, south of Lake Tahoe, where molybdenite occurs together with powellite and scheelite in tactite (King 1966).

Harvard 107537 311 Drift stope level, Climax, Colorado 2H
In the ore zone, which forms a dome-shaped cap of intensely silicified rocks over a quartz monzonite, there are three different kinds of veins; sericite-topaz veins, pyrite-topaz-quartz veins, and molybdenite-quartz veins. This third type also contains pyrite, sericite, orthoclase, and fluorite. The main Climax ore is an altered granite. The molybdenite occurs mostly in fine veinlets with molybdate, wolframite, topaz, cassiterite, monazite, pyrite and chalcopyrite (Killefer and Linz, 1952, p. 5).
OCCURRENCE OF POLYTYPES OF MOLYBDENITE

Harvard 81614  Fairplay, Park Co., Colorado  
This locality simply has been mentioned (Endlich, 1878).

Harvard unnumbered Mountain Lion Mine, Magnolia Dist.,  
Boulder Co., Colorado.  
Molybdenite is found on the lower levels on the borders of a large pegmatite dike  
associated with massive white quartz and small amounts of chalcopyrite (Worcester,  
1919).

Harvard 104570  Near St. Peters Dome, El Paso Co., Colorado  
The specimen indicates that molybdenite occurs here in pegmatite.

Harvard 98594  Middle Fork, south of Arkansas River,  
Chaffee Co., Colorado.  
Many different kinds of molybdenite deposits are known from this area. Nothing  
definite can be stated about the genesis of this particular specimen.

Harvard 18212  
Harvard 18213  Vinalhaven, Knox Co., Maine  
Harvard 88638  
Molybdenite occurs here in quartz veins and in the rapakivi granite (Stewart, 1956,  

Harvard 98290  Sanford, York Co., Maine  
In this specimen molybdenite occurs together with vesuvianite.

Harvard unnumbered Tunk Pond, Cherryfield, Hancock Co.,  
Maine.  
Molybdenite apparently accompanies a series of pegmatite dikes (Hussey, 1958;  

Harvard unnumbered Cooper, Washington Co., Maine  
Molybdenite occurs here in pegmatite dikes and disseminated in the surrounding  
granite (Kirkemo et al., 1965, p. 61).
Molybdenite is found in the granites and pegmatites of this Cape Ann locality (Warren and McKinstry, 1924).

Molybdenite occurs in a granite pegmatite.

Molybdenite occurs together with muscovite and apatite at this old pegmatite locality (Jackson, 1844).

Iron ores occur here in a gneiss penetrated by pegmatites (Bayley, 1910, p. 279). Associated with the ore are molybdenite, pyrite, chalcopyrite, garnet and apatite.

The study specimen is in an amphibolite.

The specimen is in scapolite, from limestone in the wallrock.
The specimen is a cleavage piece from the shaft pillar.

Harvard unnumbered From the 1200' level of Sterling Mine, 2H₁ Franklin, New Jersey.

In this specimen the molybdenite occurs with sphalerite in a dark silicate matrix.

Harvard unnumbered "N.E. New Mexico" The locality designation is indefinite. 2H₁ This is possibly a "porphyry copper" specimen.

U.S.N.M. 62232 Tilly Foster Mine, Putnam Co., New York 2H₁ Molybdenite occurs sparingly as a contact mineral in the serpentine of a metamorphosed limestone (Newland, 1921, p. 163). Other minerals observed include magnetite, chondrodite, and clinohumite.

U.S.N.M. 83349 Demming, McDowell Co., North Carolina 3R Molybdenite is found with quartz in a muscovite-biotite schist. (Horton, 1916, p. 88).

Harvard 88520 Easton, Pennsylvania 2H₁ Franklin limestone has been intruded by granite forming pegmatite veins in the limestone. Molybdenite occurs in the serpentine formed at the contacts.

Harvard 100826 Frankford, Philadelphia, Pennsylvania 2H₁ + 3R ~ 2:1 Molybdenite occurs in minor amounts in a granitized hornblende gneiss intrusive in high-grade metamorphosed Wissahickon Schist (J. W. Frondel, personal communication).

Harvard 88910 Chester, Pa. 2H₁ Molybdenite occurs in quartz veins in a hydrothermally emplaced granodiorite (Postel, 1940).

Harvard 97231 Little Cottonwood Canyon, Utah 2H₁ The intrusive rocks at this locality are jointed and mineralized along the joints (Butler...
Pyrite is the most common sulfide, but chalcopyrite, galena and molybdenite also occur.

Molybdenite occurs in syenite at its contact with gneiss on the crest of Granite Hill (Eggleston, 1918). "The molybdenite scales are of medium size, often thickly powdered, like the inclosing syenite, with yellow molybdenite."

In this area molybdenite occurs in a granite associated with pyrite (Horton, 1916, p. 83. U.S.G.S. 1966), but the genesis of the study specimens, which are mostly cleavage pieces, is not indicated.

Molybdenite occurs as coarse flakes in a pegmatite in a granite (Jones, 1917).

The following is a short description of the Canadian occurrences (Vokes, 1963). Deposits of molybdenite occur in a belt from southern Gatineau and Pontiac Counties in Quebec through Renfrew and Haliburton Counties in Ontario in rocks, apparently of metasomatic origin, in the Grenville province of the Canadian shield. Molybdenite is associated with pyroxenite bodies, consisting mainly of diopside with some scapolite, plagioclase, and brown mica. The pyroxenite generally is included in or adjoins the Grenville limestone. Pegmatites sometimes occur with the pyroxenites. The genesis of the pyroxenite is disputed, some favoring a magmatic origin, others a metamorphic-metasomatic origin. It has not been proven that there is any genetic connection between the pyroxenites and the accompanying iron-sulfur-molybdenum mineralization. The molybdenite, the pyrite and/or pyrrhotite, and sometimes small amounts of chalcopyrite, occur as veins in breccia fillings in the pyroxenites.

It has not been possible to locate this mine or prospect. However, since in the study
specimen molybdenite occurs together with scapolite and pyrite, it may be assumed this is a “pyroxenite occurrence.”

Harvard 92168   Spain Mine, Dacre, Ontario

This deposit, treated in some detail by Vokes (1963) and Eardley-Wilmot (1925) belongs to the general pyrite-pyrrohottite-molybdenite mineralization of the region, but here the sulfides have been deposited as vertical veins in joints within the monzonite-gneiss country rock.

The following Canadian deposits represent other genetic types.

Harvard 90825   Don Rouyn Mine, Rouyn Township, 2H1 Quebec.

In this specimen molybdenite is associated with chalcopyrite. Molybdenite has been observed as vein filling in a fracture of the local Powell granite (Wilson, 1941, p. 73). No information was obtained “regarding the relationship of this occurrence of molybdenite to that of chalcopyrite, for the development of which the shaft was sunk.”

Harvard 97213   Algonquin National Park, Ontario. 2H1

This study specimen of molybdenite is a cleavage piece. No details concerning the locality are known.

Harvard unnumbered    Burnt Hill Brook, Miramichi River, New 2H1 Brunswick.

This is mainly a tungsten deposit of greisen type with cassiterite. Molybdenite is disseminated sparsely in both greisen and veins (Little, 1959).

Harvard 10193   Cananea, Sonora, Mexico 2H1
Harvard unnumbered   Sonora, Mexico 2H1+3R~1:1

In this porphyry copper deposit molybdenite occurs in three ways (Vanderwilt, 1942):
(1) Ore consisting of copper sulfides with molybdenite in an altered porphyry.
(2) Surrounding the ore, a zone of vein quartz with molybdenite and copper sulfides.
(3) Below the ore, quartz with molybdenite and pyrite.
Specimen 101931 probably is from the third type of occurrence, while the unnumbered specimen may come from the first or second type.

Harvard 81618   Tortola Island, Virgin Islands, West Indies 2H1

No occurrence of molybdenite is reported on Tortola Island (Martin-Kaye, 1959), though pegmatites and traces of copper mineralization have been observed. However, on the neighboring island, Virgin Gora, molybdenite, occurring in quartz veins with copper minerals, has been mined.
C. South America

Information on the Bolivian localities came from Ahlfeld and Schneider-Scherbina (1964).

Harvard 104637  Fenomenal, Larecaja, Bolivia.  \(2H_1\)
Tin-bearing pegmatites occur here.

Harvard 91637  Challana, Cordillera Real, Bolivia.  \(2H_1\)
Molybdenite occurs in this region with pegmatites, some containing muscovite, cassiterite, Li-phosphates and sulfides.

Harvard 103802  Murarata, Murillo y Sur Yungas, Bolivia.  \(2H_1\)
Greisen and micropegmatites with wolframite and cassiterite occur here.

Harvard 98704  Mine Andina, Murillo, Bolivia  \(2H_1\)
Quartz veins with tungsten and tin minerals occur here. Sulfides are found, also, together with fluorite.

Harvard 93068  Brazil  \(2H_1\)
The study specimen is a cleavage piece. The locality designation is too indefinite to obtain information on genesis.

Harvard 81619)  Santiago, Chile  \(3R\)
Harvard 4281  /  “Chile”  \(3R\)
The exact localities are unknown. In both specimens molybdenite occurs with sulfides. They probably belong to the “porphyry copper” type, which is common in Chile.

Harvard unnumbered  Ricran, Jauja, Dept. Junín, Peru.  \(2H_1\)
Quartz molybdenite veins occur in a granite (Petersen, personal communication).

D. Europe

Harvard 85064  Dalen Mine, Telemark, Norway.  \(2H_1+3R\sim 4:1\)
Molybdenite occurs in a quartz vein (Bugge, 1963, p. 92).

Harvard 85065 Bandaksli Mine, Telemark, Norway

Molybdenite occurs in quartz veins and quartz-pegmatite veins, sometimes with fluorite (Bugge, 1963, pp. 90–92).

Harvard unnumbered Frikstad, Iveland, Norway.

Molybdenite occurs in a pegmatite.


Molybdenite is mined here and has many types of occurrences; in quartz veins, in pegmatites, and in impregnations of the country bed-rock (Bugge, 1963).

Harvard 91575 Norway

The study specimen is only in crystals. The locality designation is too indefinite to obtain details of genesis.

Harvard 85066 Pielisjärvi, Finland

Most probably the study specimen is from the Mätäsvaara Mine in the parish of Pielisjärvi (Kranck, 1945). The enrichment of molybdenite is connected closely with pegmatitic intrusions and quartz veins from a microcline granite, which has intruded a gneiss. The gneiss itself is silicified where molybdenite is concentrated. Other sulfides are present only in very small amounts.

U.S.N.M. R7478 Striegau, Silesia

Molybdenite occurs in the granite of the Fuchsberge at Striegau. (Hintze, 1904).

Harvard 4222 Altenberg
Harvard 81623 Saxony
Harvard unnumbered

Small amounts of molybdenite, formed during the pneumatolytic stage, are found together with quartz, mica, topaz, cassiterite, arsenopyrite, native bismuth and wolframite (Cissarz, 1927–28).

Harvard 81622 Sadisdorf, Dippoldiswalde, Saxony
Small amounts of pneumatolytic molybdenite occur together with cassiterite, Li-mica and arsenopyrite in quartz veins (Cissarz, 1927–1928).

Harvard 88914 Schlaggenwald, Bohemia $2H_1$

Molybdenite is rare in the greisen (Cissarz, 1927–28).

<table>
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<tr>
<th>Location</th>
<th>2H₁ or 3R₁:1</th>
<th>Notes</th>
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<tbody>
<tr>
<td>Harvard 4291</td>
<td>$2H_1$</td>
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<tr>
<td>Harvard 4301</td>
<td>$2H_1+3R₁:1$</td>
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<tr>
<td>Harvard 81624</td>
<td>$2H_1+3R₁:1$</td>
<td></td>
</tr>
<tr>
<td>Harvard 105884</td>
<td>$2H_1$</td>
<td></td>
</tr>
<tr>
<td>Harvard unnumbered</td>
<td>$2H₁$</td>
<td></td>
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</tbody>
</table>

Molybdenite has not been found at this particular locality (Hintze, 1904 and Cissarz, 1927–28), but the study specimens probably come from some of the many localities in the neighborhood of Zinnwald and may all belong to the same group of greisen occurrences.

Harvard 4261 Schmirn, Tyrol, Austria $2H_1$

Molybdenite occurs in quartz veins in gneiss (granitic rocks?) in this valley (Hintze, 1904, p. 414).

U.S.N.M. 78904 Hallein, Austria $2H_1$

There is no information in the literature that molybdenite has been found around this salt deposit, and the locality designation is, therefore, in doubt.

U.S.N.M. R 411 Sasca Montană, Romania $2H₁+3R₁:1:4$

The locality is given, also, as Szazka, Banat, Hungary.
Here the molybdenite occurs in both skarn and copper porphyry type deposits associated with a granodiorite (banatite) intrusion. Chalcopyrite is the dominant ore mineral with molybdenite, bornite, pyrite, digenite, tetrahedrite, pyrrhotite, sphalerite and galena (Superceanu, 1969).

<table>
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<th>Location</th>
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<th>Notes</th>
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<tr>
<td>U.S.N.M. 94296</td>
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<td></td>
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<tr>
<td>Harvard 88814</td>
<td>$2H₁$</td>
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</table>

The two specimens probably are from the same locality, since the name Iglesias often is used for the whole district. At Castangias molybdenite occurs in pegmatite veins in a granite about 20 km N.E. of Iglesias (Vardabasso, 1950, Fig. 64 and section in Fig. 65).
Nothing about the molybdenite of this district has been found in the literature, but from information regarding the tungsten mineralizations it is probable that molybdenite occurs in pegmatites or greisen.

E. Africa

Molybdenite is found only in a metamorphosed garnet-rich limestone near a contact with granitic rocks (Von der Weid, 1941). In this skarn deposit accessory minerals are hematite, pyrite, pyrrhotite, galena and arsenopyrite.

The locality designation is indefinite and the study specimen is a crystal, so no information concerning genesis can be given.

In this well-known mine molybdenite is found disseminated in graphitized dolomite, as small particles together with green sphalerite, germanite, and renierite (Sohnge, 1964).

“Olionsongate” is either a misspelling or a transliteration of the deposit Otjonzonjati (Westphal, 1914; Martin, 1965). Molybdenite occurs here sparsely, together with chalcopyrite and other sulfides in mineralized quartz and quartz feldspar breccia veins in biotite schists.

F. Asia

No information was obtained for this locality. This label may refer to some other locality in Ceylon.

U.S.N.M. 76330 Colombo, Ceylon 2H1

U.S.N.M. 98099 Chicoi River, Transbaikalia, U.S.S.R. 2H1
Molybdenite occurs here in greisen and in quartz veins close to granites (Von zur Mühlen, 1926).

U.S.N.M. 88971 Chekiang, China $2H_1+3R\sim 1:2$

Pegmatite veins containing molybdenite occur in great number in this region (Wong, 1920).

U.S.N.M. 105878 Mt. Kongo, Korea $2H_1$

This locality is identical with the Kumgang molybdenum mine (Gallagher, 1963, p. 19), where molybdenite occurs in flakes up to 5 cm across in vertical quartz veins in a biotite granite. Wolframite also is found in the veins.

Harvard 108539 Hirasi mine, Gifu Prefecture, Japan. $2H_1$

The deposit is in quartz veins ranging from the hydrothermal to the pegmatite stages; also, as dissemination in granitic rocks (Geol. Survey Japan, 1960). In addition to molybdenite the ore contains small amounts of pyrite and rare sphalerite and native bismuth.

U.S.N.M. 61448 Shirakawa, Hida, Japan. $2H_1$

This is probably the same locality as that for specimen Harvard 108539, since the Hirase mine is situated on Shirakawa (Geol. Survey Japan, 1960).

U.S.N.M. 47143 Kosha, Japan. $2H_1$

This may be a misspelling or a confused transliteration, for no mention of this locality has been found in the literature.

G. Australia

In New South Wales so-called pipes occur in many granite bodies (Garrety, 1953) and their chief minerals, besides quartz, are molybdenite, native bismuth, wolframite, arsenopyrite, chalcopyrite, cassiterite, and tetradymite.

U.S.N.M. 48788 New England District, N.S.W. $2H_1+3R\sim 9:1$

The locality designation of this specimen is indefinite.
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U.S.N.M. 90739  Allies Mine, Bow Creek, Deepwater, 2H₁
N.S.W.

The pipe of this mine is within a granite, but very close to its margin.

Harvard 97214  Broken Hill, N.S.W.  2H₁

This locality is a different type of deposit from those mentioned above. Here molybdenite occurs embedded in quartz, sphalerite and chalcopyrite.

Harvard 98591}  New Zealand  2H₁
Harvard 98593]  2H₁

The locality designation is indefinite, and the study specimens are cleavage pieces, so no comment can be made about their genesis.

METHOD OF ANALYSIS

The X-ray diffraction samples were prepared by scratching the molybdenite specimens with a fine needle and sprinkling the very small flakes thus obtained onto a piece of double-faced scotch-tape on a glass slide. This procedure reduced greatly the preferred orientation of the flakes. In some diffraction patterns there was a weak reflection from the scotch-tape at 2θ = 28.7°, if the tape was not covered entirely by the sample. The X-ray patterns were compared directly with the diagrams of the theoretical polytypes in Part I of this study, and with theoretical mixtures of 2H₁+3R (Figure 1).

DISCUSSION

It has been suggested (Khurshudyan, 1966) that the 3R polytype of molybdenite is characteristic of ores from moderate to low temperature deposits of mainly quartz-molybdenite-chalcopyrite formations, although it has been found in other formations, and, therefore, the main factor determining the modification of molybdenite appears to be the temperature at which the deposit has been produced. Further, from a study of molybdenite from ore deposits and accessory molybdenite in molybdenum-bearing igneous rocks of the Armenian plutons (Khurshudyan et al., 1969), 3R was typical of quartz-molybdenite-chalcopyrite formations in the medium-low temperature deposits and rare in high temperature formations. On the other hand, an investigation of 308 samples from more than 90 deposits (Chukhrov et al., 1968) showed that 3R was present in both high and low temperature deposits. Hence, it was proposed that temperature was not a controlling factor of molybdenite modifications, but that because 3R has a higher period of repetition than 2H and, therefore, is subject to weaker structural control,
the formation of 3R could be promoted by a slower decrease of temperature or by the presence of mineralizers.

Of the 108 specimens in this investigation, about 80 percent were the $2H_1$ polytype. The majority of $2H_1$ samples came from quartz veins or pegmatites associated with granitic rocks or granite contacts. Minor amounts of sulfides, such as pyrite and chalcopyrite, accompanied the
molybdenite in some of these deposits. $2H_1$ has been found, however, in every geological environment known for molybdenite. Three specimens were of the $3R$ polytype, two of them from the same locality, probably a porphyry copper deposit. In the third specimen the molybdenite occurred with quartz in a muscovite biotite-schist. Nineteen specimens were mixtures of $2H_1+3R$. A ratio of $2H_1$ to $3R$ is given for each sample (see description of the localities). This proportion is only approximate and varies, though not greatly, in diffractometer runs on different samples of the same specimen. In Figure 2, X-ray diffraction patterns are shown for $2H_1$, $3R$, and some mixtures of these two polytypes found in the natural material. By comparison of these patterns with the theoretical diagram in Part I of this study it is easy to distinguish between the mixtures of $2H_1+3R$ and polytypes of higher symmetry. In half of the mixtures the $2H_1$ polytype was dominant, and these specimens came generally from quartz veins, pegmatites, or granite contacts. The specimens with $3R$ dominant, or present in a significant amount, came from a variety of geological environments. From the present study, then, a definite correlation between genesis and polytype occurrence can not be made, though copper mineralization seems to play an important role. No new modifications of naturally-occurring molybdenite were found, but study of more deposits may yield other polytypes.

The growing interest in molybdenite has been spurred by the search for new sources of the rare element rhenium, for which molybdenite serves, to date, as the most important host. Fleischer (1959) thought that "no generalizations are yet possible as to correlations of rhenium content with geological conditions of formation," but in 1960 he pointed out newer analyses (Zhirov and Ivanova, 1959) suggested "that the content of rhenium in molybdenites increases as one goes from high-temperature to medium-temperature deposits." There were, however, unexplained large variations of rhenium concentration from porphyry copper deposits. Since 1960 many investigations have been made (largely in U.S.S.R.) of rhenium enrichment in molybdenite. The results of these studies, summarized by Tischendorf et al. (1968), lead more and more to the conclusion that the enrichment of rhenium is greatest in copper-molybdenum formations. It is of interest to note that analyses of molybdenite from porphyry copper type deposits of Sasca-Montană, Romania (Superceanu, 1969) yielded as much as 0.13 percent rhenium, and this investigation's specimen from that locality (U.S.N.M.R 411) is a mixture of $2H_1+3R \sim 1:4$ (Figure 2). A correlation between the presence of copper mineralizers with reference to rhenium enrichment and the occurrence of $3R$ and $2H_1+3R$ mixtures of molybdenite is
Fig. 2. X-ray diffraction patterns\(^1\) of some naturally-occurring molybdenites.

1.) Harvard unnumbered, Mt. Lion Mine, Colorado; \(2H_1\)
2.) Harvard 96916; \(2H_1:3R \sim 9:1\)
3.) Harvard 4301; \(2H_1:3R \sim 1:1\)
4.) U.S.N.M. R411; \(2H_1:3R \sim 1:4\)
5.) Harvard 81619; \(3R\)

\(^1\) Copper radiation, with nickel filter.
suggested. This is supported by the recent work by Zelikman et al. (1970). It may well be that additional finds of 3R molybdenite will lead to new sources of rhenium.

Acknowledgments

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References


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