Short communication

Finding of rhombohedral modification (3R-type) of molybdenite from Japan. MAKOTO WATANABE and AKIRA SOEDA, *Institute of Geology and Mineralogy, Faculty of Science, Hiroshima University, Hiroshima 730.*

ABSTRACT

The 3R-type modification of molybdenite was found as the first occurrence in Japan by means of X-ray powder diffraction method. Three examples are described here: (1) products of fumarolic activity on the Satsuma-Iwo-jima, southern Kyushu, (2) samples in high temperature hydrothermal wolframite-bearing quartz veins of the Yamate (Shitekurayama) mine, Okayama Prefecture, and (3) those in contact metasomatic molybdenum deposits of the Okawame mine, Iwate Prefecture. All the specimens examined are admixture of the 3R and $2H_1$ polytypes with varying ratios.

Introduction

A number of studies on naturally-occurring molybdenite polytypes have so far been carried out by Traill (1963), Khurshudyan *et al.* (1969), Chukhrov *et al.* (1970), Frondel and Wickman (1970), and others, giving rise to heated controversy as to the formation condition of the molybdenite polytypes. It is also recognized that $2H_1$ polytype is predominating over 3R modification.

Crystallographic investigations of the polytypes of molybdenite have been made by Takéuchi and Nowachi (1964), Zvyagin and Soboleva (1967), Wickman and Smith (1970), and others.

However, a little has been known on the polytypes of molybdenite in Japan. It is the only report published to date on the occurrence of molybdenite polytype in Japan that Frondel and Wickman (1970) described the $2H_1$ polytype from the Hirase mine, Gifu Prefecture. In the present paper, some preliminary results on the occurrence of

rhombohedral modification of molybdenite, relatively rare in nature, are described.

Method of study

X-ray powder diffraction analyses have been made by the scotch-tape method devised by Frondel and Wickman (1970). Radiation and recording conditions are as follows: Ni-filtered $\text{CuK}\alpha$ radiation, 30 kV, 15 mA; slits 1.0, 0.6, 1.0; time const. 2 sec; 800 cps; scan speed $1^\circ (2\theta)/\text{min}$; detector G. M. C., at room temperature (27° to 29°C).

The determination of molybdenite polytype was made following the calculated patterns by Wickman and Smith (1970), the X-ray diffraction patterns for naturally-occurring molybdenites by Frondel and Wickman (1970), and the indexing listed in ASTM cards. The naming of polytypes is based on Wickman and Smith (1970).

Results

Three examples of rhombohedral modification of molybdenite are described in the following. They are invariably admixtures of the 3R-type modification and 2H_1 polytype. With the exception of Fig. 1 (1-d), the remaining are the reflection patterns for the mixtures of 2H_1 and 3R polytypes with varying ratios. In the case of mixture, the only six reflections (101, 012, 104, 015, 107, 108) are typical of 3R polytype in the 2θ range examined (30 to 62°) because of a close similarity in their reflections. In Fig. 1 (1-a), the indices of 3R polytype are parenthesized.

- (1) Molybdenite from the Satsuma-Iwo-jima, southern Kyushu (Spec. No. SI751015-03)

According to Dr. H. Sakai (private communication, 1977), molybdenite occurs as sublimate-like material, possibly formed from "molybdenum blue" with decreasing temperature and increasing sulfur fugac-

Fig. 1. X-ray diffraction patterns for mixtures of $2H_1$ and $3R$ polytypes of molybdenite from Japan. (1-a) : Satsuma-Iwo-jima, (1-b) : Yamate (Shitekurayama) mine, (1-c) : Okawame mine, (1-d) : Higashiyama mine ($2H_1$ alone).

ity, in and around the high temperature fumaroles (about 500°C). Molybdenite examined is fine-grained and granular aggregates with small amounts of quartz, tridymite, cristobalite, and anhydrite. In Fig. 1 (1-a), an X-ray diffraction pattern for the specimen is given. As seen in the figure, characteristic reflections of admixture of the 3R and 2H₁ polytypes lie in the 2θ ranges of 37° to 42° and 47° to 53°. Judging from the X-ray diffraction pattern for the molybdenite standard by Frondel and Wickman (1970), the mixing ratio of 3R to 2H₁ polytypes of the sample is considered as more than unity. For comparison, also presented in the figure is a typical 2H₁ polytype from the Higashiyama mine, Shimane Prefecture (1-d).

(2) Molybdenite from the Yamate (Shitekurayama) mine, Okayama Prefecture (Spec. No. YA770411-01)

The ore deposit of the mine was described as a pneumatolytic quartz vein (Henmi *et al.*, 1958). Molybdenite was found in a quartz-muscovite vein with trace amounts of pyrite, chalcopyrite, cassiterite, topaz, and chlorite in altered porphyritic granite of Cretaceous age. The wolframite is known to have composition of about 80 mol. % FeWO₄ (Soeda *et al.*, 1976). Molybdenite consists of small flakes of less than 0.5 cm long and aggregates, mainly occurring adjacent to the vein walls. The X-ray diffraction pattern for this sample is also shown in Fig. 1 (1-b), with some contamination of muscovite. Like the case of the above-mentioned Satsuma-Iwo-jima sample, rhombohedral modification, to a considerable degree, is mixed with the 2H₁ polytype.

(3) Molybdenite from the Okawame mine, Iwate Prefecture (Spec. No. OK770604-10)

The ore deposits of the mine are of contact metasomatic origin and had been mined for molybdenum. Molybdenite investigated is from a quartz vein in green skarn mainly composed of clinopyroxene, epidote, and quartz, and occurs as aggregates of flakes of a little less than 1 cm long. Dissemination ores are also found in the green skarn

(Mr. M. Hori, private communication, 1977). The X-ray diffraction pattern for the sample is presented in Fig. 1 (1-c). Because the pattern is very similar to that of $2H_1$ polytype shown in the same figure (1-d), the $2H_1$ modification is predominant over the 3R polytype in the specimen.

We have reported here three examples of rhombohedral molybdenite mixed with $2H_1$ polytype from different geological environments. Among them, occurrences of some samples such as those from the Satsuma-Iwo-jima can not be explained by genetical conditions of rhombohedral molybdenite so far proposed, for example, copper mineralization and concentration of rhenium of ore fluids (Fron del and Wickman, 1970), or slow cooling rate or the presence of mineralizing agents (Chukhrov *et al.*, 1970) contributing to the production of 3R and mixtures of 3R and $2H_1$ polytypes. However, further investigations are needed as to controlling factor(s) of the polytypes of molybdenite. It is not ascertained at present whether two different polytypes coexist as aggregates or as repeated alternations of different polytypes within a single crystal. Systematic investigations on the molybdenite polytypes from the view point of ore genesis are now in progress.

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