LETTER

K-Ar age of molybdenum mineralization in the east-central Kitakami Mountains, Northern Honshu, Japan: Comparison with the Re-Os age

SHUNSO ISHIHARA, KEN SHIBATA and SHIGERU UCHIUMI

Geological Survey of Japan, Higashi 1-1-3, Tsukuba, 305, Japan

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Three K-Ar ages were determined on rocks and minerals from the mineralized areas in the east-central part of the Kitakami Cretaceous granitic terrain, where a Paleogene mineralization age was reported recently on molybdenite by the Re-Os method. The present result showed an early Cretaceous age of 114 ± 4 Ma for the same molybdenite deposit. A rather large discrepancy was found between the Re-Os ages for molybdenite and the K-Ar and Rb-Sr ages for silicate minerals from the same ore deposits of Mesozoic-Cenozoic ages in the Circum-Pacific region, indicating that the Re-Os method needs further examination.

INTRODUCTION

Early Cretaceous granitoids of the Kitakami Mountains, northern Honshu, Japan, have been well dated radiometrically, and more than 80 age determinations are so far available mostly on rock-forming biotites. The obtained mineral ages are concentrated in 110–125 Ma, which are generally in accord with the results of the Rb-Sr whole-rock method (Shibata *et al.*, 1978). Ages of molybdenum and tungsten deposits associated with the granitoids were considered to be the same as those of the granitoids, because of their close spatial connection (Ishihara, 1973).

Recently, however, Miyake *et al.* (1987) reported a Paleogene age, 69.3 Ma, for molybdenite from the Hokuto deposit using the Re-Os method. This deposit is located in the east-central part of the Kitakami Mountains (Fig. 1), where Paleogene (51.5 and 62.1 Ma, Shibata *et al.*, 1977) extrusive and intrusive magmatic activities have been known locally, and where a brecciated dike has received a weak

copper mineralization of a Paleogene age (38.4 Ma, Ishihara *et al.*, 1988). No mineralized materials have directly been dated for the ore deposits hosted in the early Cretaceous granitoids. They must therefore be dated, especially in the east-central part, in order to confirm the two stages of molybdenum mineralization. In the present study, vein-forming mineral and altered rocks from the Hokuto and Kamaishi ore deposits were examined by the K-Ar method with the analytical procedure described in Shibata and Ishihara (1974). The results will be compared with the Re-Os age obtained by Miyake *et al.* (1987).

ANALYZED SPECIMENS

Hokuto deposit: This deposit (N39°35'27"; E141°58'54") located in Horinai, Miyako city (previously Tsugaruishi village), is the largest known molybdenum deposit in northeastern Japan. Several quartz veins cropped out together with limonite gossan and molybdenum ochre in

Fig. 1. Distribution of the early Cretaceous granitoids and Paleogene volcanic and intrusive rocks in the east-central part of the Kitakami Mountains. The geology was taken from Yoshida *et al.* (1983), and Kanisawa and Ishikawa (1987); the age data are from Shibata *et al.* (1977), Ishihara *et al.* (1988) and this study.

mountain slope up to 200 m above sea level (Watanabe, 1942). The veins occur in a magnetite-series hornblende-biotite granodiorite of the Omoe pluton. The Omoe granodiorite has color index of 9.0–10.4, but the granodiorite near the veins may be hornblende free and is leucocratic (the color index of 5.4–8.5, Ishihara, 1973).

The veins strike N15°W and dip 60°E. Major four veins were mined up to 150 m along the strike and 80 m down along the dip. The average width varied from 10 to 40 cm and the average grade of the four veins ranged between 1.5 and 3.2% MoS₂ (JMIA, 1968). Sericite, chlorite and clay minerals are reported from the alteration envelop and vein minerals are composed largely of quartz and small amounts of molybdenite and

K-feldspar.

Analyzed samples are biotite separated from a fresh hornblende-bearing biotite granodiorite and K-feldspar separated from a K-feldspar (1 × 2 cm)-bearing quartz vein.

Kamaishi deposits: The Kamaishi ore deposits are known as the best example of skarn-type copper-iron deposits in Japan. The ores occur in skarns developed between late Paleozoic limestone and mafic volcanics and early Cretaceous granitic rocks (Hamabe, 1979). The intrusive rocks are classified into the Ganidake granitic complex which consists of a major volume of granodiorite and minor gabbroids, and a later intrusion of the Kurihashi granodiorite (Hamabe and Kuwahata, 1977). K–Ar biotite age shows no difference between the two bodies, i.e., 122 Ma for the Ganidake granitic complex, and 118, 123, 125 and 130 Ma for the Kurihashi granodiorite (Shibata and Miller, 1962; Kawano and Ueda, 1965).

The analyzed sample was taken from a mineralized granodiorite of the Nippo D₃ copper deposit, where bornite-bearing chalcopyrite veinlets of 2–3 mm wide occur in hydrothermally altered zone (4–5 cm wide) of a fine-grained biotite-hornblende granodiorite (Fig. 2), which may belong to the Kurihashi pluton (Hamabe and Kuwahata, 1979). Under the microscope, both zoned and unzoned plagioclase contain fine specks of sericite, and mafic silicates have been almost completely altered to chlorite and carbonate minerals.

RESULTS AND DISCUSSION

Results of the K–Ar age determination are listed in Table 1. Age of the biotite from the host granodiorite of the Hokuto molybdenum deposit is 116 ± 4 Ma, corresponding to the early Cretaceous period like other K–Ar ages reported from the Kitakami Mountains. From the Omoe granodioritic pluton, three biotite ages have been reported; 125 ± 6 Ma (Shibata and Miller, 1962), 120 and 124 Ma (Kawano and Ueda, 1965). Thus, the present result is identical to the previous data within the analytical error.

Fig. 2. Copper-stockworked and altered granodiorite from the Kamaishi mine. A whole-rock sample from the altered part was dated by the K-Ar method (Sample No. KY-616). Cp is chalcopyrite.

Table 1. K-Ar ages of mineral and whole rock samples from the Hokuto and Kamaishi deposits, Kitakami Mountains

Nos.	Rocks	Minerals	K ₂ O (%)	Rad ⁴⁰ Ar (10 ⁻⁶ ml STP/g)	Atm ⁴⁰ Ar (%)	Age (Ma)
KT644A	Granodiorite	Biotite	8.07	31.2	7.8	116±4
KT647	Ore vein	K-feldspar	9.45	35.8	21.2	114±4
KT616	Altered granodiorite	Whole rock	2.07	7.62	26.3	111±4

Localities: KT644A and KT647, Mine's dump of the Hokuto mine (39°35'27", 141°58'54"). KT616, Southwest orebody of the Nippo D₃ ore deposit, 180 mL, 5th Step, Kamaishi mine (39°18'34", 141°40'31"); The mine's grid of +1714 and -1320). The errors in K-Ar age are given on 1σ level.

Age of the vein-forming K-feldspar is 114±4 Ma which coincides with that of the host granodiorite. Thus, the molybdenum veins at Hokuto must have formed not at Paleogene time but during the deuteric stage of the early Cretaceous granodiorite emplacement.

The whole-rock K-Ar age of the altered and copper-mineralized granodiorite at Nippo, Kamaishi mine, was determined as 111 Ma. This is slightly younger than the K-Ar ages for biotite from the Kurihashi pluton of 118–130 Ma, but

still indicates that the mineralization belongs to the early Cretaceous igneous cycle.

Figure 3 compares the ages determined by the Re-Os and conventional (K-Ar, Rb-Sr or U-Pb) methods for four molybdenite-bearing ore deposits, for which Miyake *et al.* (1987) reported the Re-Os ages on molybdenites. The age data were taken from literature except the age of the Hokuto deposit (Hk) obtained by the present study. The cited age data published before 1977 were recalculated with the new decay constants

Fig. 3. Comparison of Re-Os ages on molybdenite and K-Ar, Rb-Sr or U-Pb ages on vein-forming and alteration minerals from the same ore deposits. B, Bethlehem, Canada; Hi, Hirase, Japan; Hk, Hokuto, Japan; P, Preissac, Canada. The Re-Os ages are taken from Miyake *et al.* (1987), K-Ar age for the Hirase deposit is from Shibata and Ishihara (1974), that for the Hokuto deposit is from this study, K-Ar and Rb-Sr ages for the Bethlehem deposit are from McMillan *et al.* (1985), and U-Pb age for the Preissac deposit is from Miyake *et al.* (1987). The solid line indicates 1:1 correlation of the two methods.

of Steiger and Jäger (1977). As is seen in the figure, the results by the two methods agree well for the Precambrian samples (P), while they show a poor correlation for the Mesozoic to Cenozoic ore deposits (B, Hk and Hi).

In the Bethlehem porphyry copper deposits, Miyake *et al.* (1987) obtained an early Permian age of 272 Ma for accessory molybdenite from the ore deposit, but the Rb-Sr and K-Ar ages for the Guicheon batholith were reported to be early Jurassic ages of 205 ± 10 and 202 ± 8 Ma, respectively (McMillan *et al.*, 1985). Thus, the Re-Os age is shifted to the older side.

In the Hokuto deposit, the molybdenite was dated at 69.3 Ma by the Re-Os method (Miyake *et al.*, 1987), but the vein K-feldspar of this study was dated at 114 Ma. In the Hirase molybdenite-quartz vein deposit, Miyake *et al.* (1987) found that the molybdenite had a Re-Os age of 45.3

Ma, but K-Ar age for sericite from the altered envelop to the ore vein was dated as 61.2 Ma (Shibata and Ishihara, 1974). Thus, the Re-Os ages are younger than the K-Ar ages in these examples.

Recent progress in the development of ICP mass spectrometer made the Re-Os age determination useful for the geological materials. Detection limit of both Re and Os by the ICP mass spectrometer is said to be 1 ppb (Shimizu, 1986), and all the samples analyzed by Miyake *et al.* (1987) contain Re more than 10 ppm and Os more than 4 ppb. Yet, the conventional methods of radiometrical age determination have well established an early Jurassic age for the Bethlehem, an early Cretaceous age for the Hokuto and an early Paleogene age for the Hirase ore deposits, which are all accordant with geologic occurrence. Thus, the Re-Os ages for these three deposits need to be re-examined together with mineralogical studies, such as polytypes and secondary alteration (Luck and Allègre, 1982), of the analyzed molybdenites.

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