Timing of Au–Ag mineralization and related volcanism at Otoke, Yamagata Prefecture, Northeast Japan

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K–Ar ages of Au–Ag mineralization and hydrothermal alteration at the Otoke deposit were determined to be 3.93 ± 0.15 , 3.99 ± 0.10 , 4.10 ± 0.10 and 4.15 ± 0.10 Ma for four sericite separates, proving that the Au–Ag bearing quartz veins at deep level and the sericite zone of the clay deposit at the surface of present level were formed contemporaneously. The ages are also close to those of Au–Ag–Pb–Zn mineralization at the Yatani deposit, 3 km northeast of the Otoke deposit, suggesting that mineralization in both areas occurred within a series of hydrothermal systems. The eruption ages for welded tuff of the upper part of the Otoke Formation were determined to be 4.85 ± 0.13 Ma (biotite, K–Ar age) and 4.60 ± 0.30 Ma (zircon, fission track age), predating the mineralization.

Keywords: Otoke, K–Ar age, Fission track age, Au–Ag mineralization, Sericite

I. Introduction

The Otoke area is located in the southern margin of Yamagata Prefecture (Fig. 1). It has been known for clay deposits from late 19th century (Tanemura and Horiuchi, 1958). Since Au–Ag quartz veins were found in 1991, the area has become an active site for Au–Ag exploration (Shoji, 1992).

The early geological research for the area were done mainly on mineral deposits, such as the Otoke clay deposit, the Yatani Au–Ag–Pb–Zn deposit and the Kuroko type deposits (Tanemura and Horiuchi, 1958; Taniguchi, 1969; Hattori, 1975; Hayakawa *et al.*, 1977; Sato *et al.*, 1978). Shikazono (1985) reported K–Ar ages of 3.25–3.61 Ma for Au–Ag and Pb–Zn ores from the Yatani mine, which lies 3 km northeast of the Otoke deposit. He also

obtained 5.16 ± 1.95 Ma for a clay sample from the Otoke mine. There are several different opinions about stratigraphical division of the volcanic rocks in this area. Although the age of volcanic rocks in the area was recently discussed in some papers (Nishizaka and Yoshimura, 1988; Yamamoto, 1994), the age data are still scarce because of intense hydrothermal alteration of the volcanic rocks.

With a focus on defining the ages of Au–Ag and clay mineralization in the hydrothermal system at Otoke, and related volcanism, this paper presents age relationship between the Otoke clay deposit on the present surface and the Au–Ag quartz veins at about 700 m deep level of the deposit, and discuss the stratigraphic relationship of the host rocks of Au–Ag quartz veins at Otoke with those at the Yatani Au–Ag–Pb–Zn deposit.

Fig. 1. Simplified geologic map of the Otoke area with the localities of the samples dated (modified after Taniguchi, 1969; Sato *et al.*, 1978; Suzuki *et al.*, 1986).

II. Outline of geology

The Otoke area is characterized by a thick pile of Neogene volcanic rocks of dacitic to rhyolitic compositions, which is called the Otoke Formation (Hayakawa *et al.*, 1977). The Otoke Formation consists mainly of lapilli

tuff and tuff breccia with large mudstone blocks of the lower sequence, coaly shale of the middle sequence, and densely welded tuff and andesite of the upper sequence. Quartz-porphyry intrusions expose in the southern part of the area and were found by drilling at the south of the clay deposit.

The highest altitude near the clay deposit is about 1,360 m above sea level, and the drill hole 6MATN-1, which is located 2 km south of the Otoge mine, had penetrated to 500 m above sea level, but basement was not revealed. The thickness of the Otoge Formation is more than 900 m. The Otoge Formation distributes in an area of about 8×8 km and is surrounded by marine sedimentary strata of early-middle Miocene.

Nishizaka and Yoshimura (1988) proposed a model that the Otoge Formation deposited in a collapse caldera, which was formed during the late Miocene. Yamamoto (1994) described the intracaldera deposits and named the caldera "the Otoge caldera". North of the Otoge Formation is separated from the Karasugawa Formation of middle Miocene and old granite by the Takakurayama fault (Sato *et al.*, 1978). East and south of it contact with the Mayoizawa and Ninosawa Formations of middle Miocene unconformably (Suzuki *et al.*, 1986). We have no information about the nature of the western margin (Fig. 1).

In the area, most of volcanic rocks have undergone intense hydrothermal alteration. The alteration is characterized by early high temperature acidic pyrophyllite alteration, which is observed at the present surface (about 1,000 m above sea level), and was also revealed at 600–800 m deep level by drill holes. The kaolinite zone is also observed at the shallower part, where the major part of the Otoge clay deposit are formed. Although welded tuff appears to be fresh locally, glass in matrix is in part altered into zeolite and interstratified chlorite/smectite (Zeng *et al.*, 1993).

Near neutral pH alteration, which associated with Au-Ag mineralization, has overprinted on the early acidic alteration. Several Au-Ag quartz veins were found at a level of 600 to 800 m. A better portion of the veins for exploration is 1.3 meters wide, and contains 161.5 g/t

Au and 3,997 g/t Ag (Shoji, 1992).

III. Samples and analytical methods

Two samples, H3-3-705 m and H3-3-706 m, of Au-Ag quartz vein were collected from the inclined drill hole H3-3 located 300 m southeast from the open pit of the Otoge clay mine. The specimens are composed mostly of quartz with minor sericite, rhodochrosite and metallic minerals, which form silver-bearing fine black bands locally. Most of the sericite have the grain size of about 5 μm , and some flakes in vugs are more than 30 μm in diameter. The sericite contains 0–5% expandable layers in its crystal structure.

Another two samples, Ot-01 and Ot-11c, were collected from the surface. The sample Ot-01 was collected from the silicified zone in the central part of the clay deposit, and white in color, consisting mainly of sericite and quartz, and minor sulfide minerals (Watanabe *et al.*, 1994). The gold content of the rock is about 2 g/t. The sample Ot-11c was collected from the sericite zone, which surrounds the silicified zone. The sample is grayish-green in color and has the mineral assemblage similar to that of the sample Ot-01. Sericites in both samples show irregular platy form (<2 μm in diameter) and contain 5–10% expandable layers.

The sample was crushed, mixed with distilled water and disaggregated by an ultrasonic probe. The suspended solution was left for 30 minutes to 2 hours to settle the non-sericite fraction. Then, the sericite was concentrated by centrifugation from sericite-bearing suspension, and dried by freeze-dry method. Representative X-ray diffraction patterns of sericite are shown in Fig. 2.

To define the age of volcanism, a sample of welded tuff (Ot-15f) was collected. Because of the intense hydrothermal alteration in the area, only one sample was collected from about 150 meter east of the Otoge tunnel where the

Fig. 2. X-ray powder diffraction patterns of sericite from samples Ot-11c and H3-3-706m. Broken line is with ethylene glycol treatment.

hydrothermal alteration is quite weak. The sample presents gray to dark gray color. It consists mainly of quartz, plagioclase, biotite, glass and small amounts of augite, magnetite, zircon, mordenite and interstratified chlorite/smectite. Biotite was used for K-Ar dating and zircon was used for fission track age determination. Biotite is fresh, and the maximum size is 2 mm in diameter. The separation process of biotite is as follows: the sample of welded tuff (Ot-15f) was powdered to 350–150 μm , and biotite was concentrated by flotation under the condition of pH 2–3. After drying, the concentrated fraction was put on a filter paper. The paper was inclined and tapped slightly to exclude the non-biotite fraction. The procedure was repeated for several times, and then the almost pure biotite sample was obtained. Zircon was separated from the cru-

shed sample of welded tuff by magnetic separation and heavy-liquid techniques.

K-Ar age analysis was carried out at Research Institute of Natural Sciences, Okayama University of Science with the method by Itaya *et al.* (1991). Potassium analysis was done using a flame photometer. Argon was measured with a 15 cm sector type of mass spectrometer using an isotope dilution method. The corrected error of ^{38}Ar is less than 1%. The physical constants used for calculation are after Steiger and Jäger (1977): $\lambda_e = 0.581 \times 10^{-10} \text{ y}^{-1}$; $\lambda_b = 4.962 \times 10^{-10} \text{ y}^{-1}$; $^{40}\text{K}/\text{K} = 0.01167 \text{ atom \%}$.

Fission track dating was done by the Kyoto Fission-Track Co., Ltd. with ED2 method (Gleadow, 1981). Zircon crystals mounted in a PFA teflon disk were etched in an eutectic mixture of KOH and NaOH at 225°C for 35 h. The disk attached with muscovite detector was irradiated with a thermal neutron fluence of about $7.7 \times 10^4 \text{ cm}^{-2}$ at a rotary specimen rack in TRIGA Mark II reactor of Rikkyo University. Age calibration was done with zeta value of 372 ± 5 .

IV. Results and discussions

1. Results

K-Ar ages of sericite are 3.99 ± 0.10 and $3.93 \pm 0.15 \text{ Ma}$ for the Au-Ag quartz vein from a drill hole, and 4.15 ± 0.10 and $4.10 \pm 0.10 \text{ Ma}$ for the sericite zone from the present surface (Table 1). The welded tuff, which represent the upper unit of the Otoe Formation, yields a biotite K-Ar age of $4.85 \pm 0.13 \text{ Ma}$ (Table 1), and a zircon fission track age of $4.60 \pm 0.30 \text{ Ma}$ (Table 2).

2. Timing of mineralization

The hydrothermal alteration in the area is divided into two stages on the bases of mineral assemblages and the occurrences of alteration zones, that is, early acidic alteration and later neutral pH alteration associated with Au-Ag

Table 1. K-Ar ages of sericite separates from clay and ore deposits, and of biotite separates from welded tuff in the Otoge area

Sample No.	Original rock	Analyzed mineral	K(wt.%)	Rad. Ar (10^{-8} STP/g)	Non Rad. Air(%)	Age (Ma, $\pm 1\sigma$)
H3-3-706m	Quartz vein	sericite	6.96 $\pm$ 0.14	106.2 $\pm$ 3.5	63.6	3.93 $\pm$ 0.15
H3-3-705m	Quartz vein	sericite	6.30 $\pm$ 0.13	97.6 $\pm$ 1.4	28.5	3.99 $\pm$ 0.10
Ot-11c	clay deposit	sericite	6.98 $\pm$ 0.14	117.9 $\pm$ 1.3	10.1	4.15 $\pm$ 0.10
Ot-01	clay deposit	sericite	7.41 $\pm$ 0.15	112.6 $\pm$ 1.6	4.4	4.10 $\pm$ 0.10
Ot-15f	welded tuff	biotite	5.95 $\pm$ 0.12	112.1 $\pm$ 2.0	39.2	4.85 $\pm$ 0.13

Table 2. Fission track age of zircon from welded tuff at Otoge

Sample No.	Number of crystals	Spotaneous $P_s(\text{cm}^{-2})^*$	N_s^*	Induced $P_i(\text{cm}^{-2})^*$	N_i^*	Dosimeter $P_d(\text{cm}^{-2})$	N_d	U (ppm)	Age** (Ma, $\pm 1\sigma$)
Ot-15f	30	8.07 $\times 10^5$	546	5.05 $\times 10^6$	3416	7.65 $\times 10^4$	1178	530	4.6 $\pm$ 0.3

* P and N are density and number of fission track counted, respectively. s =spontaneous, i =induced, d =dosimeter.

** The ages was calculated using ED2 method with dosimeter glass SRM612 and zeta of 372 $\pm$ 5.

mineralization (Zeng *et al.*, 1993). The K-Ar ages of 3.93 and 3.99 Ma obtained from a quartz vein are slightly younger than the ages of 4.10 and 4.15 from the sericite zone at the clay deposit. However, the differences are within analytical errors, suggesting that the ages of sericite formation both in the clay deposit at the shallower part and the Au-Ag vein at deeper part are almost the same. A similar K-Ar age of 3.96 $\pm$ 0.10 Ma was reported for a sericite-rich sample from the open-pit of the Otoge clay mine (Watanabe *et al.*, 1994). Although we could not measure the K-Ar age of early acidic alteration for the lack of K-bearing minerals, the two stages of alteration seem to be a series of evolutionary process.

The mineralization age of about 4 Ma at Otoge is older than that of the Yatani Au-Ag-Pb-Zn deposit (3.3-3.6 Ma; Shikazono, 1985). If we consider the analytical errors, the mineralization ages in the two areas may overlap partly. In addition, the Au-Ag mineralization in the two areas has many similarities, such as

mineral assemblage, ore forming elements, alteration and elevation of ore zone (Hattori, 1975; Watanabe *et al.*, 1994; Zeng *et al.*, 1994). This suggests that mineralization in both areas occurred within a series of mineralization systems.

3. Age of welded tuff

The reliability of the zircon age of 4.60 Ma is high because of enough track counts due to the high uranium content in the zircons and no sign of detrital grain contamination. Most crystal fragments in the welded tuff remain fresh, though part of glass in the matrix has altered to mordenite and interstratified chlorite/smectite, which are typical low temperature (about 150°C) alteration minerals. Generally, the low temperature does not affect the fission track age of zircon. Besides, the K-Ar age of 4.85 Ma for biotite coincides with the fission track age for zircon. These results probably represent eruption age of the volcanic rock of the upper unit of the Otoge Formation. MITI (1994) reported a K-Ar age of 4.2 Ma for

Fig. 3. Comparison of stratigraphies of the Otoe area, which have been reported by Taniguchi (1969), Hayakawa *et al.*, (1977), Suzuki *et al.*, (1986), Nishizaka and Yoshimura (1988) and this study. Ka, Karasugawa Formation; Ku, Kuroiwa Formation; Ma, Mayoizawa Mudstone Member; Ni, Ninosawa Formation; Ot, Otoe Formation; Ot-L, Lower Member of the Otoe Formation; Ot-U, Upper Member of the Otoe Formation; Ot-T, Otoe Tuff; Ya, Yatani Formation; MM, Middle and lower Miocene strata, including Ma, Ni and Ka.

biotite from the welded tuff.

Yamamoto (1994) also reported an age of 3.3 ± 0.2 Ma for matrix glass of welded tuff, 2.5 km southeast of the Otoe clay deposit. He argued, however, that radiogenic Ar might be lost from the glass during mineralization in the area.

4. Stratigraphy

The age of volcanic rocks in the Otoe area was first suggested to be Miocene by Tanemura and Horiuchi (1958) on the basis of regional correlation of strata. They also assumed that the stratiform clay deposit at Otoe was formed along an unconformity within the volcanic rocks. Taniguchi (1969) divided the volcanic rocks in the area into the Otoe Formation and the conformably underlying the Yatani Formation. Hayakawa *et al.* (1977) called them the Otoe Formation collectively, and divided it into the Upper and Lower Members with the assumed unconformity between them. Suzuki *et al.* (1986) called the volcanic rocks the Otoe Tuff.

Taniguchi (1969) described foraminiferal fossils of middle Miocene age in black mudstone lenses intercalating in the volcanic rocks

of the Yatani Formation which belongs to the Lower Member of the Otoe Formation by Hayakawa *et al.* (1977). The tuff breccias of the Yatani Formation include abundant heterogeneous breccias and huge blocks of black mudstone. These characteristics suggest that the materials are collapse megabreccias in the Otoe caldera. Therefore, the black mudstone lenses containing foraminiferal fossils might be exotic materials from basement rocks as suggested by Yamamoto (1994).

The first radiometric age data of the Otoe Formation were reported by Nishizaka and Yoshimura (1988), who gave 6.64 ± 0.52 and 7.41 ± 0.45 Ma FT zircon ages. Although the age data were obtained for the tuff breccia from the lowermost part of the Upper Member of the Otoe Formation, they suggested that the data might represent the age of the whole Otoe Formation because there is almost no difference in lithology between the Upper and Lower Member. In addition, the existence of the unconformity between the Upper and Lower Members could not be observed on the surface nor in drill cores. In lithological features, the Upper Member has similarity to the

Lower Member of the Otoge Formation or the Yatani Formation (Fig. 3). In this study, we obtained 4.6–4.85 Ma for the welded tuff which is distributed at the upper part in the district. Considering the ages of 6.6 and 7.4 Ma for pyroclastic rocks of the lower horizon (Nishizaka and Yoshimura, 1988), the age of the Otoge Formation ranges from late Miocene to early Pliocene.

Quartz porphyry bodies, which intruded into the volcanic pile in and adjacent to the Otoge caldera, show spatially close relationship with acidic alteration and were altered themselves. It is possible that the parent intrusive body, which is related to the quartz porphyry and Au-Ag mineralization, exists beneath the caldera. Although the age of intrusion is not known, the Pliocene welded tuff in the upper level might represent the result of resurgent activity of the caldera and initiation of hydrothermal activity.

V. Conclusions

(1) Four K-Ar ages were determined for sericite from altered rocks and veins in the Otoge area. The age of sericitization on the surface is 4.10–4.15 Ma. The age of Au-Ag mineralization in deep veins is 3.93–3.99 Ma. Considering the relative analytical errors, the clay deposit and Au-Ag bearing veins formed contemporaneously.

(2) The Au-Ag mineralization age at the Otoge area is close to that of the Yatani Au-Ag-Pb-Zn deposit. Connecting with the other features and regional geology, it is conceivable that both deposits were formed within a series of hydrothermal systems.

(3) The newly obtained K-Ar biotite age (4.85 Ma) and zircon FT age (4.6 Ma) and reported ages suggest that the age of the Otoge Formation ranges from late Miocene 7.41 to early Pliocene 4.6 Ma.

(4) The age of welded tuff over the upper

Otoge Formation may represent the resurgent magmatic activity responsible to mineralization at the area in early Pliocene.

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東北日本山形県大峠の金銀鉱化作用および関連した火山活動の年代

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大峠鉱床における金銀鉱化作用と熱水変質作用の年代を4個のセリサイト試料についてK-Ar法で測定した結果、 3.93 ± 0.15 , 3.99 ± 0.10 , 4.10 ± 0.10 , 4.15 ± 0.10 Maが得られた。これにより深部の含金銀石英脈と現在の地表に存在する粘土鉱床のセリサイト帯が同じ時期に生じたことが示された。この年代は大峠鉱床の北東3 kmに位置する八谷鉱床の金銀鉛亜鉛鉱化作用の年代と近いものであった。したがって、両地域の鉱化作用が一連の熱水系の中で生じたという可能性がある。大峠層上部の溶結凝灰岩の年代として 4.85 ± 0.10 Ma (黒雲母, K-Ar年代)と 4.60 ± 0.30 Ma (ジルコン, フィッション・トラック年代)が得られた。これらの年代は大峠地域の火山活動の最後の時期を表している。

Karasugawa Formation 烏川層, Kuroiwa Formation 黒岩層, Mayoizawa Mudstone Member 迷沢泥岩部層, Ninosawa Formation 二の沢層