Sulfur of Kuroko Deposits—A Deep Seated Origin?*

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Abstract: Lateral zoning of Miocene ore deposits of the Green Tuff belt is discussed in two mining areas, with reference to newly obtained sulfur isotopic evidence. The ore deposits show a distinct lateral zoning around the Miocene tonalite-granodiorite stocks in the Hokuroku district, having xenothermal-type copper vein or normal copper vein deposits in the center and the kuroko type at the margin. Rock sulfur of the granitoids has an average \( \delta^{34}S \) of about +6 permil and the vein and kuroko sulfur is somewhat depleted in \( ^{34}S \). Rhyolites associated with the kuroko mineralization have similar \( \delta^{34}S \) values to the granitoids. There is possibility that the Miocene plutonic and volcanic rocks as well as the ore-forming sulfur have been derived from a common deep-seated source material.

Introduction

A magmatic origin was once simply assumed for the sulfur of kuroko mineralization. The currently favored view, however, is that all the sulfur came from the Miocene seawater sulfate through certain process of inorganic reduction under isotopic equilibrium (OHMOTO et al., 1970; KAJIWARA, 1971). There is an alternative hypothesis of a deep seated origin for the kuroko sulfur proposed by analogy between the Quaternary sulfur deposits and Miocene kuroko deposits (ISHIHARA et al., 1974; ISHIHARA, 1974).

Genetic link between Cretaceous granitoids and ore deposits of so-called granitic affinity is well documented in their spatial and temporal relationship, and recently by sulfur isotope data (SASAKI and ISHIHARA, 1978). Miocene mineralization of the Green Tuff belt is thought generally to be connected with the volcanic activity so as to the kuroko mineralization of rhyolite (HORIKOSHI, 1969), and not much attention has been paid to possible bearing of the Miocene granitoids on the Green Tuff mineralization. The scope of the present paper is to review spatial relationship among Miocene granitoids, vein-type deposits and kuroko deposits, and to describe sulfur isotopic composition of the granitoids, rhyolite and ore deposits of the Green Tuff belt; and then to discuss the provenance of sulfur of metallic ores of kuroko deposits.

Geological Evidence

Many similarities have been seen on volcanic rocks and plutonic rocks of the Green Tuff belt. For instances the volcanic rocks include andesite and basalt, other than felsic rocks. The plutonic rocks consist of tonalite and granodiorite and subordinate amount of diorite and gabbro. Wherever the volcanic rocks are typical low-alkali tholeiite (e.g., Izu-Kofu area), the plutonic rocks are trondjemitic; wherever sub-alkalic volcanic rocks are present, (e.g., Ani mine area), the plutonic rocks are rich in \( K_2O \) (S. ISHIHARA, unpublished data).

Except for the Fossa Magna region, Miocene granitoids occur as small stock and often have a volcanic texture at their margin. OIDE and ORIMOTO (1966), indeed, considered that this is characteristic of plutonism of the Green Tuff belt, and called it a volcano-plutonic complex. Thus the plutonism seems to be closely associated with the volcanism.

Miocene vein-type deposits are much more extensively distributed than kuroko deposits in the Green Tuff belt. When so-called high-temperature minerals were found, there were proposals that these were a xenothermal type...
associated genetically with Miocene granitoids (SKAKIBARA, 1958; SEKINE et al., 1958). The proposals are much clearer now that the veins containing Bi-minerals, W-minerals, magnetite, sphalerite star-bearing chalcopyrite and/or cubanite are known to occur close to the Miocene plutons (YAMAOKA, 1976). In the Hokuroku district, SAKAKIBARA (1958) stressed that chlorite-quartz-chalcopyrite veins tend to be present near Miocene granitoid, whereas sphalerite-galena veins and kuroko deposits are distributed outwards along fault zones.

In the Hokuroku district (Fig. 1), basement rocks are distributed around the “Hokuroku Miocene basin,” which has been identified as a Miocene submarine caldera (OHMOTO, 1977, 1978). Unlike those other Tertiary calderas in Southwest Japan, such as Tama-gawa (MURAKAMI, 1968) and Hamada (MATSUI et al., 1978), the intrusive rocks

Fig. 1  Distribution of Miocene intrusive rocks and ore deposits in the Hokuroku district, northern Honshu. Original data taken mostly from OZAWA (1978) and partly from FUJIT et al. (1976), and the xenothermal type from YAMAOKA (1976)
do not occur along the caldera wall but in the surrounding part of the Hokuroku basin associated with the basement rocks. Vein-type and network-type deposits tend to cluster around the intrusive rocks of plutonic type, and kuroko deposits are present afar from any pluton, major ones of which are distributed in subsided zones bounded by major faults.

There is a tonalite stock in the central portion, which corresponds to the Takamori uplifted zone of Fujii et al. (1976). Base metal veins (mainly copper) occur close to the stock, while lead-zinc predominant kuroko deposits (e.g., Fukazawa), stratabound manganese deposits and gold veins are distributed in the fringe part. This spatial relationship appears to suggest some genetic connection between the kuroko deposits and the tonalite or its differentiates.

Yajima (1977) demonstrated several metal zonings on vein-type and kuroko-type deposits around Miocene intrusive rocks in southwestern Hokkaido (Fig. 2). In the Teine-Toyoha-Chitose mining area, he found the zoning of Pb-Zn → Au-Ag → kuroko deposits outwards, whereby the Jozankei granodiorite porphyry is located in the center. The kuroko-type deposits are distributed in the fringe parts in each of these zonings. The zoning patterns are somewhat similar to those observed in the Miocene Hokuroku basin.

Age of the Miocene granitoids has been generally considered as the Onnagawa stage or the Funakawa stage, which is later than the Nishikurosawa stage for the formation of kuroko deposits. The vein-type deposits are known to have formed from the Nishikurosawa stage to the Funakawa stage, in which the highlight is said to be in the Onnagawa stage (Yamaoka, 1976). Thus more detailed study is necessary to clarify the time sequence between each pulsation of the magmatic activity and associated mineralization.

There are no radiometric datings on porphyry rocks but some on granitoids and vein-forming materials (Yamaoka, 1976). The stage of intrusive rocks was mostly determined by the cross-cutting relationship with the intruded Miocene strata in which ore deposits occur. In the central part of the Hokuroku district, Kouda and Koide (1978) were able to determine several intrusive pulses of basaltic to dacitic magmatism including the Otaki tonalite (Fig. 1). Kuroko mineralization precedes but vein-type mineralization is later than the tonalite intrusion. At Toyoha mine in Hokkaido, El Shatoury et al. (1975) considered the mushroom-shaped quartz porphyry occurring nearby the Tajima vein is genetically connected with the Pb-Zn-Ag mineralization. Thus, detailed time sequence and spatial relationship are complicated in these two areas. However, the overall lateral metal zoning mentioned previously would strongly indicate that the granitoids and ores were supplied from a common source material through a process of multiple pumping.

Sulfur Isotope Evidence

The isotopic composition of sulfur in kuroko deposits is variable. However, the mean values for individual deposits seem to be fairly consistent. Thus, $\delta^{34}S$ values of mill concentrates of pyrite from several representative kuroko deposits in the Hokuroku district fall in a remarkably narrow range with an average
of +4.6 permil (Sasaki and Kajiwara, 1971). This value may well approximate the average isotopic composition of kuroko sulfur, since more than 90 percent of whole kuroko sulfides are considered to be pyrite.

Recent isotopic studies on rock sulfur of Japanese granitoids (Sasaki and Ishihara, 1978) revealed that the two series of granitoids defined by Ishihara (1977), the "magnetite-series" and the "ilmenite-series," are characterized with different isotopic trends. The magnetite-series granitoid has the positive $\delta^{34}S$ values clustering around +4 to +5 permil, while the ilmenite-series rock has the sulfur more enriched in $^{32}\text{S}$ with the $\delta^{34}S$ ranging from -2 to -11 permil. It was further established that the ore deposits of granitic affinity show isotopic trends parallel to the host rock-series, strongly suggesting that the sulfurs in rock and ore have a common source.

The Miocene granitoids from the Green Tuff belt are known to be of the magnetite-series (Kanaya and Ishihara, 1973; Ishihara et al., 1976). Their $\delta^{34}S$ data available to date are listed in Table 1 together with the results for some relevant materials. Specimens of the Green Tuff granitoid are rarely free from any hydrothermal alteration. Unaltered specimen from Tanigawadake (TN-154), which was taken through tunnel construction for the New Joetsu Railway, yields $\delta^{34}S$ value of +5.7 permil; the value in accord with the general trend for the magnetite-series granitoid mentioned above.

A composite sample for a molybdenite-chalcopyrite-pyrite-pyrrhotite-magnetite stockwork ore (TN-163) gives $\delta^{34}S$ of +3.0 permil, which is somewhat lighter than the value of +5.7 permil for rock sulfur. Similar relationships may be pointed out for the Jozankei area, southwestern Hokkaido (Fig. 2) and for the Ani mine area, Akita Prefecture (Fig. 1). The Jozankei granodiorite porphyry, which is located in a center of the Teine-Toyohachitose mining district yields +6.0 permil, whereas sulfides of the Toyohachitose veins were reported to have an average of +4.6 permil (Kiyosu, 1974). In the Ani mine area chalcopyrite-pyrite-gold veins occur in a small stock of granodiorite and intruded Miocene volcanic rocks. The granodiorite which has been slightly altered throughout the mass gives +9.1 permil and the average of sulfides

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<tr>
<th>Sample No.</th>
<th>Material and locality</th>
<th>$\delta^{34}S$ (%)</th>
<th>S (%)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Whole rock</td>
<td>Sulfide</td>
</tr>
<tr>
<td>TN-154</td>
<td>Granodiorite, Tanigawadake, Niigata Pref.</td>
<td>+5.7</td>
<td>—</td>
</tr>
<tr>
<td>TN-163</td>
<td>Moly-cp-py-po-mt stockwork ore, ditto</td>
<td>+3.0</td>
<td>—</td>
</tr>
<tr>
<td>AN-3</td>
<td>Granodiorite, Ani mine, Akita Pref.</td>
<td>+9.1</td>
<td>—</td>
</tr>
<tr>
<td>HK-1</td>
<td>Granodiorite porphyry, Jozankei, Hokkaido</td>
<td>+6.0</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>Akamori dacite (&quot;younger rhyolite&quot;) Kosaka mine, Akita Pref.</td>
<td>+4.5</td>
<td>—</td>
</tr>
<tr>
<td>7a</td>
<td>Lava dome rhyolite, ditto</td>
<td>$-1.7(-1.5^*)$</td>
<td>-2.2</td>
</tr>
<tr>
<td>19a</td>
<td>Torigoe rhyolite (&quot;older rhyolite&quot;), ditto</td>
<td>$- (+6.5^*)$</td>
<td>+6.3</td>
</tr>
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—, not determined. A. Sasaki analyst.

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|                  | Whole-rock sulfurs was extracted as H$_2$S with "Kiba reagent" (Sn$^{2+}$-strong phosphoric acid) and was collected as Ag$_2$S for weighing, then converted to SO$_2$ for isotope analysis (Sasaki et al., 1976). Extraction of sulfate sulfur was practised with "Thode solution" (Thode et al., 1961). An hour long digestion with this reagent decomposes all sulfates in the sample but leaves pyrite (sole sulfide in the present specimens) almost unattacked.
from the veins is estimated around +4 permil (Tatsuura, 1965; unpublished data by A. Sasaki).

Since the igneous activity directly connected with kuroko mineralization is believed to be of rhyolitic, a preliminary examination was made on three representative "rhyolite" samples in the Kosaka mine area (Fig. 1) for their sulfur isotopes. The samples, one of each of "older rhyolite," "younger rhyolite" and "lava-dome rhyolite," were taken from the specimens of Tatsuura and Clark (1972). The isotopic results are shown in Table 1. Most of the kuroko rhyolites are severely altered. This fact as well as the shallow formative condition of the rocks must leave uncertainty in our evaluation of the isotopic data.

The older and younger rhyolites have $\delta^{34}S$ values of +6.5 and +4.5 permil, respectively; both being practically similar to the values assumed for the sulfur of Miocene granitoid-ore system. The lava-dome rhyolite, on the other hand, yields a value of −1.7 permil for the whole rock sulfur. Any interpretation for this result may be premature at this moment. However, starting from the total sulfur of +6 permil, it would not be too surprising to see this kind of value in a system more or less open for sulfur and with relatively high oxidation state.

From the foregoing, it may be said that the sulfur of Miocene granitoids in the Green Tuff belt has an average $\delta^{34}S$ about +6 permil and the vein sulfur has somewhat lower isotopic values, say +3 to +5 permil, which are practically identical with those values of the rhyolite–kuroko system. This isotopic similarity appears to be more than just a coincidence, particularly when the geologic evidence mentioned before is taken into consideration.

**Concluding Remarks**

There appears to be evidence that the Miocene "Green Tuff" mineralization in Japan of so-called volcanic affinity is also tightly connected with coeval plutonic activity. Tectonic setting of the Miocene igneous activity parallel to the Japan Trench, about 300 km apart at present, and abundant basalt-equivalent involvement in this igneous system favors a deep source model, such as the upper mantle (Shuto, 1976) or the lower continental crust (Doi, 1978), but most possibly the upper mantle plus some crustal contamination (Ishihara, 1978). As the isotopic evidence strongly suggests that the ores and the igneous (both plutonic and volcanic) rocks have a common source for their sulfur, the majority of metallic ore sulfur is also likely to have been derived from a deep seated source. Contribution from the immediate host rocks and the underlying basement rocks seems to be little if any.

Intense Miocene mineralization, especially of kuroko type, in such particular area as the Hokuroku basin would probably be the result of certain specific cause. Regional availability of sulfur from depth, which is demonstrated by immense Quaternary sulfur deposition at the Matsuo mine (Ishihara et al., 1974) could have been an essential factor. The same relationship is seen in the Toyoha–Horobetsu pair of southwestern Hokkaido, which is considered as the second target area in the Miocene mineralization.

A submarine hydrothermal system of predominantly seawater origin seems to explain many aspects of the kuroko mineralization. The sulfur isotopic feature has thus been most cleverly explained with the "seawater hypothesis," which concludes all the sulfur to be of marine sulfate origin (Ohmoto et al., 1970; Kajiwara, 1971). However, the evidence presented in this paper may, at least, throw some doubt on any model that assumes simple reduction of seawater sulfate in relatively shallow hydrologic processes.

Within one magma plume area, igneous activities and mineralizations may be related to individual pulses from the evolving source magma. The Miocene plutons are generally tonalitic that may have not been differentiated enough to concentrate ore components in the aqueous phase. It appears reasonable that the major mineralizations occur in more distinct affinity with dacitic or rhyolitic activity.
Studies of dacitic intrusives in the magma plume area would be useful for further understanding of the Green Tuff mineralization including the subject discussed in this paper.

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黒鉱鉱床のイオウ——深所起源？

石原 舜三・佐々木 昭

要旨：黒鉱鉱床を含むグリーンタフ帯の鉱体の分布を北陸地域を中心に、岩石と鉱体のイオウ同位体比と共に考察した。鉱床は中新世花崗岩類を中心とする礫岩帯を示し、北陸地域では貫入岩の近くに鉱脈が、周辺に黒鉱、マンガン、金の鉱床が分布する。グリーンタフ帯花崗岩類に含まれる岩石イオウはδ34S + 6 パーセント前後の一価を示し、鉱石イオウは鉱脈、黒鉱鉱床共に、+ 4 パーセント前後で若干低い。この岩石—鉱石イオウにみられる関係は白亜系で成因的に難連性がよくわかっている岩石—鉱床ペアと同様なものである。

グリーンタフ帯の鉱床に直接に関係する成岩類は一般に鉱床近傍の火山岩類と思われているが、上記の大局的な空間的配置とイオウ同位体比にみられる対応性は、これら火山岩類が完結的には花崗岩類と共通の起源を有し、繰返すマグマ活動により生じた個々の現象であることを示している。花崗岩質マグマは深所から運ばれたから、上記は鉱床中のイオウも深所に由来することを意味する。黒鉱鉱床の金属硫化物鉱体のイオウの多くは、生の海水、母岩、その直下の基盤などの表層物質ではないが、より深所からもたらされた可能性が大きい。大規模硫化物鉱床地域は深所からの充分なイオウの供給があった地域である。