NOTE

Sulfur and oxygen isotope ratios of anhydrite from the Iratsu peridotite-hornblendite-epidote amphibolite complex, central Shikoku, Japan

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Sulfur and oxygen isotope ratios were determined for eight anhydrite samples (seven from silicate rocks and one from a marble) from the Iratsu peridotite-hornblendite-epidote amphibolite complex, central Shikoku, Japan. The δ³⁴S values of anhydrite are in the range from +4.7 to +11.0‰. The δ¹⁸O values of anhydrite from the silicate rocks are in the range from +8.6 to +10.2‰ and that from the marble is +12.4‰. The fairly uniform δ¹⁸O values may indicate that these anhydrites were re-equilibrated with respect to oxygen isotopes with host rocks during the Sambagawa metamorphism. The rather variable, high δ³⁴S values of anhydrite suggest that it is not cognate with the original rocks from which the host rocks were derived. The obtained δ³⁴S values do not provide a straightforward solution concerning the source of sulfur for these anhydrites.

INTRODUCTION

Recently it has been revealed that a considerable fraction of sulfur exists as sulfate in most ocean-floor basalts (Grinenko et al., 1975; Sakai et al., 1982, 1984). Speciation of sulfate, however, has not been made, because these basalts usually contain less than 1500ppm total sulfur. Sulfate minerals are not commonly found in igneous rocks, especially in mafic and ultramafic intrusives. The occurrence of anhydrite in mafic and ultramafic intrusives has been reported so far from only two localities: the Noril’sk-I picrite diabase, USSR (Grinenko and Grinenko, 1967) and the Iratsu complex, Japan (Shibata, 1972). The sulfur isotope data of the Noril’sk anhydrite supported the view that the anhydrite was derived from accidental inclusions of evaporite incorporated into magma (Grinenko and Grinenko, 1967). The Iratsu complex suffered the Sambagawa metamorphism of the epidote amphibolite facies. Nevertheless, the mode of occurrence of anhydrite indicates that it is not a metasomatic mineral formed during the metamorphism (Shibata, 1972). In the present study, sulfur and oxygen isotope ratios of anhydrite from the Iratsu complex have been measured with a hope of elucidating the origin of the anhydrite.

OUTLINE OF GEOLOGY

The Iratsu peridotite-hornblendite-epidote amphibolite complex occurs in the Sambagawa metamorphic belt in central Shikoku. This complex has a lentoid body extending E-W across the peak of Mt. Higashi-akaishi, and is surrounded by pelitic and basic schists (the Upper Member of the Minawa Formation) of the epidote amphibolite facies (Hide et al., 1956; Hara et al., 1977; Banno et al., 1978).

During the years 1967–1968, a 2300m deep drill hole was drilled at Site S-7 located on the uppermost horizon of the Iratsu complex and about 2km north of Mt. Higashi-akaishi (Metallic Minerals Exploration Agency of Japan (MMEAJ), 1969). Anhydrite occurs in specimens recovered from this drill hole (Shibata, 1972). In the Mt.
Higashi-akaishi district, the Mt. Higashi-akaishi dunite mass and the Iratsu epidote amphibolite mass have been mapped as two distinct, separate masses (e.g., Yoshino, 1961). The MMEAJ investigators who made petrographic descriptions of the specimens recovered from the S-7 drill hole, however, noted that peridotite, hornblendite and epidote amphibolite observed in this drill hole are so intricately associated with one another that the rocks cannot be readily differentiated into two distinct masses (Metallic Minerals Exploration Agency of Japan, 1969). Thus, they coined the name “Iratsu complex” to designate the peridotite-hornblendite-epidote amphibolite association observed in the upper portion (up to the depth of 2000 m) of the drill hole. They correlated the rest of the hole (the lower 300 m portion) with the Tonaru epidote amphibolite mass exposed separately to the west of Mt. Higashi-akaishi. Subsequently, Shibata (1972) used the name “Iratsu ultramafic complex” to designate the entire peridotite-hornblendite-epidote amphibolite association observed in the S-7 drill hole and exposed in the Mt. Higashi-akaishi district as well. More recent studies suggested that the peridotite-epidote amphibolite complex of the Mt. Higashi-akaishi district represents a cumulus peridotite-gabbro association with subsequent complex thermal history (e.g., Yokoyama and Mori, 1975; Banno et al., 1976a, 1976b; Yokoyama, 1980; Kunugiza, 1984; Takasu and Kohsaka, 1987).

More than 75 percent of the specimens recovered from the S-7 drill hole consists of ultramafic rocks (i.e., peridotites with various degrees of serpentinization, pyroxenites, and hornblendite), and the rest of the core is mainly composed of epidote amphibolite. Anhydrite occurs ubiquitously in the recovered specimens except those with olivine as a principal constituent. Thin section analyses indicate that anhydrites fill interstices of other constituent minerals, and that no other sulfate minerals are present. Also, the analysis of composition-paragenesis relations suggests that the component SO$_3$ was inert during the metamorphism related to the formation of epidote amphibolite and related rocks. Detailed accounts on petrography and occurrence of the anhydrite-bearing specimens are given in Shibata (1972), and we retain the same sample numbers as those used in his paper.

**Analytical Procedures**

For sulfur isotope analysis, powdered anhydrite-bearing rock specimens, weighing 200 mg to 1 g, were directly treated with a mixture of HI, H$_3$PO$_2$ and HCl (Thode et al., 1961). The liberated H$_2$S from anhydrite was captured as CdS and finally converted into Ag$_2$S, which was combusted to SO$_2$ in a stream of purified air.

For oxygen isotope analysis, powdered rock specimens, weighing 100 mg to 3 g, were treated with 0.1 M HCl solution to dissolve anhydrite. The marble was first decomposed by 4 M HCl solution, and the resultant solution was evaporated to dryness and then the residue was dissolved in 0.1 M HCl solution. The insoluble residues were filtered out. The filtrates were passed through a column of cation exchange resin and then BaSO$_4$ was precipitated from it. CO$_2$ was prepared from BaSO$_4$ by the graphite reduction method (Mizutani, 1971; Sakai and Krouse, 1971).

Sulfur and oxygen isotope data are given in terms of $\delta^{34}$S and $\delta^{18}$O deviations from the standards CDT and SMOW, respectively. The precision is ±0.2‰ for $\delta^{34}$S and ±0.3‰ for $\delta^{18}$O.

**Results and Discussion**

Sulfur and oxygen isotope data of anhydrite obtained are listed in Table 1, together with the type of host rocks and the modal abundance of anhydrite determined by Shibata (1972).

The $\delta^{34}$S values of anhydrite are in the range from +4.7 to +11.0‰. Anhydrite occurs in various types of host rocks and modal abundance of anhydrite varies in the range from 1.5 to 16.9 vol%, which corresponds approximately to the sulfur content from 0.3 to 3.4 wt%S.
Table 1. Sulfur and oxygen isotope ratios of anhydrite from the Iratsu complex, central Shikoku

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Host Rock</th>
<th>δ^34S (‰)</th>
<th>δ^18O (‰)</th>
<th>M.A.* (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-7-237</td>
<td>Marble**</td>
<td>+11.0</td>
<td>+12.4</td>
<td>1.5</td>
</tr>
<tr>
<td>S-7-261</td>
<td>Epidote amphibolite</td>
<td>+6.9</td>
<td>+8.9</td>
<td>7.5</td>
</tr>
<tr>
<td>S-7-77</td>
<td>Hornblende</td>
<td>+7.6</td>
<td>+10.1</td>
<td>4.6</td>
</tr>
<tr>
<td>S-7-268</td>
<td>Hornblende</td>
<td>+10.4</td>
<td>+10.0</td>
<td>5.7</td>
</tr>
<tr>
<td>S-7-320</td>
<td>Epidote amphibolite</td>
<td>+4.7</td>
<td>+9.4</td>
<td>9.0</td>
</tr>
<tr>
<td>S-7-89</td>
<td>Hornblende</td>
<td>+5.4</td>
<td>+10.2</td>
<td>13.0</td>
</tr>
<tr>
<td>S-7-94</td>
<td>Hornblende</td>
<td>+5.6</td>
<td>+8.6</td>
<td>16.9</td>
</tr>
<tr>
<td>S-7-336</td>
<td>Clinopyroxenite</td>
<td>+7.7</td>
<td>+9.5</td>
<td>2.9</td>
</tr>
</tbody>
</table>

*Modal abundance of anhydrite by Shibata (1972).
**δ^13C and δ^18O of calcite were +2.6‰ and +9.9‰, respectively.

However, there is no apparent correlation between the δ^34S value of anhydrite and the type of host rocks, nor between the δ^18O value and the modal abundance of anhydrite.

The δ^18O values of anhydrite from the silicate host rocks are in a narrow range between +8.6 and +10.2‰. The anhydrite from the marble has a δ^18O value of +12.4‰, which is somewhat higher than those for the anhydrite from silicate rocks.

Oxygen Isotope Ratios

It has generally been recognized that the oxygen isotope equilibrium is nearly attained in the silicate and oxide minerals during the regional metamorphism. It is apparent from many isotope exchange experiments that sulfate and carbonate minerals are faster in rates of most oxygen isotope exchange reactions with water than silicate minerals (Cole and Ohmoto, 1986). In the present case, therefore, it is most likely that whatever the initial δ^18O values of the anhydrite, they have been more or less modified during the Sambagawa metamorphism. The uniform δ^18O values of anhydrite may indicate the attainment of isotope re-equilibrium between anhydrite and silicate minerals in the presence of metamorphic fluids during the metamorphism. The higher δ^18O value of anhydrite from the marble may reflect the quenching of isotope equilibrium between anhydrite and calcite at lower temperatures than between anhydrite and silicate minerals.

The marble has a δ^13C value of +2.6‰ and a δ^18O value of +9.9‰. According to Wada et al. (1984) the δ^13C values of calcite in marbles from the epidote amphibolite masses of this terrain range from −8.9 to +2.8‰ and the δ^18O values from +8.6 to +17.1‰, which are in agreement with our data. They classified the marbles into a low δ^13C group of magmatic or deep-seated origin, and a high δ^13C group, which re-equilibrated with metamorphic fluids segregated from crystalline schists during the Sambagawa metamorphism. The marble in the present study is classified into the high δ^13C group.

An unrealistically low temperature of 42 ± 15°C was calculated for equilibration between anhydrite and calcite, using the equation:

\[ 10^\Delta \ln a_{\text{anhydrite-calcite}} = 0.43 \times 10^6 T^{-2} - 1.83 \]

which is derived from the fractionation factors for anhydrite-water (Chiba et al., 1981) and calcite-water (O'Neil et al., 1968), whereas the temperatures of 450 to 500°C were obtained from the carbon isotope fractionation between calcite and graphite in the marbles (Wada et al., 1984). Even if anhydrite-calcite oxygen isotope equilibrium were quenched at lower temperatures than calcite-graphite carbon isotope equilibrium, our temperature estimate seems to be too low for the equilibrium temperature. The discrepancy may be due partly to the very small temperature dependence of the anhydrite-calcite fractionation factor.

Sulfur Isotope Ratios

Sulfide minerals such as pyrite and chalcopyrite are present in most host rocks, but always in trace amounts and no other sulfate minerals are present. In addition, there is no evidence that metamorphic fluids presumably present during the Sambagawa metamorphism were sulfur-rich. Therefore, contrary to the oxygen isotope ratios discussed above, it is unlikely that the sulfur isotope ratios of the anhydrite have been modified significantly during the meta-
morphism. The observed range of $\delta^{34}$S values is common for sulfate in ocean-floor basalts (Sakai et al., 1982, 1984). However, there is an essential difference between them and the present case; i.e., sulfate in basaltic rocks always coexists with larger amounts of sulfide with $\delta^{34}$S values of total sulfur being nearly 0%, whereas in the present case the amounts of sulfide are negligibly small compared to the amounts of anhydrite.

The Iratsu complex is considered to have originally formed in the upper mantle or in the lower crust (Banno et al., 1976b). Wherever the place of the formation, the ultimate origin of this complex must be sought for in the upper mantle. It is generally accepted that the oxidation state of the upper mantle is below that of the QFM buffer and under such conditions any oxidized species of sulfur is unlikely to be present in significant amounts (Ohmoto, 1986). This is unfavorable for the hypothesis that the anhydrite is cognate with the original rocks. Recent sulfur isotope studies of the ocean-floor basalts (Grinenko et al., 1975; Sakai et al., 1982, 1984) together with sulfur isotope data of continental basaltic rocks (e.g., Smitheringale and Jensen, 1963; Schneider, 1970) suggests that the $\delta^{34}$S values of sulfur in the upper mantle is in the range between -1 and +2%. The Iratsu anhydrite has considerably high $\delta^{34}$S values compared to the upper mantle value. Even if oxidation of sulfide sulfur did take place to form sulfate under some anomalous conditions in the upper mantle, we cannot imagine any plausible process by which $^{34}$S is enriched in sulfate to the observed extent at temperatures probably higher than 1,000°C. The $\delta^{34}$S values, therefore, also suggest that the anhydrite is not cognate with the original rocks.

The Iratsu anhydrite may have crystallized from assimilated sulfur during the formation of original rocks or alternatively during some geological events after the original rocks formed. Sulfur with $\delta^{34}$S values of the observed range can be found almost everywhere in the crust; some strata-bound massive sulfide deposits, fumarolic gases, geothermal fluids, river waters, etc.

Therefore, it is impossible to estimate the source of sulfur with any confidence from the observed $\delta^{34}$S values. Just one thing we are certain is that different from the Noril'sk anhydrites, evaporite sulfate is unlikely to be the main source of sulfur in the present case, because most of the $\delta^{34}$S values of the Iratsu anhydrites are considerably lower than +10%, the minimum value of the evaporite sulfates (Holser and Kaplan, 1966).

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REFERENCES


Grinenko, V. A., Dmitriev, L. V., Migdisov, A. A. and Sharas'kin, A. Ya. (1975) Sulfur contents and


