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Hydrothermal Activity Indicated by Oxygen and Hydrogen Isotopes of Rocks and Minerals from a Paleogene Cauldron, Southwest Japan

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Abstract: $^{18}O/^{16}O$, D/H and $^{34}S/^{32}S$ ratios were determined for whole-rock and mineral samples from the Hamada cauldron in southwest Japan, a complex of volcanic and shallow-intrusive rocks of Paleogene age. The low $\delta^{18}O$ values for the whole-rock samples, ranging from −2.3 to +4.9‰ (relative to SMOW) for volcanic rocks, and from −1.8 to +7.0‰ for plutonic rocks, suggest isotopic exchange reaction with ^{18}O-poor meteoric ground waters at elevated temperatures. Isotopic fractionations between minerals indicate isotopic disequilibrium between them and preferential isotopic exchange of feldspars and biotite with hydrothermal waters. The isotopic composition of the hydrothermal waters, assuming an equilibration with sericite at 250°C, was estimated to be in the range of present-day meteoric ground waters. The temperatures of the thermal activity were estimated to be in the range of 200 to 400°C. Most part of the cauldron would have had water-to-rock ratio higher than 0.25 in weight.

The hydrothermal system established in the cauldron was reconstructed on the basis of the distribution pattern of $\delta^{18}O$ values of the rocks, which shows a concentric zoning with the lowest values in the midst of the cauldron. This concentric pattern indicates that the highest temperatures and the highest water-to-rock ratios, in other words the most intensive activity, occurred in the central part of the cauldron. A hidden pluton, a part of which crops out as small stocks, beneath the midst of the cauldron may have been the major heat source of the hydrothermal system. Low $\delta^{18}O$ values are also seen in the vicinity of the fracture zones and faults which might have given a pathway to the thermal waters. The low-^{18}O rocks have higher concentration of sulfur with low $^{34}S/^{32}S$ ratios. Low-^{34}S sulfur might have been added to the cauldron system from the basement Paleozoic sediments by convective hydrothermal waters.

Concentrations of Cu and Zn increase with decreasing in ^{18}O of the rocks when their $\delta^{18}O$ values are lower than +3‰. The enrichment of base metals in the most altered, or the most ^{18}O-depleted, rocks is about 10 times as much as in fresh rocks: 90 ppm against 8 ppm for Cu, and 250 ppm against 20 ppm for Zn. The distribution pattern of base metals in the cauldron is in accord with that of the oxygen isotopes. The base metals would have been concentrated by circulation of hydrothermal waters. Lack of dominant mineralization in the area would be due to either inadequate contribution of magmatic waters or low concentration in base metals of the intrusive magmas.

INTRODUCTION

Inasmuch as meteoric ground waters are extremely lower in ^{18}O content relative to igneous rocks (depletion as much as 15‰ is not uncommon), reaction between them in hydrothermal system would result in remarkable change in ^{18}O content for both phases. The lowering in ^{18}O content of rocks is found in present-day geothermal areas where the waters are entirely of meteoric origin (CLAYTON et al., 1968; ESLINGER and SAVIN, 1973; CLAYTON and STEINER, 1975). If the isotopic composition of rocks is well preserved during subsequent geologic events, a record of geothermal activity could be read out of the rocks even after the activity has ceased.

In recent years it has become well established by means of oxygen and hydrogen isotopic analyses that certain epizonal igneous intrusions had interacted on a large scale with meteoric ground waters (TAYLOR, 1971, 1974 a, b; TAYLOR and FORESTER, 1971). H. P. TAYLOR and his colleagues extended the water-rock interaction model to large batholithic intrusions (MAGARITZ and TAYLOR, 1976; TAYLOR and MAGARITZ, 1978). The same method is applicable to reveal the origin of fluids responsible for the formation of ore deposits and the related alteration of wall rocks (GARLICK and EPSTEIN, 1966; SHEPPARD et al. 1969, 1971; TAYLOR, 1973; O'NEIL et al., 1973).

Present-day geothermal activity is occasionally related to volcanic caldera, where large heat source and high permeability of water are available. There-

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fore, a stable isotope study of rocks and minerals from a caldera, or a cauldron of volcanic and plutonic complex, well exposed by erosion would provide information useful for understanding what is going on under the present-day geothermal areas.

In this paper we will report a large scale geothermal activity which was found by means of oxygen and hydrogen isotopic analyses of rocks and minerals in the Hamada cauldron of Paleogene age, southwest Japan (Matsuhisa et al., 1978). The isotopic results will be discussed with regard to the extent of geothermal activity, relationship between geologic structure and geothermal activity, origin of geothermal water, water-to-rock ratio in the area, and relationship between geothermal activity and ore-formation.

GEOLOGIC SETTING

The Hamada cauldron is one of several cauldron complexes of volcanic and plutonic rocks distributed on the Sea of Japan side of southwest Japan. These cauldron complexes were formed in Paleogene about 30 to 40 m.y. ago, through a succession of volcanic eruptions with intermediate to acidic composition, subsidence with ring-faults and intrusions of diorites and granites (Murakami, 1973, 1974). They are covered unconformably with submarine volcanic terranes of Miocene age in which the Kuroko ore deposits were precipitated. So, an attention should be payed to the Paleogene cauldrons as a precursor of the succeeding opening of the Sea and the formation of the Kuroko deposits in Miocene.

The general geologic map of the Hamada cauldron is shown in Figure 1. The cauldron, about 10 km wide, 18 km long, is circumscribed by faults in the basement rocks of the late Paleozoic to early Mesozoic metamorphic rocks and the late Mesozoic volcanic and plutonic rocks. In some locations talus deposits which suggest a depression of the cauldron system against the basement are observed along the faults. The northern end of the cauldron is unconformably covered with the Miocene formations.

The volcanic rocks in the cauldron consist of andesitic to rhyolitic lava and pyroclastic rocks. They have been more or less chloritized. Intensive mineralization of pyrite is observed in places where chloritization is prominent.

A granite pluton (the Kumogi pluton) and a quartz diorite pluton (the Western pluton) are intruded into the cauldron on the eastern and western rims, respectively. Numerous small stocks, few hundred meter to 1 km in diameter, of quartz diorite to granite composition are also intruded into the volcanic rocks of the cauldron.

The Kumogi pluton about 5 km wide, 13 km long has a homogeneous mineral assemblage of adamellite composition (about equal amounts of alkali feldspar and plagioclase) with partly porphyritic texture. Micrographic texture is observed mainly in the marginal part of the pluton. In the Kumogi granites, biotite has been partly or completely chloritized. The magnetite to biotite ratio in modal composition increases outward in the pluton. Iron content of biotite decreases as the magnetite content of the rocks increases. These facts suggest that biotite was probably oxidized to produce magnetite after crystallization.

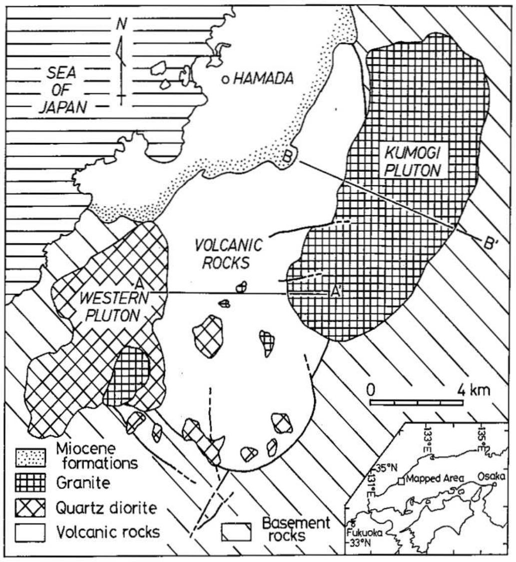


Fig. 1 Generalized geologic map of the Hamada cauldron, southwest Japan. Traverses AA′ and BB′ are taken for projection of $\delta^{18}O$ values across the cauldron in Fig. 8.

Light-colored quartz-sericite rocks with pyrite mineralization are observed in outer zone and along the fracture zones developed in the southwestern corner of the pluton. These rocks might be a product of heavy leaching of the granites by hydrothermal water. Network veins of clay minerals are seen on the surface of weathered granites. Montmorillonite and kaolinite, partly halloysite, are identified in pseudomorphs of feldspars. The formation of the clay minerals is partly superimposed on the sericite-dominant alteration, though the former lacks in the southern part of the Kumogi pluton (R. Kitagawa and S. Kakitani, written communication).

Although historic records of mining of copper and zinc are known in the area, no mines are in operation at present. Only one active hot spring, temperature 40°C and pH 10.0, is located on the northeastern flank of the cauldron.

EXPERIMENTAL

Mineral separation was done by means of hand-picking, magnetic separator and heavy liquids. It is difficult to get pure fraction of quartz because of micrographic texture. The problem of impurity will be discussed later. No attempt was made to separate clay minerals each other.

Oxygen was extracted from the rocks and minerals by reaction with bromine pentafluoride (CLAYTON and MAYEDA, 1963). Liberated oxygen was quantitatively converted to carbon dioxide using heated carbon for mass spectroscopic analysis. Oxygen isotopic ratios of the water samples were determined by the CO_2 equilibration procedure (EPSTEIN and MAYEDA, 1953).

For hydrogen isotopic analysis of hydrous minerals the water evolved from the sample at about 1,400 °C was passed through a uranium furnace heated to 700 °C and quantitatively reduced to hydrogen (FRIEDMAN and SMITH, 1958; GODFREY, 1962). Adsorbed and interlayer water was removed from the samples at 200 °C under vacuum prior to the oxygen or hydrogen extration. Hydrogen extraction from the water samples was done by the same procedure as that for hydrous minerals.

Sulfur isotopic ratios were measured on sulfur dioxide prepared from the pyrite and whole-rock samples. Small amount of sulfur in the rock samples was quantitatively recovered as hydrogen sulfide by reaction with tin (II)-strong phospheric acid (SASAKI et al., 1979).

All isotopic data are reported in the δ-notation in per mil,

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \times 1000 \qquad (^0/_{00})$$

where R is $^{18}O/^{16}O$, D/H or $^{34}S/^{32}S$. The standard for both hydrogen and oxygen is Standard Mean Ocean Water (SMOW), while that for sulfur is Canyon Diablo Troilite (CDT).

Twenty-eight analyses for oxygen isotopic ratios of the whole-rock samples were performed at the University of Chicago, while the rest of the oxygen isotopic data was obtained at the Geological Survey of Japan. The results were normalized on the basis of the $\delta^{18}O$ value of $+9.3^0/_{00}$ relative to SMOW for the NBS-28 reference quartz. Determinations for several identical samples in the two laboratories are compared in Table 1. The average deviation of measurements between the two laboratories is $0.08\ ^0/_{00}$, which is satisfactorily small as an experimental error.

Determination of the hydrogen isotopic ratios of the rocks was carried out in the U.S. Geological Survey at Menlo Park and the Tokyo Institute of Technology. The results obtained at the Tokyo Tech. are systematically higher by $4.5^0/_{00}$ on the average than those of U.S.G.S. (Table 2). As no systematic difference is found in H_2O yield between the two sets of measurements, the difference in δD values may be attributed to a systematic error in correction for mass spectroscopy. Though the difference is not significantly large for hydrogen isotopic analysis, the data in this paper were normalized to that of the Tokyo Tech. in order to accord them with the results for water samples.

Concentrations of Cu, Zn and Pb in the rocks were determined by an atomic absorption spectrometer according to the procedure described by TERASHIMA (1971).

Table 1 Comparison of oxygen isotopic data of Univ. Chicago with those of Geological Survey of Japan

Sample No.	$\delta^{18}O_{SMOW}$(‰) Chicago	GS Japan	Δ*
750512–3	+5.72	+5.42	−0.30
750511–23	+2.65	+3.01	+0.36
750410–17	−1.77	−1.65	+0.12
750328–12	+7.01	+7.05	+0.04
750606–3	+3.91	+4.16	+0.25
750609–20	+2.65	+2.63	−0.02
		Average	+0.08

* Difference between the two measurements.

Table 2 Comparison of hydrogen isotopic data of USGS, Menlo Park with those of Tokyo Inst. Technology

Sample No.	USGS, Menlo Park H_2O(wt%)	δD_{SMOW}(‰)	Tokyo Tech H_2O(wt‰)	δD_{SMOW}(‰)	Δ(‰)*
750608–8	0.66	− 99.8	0.68	− 95.1	+4.7
750328–12	0.45	− 86.0	0.41	− 85.3	+0.7
750328–8	0.53	− 91.4	0.55	− 82.6	+8.8
750319–2	0.40	− 93.6	0.38	− 88.1	+5.5
65T–38	0.56	−115.2	0.55	−112.4	+2.8
				Average	+4.5

* Difference between the two δD measurements.

Table 3 Isotopic data for the whole-rock samples from the Hamada cauldron

Sample No.	Description	$\delta^{18}O_{SMOW}$(‰)	δD_{SMOW}(‰)
Kumogi Pluton			
750319–2	Adamellite (SiO_2 = 73.5%)	+6.1	−88
750511–23	ditto (SiO_2 = 71.7%)	+2.8	
750608–8	ditto (SiO_2 = 72.5%)	+1.9	−95
760511–23A	Aplite (SiO_2 = 77.6%)	+0.2	
750410–17	Quartz-sericite rock (SiO_2 = 66.8%)	−1.8	−78
750408–16	Adamellite (SiO_2 = 72.4%)	+4.5	
750612–8	ditto (SiO_2 = 74.1%)	+4.0	
750606–3	ditto (SiO_2 = 72.8%)	+4.0	
750512–3	ditto (SiO_2 = 74.1%)	+5.6	
750606–4	ditto (SiO_2 = 71.2%)	+2.1	−96
750328–12	ditto (SiO_2 = 74.6%)	+7.0	−85
750512–18	ditto (SiO_2 = 73.7%)	+6.9	
760411–25	ditto (SiO_2 = 72.0%)	+4.3	
750408–17	ditto (SiO_2 = 72.5%)	+3.7	
750511–32	ditto	+2.8	
750609–20	ditto	+2.6	
750511–28	ditto (SiO_2 = 70.8%)	+2.5	
750411–11	ditto	+3.1	
750328–8	ditto	+3.3	−83
750427–1	ditto (SiO_2 = 70.0%)	+1.8	
750608–23	ditto	+6.4	
750408–4	ditto	+2.8	
750327–14	ditto (SiO_2 = 72.9%)	+2.8	
750601–9	ditto	+3.1	
750512–37	ditto	+3.0	
Small intrusions			
760515–11	Gabbro (SiO_2 = 49.0%)	+3.5	
760510–13	Quartz diorite (SiO_2 = 61.5%)	+2.4	
760408–4	Granodiorite (SiO_2 = 64.1%)	+0.1	
Western plutons			
750613–1	Quartz diorite (SiO_2 = 57.7%)	+5.0	
77724–9	ditto	+5.0	
77811–16	ditto (SiO_2 = 62.2%)	+1.1	
77810–2	ditto	+5.7	
7788–3	Adamellite	+6.9	
Tamagawa pluton			
7710–1	Granite	+2.9	
7710–2	ditto	+4.2	
Volcanic rocks			
760510–131	Andesite (SiO_2 = 56.2%)	−0.5	−85
760514–6	Dacite tuff (SiO_2 = 60.5%)	+4.9	−94
7764–6	ditto	+2.6	
750615–1	Rhyodacite tuff (SiO_2 = 71.3%)	+3.0	
760512–5	Rhyolite (SiO_2 = 74.6%)	−0.5	
760509–4	Ichinose quarry; andesite (SiO_2 = 51.8%)	−2.3	−94
7764–3	Rhyolite tuff	+2.0	
760407–2	Andesite	+0.2	
7765–5	Dacite tuff	+1.3	
760408–2	Andesite	+4.1	
77722–2	Rhyolite tuff	+2.3	
771122–2	ditto	+2.7	−79
750603–8	Andesite	+0.4	−90
771120–1	ditto	−0.6	
771120–2	ditto	−0.1	
760511–9	Andesite tuff breccia	−1.8	

(Continued)

Table 3. (Continued)

Sample No.	Description	$\delta^{18}O_{SMOW}$(‰)	δD_{SMOW}(‰)
771128–1	Dacite tuff	+ 2.3	
760513–9	Rhyolite	+ 0.0	
760608–6	Dacite tuff	− 1.5	
760515–2	Andesite (SiO_2 = 54.1%)	− 1.3	
Basement rocks			
750321–8	Tanohara; Mesozoic rhyolite tuff	+ 3.5	
760404–10	Hodohara; Cretaceous granite	+ 4.4	
7766–3	E of Kamijo; pelitic schist	+ 5.2	
7766–1	Chidani; pelitic schist	− 0.3	
77930–10	Oriigawa; green schist	− 0.5	
	quartz vein in schist	+13.1	
77930–5	Kitsuga dam; pelitic schist	+ 1.9	
77930–4	Kitsuga; pelitic schist	+ 0.6	
3–6–78	Composite sample of Sangun metamorphic rocks	+13.4	

ISOTOPIC RESULTS

$^{18}O/^{16}O$ and D/H Ratios of Whole-rocks

The $\delta^{18}O$ and δD values of whole-rock samples from the Hamada cauldron are given in Table 3. Some additional data for the basement rocks and the Tamagawa cauldron about 40 km southwest of the Hamada cauldron are presented in the same table.

The granites from the Kumogi pluton, in spite of the relatively uniform mineral assemblage, have a large variety of $\delta^{18}O$ values, ranging from -1.8 to $+7.0^{0}/_{00}$. The rocks from the small intrusions and the Western pluton have the same range of $\delta^{18}O$ values as that of the Kumogi pluton ($+0.1$ to $+6.9^{0}/_{00}$). Two granites from the Tamagawa cauldron which geologically and petrographically resembles the Hamada cauldron (MURAKAMI, 1969) have $\delta^{18}O$ values of $+2.9$ and $+4.2^{0}/_{00}$.

The $\delta^{18}O$ values of the volcanic rocks are -2.3 to $+4.1^{0}/_{00}$ for andesites, -1.5 to $+4.9^{0}/_{00}$ for dacite or rhyolite tuff, and -0.5 to $0^{0}/_{00}$ for rhyolites. No systematic correlation is observed between isotopic composition and rock types.

The $\delta^{18}O$ values reported here for the Hamada cauldron are lower and more diverse than those of "fresh" igneous rocks which display a relatively narrow range of $+5.5$ to $+10.0^{0}/_{00}$. Low $\delta^{18}O$ values of -5 to $+5^{0}/_{00}$ of igneous rocks are typically found in the areas such as Scottish Hebrides, Skaergaard Intrusion and Western Cascade, and believed to be an evidence of a large scale interaction between igneous intrusions and meteoric ground waters (TAYLOR, 1974a).

A rhyolite tuff and a granite from the Mesozoic basement have $\delta^{18}O$ values of $+3.5$ and $+4.4^{0}/_{00}$, respectively. Pelitic schists from the basement nearby the cauldron are distinctly depleted in ^{18}O ($\delta^{18}O = -0.5$ to $+5.2^{0}/_{00}$) as compared with "normal" pelitic schists collected from the same metamorphic terrain far from the area($+13.4^{0}/_{00}$). The $\delta^{18}O$ values of the pelitic schists gradually increase from about $0^{0}/_{00}$ at the border of the cauldron to $+5^{0}/_{00}$ at about 1.5 km from the border. A quartz segregation vein parallel to the schistosity has a $\delta^{18}O$ value of $+13.1^{0}/_{00}$, showing a large contrast to $-0.5^{0}/_{00}$ of its host rock (#77930–10).

In contrast with the wide range of $\delta^{18}O$ values, δD values of the rocks are very uniform, ranging from -96 to $-78^{0}/_{00}$ for the Kumogi granites and -94 to $-85^{0}/_{00}$ for the volcanic rocks.

$^{18}O/^{16}O$ and D/H Ratios of Minerals

The $\delta^{18}O$ and δD values of minerals separated from the Kumogi granites and veins are shown in Tables 4 and 5.

The $\delta^{18}O$ values of K-feldspar ($+1.9$ to $+7.2^{0}/_{00}$), plagioclase (-0.1 to $+6.6^{0}/_{00}$) and biotite (-3.4 to $+3.5^{0}/_{00}$)vary widely, while those of quartz ($+5.9$ to $+7.6^{0}/_{00}$) and magnetite ($+0.4$ to $+1.3^{0}/_{00}$) are in relatively narrow ranges (Table 4).

Figures 2a-d are plots of $\delta^{18}O$ value of minerals against that of their host rocks. A reference line showing 1:1 correlation is given in the diagrams. The data points for K-feldspar and plagioclase fall in the diagram close to the correlation line. Because feldspars (K-feldspar and plagioclase) exceed 60% of the modal composition of the rocks, the $\delta^{18}O$ value of whole-rock would largely be defined by that of the constituting feldspars. The data points for biotite (partly includes chlorite) are distributed parallel to the reference line in a lower-^{18}O region, which indicates isotopically concordant behavior of biotite with feldspars in the rocks.

The $\delta^{18}O$ values of quartz show a small, but continuous decrease (from $+7.6$ to $+6.5^{0}/_{00}$) with

Table 4 Isotopic data for minerals from the Kumogi pluton

Sample No.	$\delta^{18}O_{SMOW}$(‰) W.R.	Qz	Kf	Pl	Bi(Ch)	Mt	δD_{SMOW}(‰) Bi(Ch)
750328–12	+7.0	+7.6 (+7.7)	+7.2 (+7.0)	+6.6	+3.5	+0.7	−89
750319–2	+6.1	+7.3	–	–	+3.5	+1.3	−95
750512–3	+5.6	+7.5	–	+5.9	+2.3	−0.8	–
750606–3	+4.0	+7.1 (+7.9)	+3.4 (+3.4)	+3.6	+1.1	+0.4	−90
750612–8	+4.0	+6.9	+2.5	–	−0.4	–	−90
750609–20	+2.6	+6.8	–	+2.1	−3.4	+0.5	–
750511–23	+2.8	+5.9 (+6.5)	+1.9 (+1.0)	–	−3.3	+0.6	–
750511–28	+2.5	+6.7 (+7.7)	+2.5 (+0.8)	−0.1	–	+0.5	–
750427–1	+1.8	+6.5	–	+2.5	–	–	–
750410–17	−1.8	+6.5	–	–	–	–	–

Abbreviations: W.R., whole-rock; Qz, quartz; Kf, K-feldspar; Pl, plagioclase; Bi(Ch), biotite + chlorite; Mt, magnetite. Numbers in parentheses are corrected values (see text).

Table 5 Isotopic data for vein minerals

Sample No.	Description*	$\delta^{18}O_{SMOW}$ (‰)	δD_{SMOW} (‰)
77103–1	Quartz	+ 6.0	–
77930–2	Sericite, (Qz)	− 2.8	−78
77930–1	Montmorillonite ≫ Qz, Kaol, Ser	+11.1	−59
77929–1B	Ser, Mont, Kaol, Qz, Feld	+12.0	−59
77929–2B	Montmorillonite, (Qz)	+16.2	−52**

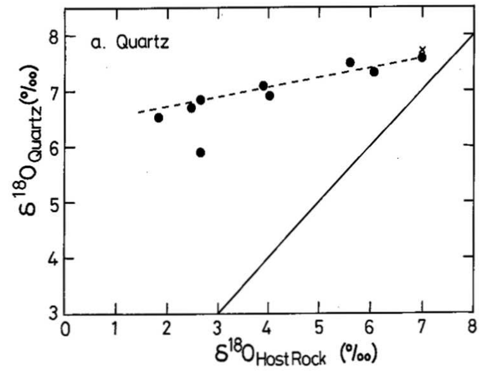
* Abbreviations: Qz, quartz; Kaol, kaolinite; Ser, sericite; Mont, montmorillonite; Feld, feldspar. (Qz) indicates existence of trace amount of quartz.

** Reproducibility of analyses: coarse grain, −53, −52‰; fine grain, −51‰.

decrease of the whole-rock $\delta^{18}O$ values. A plot of $\delta^{18}O$ vs oxygen yield for quartz is shown in Figure 3. The $\delta^{18}O$ values vary from +5.9 to +7.6‰ with virtually constant oxygen yield with an average of 16.26 μmole/mg. The theoretical oxygen yield for quartz (16.65 μmole/mg) and the reproducibility for NBS-28 quartz are compared in Figure 3 for reference. The oxygen yield for the quartz from the Kumogi granites is 2.3% lower than the theoretical yield or pure quartz. On the other hand, average oxygen yield for K-feldspar is 14.70 μmole/mg which is 2.3% higher than the theoretical yield (14.37 μmole/mg), while that for plagioclase, 14.72 μmole/mg, is within experimental error of the theoretical yield (14.80 μmole/mg for andesine). Therefore, it is likely that the insufficient and excess oxygen yield for quartz and K-feldspar is due to cross-contamination in separating the minerals from the rocks with micrographic texture.

Material balance calculation gives corrected $\delta^{18}O$ values expected for pure quartz and K-feldspar, which are shown in parentheses in Table 4. If it is assumed that contamination of 17% K-feldspar with a $\delta^{18}O$ value identical to that of its host rock to quartz fraction takes place, a correlation between $\delta^{18}O$ values of contaminated quartz fraction and host rock is predicted. The predicted correlation is shown by a broken line in Figure 2a. In the calculation the $\delta^{18}O$ value of pure quartz is taken to be +7.7‰ which is shown by a cross in the figure. An excellent agreement between the predicted correlation line and the data points proves appropriateness of the contamination model. The quartz in the Kumogi granites might have little variataion in its ^{18}O content irrespective of $\delta^{18}O$ value of its host rocks.

Clay minerals from veins have high $\delta^{18}O$ values of +11.1 to +16.2‰ except for sericite(−2.8‰). The clay samples are mixtures of montmorillonite,



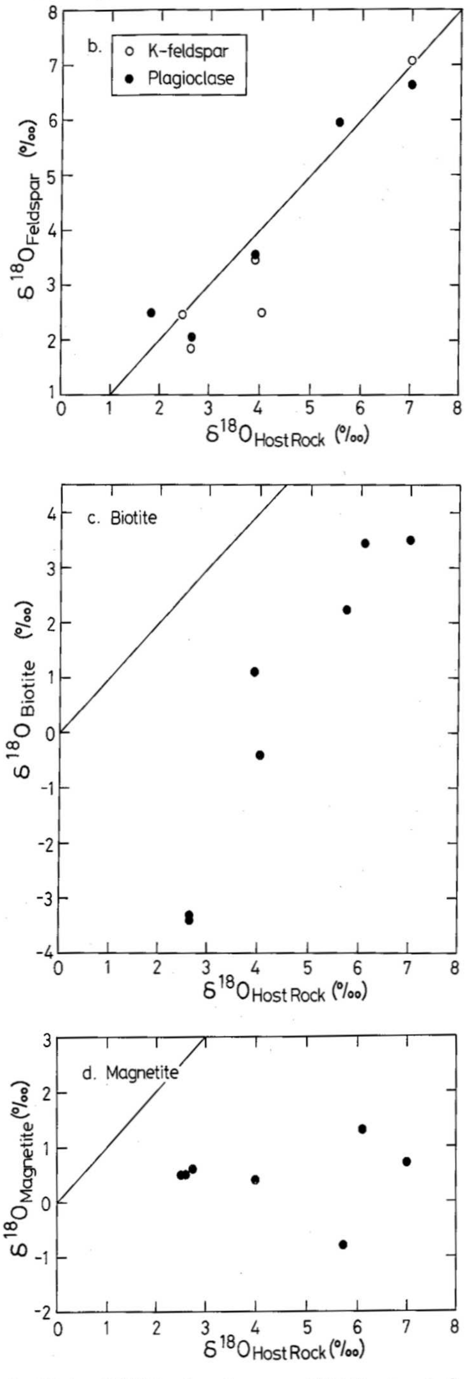


Fig. 2 Plots of $\delta^{18}O$ mineral versus $\delta^{18}O$ host-rock for quartz (a), feldspars (b), biotite (c) and magnetite (d) from the Kumogi granites. Solid lines give 1:1 correlation for reference. The broken line in (a) shows a predicted trend for quartz calculated by assuming contamination of K-feldspar (see text). The corrected $\delta^{18}O$ value for quartz is given by a cross mark.

kaolinite, sericite and quartz in various proportion (Table 5). The higher content of montmorillonite seems to be associated with higher $\delta^{18}O$ value.

The δD values of biotite are virtually constant regardless of the degree of chloritization, -95 to $-89^{0}/_{00}$, while those of clay minerals vary from $-78^{0}/_{00}$ for sericite to $-52^{0}/_{00}$ for montmorillonite. The clay minerals are enriched in D relative to biotite without exception.

$^{34}S/^{32}S$ Ratios of Whole-rocks and Minerals

The $\delta^{34}S$ values and sulfur content of whole-rocks and pyrite are shown in Table 6. They range from $+0.1$ to $+6.3^{0}/_{00}$ for the whole-rock samples. The $\delta^{34}S$ values of $+4.4$ and $+5.4^{0}/_{00}$ for two pyrite separated from a granite and a quartz vein are within this range. It is noticed that the $\delta^{34}S$ values are rather uniform except for that of quartz-sericite rock, and are in the range for the magnetite-series granitoids in Japan (SASAKI and ISHIHARA, 1979). The quartz-sericite rock has a high sulfur content (1.2%) with low $\delta^{34}S$ value

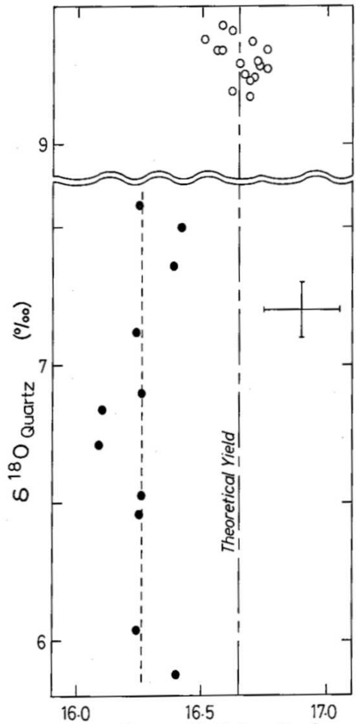


Fig. 3 A plot of $\delta^{18}O$ versus oxygen yield for quartz. Solid circles are for quartz from the Kumogi granites, while open circles are for NBS-28 reference quartz. Theoretical oxygen yield for quartz and the average oxygen yield for the Kumogi quartz are shown by a solid and a broken lines, respectively. Crossed bars present the experimental error.

Table 6 Sulfur isotopic data for whole-rock and pyrite samples from the Hamada cauldron

Sample No.	Description	$\delta^{34}S_{CDT}$(‰)
7710–1	Pyrite in granite	+4.4
77929–1A	Pyrite in quartz vein	+5.4
750328–12	Adamellite	+6.3
750328–8	ditto	+4.4
750410–17	Quartz-sericite rock	+0.1

Table 7 Isotopic data for water samples from the Hamada area

Sample No.	Location and description	$\delta^{18}O_{SMOW}$ (‰)	δD_{SMOW} (‰)
Kum-27	Near the town hall, Kanagi-cho; tap water	−7.8	−44
Kum-25	Kurakake; ground water collected from a borehole of 60m depth	−8.1	−48
Kum-24	Ino spa; spring water	−7.6	−45
Kum-6	Mimata hot springs; thermal water, 40.1 °C, pH 10.0	−9.0	−54

(+0.1‰). This suggests formation of pyrite with low-^{34}S content in hydrothermal alteration.

$^{18}O/^{16}O$ and D/H Ratios of Waters

Meteoric ground waters collected from the area have $\delta^{18}O$ values of −8.1 to −7.6‰ and δD values of −48 to −44‰. One thermal water collected at the Mimata hot springs (40.1 °C, pH 10.0) has a $\delta^{18}O$ value of −9.0‰ and a δD value of −54‰ (Table 7). These values are in the range reported for meteoric waters on the Sea of Japan side of southwest Japan (MATSUBAYA et al., 1973).

ROCK-WATER INTERACTION

^{18}O-depletion of the Rocks in the Hamada Cauldron

The $\delta^{18}O$ values of the whole-rock samples from the Hamada cauldron are plotted against SiO_2 content in Figure 4. The composition ranges of island arc tholeiites (MATSUHISA, 1979) and granitic rocks from central Japan (MATSUHISA and ISHIHARA, unpublished) are shown for reference.

In general volcanic and plutonic rocks, ^{18}O-enrichment with SiO_2 content is induced as a result of isotopic fractionation between cumulus and liquid phases (MATSUHISA et al., 1973; MATSUHISA, 1979). The granitic rocks from central Japan show a positive correlation between $\delta^{18}O$ value and SiO_2 content, suggesting this ^{18}O-enrichment process.

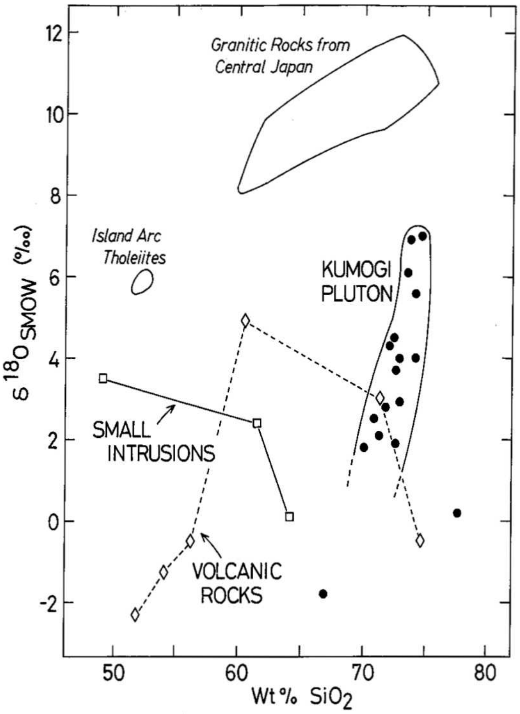


Fig. 4 Graph showing the variation of $\delta^{18}O$ values with SiO_2 content of whole-rock samples from the Hamada cauldron (solid circle = the Kumogi granites, square = small intrusions, diamond = volcanic rocks). The compositional range of island arc tholeiites (MATSUHISA, 1979) and granitic rocks from central Japan (MATSUHISA and ISHIHARA, unpublished) are compared.

On the contrary, no correlation is seen between $\delta^{18}O$ value and SiO_2 content of the rocks from the Hamada cauldron. $\delta^{18}O$ value falls from +7‰ down to −2‰ with a narrow range of SiO_2 content for the Kumogi granites. An up and down of $\delta^{18}O$ value from −2 to +5‰ is observed with SiO_2 content of the volcanic rocks. These patterns and magnitude of variation, as well as low ^{18}O content, could not be produced in igneous processes. The large, irregular variation suggests secondary isotopic exchange with an ^{18}O-poor oxygen reservoir. They would be due to isotopic exchange reaction with ^{18}O-poor meteoric ground waters at elevated temperatures (TAYLOR, 1974a).

Let us consider oxygen isotopic exchange reaction between rock and water in a closed system. If $\delta^{18}O$ values are given for rock and water at the initial stage of reaction, $\delta^{18}O$ value of rock in product would be a function of water-to-rock ratio with a parameter of isotopic fractionation factor or temperature. Figure 5 shows the change in $\delta^{18}O$ value of rock with water-to-rock ratio in the system calculated by assuming isotopic equilibrium at several different temperatures, where the initial $\delta^{18}O$ values for rock and water were taken as +7.0 and −8.0‰, respectively, and rock-water isotopic fractionation factors were approximated by those of plagioclase (An_{30})-water (Matsuhisa et al., 1979).

It is noted that if the temperature is lower than 100°C, reaction with ^{18}O-poor meteoric water results in ^{18}O-enrichment of the rocks. This means that low-^{18}O rocks could never been produced under weathering condition. According to the calculation shown in Figure 5, the rocks with δ^{18}O values of +4 to −2‰ found in the Hamada cauldron could be derived from the original rock with +7‰ by reaction with ^{18}O-poor meteoric ground water at temperatures of 200 to 400°C. The variation in δ^{18}O value depends upon water-to-rock ratio in the reaction or degree of reaction.

Oxygen Isotopic Fractionation between Minerals

Among the minerals from the Kumogi granites, oxygen isotopic fractionation diagram is shown for the quartz-K-feldspar-magnetite assemblage in Figure 6. The fractionations were calculated on the basis of the corrected δ^{18}O values in Table 4. The solid line in the diagram represents equilibrium fractionation for the assemblage (Becker and Clayton, 1976; Matsuhisa et al., 1979).

One sample (#750328–12), which was collected from the core of the pluton, is plotted on the equilibrium fractionation line at about 650°C. This sample would have preserved the equilibrium fractionation at a magmatic temperature, and represent the least altered rocks in the pluton. Therefore, the whole-rock δ^{18}O value of +7.0‰ of this sample would be close to the original isotopic composition of the Kumogi granites.

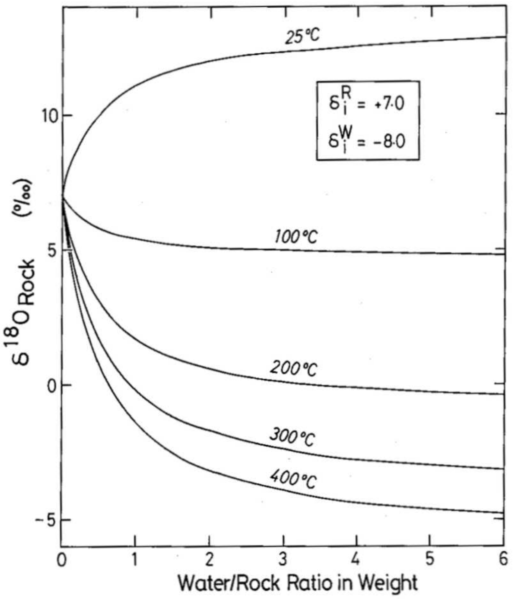


Fig. 5 A plot of calculated δ^{18}O values of rocks versus water-to-rock ratio for rock-water interaction, assuming isotopic equilibrium at several different temperatures in a closed system. The initial δ^{18}O values are taken as +7.0‰ for rock and −8.0‰ for water. Rock-water isotopic fractionation factors are approximated by those of plagioclase (An_{30})-water (Matsuhisa et al., 1979).

Other data points in Figure 6 are distributed far from the equilibrium fractionation line on the side of smaller fractionation of K-feldspar-magnetite pair. The K-feldspar-magnetite fractionation has been shrunk by lowering in ^{18}O content of K-feldspar. The isotopic disequilibrium among the minerals suggests that the isotopic exchange reaction with ^{18}O-poor water would have taken place after crystallization, and that K-feldspar, and also plagioclase as indicated in Figure 2b, would have preferentially reacted with the water.

As has been seen in Figure 2c, biotite behaves isotopically parallel to feldspars. That is, biotite may exchange its oxygen with hydrothermal water as readily as do feldspars. However, the discrepancy in measured fractionation between feldspar and biotite is so large (2.3 to 4.3‰) that it is difficult to infer a secondary isotopic equilibrium between them in hydrothermal condition.

HYDROTHERMAL SYSTEM ESTABLISHED IN THE CAULDRON

Extent of the Hydrothermal Activity

Figure 7 shows the distribution of δ^{18}O values of whole-rock samples and approximate δ^{18}O contours in the Hamada cauldron. A distinct concentric

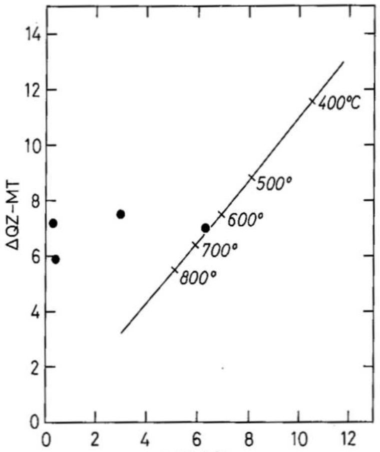


Fig. 6 Oxygen isotopic fractionation diagram for the quartz-K-feldspar-magnetite assemblage from the Kumogi granites. The line showing equilibrium fractionation was calculated on the basis of Becker and Clayton (1976) and Matsuhisa et al. (1979).

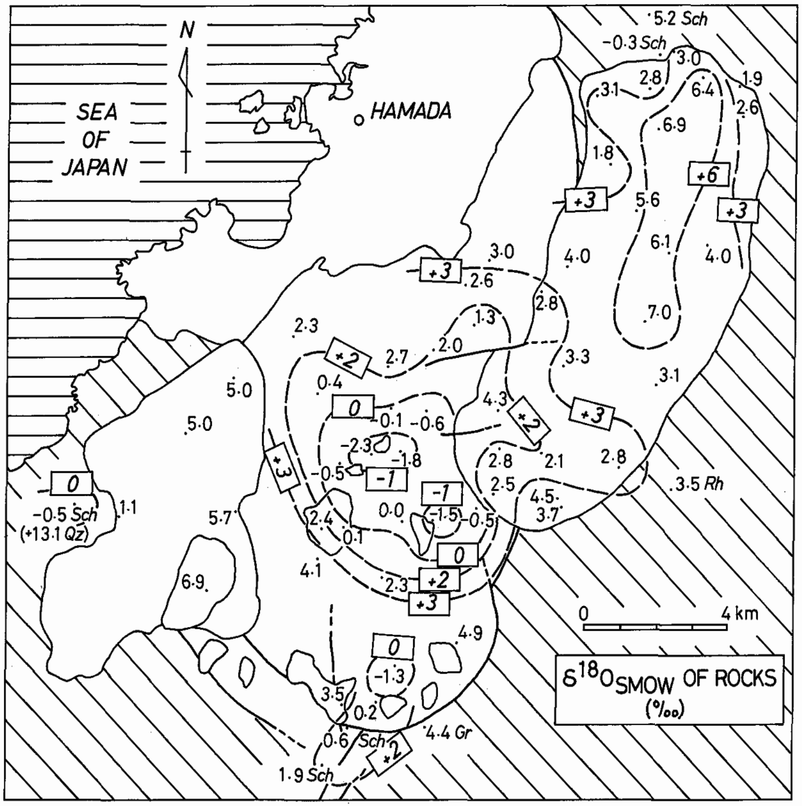


Fig. 7 Distribution of $\delta^{18}O$ values of whole-rock samples and approximate $\delta^{18}O$ contours in the Hamada cauldron. Abbreviations: Gr=granite, Rh=rhyolite, Sch=schist, Qz=quartz.

zoning of whole-rock $\delta^{18}O$ values is seen with the lowest values in the midst of the cauldron. Since the original isotopic composition of the rocks in the cauldron are presumed to have been in a narrow range, lower $\delta^{18}O$ values indicate higher water-to-rock ratio in the reaction or higher temperature at which the reaction took place.

The similar concentric zonings of $\delta^{18}O$ values have been found in the volcanic and plutonic complexes in the Western Cascade Range and the San Juan volcanic field (TAYLOR, 1971; 1974a, b). TAYLOR (1971) suggested that the igneous intrusions acted as heat engines by which ground waters were convectively circulated and reacted with rocks.

It is noticed that small granitic stocks 400 to 700 m in diameter are associated with the lowest-^{18}O zones in the Hamada cauldron. TAYLOR (1971) demonstrated that the low-^{18}O zones of the volcanic country rocks in the Western Cascade Range extend outward 3.0 units of stock diameters away from the intrusive contact. In the Tertiary complex of the Isle of Mull, Scotland, the extent of low-^{18}O zone is in accord with the limit of pneumatolysis (FORESTER and TAYLOR, 1976). If the small stocks are taken as the reference point, the extent of low-^{18}O zone is as large as 7 times of stock diameters in the Hamada cauldron. It is supposed that a hidden pluton or plutons, a part of which crops out as small stocks, beneath the midst of the Hamada cauldron may have been the heat source of the hydrothermal system.

The low-^{18}O zone extends toward the southern part of the Kumogi granite pluton where fracture zones are intensively developed in E–W direction. The thermal waters convected by the hidden pluton seem to have preferentially percolated into the Kumogi pluton through the fracture zones. Quartz-sericite rocks are prominent in the fracture zones with a dike-like appearance. Under a microscope, it is observed that sericite replaces pseudomorphic feldspar, while quartz shows an igneous texture. The relatively high $\delta^{18}O$ value of quartz (+6.0‰) and probably disequilibrium fractionation between quartz and sericite (8.8‰) suggest that quartz in the rocks is a remnant of the original granites.

The variation of $\delta^{18}O$ values along two traverses across the center of the cauldron (AA′) and the

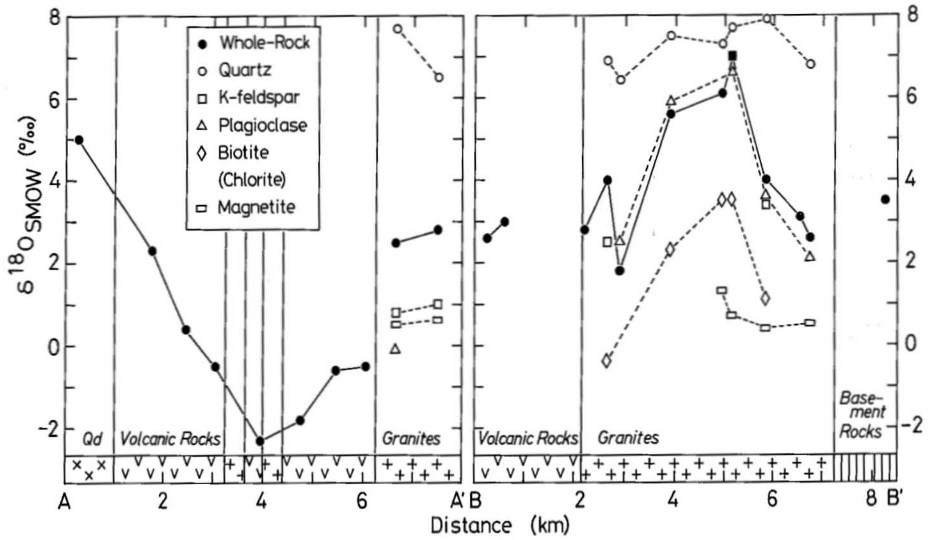


Fig. 8 The variation of $\delta^{18}O$ values of whole-rock and mineral samples along traverses across the center of the cauldron (AA′) and the Kumogi pluton (BB′). The locations of the traverses are shown in Fig. 1.

Kumogi pluton (BB′) is shown in Figure 8. The lowest $\delta^{18}O$ value in the midst of the cauldron and an increase in $\delta^{18}O$ outward are again clearly recognized.

In the Kumogi pluton, the highest $\delta^{18}O$ value of $+7.0^{0}/_{00}$ for whole-rock is seen in the core of the pluton. As has been discussed, equilibrium isotopic fractionation between minerals in the rock suggests that $+7.0^{0}/_{00}$ would be close to the original oxygen isotopic composition of the Kumogi granites.

The $\delta^{18}O$ values decrease toward the outer zones of the pluton. The oxygen isotopic disequilibrium between minerals is also prominent in the outer zones of the pluton. The rocks may have reacted with low-^{18}O waters supplied from the outside of the pluton. If the hidden pluton in the midst of the cauldron was the only heat source available and the Kumogi pluton had cooled down when the hydrothermal system was established, the $\delta^{18}O$ values in the Kumogi pluton should gradually increase with the distance from the center of the cauldron. As a matter of fact, the decrease in $\delta^{18}O$ outward is observed even in the northern and eastern parts of the pluton on the opposite side of the cauldron. This suggests that the Kumogi pluton itself was hot enough to promote rock-water interaction when water came in.

The zoning of oxygen isotopic composition in the Kumogi pluton accords with the zoned pattern of degree of oxidation of the rocks. The oxidation agent would be the meteoric ground waters supplied from the outside and heated by the pluton itself.

Extent of the rock-water interaction toward basement rocks is recognized at least 1 km from the rim of the cauldron. The basement pelitic schists, which had originally $\delta^{18}O$ value of $+13.4^{0}/_{00}$ on the average, have been depleted in ^{18}O as low as $\delta^{18}O$ of $-0.5^{0}/_{00}$. This large decrease in ^{18}O suggests that rock-water interaction might have extended far beyond 1 km from the rim. Development of radial faults and intrusion of small stocks at the southern rim of the cauldron seem to have enhanced the reaction of the basement rocks with hydrothermal waters.

It is interesting that a quartz vein 5 to 10 cm thick in a schist with $\delta^{18}O$ value of $-0.5^{0}/_{00}$ has a $\delta^{18}O$ value of $+13.1^{0}/_{00}$ (#77930–10). Its $\delta^{18}O$ value is almost identical to that of the original host rock. It seems likely that the quartz crystallized during metamorphism might have preserved its oxygen isotopic composition through the hydrothermal alteration. Here we have another example that quartz is resistant to isotopic exchange after crystallization (Clayton et al., 1968).

Origin of the Thermal Water

We have a sericite (#77930–2) which seems to have crystallized from the hydrothermal water. If isotopic equilibrium is assumed between them, isotopic composition of the hydrothermal water is calculated.

Figure 9 is a plot of δD vs $\delta^{18}O$ values for waters, rocks and minerals from the Hamada cauldron. The calculated isotopic composition for the hydrothermal water equilibrated with sericite (open square) is shown by cross marks with parameter of temperature. The calculation was made on the basis of laboratory experimental data by O'Neil and Taylor (1969) for oxygen and Suzuoki and Epstein (1976) for hydrogen. It is noticed that the isotopic composition of the

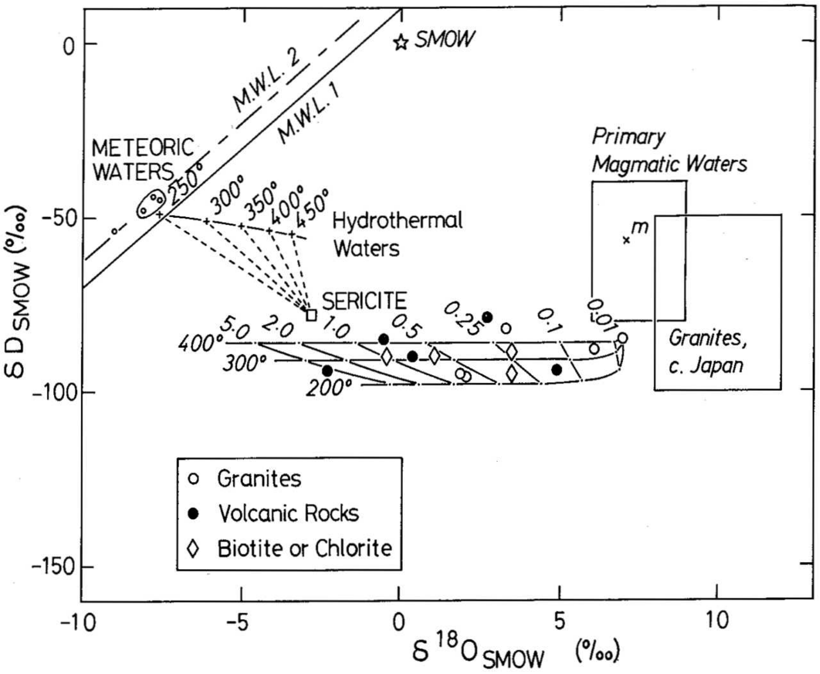


Fig. 9 A plot of δD versus $\delta^{18}O$ for waters, rocks and minerals from the Hamada cauldron. The calculated isotopic composition of the hydrothermal waters equilibrated with sericite (square) is shown by cross marks with parameter of temperature. The cross mark with *m* presents isotopic composition of magmatic waters calculated for the Kumogi granites. The calculated compositional range of hydrothermally altered rocks is given by solid curves with parameters of temperature and water-to-rock ratio. See the text for the details of calculations. The compositional ranges of granites from central Japan (MATSUHISA and ISHIHARA, unpublished) and primary magmatic waters by TAYLOR (1974a) are shown by rectangles. M.W.L. 1 and M.W.L. 2 stand for the meteoric water lines by CRAIG (1961) and SAKAI and MATSUBAYA (1977), respectively.

hydrothermal water goes into the region of present-day meteoric ground waters at about 250°C. It may be possible that the hydrothermal water was originated from Paleogene meteoric ground waters whose isotopic composition was close to that of the present-day meteoric ground waters.

On the other hand, magmatic water equilibrated with the original Kumogi granites (represented by sample #750328–12) might have had an isotopic composition indicated by a cross mark with *m* in Figure 9 (MATSUHISA et al., 1979; SUZUOKI and EPSTEIN, 1976). The compositional range of the hydrothermal waters with different temperatures comes close to the tie line between the magmatic water (*m*) and the meteoric water region. If the temperature at which sericite precipitated was higher than 250°C, the hydrothermal water could be a mixture of meteoric and magmatic waters.

Water-to-rock Ratio in the Hydrothermal System

The change in isotopic composition of rocks by reaction with hydrothermal water was calculated with parameters of temperature and water-to-rock ratio (Fig. 9). Because the apparent hydrogen isotopic fractionation of about 12‰ between sericite and chloritized biotite from the Kumogi pluton is close to the equilibrium fractionation (TAYLOR, 1974a; SUZUOKI and EPSTEIN, 1976), the composition of hydrothermal water responsible for chloritization of biotite would be the same as that for sericite deposition. In the calculation, the initial isotopic compositions were taken as $\delta^{18}O = +7.0‰$ and $\delta D = -85‰$ for rock, and $\delta^{18}O = -8.0‰$ and $\delta D = -47‰$ for water. The isotopic fractionation factors were approximated by that of plagioclase (An_{30})-water for oxygen (MATSUHISA et al., 1979) and that of chlorite-water for hydrogen (TAYLOR, 1974a). The rocks from the Hamada cauldron have 0.5% (in weight) water on the average, which was taken into calculation for hydrogen isotopes.

The amount of hydrogen atoms in rock is so small relative to that in water that δD value of rock approaches quichly a value in equilibration with the infinite amount of water. Therefore, δD value of rocks would indicate a reaction temperature regardless of water-to-rock ratio, if isotopic composition of water is given. The data points for the rocks from the Hamada cauldron in Figure 9 are distributed in the temperature range of 200 to 400 °C.

In the Wairakei geothermal field, New Zealand, a concentric zoning of isotherms is observed (BANWELL, 1965). ESLINGER and SAVIN (1973) indicated that the extent of enrichment in ^{18}O of thermal water varies with both temperature and rock type in the Ohaki-Broadlands geothermal field. These examples suggest that the zoned pattern of $\delta^{18}O$ values of the rocks in the Hamada cauldron also might be due to temperature distribution in the cauldron. It may partly be so. However, the variation range of the data points shown in Figure 9 is much wider than that attributed to temperature change (200 to 400°C) with a constant water-to-rock ratio. The distribution of $\delta^{18}O$ values of the rocks in the Hamada cauldron may have largely been produced by varying water-to-rock ratio. In the vicinity of the small stocks, the ratio might have been higher than 1.0. Most part of the cauldron with $\delta^{18}O$ values lower than $+3.0^{0}/_{00}$ would have had water-to-rock ratio higher than 0.25.

Another, but minor factor to vary the isotopic composition of rocks is production of sericite which has distinct isotopic composition of both oxygen and hydrogen. Some data points in Figure 9 which seem to lie along a tie line with sericite might suggest the mixing of sericite with chlorite.

Formation of Clay Minerals

The clay minerals collected from the Kumogi granites have composition enriched in heavy isotopes of both oxygen and hydrogen as compared with the host rocks (Table 5). These clays, together with sericite, are distributed on a single line in the δD vs $\delta^{18}O$ plot (Fig. 10). The sample which is most abundant in montmorillonite has the highest $\delta^{18}O$ and δD values, while sericite has the lowest. Therefore, the line would represent mixing of sericite and clays.

The intercept of the extrapolation of the sericite-clay mixing line with the kaolinite weathering line, which is obtained by modification of the SAVIN and EPSTEIN (1970)'s line on the basis of meteoric water line in Japan (SAKAI and MATSUBAYA, 1977), gives a $\delta^{18}O$ value of $+22.5^{0}/_{00}$ and a δD value of $-44^{0}/_{00}$. It seems likely that these values represent pure fraction of clays formed by weathering of the Kumogi granites. It is interesting that the values are identical to the composition of montmorillonite from the weathering profile of the Big Sur quartz diorite gneiss, California (LAWRENCE and TAYLOR, 1972).

If the isotopic fractionation factors between clay and water are taken as 1.027 for oxygen and 0.970 for hydrogen (LAWRENCE and TAYLOR, 1971), water equilibrated with the clay should have a $\delta^{18}O$ of $-4.4^{0}/_{00}$ and a δD of $-14.4^{0}/_{00}$, which are enriched in heavy isotopes relative to the present-day meteoric waters. It is supposed that the clay minerals were formed at a stage different from the hydrothermal alteration, and that the waters at that stage, presumably meteoric ground waters, had an isotopic composition enriched in heavey isotopes relative to that of the hydrothermal waters.

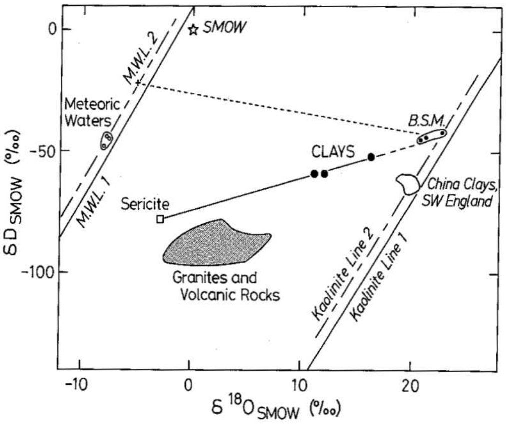


Fig. 10 A plot of δD versus $\delta^{18}O$ for clay minerals from the Hamada cauldron. Solid line gives the mixing line of clay and sericite. The compositional ranges of granites and volcanic rocks and meteoric waters were transferred from Fig. 9. Kaolinite Line 1 (SAVIN and EPSTEIN, 1970) is modified to Kaolinite Line 2 on the basis of the meteoric water line in Japan (M.W.L. 2) (SAKAI and MATSUBAYA, 1977). The compositional ranges of clays from Big Sur, California (LAWRENCE and TAYLOR, 1972) and SW England (SHEPPARD, 1977a) are shown for comparison.

Sulfur Isotopes in the Hydrothermal System

As has been mentioned, the rocks from the Hamada cauldron have $\delta^{34}S$ values in the range for the magnetite-series granitoids in Japan (SASAKI and ISHIHARA, 1979). SASAKI and ISHIHARA (1979) describe that the magnetite-series granitoids (ISHIHARA, 1977) all have positive $\delta^{34}S$ values from $+1$ to $+9^{0}/_{00}$, while the ilmenite-series rocks (ISHIHARA, 1977) are dominated by negative values between -11 and $+1^{0}/_{00}$. They attributed the trend in the ilmenite-series to the influence by isotopically light biogenic sulfur from the continental crust.

The $\delta^{34}S$ values of the rocks from the Hamada cauldron show a positive correlation with the $\delta^{18}O$ values of the rocks (Fig. 11). That is, rocks highly altered by reaction with meteoric hydrothermal waters have lower ^{34}S content. Besides, the rocks which have lower ^{34}S content show high content of sulfur up to 1.2% in weight.

It is likely that sulfur with low ^{34}S content was added to the system by hydrothermal waters. The basement Paleozoic sediments and metamorphic rocks might be the source of the isotopically light sulfur. The alternative is that ^{34}S isotope was preferentially

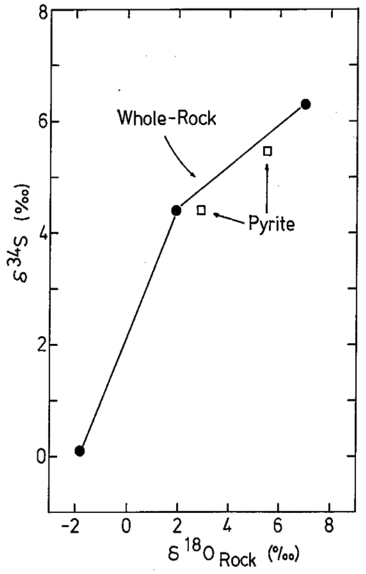


Fig. 11 A plot of $\delta^{34}S$ versus $\delta^{18}O$ for whole-rock and pyrite samples from the Hamada cauldron. The $\delta^{34}S$ values of pyrite are plotted against $\delta^{18}O$ values of their host rocks.

leached away from the system by oxidation of sulfur in hydrothermal condition.

Large euhedral crystals of pyrite from a granite and a quartz vein come close to the trend of the whole-rocks in the diagram if their $\delta^{34}S$ values are plotted against $\delta^{18}O$ values of their host rocks (Fig. 11). The source of sulfur of vein sulfides seems to be the same as that of the rocks.

ENRICHMENT OF BASE METALS IN THE CAULDRON

The porphyry copper deposits generally show a systematic concentric pattern of alteration and mineralization, being arranged outward from a potassic core through phyllic, argillic, and propylitic zones (LOWELL and GUILBERT, 1970). By means of isotopic analysis, hydrothermal waters responsible for potassic alteration were proved to be of magmatic origin, while the surrounding phyllic alteration assemblage is a product of meteoric hydrothermal system (GARLICK and EPSTEIN, 1966; SHEPPARD et al., 1969, 1971; SHEPPARD and TAYLOR, 1974). In many porphyry copper deposits, much of the chalcopyrite mineralization is centered about the boundary zone between the meteoric and magmatic hydrothermal systems (LOWELL and GUILBERT, 1970; SHEPPARD, 1977b).

The appearance of the hydrothermal alteration in the Hamada cauldron resembles that of the phyllic alteration in porphyry copper deposits. However, there exists neither potassic alteration zone nor remarkable mineralization of chalcopyrite on the surface. Possibility of mineralization in the area was preliminarily examined by analyzing whole-rock samples for copper, zinc and lead concentration.

The results are presented in Table 8. The Kumogi granites with $\delta^{18}O$ values higher than $+3^0/_{00}$ have low and uniform concentration of copper (6 to 9 ppm) and zinc (11 to 31 ppm). These base metal concentrations are identical to those of the basement rocks in other regions of Japan (ISHIHARA and TERASHIMA, 1974). In the ^{18}O-depleted granites, copper and zinc are enriched up to 66 and 165 ppm, respectively. The concentrations in copper and zinc of volcanic rocks increase up to 94 and 250 ppm, respectively, in more ^{18}O-depleted rocks.

Table 8 Cu, Zn and Pb concentrations in the rocks from the Hamada cauldron

Sample No.	Cu (ppm)	Zn (ppm)	Pb (ppm)
Granites			
750328–12	6	27	10
750319–2	9	24	15
750512–3	9	19	13
750408–17	8	31	9
750601–9	7	11	12
750327–14	21	107	97
750511–23	25	66	19
750609–20	9	26	7
750511–28	9	58	15
760510–13	66	83	26
750606–4	29	165	15
750608–8	37	59	13
760408–4	38	58	6
750410–17	14	9	16
7710–1	11	42	5
Quartz diorites			
760408–2	42	111	8
750613–1	39	99	13
77718–12	43	92	14
Quartz gabbros			
77723–3	64	110	12
77723–7	61	83	13
760515–11	52	112	21
Volcanic rocks			
77722–2	25	71	17
771128–1	32	95	8
7764–3	23	56	15
7765–5	32	58	5
750603–8	80	220	9
760513–9	36	124	17
771120–2	67	76	8
760510–131	11	173	13
771120–1	33	98	10
760608–6	41	250	104
760511–9	25	130	20
760509–4	94	111	21

The lead content of the rocks seems invariable being in the range of 5 to 26 ppm regardless of ^{18}O-content, with two exceptions of 97 ppm for a granite (#750327–14)and 104 ppm for a dacite tuff (#760608–6). In the sample #750327–14, it is observed under a microscope that minute grains of galena and sphalerite are associated with pyrite.

SILLITOE (1980) argues that caldera system may not be a convenient setting for the formation of porphyry copper deposits because of expulsion of the metal-carrying agents from the magma chambers. Indeed, the absolute concentration of base metals in the Hamada cauldron is lower by two orders of magnitude than that in porphyry copper deposits. The enrichment factor of base metals relative to background in the country rocks is about 10, which is one order of magnitude lower than that in porphyry copper deposits.

Aside from the absolute concentration, however, it is evident that base metals of the rocks are relatively enriched with depletion in ^{18}O content (Fig. 12). A concentric pattern of distribution of base metals in the cauldron is obtained, being in accord with that of the oxygen isotopes (Fig. 13). That is, the highest concentration of copper (higher than 60 ppm) is seen in the vicinity of the small granitic stocks in the midst of the cauldron. It appears that the concentration of base metals in the cauldron is closely related to the circulation of the hydrothermal waters.

If base metals were supplied from leaching of country rocks by hydrothermal waters, rocks lower in ^{18}O should have lower concentration in base metals. This is not the case in fact. The base metals would have been supplied from other source, probably from the intrusive magmas and concentrated by circulating hydrothermal waters. The lack of potassic alteration zone in the Hamada cauldron suggests that high-temperature and high K^+/H^+ condition (HEMLEY and JONES, 1964) was not established in the hydrothermal system. The high-temperature and high K^+/H^+ solution, which might be derived from intrusive magmas, would be the initial carrier of base metals, and essential to the formation of porphyry copper deposits.

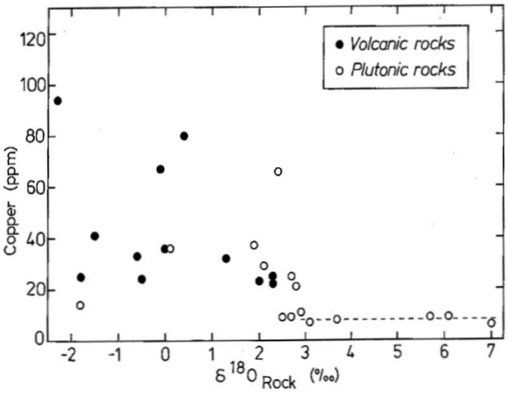


Fig. 12 Graph showing the variation of copper content with $\delta^{18}O$ values of whole-rock samples from the Hamada cauldron. The horizontal broken line presents the average concentration of copper in the rocks with $\delta^{18}O$ values higher than +3‰.

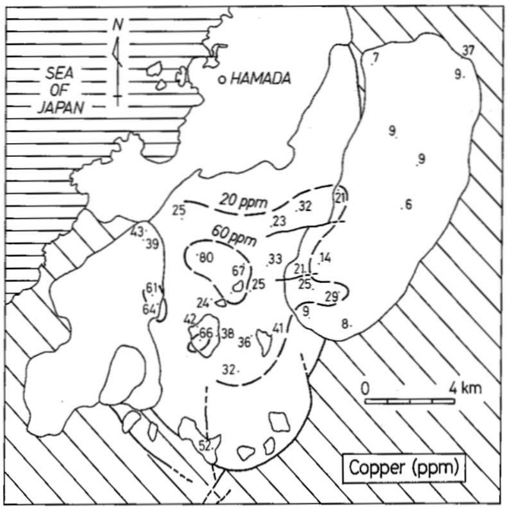


Fig. 13 Distribution of copper concentration of whole-rocks, showing approximate contours in the Hamada cauldron.

In the regional metallogenic analysis of Japan by SHIMAZAKI (1975), the Paleogene granitic terrane along the Sea of Japan coast is assigned to a Cu-poor, Pb–Zn province. In the province, however, lead-zinc ore deposits are concentrated in the Hida metamorphic terrane of central Honshu (ISHIHARA, 1978), and any important base metal deposits have not been found in the Chugoku district where the Hamada cauldron is located. It is probable that the granitic magma of the Hamada cauldron had a low concentration of base metals.

CONCLUDING REMARKS

The oxygen and hydrogen isotopic ratios of rocks and minerals from the Hamada cauldron indicate a large extent of meteoric hydrothermal activity in the cauldron. The hydrothermal activity was most intensive in the central part of the cauldron and diminished outward. A hidden intrusion in the midst of the cauldron, although the Kumogi pluton now exposed to a large extent on the eastern rim seems to have been still hot, would have been the major source of heat which promoted convective circulation of the waters and reaction with rocks. Faults and fracture zones gave a pathway to the hydrothermal waters percolating into the cauldron. The hydrothermal waters were entirely of meteoric origin or one with a little ^{18}O-enrichment caused by isotopic exchange with rocks or mixing of magmatic waters. The temperatures of the thermal waters are estimated to have been in the range of 200 to 400°C. Most part of the cauldron would have had water-to-rock ratio higher than 0.25.

^{34}S-poor sulfur was derived from the basement sediments to form sulfides by the convective thermal waters.

Formation of clay minerals under weathering condition was superimposed on the hydrothermal alteration. The clay minerals would have precipitated from meteoric ground waters different in isotopic composition from the hydrothermal waters.

The features of hydrothermal system described here would be expected at depths of the present-day calderas.

The hydrothermal system established in the Hamada cauldron resembles to that of porphyry copper deposits. Base metals seem to have been supplied from intrusive magmas and concentrated by circulating hydrothermal waters. The mechanisms of concentration of base metals in the Hamada cauldron might have been similar to that of porphyry copper deposits. However, no significant mineralization took place in the area because of inadequate contribution of magmatic waters or low concentration in base metals of the intrusive magmas.

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REFERENCES

BANWELL, C. J. (1965): Central volcanic region. *In* New Zealand Volcanology (B. N. THOMPSON, L. O. KERMODE and A. EWART, eds.). New Zealand D. S. I. R. Inform. Ser. 50, Wellington, 161–171.

BECKER, R. H. and CLAYTON, R. N. (1976): Oxygen isotope study of a Precambrian banded iron-formation, Hamersley Range, Western Australia. Geochim. Cosmochim. Acta, **40**, 1153–1165.

CLAYTON, R. N. and MAYEDA, T. K. (1963): The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. Geochim. Cosmochim. Acta, **27**, 43–52.

CLAYTON, R. N., MUFFLER, L. J. P. and WHITE D. E. (1968): Oxygen isotope study of calcite and silicates of the River Ranch No. 1 well, Salton Sea geothermal field, California. Amer. Jour. Sci., **266**, 968–979.

CLAYTON, R. N. and STEINER, A. (1975): Oxygen isotope studies of the geothermal system at Wairakei, New Zealand. Geochim. Cosmochim. Acta, **39**, 1179–1186.

CRAIG, H. (1961): Isotopic variations in meteoric waters. Science, **133**, 1702–1703.

EPSTEIN, S. and MAYEDA, T. (1953): Variation of O^{18} content of waters from natural sources. Geochim. Cosmochim. Acta, **4**, 213–224.

ESLINGER, E. V. and SAVIN, S. M. (1973): Mineralogy and oxygen isotope geochemistry of the hydrothermally altered rocks of the Ohaki-Broadlands, New Zealand geothermal area. Amer. Jour. Sci., **273**, 240–267.

FORESTER, R. W. and TAYLOR, H. P., Jr. (1976): ^{18}O-depleted igneous rocks from the Tertiary complex of the Isle of Mull, Scotland. Earth Planet. Sci. Lett., **32**, 11–17.

FRIEDMAN, I. and SMITH, R. L. (1958): The deuterium content of water in some volcanic glasses. Geochim. Cosmochim. Acta, **15**, 218–228.

GARLICK, G. D. and EPSTEIN, S. (1966): The isotopic composition of oxygen and carbon in hydrothermal minerals at Butte, Montana. Econ. Geol., **61**, 1325–1335.

GODFREY, J. D. (1962): The deuterium content of hydrous minerals from the East-Central Sierra Nevada and Yosemite National Park. Geochim. Cosmochim. Acta, **26**, 1215–1245.

HEMLEY, J. J. and JONES, W. R. (1964): Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism. Econ. Geol., **59**, 538–569.

ISHIHARA, S. (1977): The magnetite-series and ilmenite-series granitic rocks. Mining Geol., **27**, 293–305.

ISHIHARA, S. (1978): Metallogenesis in the Japanese island-arc system. Jour. Geol. Soc. (London), **135**, 389–406.

ISHIHARA, S. and TERASHIMA, S. (1974): Base metal contents of the basement rocks of Kuroko deposits—An overall view to examine their effect on the Kuroko mineralization. *In* Geology of Kuroko Deposits (S. ISHIHARA, K. KANEHIRA, A. SASAKI, T. SATO and Y. SHIMAZAKI, eds.). Mining Geol. Spec. Issue, 6, 421–428.

LAWRENCE, J. R. and TAYLOR, H. P., Jr. (1971): Deuterium and oxygen-18 correlation: Clay minerals and hydroxides in Quaternary soils compared to meteoric waters. Geochim. Cosmochim. Acta, **35**, 993–1003.

LAWRENCE, J. R. and TATLOR, H. P., Jr. (1972): Hydrogen and oxygen isotope systematics in weathering profiles. Geochim. Cosmochim. Acta, **36**, 1377–1391.

LOWELL, J. D. and GUILBERT, J. M. (1970): Lateral and vertical alteration-mineralization zoning in porphyry ore deposits. Econ. Geol., **65**, 373–408.

MAGARITZ, M. and TAYLOR, H. P., Jr. (1976): Isotopic evidence for meteoric-hydrothermal alteration of plutonic igneous rocks in the Yakutat Bay and Skagway areas, Alaska. Earth Planet. Sci. Lett., **30**, 179–190.

MATSUBAYA, O., SAKAI, H., KUSACHI, I. and SATAKE, H. (1973): Hydrogen and oxygen isotopic ratios and major element chemistry of Japanese thermal water systems. Geochem. J., **7**, 123–151.