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CRISTOBALITE MORPHOLOGY AND OXYGEN ISOTOPIC COMPOSITION VARIATION UNDER HYDROTHERMAL ALTERATION

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Abstract—From 2 to 28% opal-cristobalite was isolated from the 2–20 μm fraction of rhyolitic and andesitic tuffaceous pyroclastics from the Island of Honshu, Japan, where it had been formed in hydrothermal springs at temperatures of ~25–170°C, as calculated from the oxygen isotopic ratios ($^{18}O/^{16}O$). Three of the isolates gave X-ray powder diffractograms with strong peaks at 4.07 Å. Two of these also had very weak peaks at 4.32 Å indicative of the presence of traces of tridymite. The fourth isolate had a strong 4.11 Å cristobalite peak and a very weak 4.32 Å peak. The morphology, determined by the scanning electron microscope, varied with the formation temperature indicated by the oxygen isotopic ratio ($\delta^{18}O$), from spheroidal and spongy for the opal-cristobalite formed at ~25°C ($\delta^{18}O = 26.0$ ‰) in contrast to angular irregular plates and prisms for that formed at ~115°C (11.9 ‰), ~135°C (7.9 ‰) and ~170°C (6.8 ‰). The differences in $\delta^{18}O$ values are attributed to variation in hydrothermal temperature, but some variability in oxygen isotopic composition of the water is possible. The field-measured temperatures related roughly with the calculated fractionation temperatures except in one site, while the contrast in cristobalite morphology related well to calculated low and high fractionation temperatures. Low-cristobalite of hydrothermal origin in New Zealand ($\delta^{18}O = 9$ ‰) had characteristic rounded grains with some evidence of platiness. Co-existing quartz grains ($\delta^{18}O = 10$ ‰) showed more subhedral and irregular prismatic morphology.

INTRODUCTION

The purpose of this paper is to show the range in electron microscopic morphology and oxygen isotopic composition in opal-cristobalite formed in hydrothermal springs at varying temperatures. Opal-cristobalite from various sources ranges in $\delta^{18}O$ value (in per mil relative to SMOW, the standard terminology) from 8.8 to 34.0 ‰. It ranges from 25.5 to 29.9 ‰ in that from Helms bentonite of Texas with diatom skeletal pseudomorphology (Henderson *et al.*, 1971). The ratios of the latter reflect greater abundance of heavier oxygen isotopes than in a hydrothermal low-cristobalite from Taiwan ($\delta^{18}O = 9.3$‰) with prismatic morphology or from the A2 and C1 horizons ($\delta^{18}O = 8.3$–9.1 ‰) of Parahaki soil developed in apparently hydrothermally altered rhyolite in New Zealand (Henderson *et al.*, 1972). The oxygen isotopic compositions reported for cristobalite evidently parallel that of its SiO_2 polymorph, quartz, ranging from those of quartz from granite (9–11 ‰; Taylor, 1968) to those of quartz from chert (commonly 24–32 ‰; Degens and Epstein, 1962).

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MATERIALS AND METHODS

Opal-cristobalite was isolated from the 2–20 μm size fraction of samples of hydrothermally altered Miocene rhyolitic tuffaceous angular conglomerate pyroclastics of the Mizusawa acid clay deposit in northeastern Honshu, Japan (Takeshi *et al.*, 1969) and andesitic tuffaceous breccia in the acid solfataric zone of Mt. Hakone (east of Mt. Fuji) of central Honshu, Japan. The tuffaceous conglomerate consisted mainly of acid montmorillonite, quartz and opal-cristobalite. The tuffaceous breccia from the solfatara zone consisted mainly of alunite, kaolinite, quartz, and opal-cristobalite (Fujii *et al.*, 1966).

The morphologies of hydrothermal low-cristobalite and quartz isolated from the A2 (28–39 cm) and C1 (104–124 cm) horizons of Parahaki soil from Putahi Hill, N.Z. (oxygen isotopic ratios and lithology of which were presented earlier; Henderson *et al.*, 1972) are included here for comparison.

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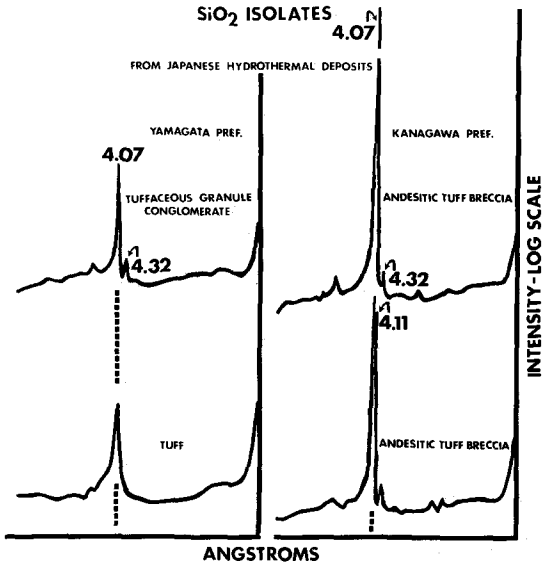


Fig. 1. X-ray powder diffractograms of opal-cristobalite isolates from hydrothermal deposits, Yamagata and Kanagawa Prefectures, Japan.

Quartz and cristobalite were isolated by the acid–base hexafluorosilicic acid (ABHF) treatment combined with heavy liquid separation with 9% polyvinylpyrrolidone in ethanol (Francis *et al.*, 1970) mixed with tetrabromoethane and nitrobenzene (Henderson *et al.*, 1972). Cristobalite was separated from quartz at 2.33 g cm^{-3}, the cristobalite going into the lighter fraction. Treatment with 6N HCl at 80°C and 0.5N NaOH at boiling were given to decrease the extraneous oxides and amorphous material. Then 30% H_2SiF_6 treatment for four days at 18°C yielded the SiO_2 polymorph isolates. The opal-cristobalite was characterized by a single sharp X-ray diffraction peak at 4.07–4.11 Å (Figure 1). Traces of tridymite usually were denoted by the 4.32 Å peak.

The oxygen isotopic composition was determined by the method of Clayton and Mayeda (1963). The scanning electron microscopy was with a Cambridge instrument. Mounting was on silver cement (E. F. Fullam, Schenectady, NY) on 12-mm Al stubs, with successive C and Au coatings.

RESULTS AND DISCUSSION

The amount of opal-cristobalite ranged widely from 2 to 28 weight % of the 2–20 μm size fraction (Table 1). The oxygen yield ranged from 89 to 97% of the theoretical value for SiO_2. Work on the isolation procedure done after these samples were prepared (Sridhar *et al.*, 1975) suggests that low oxygen yields are a result of the production of sparingly soluble fluorides by the H_2SiF_6 treatment. Their removal by water, dilute HF, and saturated H_3BO_3 treatments (resulting in 100% oxygen yield) did not change the oxygen isotopic $\delta^{18}O$ value (i.e. no oxygen was contained in the F impurities).

Oxygen isotopic composition

The $\delta^{18}O$ values have a wide range, from 6.8 to 26.0‰ (Table 1), suggesting widely different temperatures of formation. Temperatures of formation of the opal-cristobalite can be estimated, based on the following assumptions: (1) that it formed in isotopic equilibrium with the local thermal waters; (2) that the equilibrium isotopic fractionations for cristobalite–water are the same as those determined experimentally for quartz–water (Clayton *et al.*, 1972); (3) that the isotopic composition of the opal-cristobalite has

Table 1. Oxygen isotope abundance of opal-cristobalite (from fraction 2–20 μm in dia.) isolated from hydrothermally altered rhyolitic and andesitic pyroclastics of Japan

Sample Location (Sample No.)	Description of parent rock type	Opal-cristobalite Weight (%)†	(%)§	$\delta^{18}O$ (‰)	Temperature, °C Field*	$\delta^{18}O$‡
Mizasawa, Yamagata Pref., Honshu Island northeast Japan (M-9)	Miocene rhyolitic tuffaceous, granular conglomerate	1.7	95	7.9	50	~135
Same (M-39)	Granule-bearing tuff	4.8	89	26.0	50	~25
Mt. Hakone, east of Mt. Fuji, Kanagawa Pref., central Japan (H-16)	Andesitic tuff breccia, active solfataric zone	28.0	97	11.9	93–143	~115
Same (H-45)	Same (zeolitic)	3.3	92	6.8	93–143	~170

* Field observation by Dr. N. Fujii.
† Of 2–20 μm size fraction.
‡ The hydrothermal waters are assumed to be of a meteoric origin with a $\delta^{18}O$ value of −9‰ in NE Honshu and −7‰ in the Mt. Hakone region (Matsubaya *et al.*, 1973); the H_2O/SiO_2 fractionation is according to Clayton *et al.* (1972).
§ Oxygen, of theoretical SiO_2.

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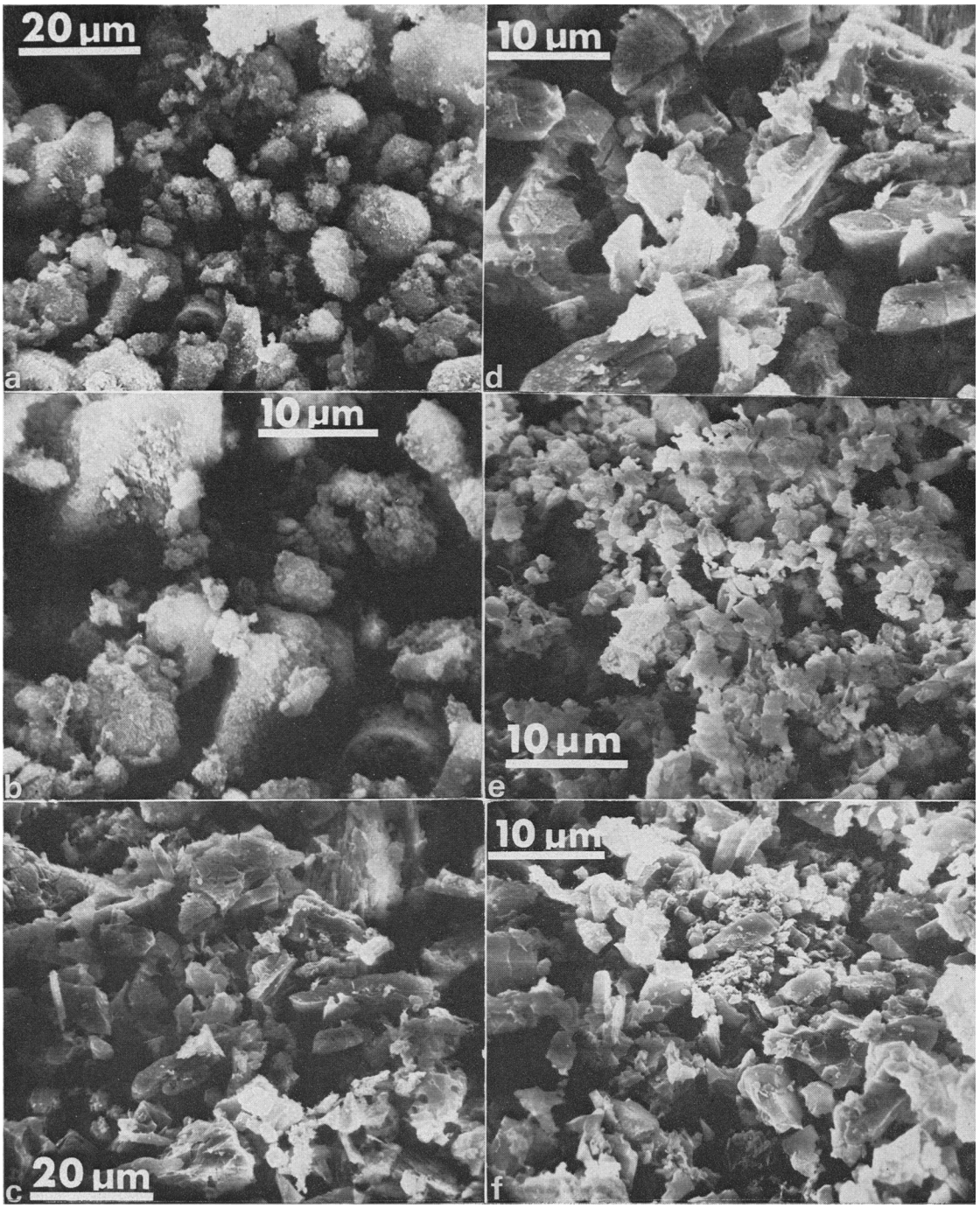


Fig. 2. Opal-crystobalite (20–2 μm in dia.) isolates, as observed with the scanning electron microscope, from the following hydrothermal deposits of Japan: (a and b) tuff, Yamagata Pref., formed at ~ 25°C; (c and d) andesitic tuff breccia, Kanagawa Pref., formed at ~ 115°C; (e) tuffaceous granule conglomerate, Yamagata Pref., formed at ~ 135°C; (f) with tridymite intergrowths, andesitic tuff breccia, Kanagawa Pref., formed at ~170°C.

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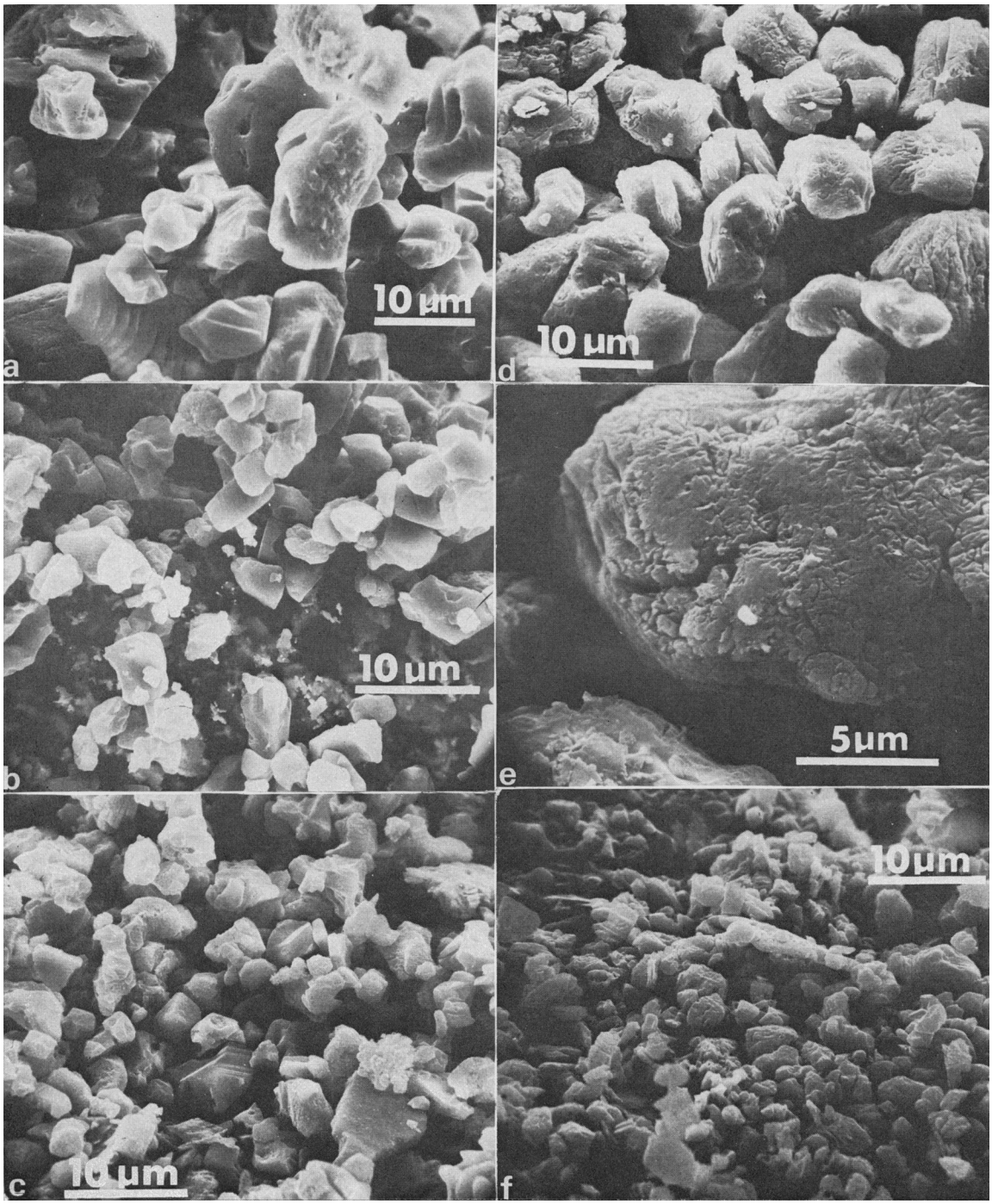


Fig. 3. Quartz (a,b,c) and low-cristobalite (d,e,f) isolates as observed by scanning electron microscopy, from the following horizons of the Parahaki sandy loam (Putahi Hill, N.Z.): (a) A2 horizon, 28–39 cm, 50–5 μm in dia.; (b) A2 horizon, 5–2 μm; (c) C1 horizon, 104–124 cm, 5–2 μm; (d and e) A2 horizon, 50–5 μm; (f) A2 horizon, 5–2 μm.

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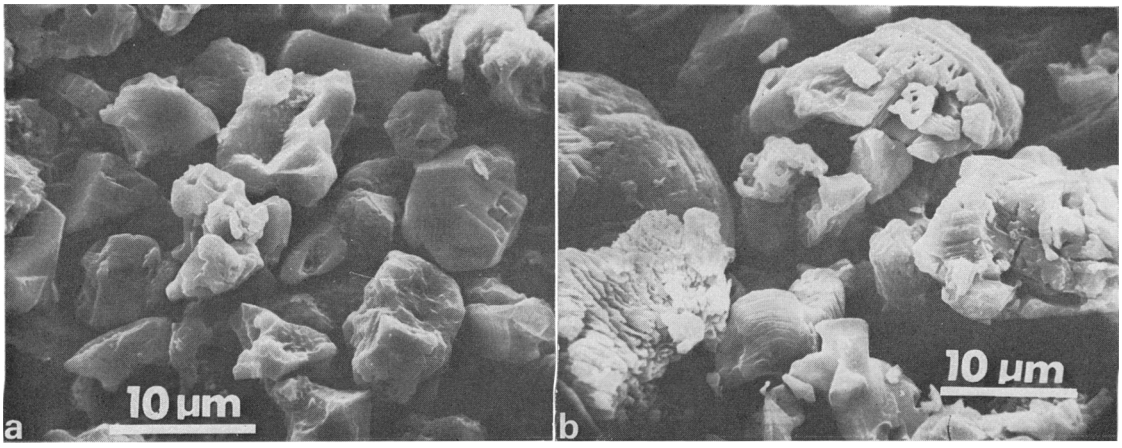


Fig. 4. Morphology of SiO_2 isolates (50–20 μm), quartz (a) and low cristobalite (b), from the Parahaki sandy loam (Putahi Hill, N.Z.), C1 horizon (104–124 cm), as shown by scanning electron microscopy.

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not been altered since its formation. The $\delta^{18}O$-values of thermal waters in northeastern Honshu are assumed to be about -9 ‰, and those of the Hakone region are assumed to be about -7 ‰, based on measurements of Matsubaya *et al.* (1973). The isotopic temperatures range from ~25°C (for $\delta^{18}O = 26$ ‰) to ~170° (for $\delta^{18}O = 6.8$ ‰). Field-observed temperatures can be only approximate at best because the temperature at the time of observation would not necessarily be that existing at the time that the opal-cristobalite formed. Nevertheless, three of the four samples are in rough qualitative agreement. The cristobalite from a tuffaceous, granular conglomerate (M-9) is indicated to have formed at a much higher temperature than the estimated field temperature, measured at a later time. That from breccia (sample H-45) probably also formed at a higher temperature than the 93–143°C estimated field measurements of fumerol gas temperatures (Takahashi *et al.*, 1966). The small amount of tridymite (SiO_2) phase is assumed also to conform to SiO_2 fractionation temperatures of quartz (Henderson *et al.*, 1972).

Particle morphology

Opal-cristobalite. The major morphological differences are between those of the low temperature (~25°C), high $\delta^{18}O$ (26 ‰) opal-cristobalite and those of the silica formed at higher temperatures (Figure 2). The low-temperature samples from granule-bearing tuff have a spongy appearance (Figure 2a,b). The morphology of the high-temperature fractions is irregular and somewhat platy (Figure 2c,d,e,f). An important point is that all specimens received the same preparatory treatment and the recorded wide differences in $\delta^{18}O$ (Table 1) and morphology (Figure 2) persisted through the preparations. Deep-sea cristobalite from nanofossils occurs as cavity-filling spherules (Weaver and Wise, 1972). Blade-like clusters and microspherules occurred in cristobalite–tridynite synthesized from silica gel at 150°C and 2000 bars during 4 weeks (Oehler, 1973). Our plates may have resulted from break-up of clusters.

Quartz. The hydrothermal quartz particles from Parahaki soil of New Zealand are subhedral (Sayin and Jackson, 1975) with some irregularity and rounding (Figure 3a,b,c, $\delta^{18}O = 9.6$‰, A2 horizon; and Figure 4a, $\delta^{18}O = 10$‰ Cl horizon). Only slight filling in of crystals would accompany the cristobalite → quartz transformation believed to be one course of quartz genesis (Murata and Nakata, 1974).

Low-cristobalite. Rounded grains with some evidence of platiness characterize the low-cristobalite of Parahaki soil (Figure 3d,e,f, $\delta^{18}O = 8.3$–9.1‰ A2 horizon; and Figure 4b, $\delta^{18}O = 8.6$‰ Cl horizon). The oxygen isotopic values for low-cristobalite and quartz are from Henderson *et al.* (1972). The low and nearly coincident values $\delta^{18}O$ values for the quartz and low-cristobalite indicate a hydrothermal rather than pedological origin of the SiO_2 which made up most of the A2 horizon of this soil formed under Kauri forest (Swindale and Jackson, 1956).

Low-cristobalite of hydrothermal origin in Taiwan (Henderson *et al.*, 1972; their Figure 3, $\delta^{18}O = 8.8$ to 9.3 ‰) presents an interesting comparison to the present study. The spongy spherules of the untreated low-cristobalite ($\delta^{18}O = 14.3$ ‰) were removed by one ABHF treatment. The treatment removed 52% of the sample, a fraction with a calculated $\delta^{18}O$ value of 18.9 ‰ which, from the present study, could be considered to be a phase of SiO_2 formed at a lower temperature than the rounded, more platy 48%, the remaining phase ($\delta^{18}O = 9.3$ ‰).

CONCLUSIONS

1. The oxygen isotopic ratios ($\delta^{18}O$ values) of 26.0, 11.9, 7.9 and 6.8 ‰ obtained for the opal-cristobalite (SiO_2) isolates from hydrothermal deposits of Honshu Island of Japan indicate that this SiO_2 polymorph was formed at temperatures of ~25, ~115, ~135, and ~170°C, respectively. The scanning electron microscopic (SEM) morphology showed marked contrast for the low-temperature sample (spheroidal, spongy) with those formed at ~115°C or above (irregular, platy). The field temperature observations for the waters and gases correspond only roughly to the indicated hydrothermal temperatures of formation of the cristobalite.

2. Co-existing hydrothermal low-cristobalite and quartz in Parahaki (Kauri podzol) soil of New Zealand, isolated from each other in the laboratory and having similar $\delta^{18}O$ values indicative of hydrothermal origin in both the A2 and Cl horizons, gave distinctive SEM morphologies (rounded and platy for cristobalite versus subhedral and blocky for quartz).

3. Fractionation of hydrothermal low-cristobalite ($\delta^{18}O = 14.3$ ‰) from Taiwan by intensive acid–base–hexafluorosilicic acid treatments to remove half the sample (reported earlier) preferentially removed the lower temperate type with spongy morphology ($\delta^{18}O$ calculated at 18.9 ‰) leaving the platy-blocky type, with $\delta^{18}O = 9.3$ ‰ corresponding to a higher formation temperature.

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