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HYDROTHERMAL ORIGIN OF SMECTITE IN VOLCANIC ASH

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Abstract—Smectite and fine-grained quartz were separated from 6 volcanic ash samples collected in Japan from Shinmoe-dake Volcano, southern Kyushu, and Mt. Usu Volcano, southern Hokkaido. Oxygen isotope ratios of smectite in the volcanic ash range from +6.9 to +12.9 per mill (‰), which are comparable to the values of smectite ($\delta^{18}O$ = +6.5 and +9.4‰) from currently active geothermal fields. Evaluation of the oxygen isotope data from smectite ($\delta^{18}O$ = +6.9 and +8.4‰) and quartz ($\delta^{18}O$ = +6.6 to +11.2‰) in volcanic ash erupted from Shinmoe-dake in 1959 indicates a hydrothermal origin at elevated temperatures (150 to 270 °C) from waters that have calculated $\delta^{18}O$ values ($\delta^{18}O$ = −3 to +5‰) that are enriched relative to local meteoric water ($\delta^{18}O$ = −7 to −8‰). This precludes an authigenic formation of the smectites under ambient temperatures in crater lakes and/or somma-atrios which had been previously proposed as a plausible mechanism. A peculiar clay flow was extruded on the somma-atrio of Mt. Usu Volcano. The isotopic composition of the clay (<0.5 μm, $\delta^{18}O$ = +12.2‰) and evidence from geophysical exploration over volcanic vents of Shinmoe-dake support the concept that extensive hydrothermal alteration is taking place within volcanic vents.

Key Words—Hydrothermal Alteration, Oxygen Isotope Composition, Smectite, Volcanic Ash.

INTRODUCTION

Fresh volcanic ash does not usually contain a significant amount of smectite. However, ash deposits that do contain smectite can cause serious problems for agricultural, forest and catchment ecosystems due to their high water retention properties, adhesiveness and dispersibility (Kanno et al. 1961; Kondo et al. 1979). Therefore, knowledge of volcanic smectite formation is not only important for establishing the origin of the smectite but also for prediction of environmental hazards related to volcanic deposits.

Several modern day volcanic ash deposits such as those from Mt. Usu Volcano, southern Hokkaido (Kondo 1963; Kondo et al. 1978), and Shinmoe-dake Volcano, southern Kyushu, Japan (Kanno et al. 1961), contain smectite. It has been proposed that the high activity of dissolved silicon and bases, and the highly reducing environment at ambient temperatures, were responsible for the authigenic formation of smectite from the pyroclastic deposits in the Mt. Shinmoe-dake crater lake and the somma-atrio of the Usu volcanoes (Kanno et al. 1961; Kondo 1963; Kondo et al. 1978). However, the interpretation that the smectite was formed by authigenic processes is at present only speculative. We present oxygen isotope ratios of smectite and fine-grained quartz separated from volcanic ash that were erupted relatively recently from volcanoes in Japan. Contrary to the previous studies, we propose a hydrothermal origin for the smectite.

SAMPLE LOCALITY AND DESCRIPTION

Three samples of altered volcanic ash from Shinmoe-dake and 3 samples of volcanic ash and 1 clay flow were collected from Mt. Usu (Table 1). In addition, 2 hydrothermal smectites from nearby active geothermal fields were collected (Table 1).

Fresh Volcanic Ash from Shinmoe-dake, Southern Kyushu

Shinmoe-dake is one of several volcanoes in the composite group of the Kirishima Volcano that erupted on February 17, 1959. The ash deposit extended eastward with an aerial width of 8 km, covering Takaharu-cho and Kobayashi city with ash 10 cm thick. The unusual nature of the ash, which had a high plasticity and high clay content, was reported by Kanno et al. (1961). The ash contains a high percentage of soluble salts (calcium sulfates) and ferrous iron. The clay fraction consists predominantly of beidellite and the coarse (2–20 μm) fraction contain a high concentration of quartz (Kanno et al. 1961). Two ash samples were collected within 6 d of the eruption (Table 1).

Mt. Shinmoe-dake Volcano previously erupted a clayey volcanic ash in 1716–1717 AD, which is termed also Sm-KP1 (Imura and Kobayashi 1991). The thickness of the Sm-KP1 ash deposit at the sample site is 2 cm (Table 1). Secondary iron hydroxides (ochre crusting) were observed within Sm-KP1 manifesting the effects of surficial weathering after deposition.

Fresh Volcanic Ash and Clay Flow from Mt. Usu

Mt. Usu consists of 2 volcanic craters. The most recent ash eruption started on August 7, 1977, and continued until October 1978. These ash deposits contain 2 to 6% clay (<2 μm), which is predominantly smectite (Kondo et al. 1979). The color of moist fresh ash was olive black to dark gray (10Y Munsel color

Table 1. Oxygen isotope composition of smectite and quartz from volcanic ash samples.

		$\delta^{18}O$ (per mill)	
Date of collection	Location	Smectite	Quartz
Fresh ashes from Shinmoe-dake			
Feb. 22, 1959	Takachiho-cho (long. 131°00'E, lat. 31°55'N), deposited on leaves of *Cryptomeria japonica*	<0.5 μm: +6.9	1–10 μm: +9.2 10–20 μm: +9.6
Feb. 23, 1959	Southern fringe of Shinmoe-dake crater (130°53'E, 31°54'N)	<0.5 μm: +8.4	1–10 μm: +11.2 10–20 μm: +11.0
Historical ash erupted from Shinmoe-dake 1716–1717 AD†			
Nov. 16, 1996	Nearby Lake Miike (130°53'E, 31°54'N)	<0.5 μm: +9.4	1–10 μm: +6.7 10–20 μm: +6.6 20–53 μm: +6.7
Fresh ashes from Mt. Usu			
Aug. 14, 1977	Sobetsu-cho (140°54'E, 42°33'N)	<0.5 μm: +12.9	
Aug. 31, 1977	Within No. 1 crater	<0.5 μm: +11.7	
Mar. 5, 1978	Eastern margin of Ginnuma	<0.5 μm: +8.3	
Clay flow on somma-atrio of Mt. Usu			
Aug. 23, 1977	Nearby Ginnuma	<0.5 μm: +12.2	
Hydrothermal smectites			
Apr. 10, 1996	Shinyu spa, Unzen (long. 130°16'E, lat. 32°44'N)	<0.5 μm: +9.4	
Apr. 11, 1996	Sujiyu spa, Kuju (long. 131°11'E, lat. 33°07'N)	<0.5 μm: +6.5	

† Sm-KP1 (Imura and Kobayashi 1991).

notation) and yielded a markedly positive reaction for ferrous iron in the field-test using dipyridyl. Previous chemical analysis showed that air-dried clays of the late Pleistocene to Recent pyroclastic deposits from Mt. Usu have a total Fe_2O_3 content ranging from 8.7 to 14.4 wt%, suggesting that the smectite is predominantly nontronite (Kondo 1963). Distinctive clay flows were extruded from 2 cracks in the somma-atrio of Mt. Usu after August 23, 1977 (Katsui et al. 1978; Kondo et al. 1979).

Smectite Formed in Currently Active Geothermal Fields

Hydrothermally altered andesitic rocks, which consist predominantly of smectite, were collected from currently active geothermal fields in Unzen and Kuju volcanic fields, central Kyushu, Japan (Table 1).

METHODS

Air-dried samples were treated with 10% hydrogen peroxide followed by dithionite-citrate and 2% sodium carbonate to remove organic matter, iron-hydroxides and noncrystalline silica (Jackson 1973). A sample-water suspension was disaggregated with an ultrasonic transducer. Fine clay (<0.5 μm) in suspension was collected after centrifugation and flocculated by adding saturated sodium chloride. Ca-saturated specimens were prepared by successive washings with 0.5 *M* $CaCl_2$, water-methanol, methanol-acetone, and finally acetone, then air-dried. These treatments have no effect on the oxygen isotopic composition of clay minerals (Yeh and Savin 1977).

The coarse material was separated into 0.5 to 10, 10 to 20 and 20 to 53 μm size fractions and dried at 105 °C. Quartz was quantitatively isolated from the separates by pyrosulfate fusion, followed by digestion with 30% fluorosilicic acid at 20 °C (Sridhar et al. 1975).

The oxygen of smectite and quartz was extracted by conventional BrF_5 and laser-microprobe methods, respectively (Clayton and Mayeda 1963; Sharp 1990). Prior to oxygen extraction, interlayer water in smectite was removed by heating at 180 °C for 3 h under vacuum. All the oxygen isotopic ratios were normalized to NBS 28 quartz reference ($\delta^{18}O$ = +9.34‰, SMOW).

Powder X-ray diffraction (XRD) analysis was performed on clay specimens (<0.5 μm) oriented on glass slides. Treatments were K-saturated, air-dried and heated to 300 and 550 °C and Mg-saturated, air-dried and solvated with glycerol.

ANALYTICAL RESULTS

X-ray Diffractometry

Powder XRD of the <0.5 μm clay fractions, which were also chemically treated and heated, revealed that the clay was predominantly smectite in all the samples. Very small amounts of mica and kaolinite were present in clay from Shinmoe-dake Volcano (data not shown).

Oxygen Isotope Geochemistry

The $\delta^{18}O$ values of 3 smectite separates from Shinmoe-dake ash range from +6.9 to +9.4‰. Smectites from Mt. Usu range from +8.3 to +12.9‰; smectites from active geothermal fields are between +6.5 and +9.4‰; and quartz separates from Shinmoe-dake ash range between +6.6 and +11.2‰ (Table 1).

DISCUSSION

The Shinmoe-dake values (+6.9 to +9.4‰) are similar to the 2 values obtained from smectites ($\delta^{18}O$ = +6.5 and +9.4‰) that are being formed in currently active geothermal fields in central Kyushu. The oxygen isotope fractionation between smectite and water has recently been refined by Sheppard and Gilg (1996) by using experimental and empirical data. By assuming an average ambient temperature for the Shinmoe-dake landscape surface of about 10 °C, we calculate that the oxygen isotopic composition of the water in equilibrium with the smectite should be −21 to −18‰, which is not in accord, however, with values measured for meteoric waters ($\delta^{18}O$ = −8 to −7‰) from the Kirishima area (Matsubaya et al. 1975). If the smectite was formed under hydrothermal conditions, say 150 to 270 °C (typical temperatures for hydrothermal smectite formation; Sheppard and Gilg 1996), the estimated fluid should have $\delta^{18}O$ values that range between −3 and +5‰, suggesting that the hydrothermal fluids are a mixture of meteoric and magmatic water. Christenson and Wood (1993) demonstrated that there is extensive hydrothermal alteration taking place between cooling magmatic material and lake water and/or fumarolic condensate in the vent of Ruapehu Volcano in New Zealand. Therefore, the interpretation that the smectite from the Shinmoe-dake ash was formed at relatively high temperatures and by fluids which were probably a mixture of magmatic and meteoric water is reasonable.

Kanno et al. (1961) suggested that smectite in the Shinmoe-dake ash was formed in a crater lake located on the top of the volcano. The $\delta^{18}O$ values (−6‰, Matsubaya et al. 1975) of water from several crater lakes in the Kirishima area may be slightly enriched relative to meteoric water due to preferential evaporation of ^{18}O. If the smectites were formed in the crater lake, as stated by Kanno et al. (1961), from water with an enriched ^{18}O content (say values of about −6‰) the temperature of the smectite formation would be about 90 to 110 °C, which is still much higher than current temperatures of the lake waters (21 to 23 °C; Fukuoka Regional Meteorological Observatory 1965).

The $\delta^{18}O$ values of 3 smectite separates from volcanic ash and the clay flow from Mt. Usu range from +8.3 to +12.9‰. The values are comparable to those of smectites from the nearby Noboribetsu active geothermal field in southern Hokkaido ($\delta^{18}O$ = +4.5 and +6.1‰; Marumo et al. 1996). If the smectite was formed by weathering, then the 5 °C (average temperature of the somma atmosphere of Mt. Usu, Maruzen 1978) fluids responsible for smectite formation should have $\delta^{18}O$ values between −21 and −17‰. If the smectite formed at temperatures between 150 and 270 °C, fluid should have $\delta^{18}O$ values between −2 and +8‰. The authigenic formation of smectite in the Mt. Usu ash, as proposed by Kondo (1963), is not plausible because $\delta^{18}O$ values of modern meteoric waters from the concerned area (−10 to −9‰; Matsuo et al. 1977) are clearly much heavier than the calculated values (−21 to −17‰). The conclusion, therefore, is that hydrothermal fluids enriched in ^{18}O relative to present day meteoric water were responsible for smectite formation in volcanic ash from Mt. Usu.

Two very peculiar clay flows were extruded onto the surface at the somma-atrio of Mt. Usu on August 23, 1977 (Katsui et al. 1978; Kondo et al. 1979; clay flow in Table 1). They have a characteristically green color when fresh, but gradually change to a brownish color due to oxidation at ambient conditions. Matsuo (1979) extracted pore and interlayer water from the clay and determined the δD values of the water. He reported that the δD values were heavier than sea water but the δD and $\delta^{18}O$ values were not shown in the report. The presence of the clay flows reveal that an iron-rich smectite mass is present under the somma-atrio of Mt. Usu. The isotopic data of the smectite (Table 1) demonstrate that it must have formed by water–rock interaction at elevated temperatures.

Significant amounts of fine-grained quartz (11 to 13 wt%) were formed in the 3 volcanic ash samples from Shinmoe-dake volcano, whereas quartz was not found in samples from Mt. Usu (Table 1). Lava of Shinmoe-dake volcano predominantly consists of pyroxene andesite with accompanying small amounts of olivine-bearing pyroxene andesite. Quartz has not been identified either as phenocryst or groundmass minerals in the lava (Sawamura and Matsui 1957), indicating that the quartz in the unusual volcanic ash from Shinmoe-dake perhaps has a secondary origin.

The $\delta^{18}O$ values of 7 quartz isolates from the Shinmoe-dake volcanic ash range from +6.7 to +11.2‰ (Table 1). There is no apparent correlation between the $\delta^{18}O$ values and particle-size. The $\delta^{18}O$ values of quartz separated from the 1716–1717 ash is about 3 to 4‰ lower than the $\delta^{18}O$ values of quartz in 1959 ash. All these values are nearly identical or slightly higher than those reported for phenocryst quartz in Quaternary volcanic ash in Japan ($\delta^{18}O$ = +7 to +9‰; Mizota and Matsuhisa 1985; Mizota et al. 1990). If the quartz and smectite coprecipitated from the same thermal fluids, oxygen isotopic fractionation between quartz (Matsuhisa et al. 1979) and smectite (Sheppard and Gilg 1996) for ash deposited in 1959 indicates formation temperatures of 340 to 430 °C from fluids with $\delta^{18}O$ values of +3.4 to +5.6‰, which is not compatible with the temperature estimates discussed above. Smectite and associated quartz do not appear to have been formed in isotopic equilibrium, and are probably products of different periods or stages of alteration.

Apparent negative oxygen isotope fractionation between quartz ($\delta^{18}O$ = +6.6 and +6.7‰) and associated smectite ($\delta^{18}O$ = +9.4‰) was noticed for a sample deposited in 1716–1717 from Shinmoe-dake. XRD analysis of the smectite revealed a slight development of interlayered Al polymers, probably due to long-term leaching under high rainfall conditions (annual precipitation 3500 mm). It is plausible that the primary oxygen isotope composition of the smectite was modified during pedogenesis.

Documents of the 1959 eruption of Shinmoe-dake volcano (Fukuoka Regional Meteorological Observatory et al. 1959) report that the eruption occurred on its western flank. Recent geophysical exploration predicts the presence of a highly water-saturated zone under the vents (Kagiyama, 1994). This supports the idea that extensive hydrothermal alteration is taking place within the volcanic vents.

Kanno et al. (1961) speculated that smectite in the 1959 ash from Shinmoe-dake Volcano was derived from "halmyrolysis" of ash that was deposited in the crater lake, similar to the diagenesis of volcanic ash on the oceanic floor. However, lake water sampled on July 28, 1934, had only trace concentrations of dissolved carbonates, chlorides and ammonia (Fukuoka Regional Meteorological Observatory 1965). Authigenic formation of smectite may not be plausible under such circumstances where activities of silicon and bases are low (trace amounts).

CONCLUSION

Oxygen isotope data from smectite and associated quartz in volcanic ash that erupted from the Shinmoe-dake Volcano, southern Kyushu, and Mt. Usu Volcano, southern Hokkaido, indicate that the smectite and quartz had a hydrothermal origin, precipitating from fluids that were mixtures of magmatic and local meteoric water. The oxygen isotope evidence precludes an authigenic formation of the smectite under ambient temperatures in crater lakes and/or somma-atrios as proposed by others. The isotopic composition of the clay from peculiar clay flows extruded on the soma-atrio of Mt. Usu Volcano and evidence from recent geophysical exploration over volcanic vents of Shinmoe-dake (Kagiyama 1994) affirm that extensive hydrothermal alteration within volcanic vents. Volcanic ash, particularly from initial phreatomagmatic eruptive events, may have substantial alteration minerals such as smectite, which may increase environmental hazards.

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