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COMPOSITION OF CLINOPTILOLITE FORMED FROM VOLCANIC GLASS DURING BURIAL DIAGENESIS

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Abstract—The composition of clinoptilolite formed from volcanic glass was investigated from cuttings collected from the offshore MITI-Somaoki borehole, 52 km east of Soma City, Japan. Unaltered volcanic glass and clinoptilolite-replaced glass were found coexisting in the same silicic tuff at 1000 m depth, but unaltered volcanic glass and clinoptilolite did not coexist in individual glass shards, and each material analyzed in this study was pure. The SiO_2 and Al_2O_3 contents of the pure clinoptilolite and the pure, unaltered glass were 69.32 and 13.05 wt. %, and 70.03 and 11.54 wt. %, respectively. The SiO_2 content was almost the same and the Al_2O_3 content was greater in the clinoptilolite-replaced glass compared with the unaltered volcanic glass. As a result, the SiO_2/Al_2O_3 ratio in the clinoptilolite-replaced glass ($SiO_2/Al_2O_3 = 5.31$) was slightly lower than that of the unaltered volcanic glass ($SiO_2/Al_2O_3 = 6.07$). The extra-framework cation composition of the clinoptilolite-replaced glass was three times richer in K (K_2O = 7.84 wt. %) than the unaltered volcanic glass (K_2O = 2.59 wt. %). The cation selectivity of clinoptilolite, which shows a preference for K to Ca and Na, played an important role in the concentration of K in clinoptilolite during clinoptilolite formation from volcanic glass, although the initial pore waters and the volcanic glass were not especially relative K.

Clinoptilolite-replaced glass in the calcite-cemented tuff at 1100 m depth was not enriched in Ca, suggesting that the exchangable-cation composition of clinoptilolite did not change by exposure to Ca-rich solutions at this depth. Apparently, the exchangable-cation composition of clinoptilolite, once formed, is relatively stable and difficult to change, even under conditions in which calcite is precipitating on clinoptilolite crystals.

Key Words—Burial Diagenesis, Cation Exchange, Clinoptilolite, Volcanic Glass, Zeolite.

INTRODUCTION

Volcanic glass is the main constituent of many tuffs and tuffaceous rocks. It easily reacts with pore water and is remarkably unstable during post-depositional diagenesis. Authigenic smectite and opal form during early diagenesis and outline silicic volcanic-glass shards. Clinoptilolite commonly replaces volcanic glass, and as diagenesis proceeds, it alters to analcime and/or heulandite (Iijima and Utada, 1971; Iijima, 1986). The transformation mechanism and the change in chemical composition from clinoptilolite to heulandite and/or analcime was studied by Ogihara and Iijima (1989, 1990) and Ogihara (1996), but few studies have compared the composition of clinoptilolite with the composition of the original volcanic glass directly because the assemblages of clinoptilolite coexisting with original volcanic glass have not been found.

This study compares the chemical composition of clinoptilolite and original, unaltered volcanic glass coexisting in a single tuff from the offshore MITI-Somaoki borehole northeast of Honshu Island, Japan.

MATERIALS

The offshore MITI-Somaoki borehole (Figure 1) is located 52 km east of Soma City on the east coast of northeastern Honshu Island, Japan. The depth of water was 137.2 m, and the destination depth of the well was 3500 m. Early to middle-Miocene marine strata occur between 581–1652 m in depth (Japan National Oil Corporation, 1990). Cuttings of light-gray tuff and tuffaceous mudstone, interbedded with olive-gray mudstone, were collected at 100-m intervals. Several pieces rich in tuffaceous material were chosen by hand from the cuttings for chemical analysis.

ANALYTICAL METHODS

Bulk samples were examined by X-ray diffraction (XRD) analysis using a MAC Science MXP3 X-ray powder diffractometer. Polished thin sections made from cuttings were investigated by petrographic microscope and scanning electron microscope (SEM) using a JEOL-JSM840 microscope, and the chemical composition was determined by an energy-dispersive X-ray spectrometer (EDX) using a LINK-AN1000 spectrometer. The analytical parameters were 15 keV and 10^{-10} A, a scanning area of 3.3–4.3 μm, and an analytical time of 100 s. Owing to dehydration under vacuum conditions in the electron microscope and the sample dessicator, the water content of clinoptilolite decreases to ~0.66–0.75 of normal values.

The present study uses the nomenclature of Boles (1972). Clinoptilolite is distinguished for a framework composition of Si/Al > 4.0, and heulandite for Si/Al < 4.0.

DISTRIBUTION OF VOLCANIC GLASS AND CLINOPTILOLITE

Clinoptilolite was detected in the cuttings from 1000 to 1700 m depth by petrographic-microscope obser-

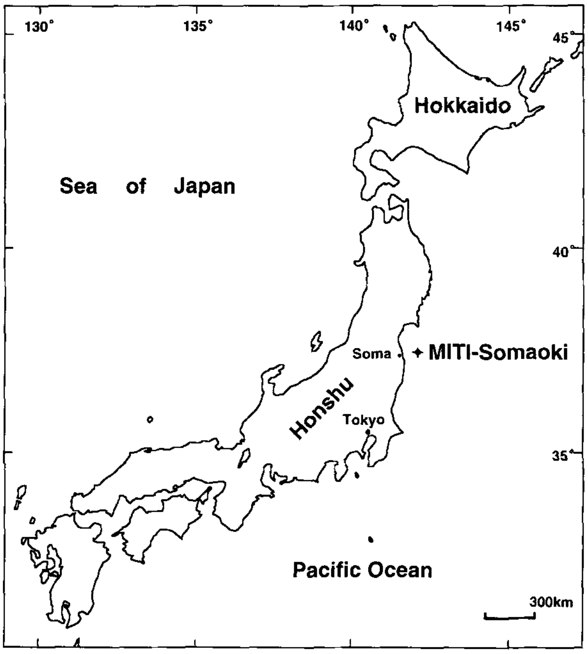

Figure 1. Location map of investigated offshore MITI-Somaoki borehole.

vation and XRD analysis. Because the samples of bulk cuttings included small amounts of clinoptilolite, only the (020) base peak of clinoptilolite was detected by XRD analysis. Unaltered volcanic glass was observed from 100 to 1300 m depth. Clinoptilolite and the precursor volcanic glass coexisted in the same tuff at 1000 m.

SEM OBSERVATION

Figure 2 is a back-scattered image of unaltered volcanic glass at 1000 and 1300 m depths (A and B, respectively) and clinoptilolite-replaced bubble-wall shards at 1000 and 1100 m depths (C and D, respectively). The external shape of the unaltered and clinoptilolite-replaced volcanic glass shows a distinct bubble-wall texture, indicating "foaming" at the time of eruption (Pirsson, 1915). Unaltered volcanic glass and clinoptilolite-replaced volcanic glass were easily distinguished in a polished surface by SEM. The polished surface of the unaltered volcanic glass appeared smooth (Figure 2A and 2B), whereas the clinoptilolite-replaced volcanic glass showed cracks caused by cleavage and crystal boundaries (Figure 2C and 2D). Prismatic clinoptilolite crystals, having a maximum length of 10 μm, were oriented perpendicular to the outer margin of the volcanic glass and projected towards the center of the vitric shards. Some vesicles were completely filled with clinoptilolite.

Unaltered volcanic glass and clinoptilolite were found to coexist at 1000 m; at this depth, most of the glass shards were altered to clinoptilolite, but $\sim$10% were unaltered. The altered glass shards was generally the smaller shards ($<$70 μm) whereas the larger shards ($<$100 μm) were unaltered. Unaltered volcanic glass could not be distinguished from clinoptilolite-replaced volcanic glass by the external form alone, but both were easy to identify by comparing a polished surface. In addition, clinoptilolite and unaltered volcanic glass did not coexist in individual glass shards. The glass shards were either unaltered or fully replaced by clinoptilolite.

Calcite cement was observed surrounding clinoptilolite-replaced volcanic glass at 1100 m depth. This cementation occurred on the surface and within the clinoptilolite-replaced glass shards. Some clinoptilolite-replaced shards were completely coated by calcite cement (Figure 2D). Calcite precipitation from Ca-rich pore water obviously occurred after clinoptilolite formation.

ANALYTICAL RESULTS

Table 1 shows the EDX compositions of unaltered volcanic glass and clinoptilolite at each depth. All clinoptilolite particles found in this borehole were characterized by high K. Figure 3 shows the Al_2O_3-normalized chemical composition with depth. The clinoptilolite particles had lower SiO_2/Al_2O_3 ratios and much lower CaO/Al_2O_3 and Na_2O/Al_2O_3 ratios than did the precursor volcanic glass. In contrast, the clinoptilolites had much higher K_2O/Al_2O_3 ratios than did the volcanic glass.

The cation composition of the clinoptilolite-replaced shards surrounded by calcite cement (1100 m depth) was not rich in Ca, and no difference in chemical composition between calcite-cemented (1100 m) and non-calcite-coated clinoptilolite-replaced shards (1000 and 1400 m) was noted.

Because all samples used in this study were cuttings, bulk chemical compositions were not determined, but no K-rich minerals were found during the petrographic microscope or SEM examinations of the cuttings, except K-rich clinoptilolite.

DISCUSSION

The distributions of unaltered volcanic glass and clinoptilolite-replaced volcanic glass overlap over a wide depth range (1000–1300 m). The temperature range at which volcanic glass transforms to clinoptilolite is 41–55°C, according to Iijima (1986), based on the data of present-day burial diagenesis in deep boreholes. The temperature at 1000 m, the depth at which clinoptilolite appears, was 45°C, and at 1300 m, the deepest point at which unaltered volcanic glass was observed, was 51°C. Both temperatures are within the transitional-temperature range mentioned above. Thus, clinoptilolite appears to have formed from volcanic glass under usual burial diagenetic environments.

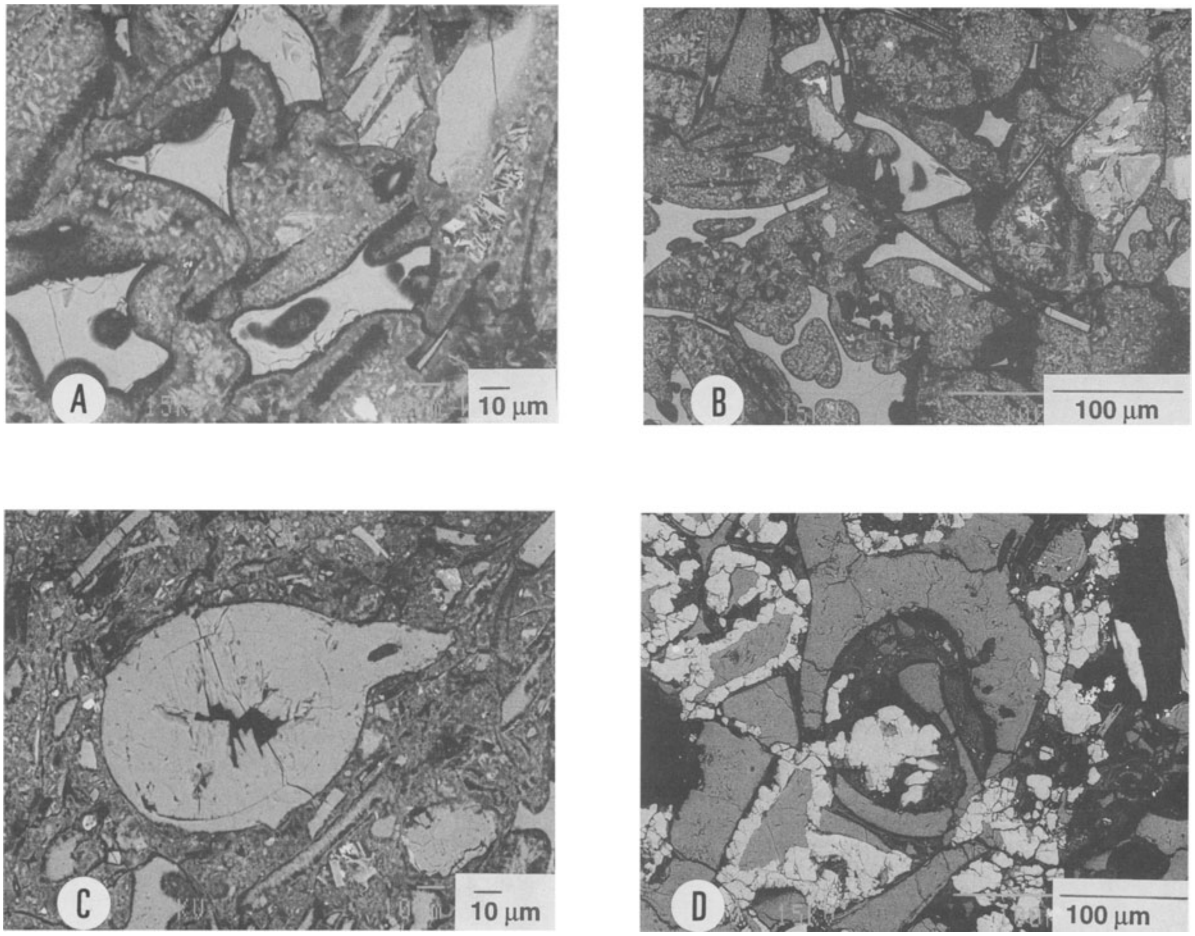

Figure 2. SEM photomicrographs (back-scattered electron images) of polished thin sections from the offshore MITI-Somaoki borehole. Unaltered volcanic glass shows vitroclastic texture (A: 1000 m, B: 1300 m). Altered vitric tuff shows glass shards replaced by fine tabular clinoptilolite (C: 1000 m, D: 1100 m). Glass shards replaced by clinoptilolite (dark gray) are cemented by calcite (light gray) at 1100 m (D).

Table 1. Average EDX analyses of unaltered volcanic glass and clinoptilolite from offshore MITI-Somaoki borehole.

	Unaltered volcanic glass				Clinoptilolite		
Depth (m)	800	900	1000	1300	1000	1100	1400
SiO_2[1]	69.86	66.15	70.03	71.32	69.32	67.67	66.73
TiO_2[1]	0.10	0.68	0.19	0.10	0.00	0.00	0.00
Al_2O_3[1]	12.34	13.50	11.54	12.18	13.05	13.06	14.02
Fe_2O_3[1]	1.86	3.09	1.94	2.07	0.00	0.00	0.00
MgO[1]	0.22	0.63	0.11	0.10	0.05	0.10	0.00
CaO[1]	1.48	2.71	1.27	1.40	0.19	0.65	0.84
Na_2O[1]	3.12	3.07	3.24	3.47	1.45	1.05	1.58
K_2O[1]	3.11	1.82	2.59	2.68	7.84	8.52	8.78
Total	92.08	91.64	90.92	93.33	91.89	91.06	91.94
SiO_2/Al_2O_3	5.66	4.90	6.07	5.85	5.31	5.18	4.76
CaO/Al_2O_3	0.12	0.20	0.11	0.11	0.01	0.05	0.06
Na_2O/Al_2O_3	0.25	0.23	0.28	0.28	0.11	0.08	0.11
K_2O/Al_2O_3	0.25	0.14	0.22	0.22	0.60	0.65	0.63
Si/Al (atom%)	4.80	4.16	5.15	4.97	4.51	4.40	4.02

[1] wt. %.

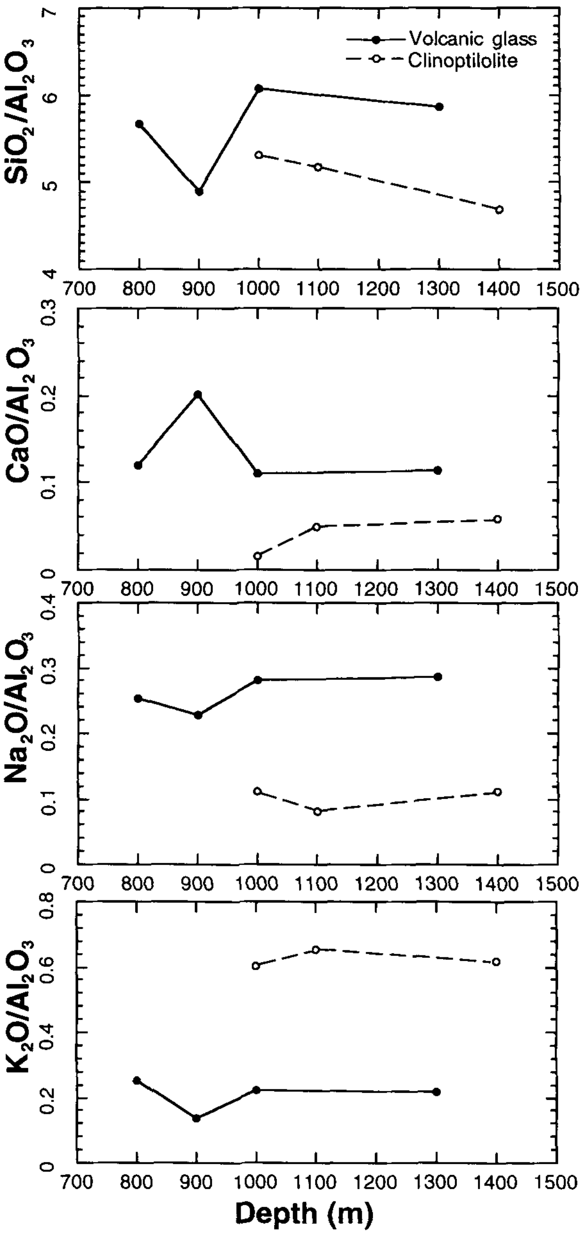

Figure 3. Compositional changes (wt. %) of volcanic glass and clinoptilolite (Al_2O_3-normalized SiO_2, CaO, Na_2O, and K_2O) with depth from the offshore MITI-Somaoki borehole.

Unaltered volcanic glass and clinoptilolite-replaced volcanic glass coexist in the same tuff at 1000 m. The size of the unaltered glass shards was larger than the size of clinoptilolite-replaced glass. Thus, smaller particles of glass were apparently altered to clinoptilolite more readily than larger particles.

The chemical composition of clinoptilolites formed by burial diagenesis is remarkably variable, with the Si/Al ratio depending on the composition of the precursor volcanic glass, which can be estimated indirectly by the anorthite content of coexisting plagioclase (Ogihara and Iijima, 1990). In the present study, the clinoptilolite had a slightly lower SiO_2/Al_2O_3 ratio than did the precursor volcanic glass. However, the difference in Si and Al abundances between the precursor volcanic glass and the clinoptilolite was very small. The SiO_2 content at 1000 m depth was 70.03 wt. % in the precursor volcanic glass and 69.32 wt. % in the clinoptilolite. The Al_2O_3 content was 11.54 wt. % in the glass and 13.05 wt. % in the clinoptilolite (Table 1).

The extra-framework composition of the clinoptilolite is quite different from that of the precursor glass. The K-rich clinoptilolite apparently originated from volcanic glass having a composition richer in Na_2O than in K_2O. At 1000 m depth, the CaO, Na_2O, and K_2O contents of the precursor unaltered volcanic glass were 1.27, 3.24, and 2.59 wt. %, respectively. The composition of the clinoptilolite in the same tuff, however, was 0.19 CaO, 1.45 Na_2O, and 7.84 K_2O wt. % (Table 1). The K content of the clinoptilolite, which fully replaced glass shards, was three times higher than that of the precursor glass.

K-rich clinoptilolite from Japan was reported by Minato and Utada (1971) and Ogihara and Iijima (1990). These authors suggested that either the precursor volcanic glass was originally rich in K, or K was derived from K-rich pore water. The K in the clinoptilolite in the present study, however, does not appear to have been derived solely from the precursor glass because the amount of K in the glass shards was insufficient to account for the amount of clinoptilolite present, despite the similar volumes of the glass shard and the replacing clinoptilolite.

Pore-water composition has been reported to play an important role in establishing the extra-framework cation composition. The extra-framework cations in clinoptilolite from alkaline saline-lake deposits, characterized by extremely Na-rich pore water, are mainly Na (Sheppard and Gude, 1968). Clinoptilolite formed in Ca-rich pore water in calcareous, deep-ocean sediments contains more Ca than does clinoptilolite formed in non-calcareous sediments, and most clinoptilolite from non-calcareous sediments are rich in K (Stonecipher, 1978). The most K-rich clinoptilolite from deep-ocean sediment from the Deep Sea Drilling Project site 105 have 77% K in their cation sites (Stonecipher, 1978). Ames (1960) suggested cation selectivity of K > Ca > Na and Ca > Mg in clinoptilolite. Boles and Wise (1978) also reported the extreme fractionation of the extra-framework cation in clinoptilolite from deep-ocean sediments, with the K concentration in clinoptilolite being 80 times that of the Na, 50 times that of the Ca, and 55 times that of the Mg of the initial sea water.

The clinoptilolite rich in K studied here appeared to have formed by a reaction of volcanic glass in tuffs with trapped sea water during burial diagenesis. The cation selectivity of clinoptilolite, which shows a preference for K to Ca and Na, played an important role in the concentration of K in clinoptilolite during its formation from volcanic glass. K-rich clinoptilolite can be formed from non-K rich volcanic glass reacting with pore water not rich in K during burial diagenesis.

The cation-exchange property is a most important characteristic of zeolites; however, the clinoptilolite found in calcite-cemented tuff at 1100 m depth in the present study is not Ca-rich, although it had certainly been in contact with Ca-rich pore water during calcite cementation. The same non Ca-exchanged clinoptilolite in calcite-cemented zeolitic tuff was found from the offshore MITI-Kesennumaoki borehole (Ogihara and Iijima, 1989). Thus, cation composition of clinoptilolite, once formed, appears to be relatively stable and is not easily change during burial diagenesis. This result is in contrast to the work, for example, by Broxton *et al.* (1987) where it is suggested that the exchangeable-cation contrast of a zeolite is influenced by the cation contrast of the ground water passing through the deposit.

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