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STRUCTURAL WATER IN VOLCANIC GLASS

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Abstract—High-resolution transmission electron microscopy has revealed spherical and hemispherical structures on the surface of partly hydrated volcanic and synthetic glasses. These structures contrast with the bulk of the glass in showing lattice-fringe images indicative of the early stages of crystallization. Heavy-ion Rutherford scattering analysis of the noncrystalline volcanic glass indicates a structural water with hydrogen and deuterium. Depth profiles show that the glass grains contain structural water without adsorbed water on the surface. The presence of structural water in volcanic glass must be of interest to the formation of primitive clays. The spherical and hemispherical structures favor production of clay precursors in the presence of water.

Key Words—Glass, Heavy-ion Rutherford scattering, High-resolution transmission electron microscopy, Structural water.

INTRODUCTION

Crystallization of hydrous silicates from natural glass is not well understood. A primitive crystallization process involving precursors has been revealed by high-resolution electron microscopy. Poorly crystalline, hollow spheres have been described as precursors to crystalline clay minerals during the hydration of feldspar and some volcanic glasses (Eggleton and Keller, 1982; Tazaki and Fyfe, 1985, 1987; Eggleton, 1987; Palmer *et al.*, 1988). The present study examines the crystallization process in hydrated dacitic volcanic glass using scanning electron microscopy (SEM) equipped for energy-dispersive analysis (EDAX), differential thermal analysis (DTA), and high-resolution transmission electron microscopy (HRTEM).

MATERIALS AND METHODS

Glass samples

Dacitic volcanic glass was collected from a volcanic ash layer from the Mt. Daisen volcano at Daisen-Ike in Tottori prefecture, SW Japan. The overlying soil is the Daisen loam, dated at 17,200 ± 400 y.B.P. (Matsui and Inoue, 1970). Clean glass grains were hand-picked from the volcanic ash under the microscope. Another dacitic volcanic glass from Mt. Aira volcano and a synthetic waste-form glass (Zhou *et al.*, 1987) showing domain structure in the noncrystalline glass matrix were also investigated for comparative microstructural study. Bulk glass grains were mounted on a sample stub with double-sided tape and coated with Au for SEM. Clay-size fraction (<2 μm) were used on a microgrid for HRTEM.

Analytical methods

The glass grains were ground in a porcelain mortar, then studied by XRD using a RIGAKU instrument, by SEM using a JEOL JSM-T220A instrument operating at 20 kV, and by TEM using a JEOL JEM 2000EX operating at 160 kV. For DTA and TGA, 100 mg of powdered glass was analyzed with a Shimadzu DTG-40 instrument, heating from 25°–1000°C. Hydrogen and deuterium distribution in the glass were examined by heavy-ion Rutherford scattering using the RIKEN heavy-ion linear accelerator (RILAC) (Nagai *et al.*, 1987; Aratani, 1988). A 50 MeV Ar^{4+} or Cu^{2+} beam of 50 nA were used as incident particles. The beam size was about 1.5 mm × 3 mm on a target angled at 45°.

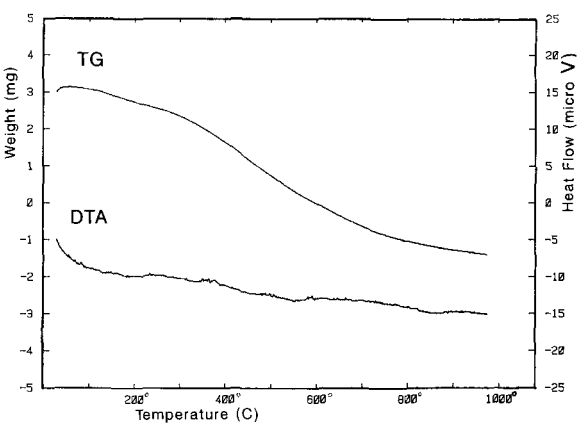


Figure 1. Differential thermal analysis (DTA) and thermogravimetry (TGA) of glass grains.

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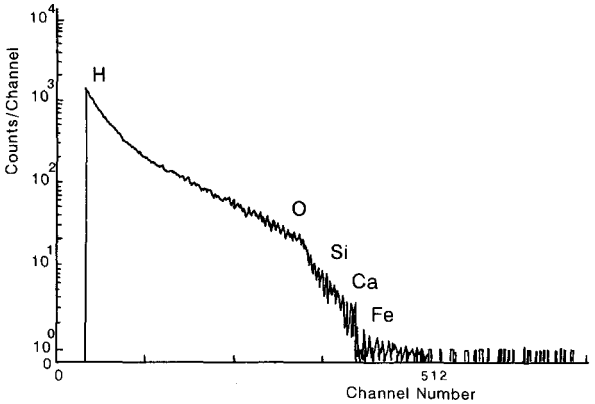


Figure 2. Energy spectrum of the volcanic glass using HIRS showing uniform distribution of structural water.

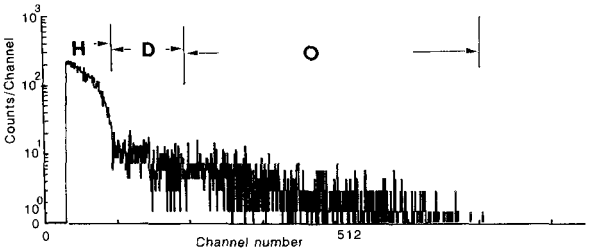


Figure 3. Energy spectrum of recoiled hydrogen, deuterium and oxygen ions (35° to the incident argon ion beam).

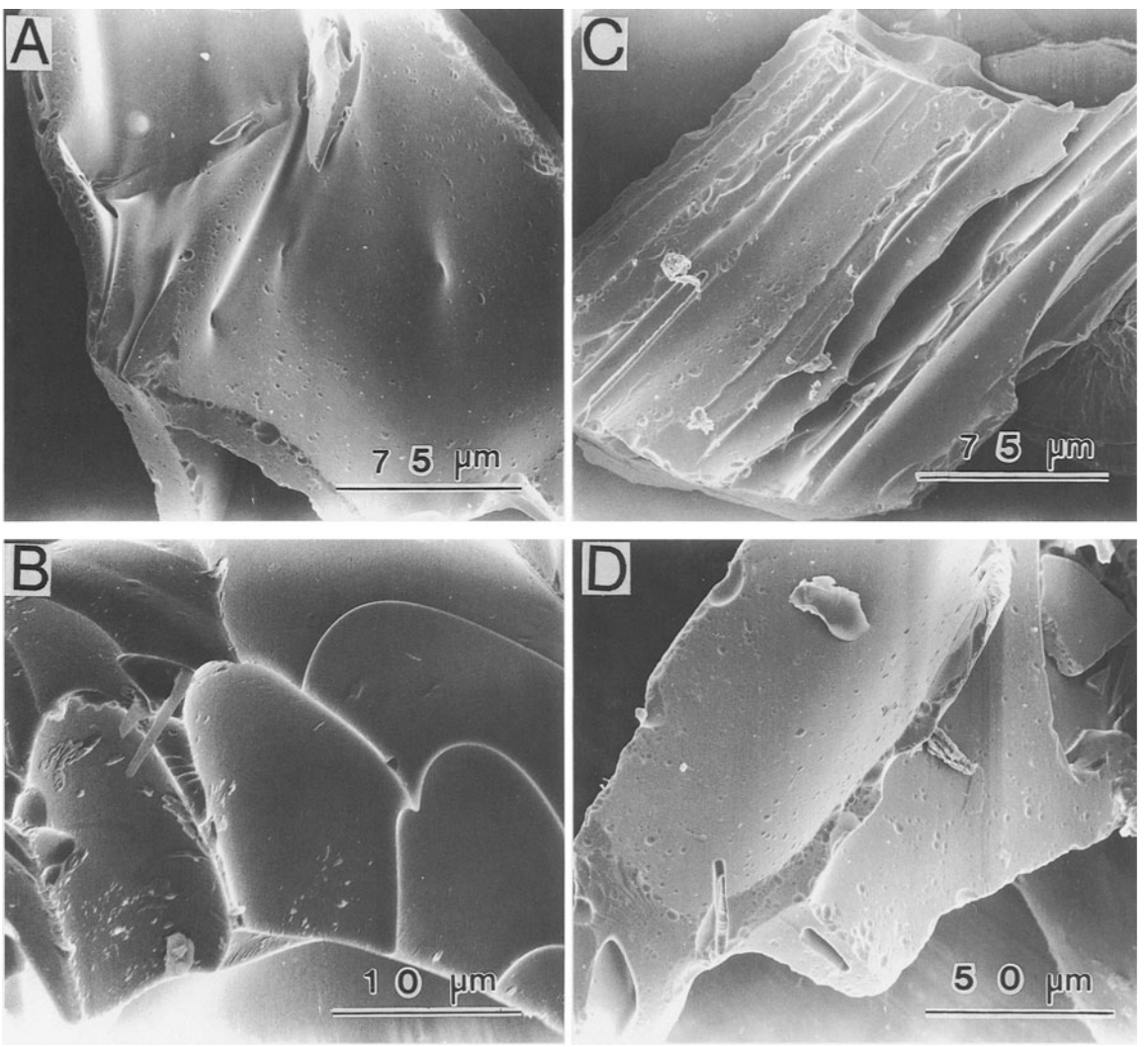
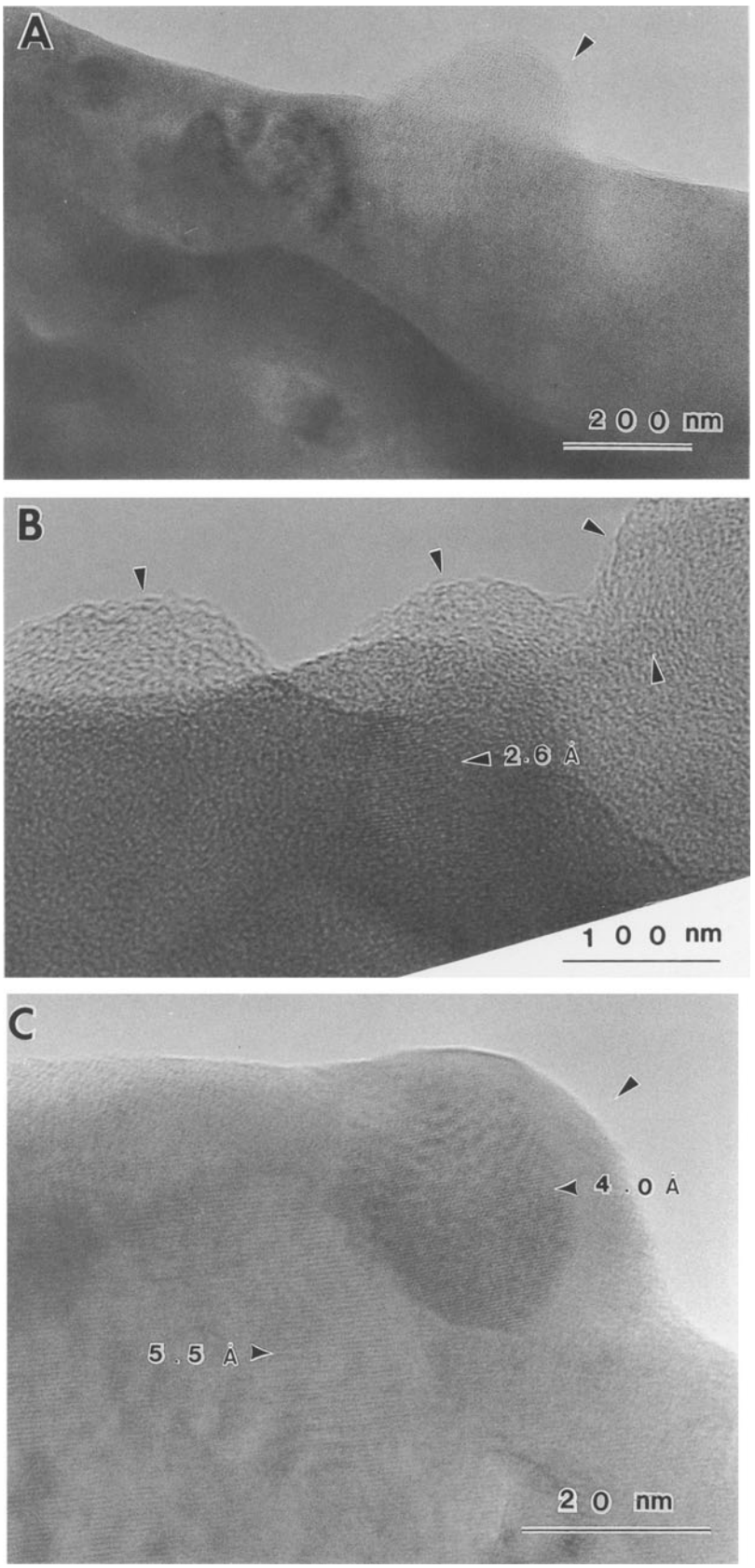


Figure 4. Scanning electron micrographs of glass grains showing planar surface with small vesicles (A and D), curviplanar fractures (B) and elongated vesicles with pockets (C).

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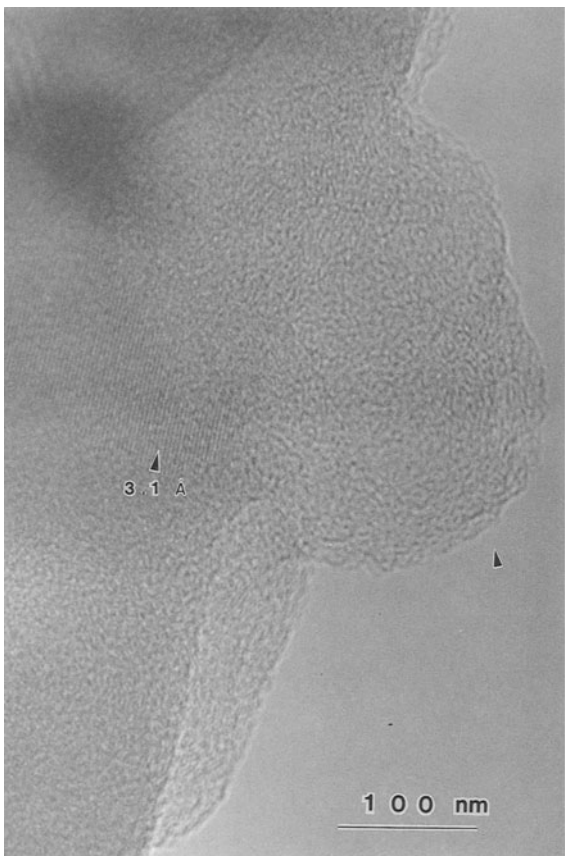


Figure 6. High-resolution transmission electron micrograph of glass showing swelling hump (arrow) and domain structure of 3.1 Å.

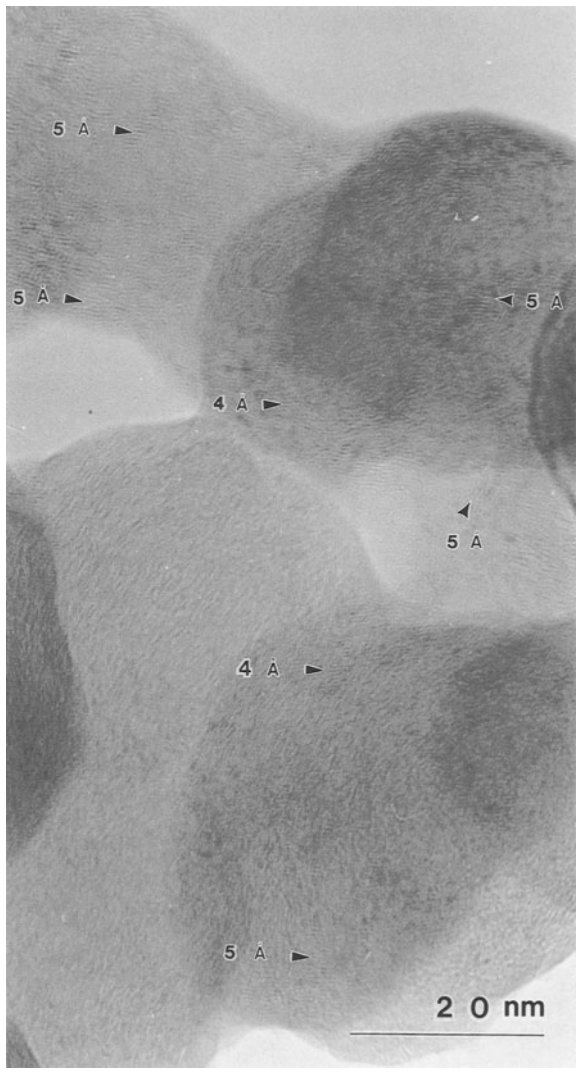


Figure 7. High-resolution transmission electron micrograph of spherical domain structure of 4–5 Å d-spacings (arrows).

RESULTS

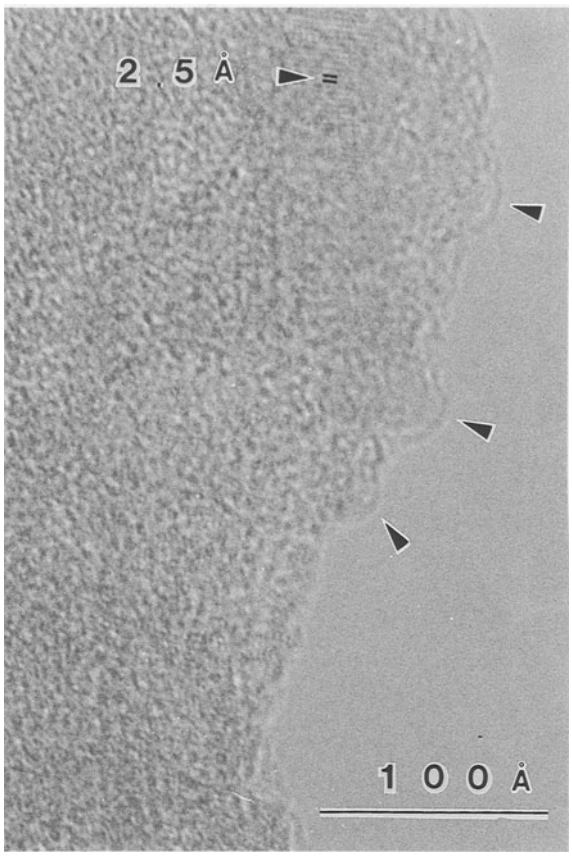
Quantitative energy dispersive analyses of the glass grains gave 77–78% SiO_2, 12–13% Al_2O_3, 1.1–1.9% FeO, 1.0–1.3% CaO, 3.3–3.9% Na_2O and 3.0–3.3% K_2O suggesting fresh dacitic glass. The DTA curve, free from any visible endo- and exothermic peaks, is indicative of neither clay minerals nor crystalline materials (Figure 1). The thermogravimetric curve indicates a loss on ignition of about 4%. The XRD data showed a broad and strong enhancement of background radiation in the 19°–36° 2θ range. This broad hump suggests that the sample contains a substantial amount of short-range order material.

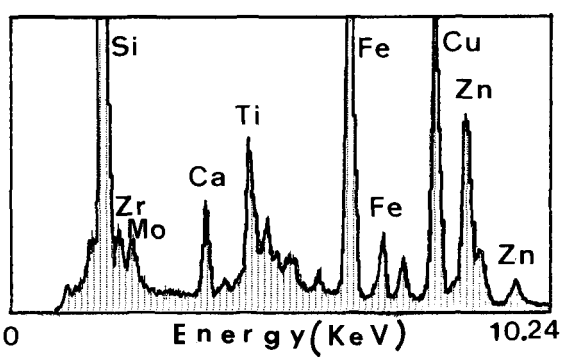
Heavy-ion Rutherford scattering (HIRS) depth profiles indicate H, O, Si, Ca and Fe contents of the volcanic glass (Figure 2). The profile showed no significant difference between the outside and the inside of the structure (see smooth slope between H and O in Figure 2). The hemispherical hydrogen slope shows that hydrogen atoms are distributed uniformly in the glass with no evidence of surface absorption. The data indicate that the structural water is in uniform structural distribution with O, Si, Ca and Fe. High-resolution of HIRS data showed not only hydrogen, but also a deuterium ion spectrum (Figure 3).

Another volcanic glass of similar age, collected from Mt. Aira in southern Kyushu, Japan, was also analyzed by HIRS for comparison. Spectra of the Aira glass also showed the presence of structural hydrogen, even though the amount of water was five times less than for the volcanic glass from Mt. Daisen.

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Figure 5. High-resolution transmission electron micrographs of swelling humps (arrows) on glass surface. A; structureless hump, B; spheres with domains of 2.6 Å, C; lattice images of 4.0 and 5.5 Å in sphere.

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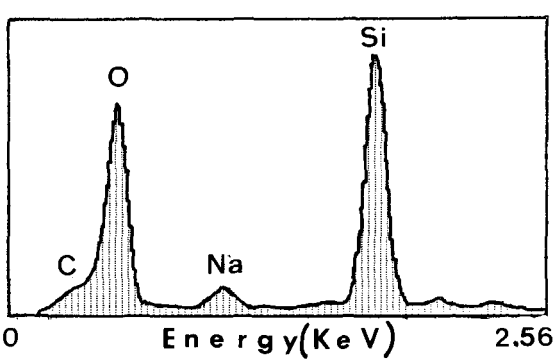


Figure 8. High-resolution transmission electron micrograph (upper) and its energy dispersive X-ray spectra of synthetic waste-form glass. HRTEM showed swelling humps (arrows) and 2.5 Å domain structure in the truly noncrystalline glass matrix.

SEM photographs of the glass grains show nearly planar surfaces that have irregularities and small vesicles (Figure 4A, D). Note the smooth, curved, and hollow surface textures forming sharp edges on the grains. Many of the vesicles are cut by curviplanar fractures (Figure 4B), and according to Heiken and Wohletz (1985), result from hydrovolcanic fragmentation of the melt. The well-developed elongate vesicles have pockets of coalesced vesicles with thin walls (center, Figure 4C). Note that these glass grains have no crystalline material, cracks, or hydrated films.

Growth phenomena and structural transformations can be traced in detail using HRTEM as illustrated in Figures 5–7. Although the glass phase structure is too small to resolve, there is evidence of short-range domain structure showing broad, diffuse rings in electron diffraction patterns. Small areas within the glass phase showed swelling humps on the surface (Figure 5) ranging from 20 to 200 nm in diameter. They have no void space or bubbles. These areas were not damaged by the electron beam, and high-resolution photographs revealed lattice images having 2.6, 3.1, 4.0 and 5.0–5.5 Å spacings (Figures 5B, C, 6, 7). Other areas are almost completely structureless. The domains having these spacings were randomly distributed (Figure 7). These spherical structures or clay precursors appear similar to those that form on allophane and in lateritic pisolites during the initial stages of weathering (Eggleton, 1987).

The hydrated surface of a synthetic nuclear-waste-form glass was observed for comparative purposes (Figure 8). The composition of the glass has been analyzed by EDAX (Figure 8). The nuclear-waste-form glass (Zhou *et al.*, 1987) also showed spherical humps associated with domain structure in small areas, even after two episodes of fusion and annealing for 3 hr at 550°C. HRTEM showed short-range order with a 2.5 Å spacing.

DISCUSSION AND CONCLUSIONS

Natural glasses of obsidian, perlite and pitchstone contain $H_2O \lesssim 2\%$, 2–5% and $\gtrsim 5\%$, respectively. The H_2O can be introduced into silicate glass under hydrothermal conditions as follows (Moriya, 1981):

$$\begin{array}{c} | \quad | \qquad\qquad | \qquad | \\ -Si-O-Si- + H_2O\,(g) \rightarrow -Si-OH + HO-Si-. \\ | \quad | \qquad\qquad | \qquad | \end{array}$$

The structural water must agree with observed TGA patterns. The TGA of the glass shows a sharp endo-

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thermic peak at 150°C and a broad peak at 300°–500°C. In this study the TGA of the volcanic glass shows that most water loss occurs below 500°C, but is continuous. The DTA appears to show no discrete hydrous phase in major quantities. The thermogravimetric curve indicated an ignition loss of 4%, which was not due to adsorbed water showing no endothermic peak at 100°–200°C. It seems certain that the glassy material contains hydrated phases.

HIRS is a powerful technique for the identification of structural or adsorbed water. In this study HIRS shows that hydrogen is present throughout the glass and is not surface concentrated. The hydrogen could be present as OH or $(OH)_4^{4-}$ replacing $(SiO_4)^{4-}$. However, HRTEM observation revealed spherical humps on the surface of the glass having partial ordering of domain structure in the small area. The structural water is related to these humps and domains on the glass, which were stable to electron beam damage. There are micro-domains (20 nm) with a variety of spacings. HRTEM provided lattice-fringe images of about 3, 4 and 5 Å separations, while other areas were almost structureless. The glass shows a wide range of micro-domains, created near or at hydrogen sites which are interpreted as support for clay precursors, or other precursors (e.g., SiO_2).

The observed areas of highly regular fringes require the presence of at least a small proportion of crystallites and enriched Fe in the primitive clay phase (Rudee, 1976; Zarzycki, 1977; Williams, 1984; Tazaki *et al.*, 1989). The crystallization appeared to be induced by foreign impurities or defects on the substrate surface already existing prior to deposition (Wong and Angell, 1976; Aratani, 1988). In addition, much of the structural water should be contributed to produce clay minerals in the hump and spherical areas, which were regarded as network forms in the glass. Tateyama *et al.* (1982) discussed the relationship between volcanic glass structure and the bloating properties. The structures of the glass were analyzed by using the method of radial distribution function. The peaks of 1.62, 2.7, 3.2, 4.0 Å were attributed to the spacings of Si-O, O-O, (Si-1st)-Si, and (Si-2nd)-O in tetrahedral structure of the glass, respectively. In this study these values are in approximate agreement with those values obtained by HRTEM of 2.6, 3.1 and 4.0 Å (Figures 5B, 6, 7). The crystallites might transform into the layer structure of primitive clays by cutting the Si-O-Si network structure into Si-OH and HO-Si, as illustrated in previous work (Tazaki *et al.*, 1989). In the case of structural water in the octahedral layer, the lattice image (e.g., 5–5.5 Å in Figures 5C, 7) should be larger than 3.3–4.0 Å, which is in the tetrahedral layer. The presence of structural water in volcanic glass must be of interest to the formation of primitive clays. The spherical and hemispherical structures favor production of clay precursors in the presence of water.

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