

VOLCANIC ORIGIN OF A CRISTOBALITE IN THE TE NGAE TEPHRIC-LOESS FROM NORTH ISLAND, NEW ZEALAND

Key Words—Cristobalite, New Zealand, Pedogenesis, Stable isotope(s).

Fine-grained cristobalite has been reported in the Hamilton Clay Loam and Naike Clay, both of which are derived from volcanic ash (New Zealand Department of Scientific and Industrial Research, 1968) and the Te Ngae tephric-loess in Rotorua (Naruse and Inoue, 1983), North Island, New Zealand. Lowe (1986) studied the mineralogy of four pedons developed on late Quaternary volcanic ashes in the Waikato region, New Zealand. Abundant cristobalite was observed only in the clay and silt fractions from the Rototuna pedon with poor drainage and Lowe (1986) interpreted the cristobalite as being of authigenic origin, formed under alternating dry and wet conditions. Nevertheless, no conclusive evidence has been provided for the origin of cristobalite in tephra-derived soils and sediments of the region. Lowe's interpretation is in conflict with our previous study (Mizota *et al.*, 1987), in which we concluded that cristobalite in soils formed by weathering of volcanic ash in temperate and tropical regions was of primary igneous origin.

MATERIALS AND METHODS

Stratigraphic correlation of volcanic ash deposits in the region using a widespread marker tephra, Aokautere Ash, around Hamilton City (Lowe, 1986) and Rotorua (Sase *et al.*, 1988) show that the Te Ngae tephric-loess forms the same horizon as that of a Rototuna pedon. A Te Ngae tephric-loess sample was collected from the Te Ngae Road Section (Sase *et al.*, 1988), northeast of Rotorua, North Island, New Zealand. Naruse and Inoue (1983) estimated a cristobalite content of 27% in the <20 μm fraction. The age of the Te Ngae loess is estimated to be 42 Kyr (Lowe, 1986). Cristobalite was separated from coexisting minerals by selective chemical dissolution and heavy liquid separation (Mizota *et al.*, 1987). The purity of the mineral separates was tested by X-ray powder diffractometry and oxygen yield during preparation of CO_2 for mass spectrometry. The oxygen of the cristobalite was extracted for isotopic analysis using the BrF_5 (Clayton and Mayeda, 1963).

RESULTS AND DISCUSSION

Quantities of size-separates and their mineral assemblages are shown in Table 1. Cristobalite is abundant

in the 1–10, 10–20, and 20–53 μm size fractions, but was not observed in the fractions coarser than 53 μm . X-ray diffraction patterns of three cristobalite separates from the Te Ngae tephric-loess are shown in Figure 1. Cristobalite concentrates gave very sharp and strong diffraction peaks at 4.50, 4.08, and 3.80 \AA , indicating high crystallinity. All the concentrates contain small amounts of tridymite (4.30 \AA). Cristobalite-rich concentrates in the 1–10, 10–20, and 20–53 μm fractions have $\delta^{18}\text{O}$ values of +8.4, +8.1, and +7.6‰, which are comparable to those (+5.3‰–+11.0‰; Mizota *et al.*, 1987) previously reported for cristobalite of five soil samples of igneous origin. The oxygen isotopic data definitely suggest volcanic origin of a cristobalite in the Te Ngae tephric-loess. If the cristobalite in the weathered volcanic materials had formed pedogenically, the oxygen isotopic composition would be expected to be +32‰–+34‰ based on the assumptions of the equilibrium oxygen isotopic fractionation between amorphous silica and water (Kita *et al.*, 1985; Leclerc and Labeyrie, 1987), a mean annual air temperature of 13 to 15°C (Lowe, 1986), and oxygen isotopic composition of pore waters dominated by meteoric contributions (–5.7‰––6.4‰; Taylor *et al.*, 1977). Even assuming ^{18}O enriched waters (lake waters without drainage; –1‰; Taylor *et al.*, 1977) resulting from surface evaporation, the expected $\delta^{18}\text{O}$ values of cristobalite are +37‰–+39‰, which are clearly different from the val-

Table 1. Weight % abundance and mineral assemblage of size separates from a Te Ngae tephric-loess sample.

	Size fractions (μm)		
	1–10	10–20	20–53
Weight % ¹	18.8	10.8	20.8
Weight % ²	5.4	28.1	17.5
Mineral composition ³	Cb \gg Tri, Qz	Cb \gg Tri	Cb \gg Tri

¹ On the basis of air-dried fine earth (<2 mm).

² After acid-alkali-hydrofluorosilicic acid digestions and heavy liquid separation. On the basis of oven-dried separates treated with hydrogen peroxide and dithionite-citrate.

³ Determined by visual estimation of peak heights characteristic for each mineral species.

Abbreviations: Cb = cristobalite, Qz = quartz, Tri = tridymite.

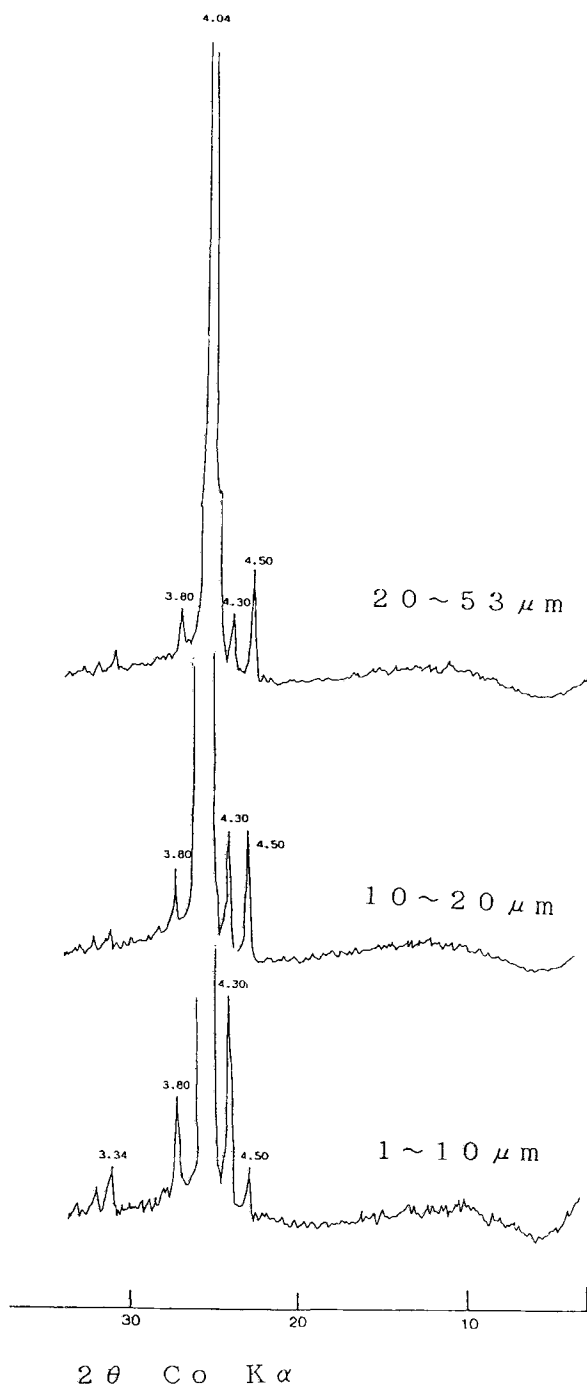


Figure 1. X-ray diffractograms of cristobalite-rich size-separates. Numbers indicate values of diffraction peaks in Å.

ues obtained in the present study. The conclusion is that pedogenic transformation of amorphous to crystalline silica is unlikely within the relatively short time since the deposition of the parent volcanic ashes (42 Kyr; Lowe, 1986), even with the intense seasonal en-

richment of silica in the Rototuna pedon. Pedogenic formation of amorphous silica (opaline silica) in surface horizons of older volcanic ash soils from tropical and temperate regions was shown by a stable isotope technique (Mizota *et al.*, 1991).

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