

## EXPERIMENTAL ALTERATION OF VOLCANIC TUFF: SMECTITE FORMATION AND EFFECT ON $^{18}\text{O}$ ISOTOPE COMPOSITION

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**Abstract**—Three samples of volcanic tuff were hydrothermally altered at  $\sim 82^\circ\text{C}$  in a soxhlet apparatus for periods from 745 to 2706 h. The samples correspond to partially altered specimens of volcanic tuff with 6 wt. % (T3a) and 9 wt. % (T3b) smectite and to the calcination product of the latter (T3c). The calcination treatment melted the smectite in the sample. Untreated samples and alteration products were studied by X-ray diffraction (XRD), differential thermal analysis (DTA) and thermogravimetry (TG), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis, and oxygen isotope analysis. DTA-TG of the  $<2\text{-}\mu\text{m}$  size fractions showed that there was a small increase of smectite relative to glass after alteration for samples T3a and T3b, with the amount of smectite increasing exponentially with time. No smectite formed in sample T3c. These results suggest that smectite acts as a nucleation site for the precipitation of new smectite. The amount of glass in the  $<2\text{-}\mu\text{m}$  size fraction increased, although slightly decreased relative to smectite. SEM-EDX analysis showed smectite with the approximate structural formula of  $\text{Na}_{0.22}\text{K}_{0.08}\text{Mg}_{0.12}\text{Ca}_{0.03}^{\text{VI}}(\text{Al}_{1.47}\text{Fe}_{0.05}\text{Mg}_{0.48})^{\text{IV}}(\text{Si}_{3.97}\text{Al}_{0.03})\text{O}_{10}(\text{OH})_2$ .

Oxygen isotope composition of the  $<2\text{-}\mu\text{m}$  size fraction became enriched in  $^{18}\text{O}$  by alteration, the  $>2\text{-}\mu\text{m}$  size fraction of T3b did not vary, and that of T3c was depleted in  $^{18}\text{O}$ . Our results are consistent with three processes during alteration: 1) oxygen isotope exchange between volcanic glass and water, 2) neo-formation of smectite, and 3) hydration and consequent hydroxylation of the calcined glass.

**Key Words**—Alteration Mechanism of Volcanic Tuff, Oxygen Isotope Exchange, Smectite, Tuff.

### INTRODUCTION

Volcanic glass is altered to bentonite by the effect of water. The conditions under which this alteration occurs can be very different depending on the nature of the water supply: rain, sea, groundwater, or a hydrothermal system which supplies steam as well as water. The alteration mechanism of tuff into bentonite is not well understood. Considering the variety of conditions in which alteration occurs, it is likely that the alteration mechanism varies. Processes probably range from diffusion of water and ion diffusion and rearrangement to dissolution and precipitation of new phases. Tuff composition may also influence the alteration mechanism. Caballero *et al.* (1992) found that different silica contents in the tuff resulted in smectites having various chemical compositions. Although the main factors controlling smectite chemical composition are the chemical and mineralogical composition of the tuff, water chemistry, and temperature, the results of Caballero *et al.* (1992) may be related also to different alteration mechanisms.

Tuff alteration is studied mainly experimentally because reaction conditions may be controlled, and the alteration process may be studied at its earliest stages. Electron microscopy is used to view changes in texture, morphology, and structure of the altered specimens, and X-ray diffraction (XRD) is used to identify the nature of the developing phases as well as their crystallinity, rate of formation, *etc.* Some studies of

glass alteration do not use volcanic glass, but some of their results may be applied to tuff alteration. Studies have shown the formation of protocrystalline domains in glass with different lattice spacings that may be clay precursors (Tazaki *et al.*, 1989, 1992; Kawano and Tomita, 1992). On the other hand, Crovisier *et al.* (1992) proposed a mechanism of congruent dissolution of glass and precipitation of palagonite and a clayey material for altered hyaloclastites from Iceland. The alteration products vary depending on time, water/rock ratio, rainfall distribution, or solution pH, which suggests also possible variations in alteration processes. Kawano and Tomita (1992) carried out alteration experiments of volcanic glass at  $150\text{--}200^\circ\text{C}$  and found that the glass was transformed into allophane, which later transformed into smectite. Kawano *et al.* (1993) also detected allophane between  $150\text{--}225^\circ\text{C}$  as the initial alteration product of obsidian in deionized water. Subsequently, allophane transformed to a noncrystalline fibrous material, which later crystallized to smectite. Thomassin *et al.* (1989) found that basaltic glass altered with seawater at  $50^\circ\text{C}$  by transforming to hydrotalcite, serpentine, and smectite in water-dominated systems, and by transforming to a poorly crystallized nontronite in glass-dominated systems. Berggaut *et al.* (1994) identified as illite-smectite the poorly crystalline product of naturally altered basic pyroclastics. They attributed the formation of illite-smectite to the alternation of humid and dry seasons, which acted as

Table 1. Chemical analysis of the three starting materials used in the alteration experiments. Data are expressed as oxide percentage.

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	H <sub>2</sub> O <sup>+</sup>	Total
T3a	65.21	14.90	1.37	2.48	1.03	3.72	5.25	6.32	100.28
T3b	64.86	13.28	1.12	2.01	1.22	4.22	7.25	5.30	99.26
T3c	71.63	16.08	1.43	2.30	0.84	4.14	6.27	0.14	100.53

wetting and drying cycles in soils. Zevenbergen *et al.* (1996) studied the effect of natural alteration on glass that had been produced by incineration of waste, which was mainly composed of glassy constituents, and found illite as the major alteration product. They concluded that the clay-mineral product is determined by the pH of the leaching solution. Tomita *et al.* (1993) also identified pH as a primary factor controlling the products of glass alteration. They hydrothermally altered volcanic glass from pumice at temperatures between 90–100°C in NaOH solutions and found that smectite and zeolites formed depending on glass/NaOH ratios. The neoformed smectite was iron-rich and had an unusually high stacking order.

Oxygen isotope data of the alteration products of volcanic tuff may give information about the transformation mechanism. These data may be used to assess the influence of the oxygen isotope composition of the original tuff and of water on the oxygen isotope composition of the product. Oxygen isotope composition of bentonite (after the complete alteration of the tuff) depends only on the isotope composition of the percolating water and the temperature at which the alteration occurs (Savin and Epstein, 1970a, 1970b; Savin, 1980). In principle, this suggests dissolution of the original tuff and precipitation of the alteration products. However, the large volumes of water required for the alteration of tuff suggest that complete oxygen isotope exchange between the solid and water may occur even if complete dissolution of the original tuff does not occur, that is, even if the transformation process consists of atom rearrangement through the formation of protocrystalline intermediates. For this reason, oxygen isotope data might provide information about alteration mechanisms and processes only during the initial stages of alteration. Giletti (1985) proposed a mechanism for isotope exchange between minerals and water by diffusion through the crystal lattice, without structural or chemical changes. The rate of such an exchange for oxygen in minerals is very slow at low temperatures (O'Neil and Kharaka, 1976; James and Baker, 1976; Cole and Ohmoto, 1986; Linares, 1987), but exchange is probably more efficient in volcanic tuff because of the lack of crystallinity.

In this paper, we present an experimental study of volcanic tuff alteration in simulated natural conditions. The study includes quantification of reaction progress and oxygen isotope analysis to obtain understanding of the processes occurring during tuff alteration.

## MATERIALS AND METHODS

The starting materials were two specimens of vitreous volcanic tuff (T3a, T3b) from Cabo de Gata, Almería, south-eastern Spain. The samples correspond to the acid member of the potassic calc-alkaline series of the Neogene explosive volcanism. Bulk samples were crushed and gently ground in an agate mortar. Samples are partially altered to smectite. A third sample (T3c) was obtained by calcination of T3b at 1000°C for 2 h to decompose the smectite in it.

Each sample was chemically analyzed by the wet methods of Shapiro (1975), with small modifications: Si, Al, and Fe were determined colorimetrically; Ca and Mg were titrated using EDTA solutions; and Na and K were measured by flame spectrophotometry. Structural water was determined by dehydrating the samples at 110°C overnight and subsequent calcination at 1000°C for 2 h. The results of the chemical analyses are shown in Table 1. High K content is related to their formation during the last volcanic episode (fortunite-verite rock type) in the area (López and Rodríguez, 1980). The large amount of H<sub>2</sub>O<sup>+</sup> in samples T3a and T3b probably includes hydration water owing to incomplete loss of water adsorbed in both smectite and glass, together with the actual hydroxyl water in both phases.

Mineralogy was analyzed by XRD using a Philips 1730 diffractometer, equipped with a Cu X-ray tube and a graphite monochromator. Diffraction patterns were obtained on both random powder and oriented clay-mineral aggregate mounts intercalated with ethylene glycol. They showed that samples T3a and T3b contain small amounts of smectite and trace amounts of K-rich feldspar, plagioclase, and cristobalite, whereas the T3c material does not contain any crystalline phase. Differential thermal analysis and thermogravimetry (DTA-TG) were performed in a simultaneous thermal analyzer (Netzsch STA 409 EP) under the following experimental conditions: ~50 mg of sample were placed in alumina crucibles, and heated at a rate of 10°C min<sup>-1</sup> in air, with alumina as reference material. The amount of smectite in the samples was determined by TG by using weight loss from dehydroxylation and assuming an ideal hydroxyl water content of 5%. The content of smectite was measured in the <2-μm size fraction. This fraction was obtained by suspending the sample in water and centrifuging the suspension. The supernatant containing the <2-μm

Table 2. Alteration time, size fraction, and mineralogical data of untreated materials and products. Each untreated sample is followed by its alteration products.

Sample	Alter. time (h)	% <2 $\mu\text{m}$ <sup>1</sup>	% Sm (<2 $\mu\text{m}$ ) <sup>2</sup>	% Sm <sup>3</sup>
T3a	0	15	38.7	5.8
3	800	18	37.7	6.8
1	1743	19	39.6	7.4
2	2212	27	43.5	11.6
4	2355	38	46.1	17.3
T3b	0	21	43.9	9.2
6	745	20	46.1	9.4
8	1688	29	44.2	12.8
7	2492	34	51.8	18.8
T3c	0	15	0	0
11	1937	23	0	0
10	2706	38	0	0

<sup>1</sup> wt. % of <2- $\mu\text{m}$  size fraction.

<sup>2</sup> wt. % of smectite in the <2- $\mu\text{m}$  size fraction.

<sup>3</sup> wt. % of smectite <2  $\mu\text{m}$  in size in the whole sample (calculated).

size fraction was collected in several extractions until the liquid was clear. The <2- $\mu\text{m}$  size fraction was heated at 60°C for a few days and the dry solid ground. The smectite content in the starting material is given in Table 2.

The alteration of the three samples (20 g in each experiment, <63- $\mu\text{m}$  size fraction) was performed in a soxhlet apparatus (Figure 1). Water is evaporated from the lower flask (C) and, after condensing in the coil (A), reaches the reaction chamber where the sample is confined within a dialysis bag (B), which permits the circulation of water and dissolved ions. The temperature of the water in the reactor is 82  $\pm$  2°C. The reactor is filled with water until the 250-mL level, then the reaction chamber is siphoned to the lower flask. The reaction chamber is refilled with fresh water in a new cycle approximately every hour. The total volume of water in the apparatus is 400 mL.

The system works as a step reactor. The soluble alteration products can pass through the dialysis membrane to the solution, where they are periodically removed to flask (C). The alteration solution is regenerated in each cycle. In this way, the solution surrounding the solid sample is prevented from reaching a high saturation state. On the other hand, this system prevents the immediate removal of released ions from the solution in contact with the sample within the dialysis bag. Four samples of the T3a starting material, three of T3b, and two of T3c were processed at time periods varying from ~700 to ~2700 h (Table 2).

After the experiments, the dialysis bags were dried and weighed. The <2- $\mu\text{m}$  size fraction was separated following the procedure described above. Both size fractions, <2 and >2  $\mu\text{m}$ , were dried at 60°C and ground. The alteration products were studied by XRD

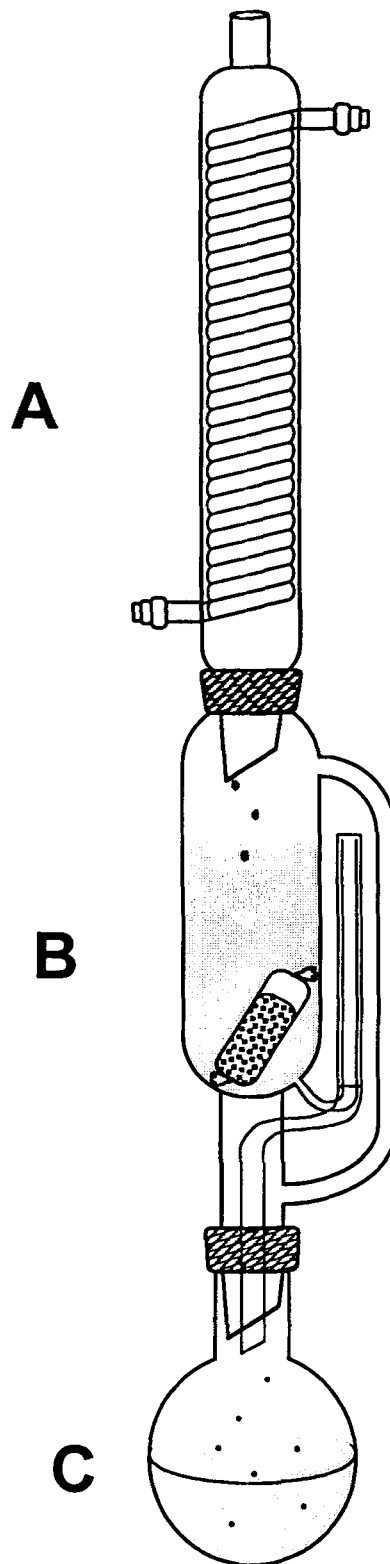


Figure 1. Soxhlet reactor. Water is evaporated in C. Water vapor is condensed in A and falls into B, where it is in contact with the sample. When the water level reaches a certain value it is siphoned into C and a new cycle begins.

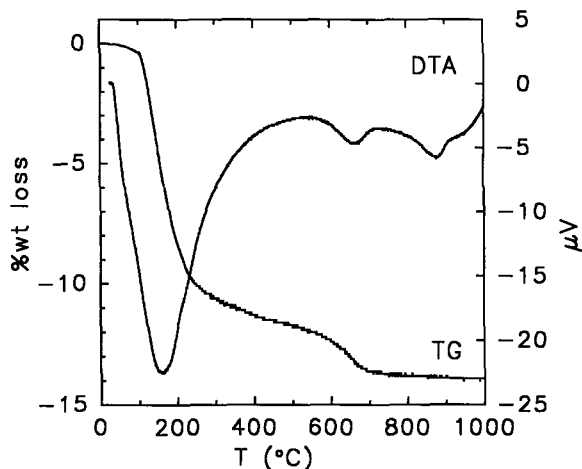


Figure 2. DTA and TG analysis of alteration product 7.

and DTA-TG under the same conditions used for the starting materials.

The  $<2\text{-}\mu\text{m}$  fraction of samples and products were studied by scanning electron microscopy (SEM) (Zeiss 850) and analyzed by energy dispersive X-ray analysis (EDX) (Link Q 2000). Operating conditions were: 20 kV; working distance, 7 mm for SEM observation; working distance, 26 mm for EDX analysis. The solid sample was suspended in water (0.1%) and 50  $\mu\text{L}$  of suspension were placed on an Al stub covered with a carbon film to avoid Al interference during chemical analysis. Samples were covered with carbon for chemical analyses and later with gold for morphological study. Semiquantitative analyses were performed using Co as a standard. Care was taken to analyze only isolated particles to avoid chemical interferences from adjacent grains.

Oxygen isotopic composition was determined in the starting material and the products of T3b and T3c, in both size fractions,  $>2$  and  $<2$   $\mu\text{m}$ , as well as in the water before and after the experiment. The solids were heated in vacuum at 200°C for 2 h to remove hydration water. Oxygen was extracted by reaction with  $\text{F}_3\text{Cl}$  at 600°C and converted to  $\text{CO}_2$  on graphite at 550–600°C, following the method of Borthwick and Harmon (1982). The method of Epstein and Mayeda (1953) of isotope equilibrium  $\text{CO}_2\text{-H}_2\text{O}$  was followed for the water-sample analysis. The determined error of the method is  $\pm 0.2\%$  in  $\delta^{18}\text{O}$ .

## RESULTS

The XRD analyses of the products did not detect any appreciable change with respect to the original tuffs T3a and T3b, showing the presence of smectite and trace amounts of cristobalite, K-rich feldspar, and plagioclase. The calcined tuff (T3c), after alteration, showed trace amounts of cristobalite, K-rich feldspar, and plagioclase, but no smectite.

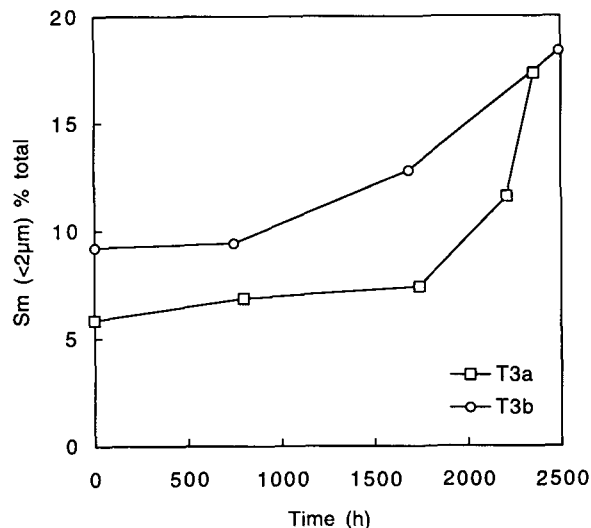


Figure 3. Evolution of smectite  $<2$   $\mu\text{m}$  in size present in the entire fraction of T3a and T3b with alteration time.

The DTA-TG analysis of the original and altered tuff samples allowed quantification of the amounts of smectite present before and after the experiments. Figure 2 shows the DTA and TG diagrams of sample 7 as an example (see Table 2 for reaction conditions). There are two endothermic events accompanied by weight loss. The low-temperature event, at  $\sim 140^\circ\text{C}$ , corresponds to hydration-water loss. The event at  $\sim 650^\circ\text{C}$  is due to smectite-hydroxyl loss. The DTA features above  $800^\circ\text{C}$  are related to smectite decomposition and formation of new phases. These events are not accompanied by weight loss or gain. The DTA-TG diagram of calcined tuff (T3c), where no smectite is present, does not show any thermal event. The ideal amount of water lost from dehydroxylation of 2:1 phyllosilicates is  $\sim 5\%$  in weight based on dry clay, although variations have been reported (Schultz, 1969; Newman and Brown, 1987; Cuadros *et al.*, 1994). We assumed that the smectites contain 5 wt. % water and then we converted weight loss in TG to the smectite content (Table 2, column 4). No smectite was observed in the calcined sample after alteration. The DTA-TG analyses were performed using the  $<2\text{-}\mu\text{m}$  size fraction where smectite is concentrated, so that weight loss is higher and the measurement is more accurate. We determined the total amount of material in the  $<2\text{-}\mu\text{m}$  size fraction in the samples, which includes both unaltered glass and smectite (Table 2, column 3). Using this value and the amount of smectite in the  $<2\text{-}\mu\text{m}$  size fraction, we calculated the amount of smectite with a size  $<2$   $\mu\text{m}$  in the whole sample (Table 2, column 5). The amount of smectite present in the original and altered materials with respect to alteration time is shown in Figure 3. For both samples, the rate of smectite formation increases with time.

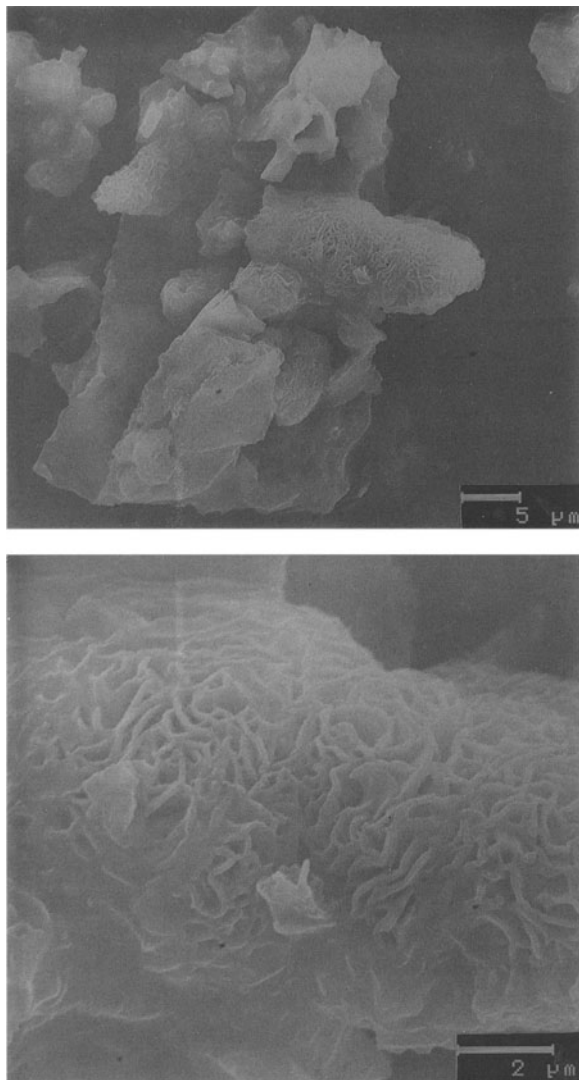


Figure 4. SEM photographs of alteration product 7. The upper photograph shows a glass grain with smectite overgrowth. The bottom photograph is detail from the largest smectite grain in the upper image.

The SEM examination of sample T3a and the altered sample 7 showed glass grains of variable size to  $\leq 30 \mu\text{m}$  in their largest dimension. These grains were sometimes covered with smectite particles which were recognized by their honeycomb structure. Figure 4 is from sample 7 and shows one glass grain with smectite overgrowths as well as detail of one smectite grain. Semiquantitative EDX chemical analyses of smectite grains were averaged and the corresponding structural formula for the smectite calculated. This structural formula is only approximate. No morphological or chemical variations could be detected to differentiate the original and neofomed smectites. The average composition is 63.54%  $\text{SiO}_2$ , 20.43%  $\text{Al}_2\text{O}_3$ , 1.47%  $\text{Fe}_2\text{O}_3$ , 6.41%  $\text{MgO}$ , 0.50%  $\text{CaO}$ , 1.80%  $\text{Na}_2\text{O}$ , 1.05%  $\text{K}_2\text{O}$ ,

Table 3. Alteration time and isotope data (in ‰) of untreated materials and products. Each untreated sample is followed by its alteration products.

Sample	Alter. time (h)	$\delta^{18}\text{O}$ in $>2\text{-}\mu\text{m}$ fraction	$\delta^{18}\text{O}$ in $<2\text{-}\mu\text{m}$ fraction
T3b	0	11.45	12.20
8	1688	11.00	14.78
7	2492	11.27	14.40
T3c	0	14.23	16.90
11	1937	11.92	18.33
10	2706	12.19	18.68

5.00%  $\text{H}_2\text{O}^+$  (structural water assuming ideal smectite chemistry). Comparison to the composition of the entire T3b sample (Table 1), which contains both unaltered tuff and smectite (Table 2), shows that Al and Mg are concentrated in the smectite with respect to the whole sample. Potassium, Na, and Ca are depleted in smectite to varying degrees. Structural water ( $\text{H}_2\text{O}^+$ ) content is similar in both analyses. The resulting structural formula is  $\text{Na}_{0.22}\text{K}_{0.08}\text{Mg}_{0.12}\text{Ca}_{0.03}^{\text{VI}}(\text{Al}_{1.47}\text{Fe}_{0.05}\text{Mg}_{0.48})^{\text{IV}}(\text{Si}_{3.97}\text{Al}_{0.03})\text{O}_{10}(\text{OH})_2$ . Aluminum was assigned to tetrahedral positions to complete an occupancy of four, then Mg was assigned to octahedral sites to complete an occupancy of two, and the remaining Mg was assigned to the interlayer. The negative layer charge is in the upper range for smectites (Newman and Brown, 1987). The tetrahedral substitution is low and most of the charge arises from the octahedral sheet, and the smectite is thus classified as montmorillonite.

The analyses of the oxygen isotope composition for some of the starting materials and products are shown in Table 3. Note that the two size fractions of the calcined sample before alteration (T3c) are enriched in  $^{18}\text{O}$  with respect to the corresponding fraction in the natural sample (T3b). This is probably owing to the preferential evolution of  $^{16}\text{O}$  during hydroxyl loss (Bechtel and Hoernes, 1990).

We calculated an oxygen isotope balance in the four experiments, and we always found an excess of  $^{16}\text{O}$ , indicating that the system was not completely closed. The reasons for this relate to: (1) the isotope exchange between water and the glass walls of the reactor, enhanced by dissolution and reprecipitation reactions of the reactor glass, and (2) the transport and precipitation of ions to the lower body of the reactor (Figure 1). The oxygen isotope composition of the water in contact with the tuff is lighter than the bulk water composition, owing to the fractionation inherent to evaporation. Only water evaporated from the lower flask in Figure 1 reached the tuff and reacted with it. The  $\delta^{18}\text{O}$  value for the evaporated water is unknown. Due to the above uncertainties, the isotope composition of water was not used and the focus was on the changes in the solids. The  $\delta^{18}\text{O}$  value for the bulk original water is  $-8.20\text{‰}$ . The corresponding value after

the alteration processes ranged between  $-9.20$  and  $-11.67\%$ .

After the alteration experiments, examination of the products of the  $>2\text{-}\mu\text{m}$  size fraction of T3b showed that they maintained their original oxygen isotope composition, but the products of sample T3c were depleted in  $^{18}\text{O}$ . The observed values are in agreement with those measured by Hoefs (1980) for various volcanic rocks (andesites, dacites, and tuffs) whose  $\delta^{18}\text{O}$  values varied between  $7\text{--}9\%$  for non-altered rocks, and were above  $10\%$  for rocks undergoing alteration. In contrast, all  $<2\text{-}\mu\text{m}$  size fractions became enriched in  $^{18}\text{O}$ , independently of the fact that the original sample T3b contained smectite and additional smectite was produced during alteration (samples 7 and 8). Smectite was not present in the calcined starting material T3c or in its alteration products (samples 10 and 11).

### DISCUSSION

We quantified the amount of smectite in the untreated and altered samples by TG as described above. It can be argued that this method may be biased because vitreous volcanic tuff may contain small amounts of hydroxyl groups, especially if it has undergone some alteration, as is the case of these samples. Tazaki *et al.* (1992) showed a DTA-TG curve of a volcanic tuff in which there is a weight loss from  $300$  to  $800^\circ\text{C}$  of  $\sim 3\%$  of the total sample mass and there are no clear endothermic events. Weight loss is surely due to dehydroxylation and it indicates that hydroxyl loss in tuff occurs in a wider temperature range than in smectite. The range may be sufficiently wide that dehydroxylation is not recorded in DTA. Our DTA-TG curves are like those of smectite, with localized thermal events. Hence, we assume that if hydroxyls are present in the unaltered glass, then they are in small quantities. Thus, the hydroxyl-loss event at about  $650^\circ\text{C}$  in the DTA-TG curves of this study corresponds to smectite dehydroxylation only, and these curves can be used to quantify smectite present.

The rate of formation of smectite increased with time (Figure 3), probably because of the progressive concentration of released ions inside the dialysis bag. When the experiment starts, the water in contact with the sample is ion free. Ion content in the solution increases with dissolution of tuff. Some ions migrate across the walls of the dialysis bag to the external solution, which is siphoned periodically into the lower flask of the soxhlet reactor. The increase of ion concentration in the solution in contact with the sample is thus the result of the rate of tuff dissolution minus the rate of ion diffusion through the walls of the dialysis bag. If the dissolution rate of volcanic glass is higher than the ion diffusion through the bag membrane, ion concentration will increase with time. Probably, the rate of smectite formation reflects the rate of ion con-

centration because smectite precipitation from solution requires that the saturation level is reached. Initially ( $<1000$  h), ion concentration in solution increases, but the solution is not saturated with respect to smectite, and there is no significant smectite formation. Later, the saturation concentration is probably reached and smectite forms.

Smectite formed only in the non-calcined samples, where smectite existed previously (Table 2, columns 4 and 5). The preexistent smectite probably acts as a template facilitating smectite neof ormation. This is consistent with our SEM-EDS results, which could not discriminate between existent and neof ormed smectite. Smectite precipitation is thus the rate-limiting step in its formation. Another possible explanation is that calcination of the tuff decreases the surface area thereby causing the rate of tuff dissolution to decrease. In this way smectite formation is delayed because the ion concentration threshold is reached at a later time. Longer experiments may resolve this issue because they would document smectite formation in the calcined sample with respect to alteration time.

For the longest experiments, the calculated increase in smectite with a size fraction  $<2\text{ }\mu\text{m}$  for the whole of each sample is between twofold and threefold (Table 2, column 5), whereas the corresponding increase observed for the  $<2\text{-}\mu\text{m}$  size fraction is only 1.2 as much (Table 2, column 4). The latter value compares the relative amount of smectite and glass present in the  $<2\text{-}\mu\text{m}$  size fraction. The former value compares the relative amounts of smectite with size of  $<2\text{ }\mu\text{m}$  and the remaining material (smectite  $>2\text{ }\mu\text{m}$  in size and glass) in the entire sample. The neof ormed smectite will likely be in the  $<2\text{-}\mu\text{m}$  size fraction. For this reason, the much higher relative increase of smectite corresponding to the entire sample must be due to the fact that, in the  $<2\text{-}\mu\text{m}$  size fraction, the amount of glass increases together with that of smectite, thus causing a smaller relative increase of smectite in this fraction. The amount of glass  $<2\text{ }\mu\text{m}$  in size can increase simply by mass loss of tuff grains owing to dissolution.

We considered that oxygen isotope fractionation between water and the solid occurred through two fundamental processes: precipitation of smectite and oxygen isotope exchange between glass and water. Isotope exchange between preexisting smectite and water was considered to be sufficiently low as not to affect our experimental isotope values. This is very likely due to the low temperature and short alteration time (James and Baker, 1976). In fact, O'Neil and Kharaka (1976) did not find any oxygen isotope exchange between water and montmorillonite at  $300^\circ\text{C}$  after 9000 h. The influence of the trace amounts of cristobalite, K-rich feldspar, and plagioclase in the oxygen isotope exchange reactions is probably negligible because of their low concentrations. Besides smectite, non-crys-

talline phases may also have formed during alteration, but SEM observation did not show any such phase.

The processes occurring in sample T3b are probably the following: (1) oxygen isotope exchange between volcanic glass and water. This process would cause an  $^{18}\text{O}$  enrichment of the solid and would be favored in the finest size fraction owing to its larger relative surface area. (2) Neof ormation of smectite, which would also cause  $^{18}\text{O}$  enrichment of the solid and would operate only in the finest fraction. Hence, the two processes can account for the observed changes in oxygen isotope composition of the solids in the  $<2\text{-}\mu\text{m}$  size fraction. These processes were less important in the  $>2\text{-}\mu\text{m}$  size fraction (lower surface to volume ratio) and the oxygen isotope composition is not appreciably changed during alteration.

In sample T3c, the changes of oxygen isotope composition during alteration are opposite in the  $<2$  and  $>2\text{-}\mu\text{m}$  size fractions. In this sample there is no smectite formation. We interpret the  $\delta^{18}\text{O}$  decrease in the  $>2\text{-}\mu\text{m}$  size fraction to be the result of hydration and subsequent hydroxylation. Sample T3c was dehydrated (calcined) and, hence, the main process expected during alteration is water penetration and reaction on the surface of the grains. The  $\text{H}_2\text{O}$  molecules, with a lower  $\delta^{18}\text{O}$  value, would produce a hydrated glass more depleted in  $^{18}\text{O}$ . This is not an oxygen exchange process, but rather a process of addition of oxygen with a different isotope ratio. This process is probably detectable only in the initial alteration. When alteration time is sufficient, oxygen exchange between glass and water displaces the oxygen isotope composition toward that of equilibrium and the glass becomes enriched in  $^{18}\text{O}$ . The effect observed here should not be detected in naturally altered samples. In fact, Cerling *et al.* (1985) analyzed altered volcanic glass in which all alteration products were removed and found that the glass  $\delta^{18}\text{O}$  values increased with increasing hydration level. The hydration process does not occur in sample T3b because the tuff was hydrated previous to the alteration experiments. In sample T3c there was also glass-water exchange of oxygen, which promotes an increase of  $\delta^{18}\text{O}$  values in the glass, but the more extensive hydration process caused overall  $^{18}\text{O}$  depletion. On the other hand, glass-water exchange occurred to a greater extent in the  $<2\text{-}\mu\text{m}$  size fraction, likely due to its larger surface to volume ratio, and alteration resulted in a  $\delta^{18}\text{O}$  increase.

In summary, experiments of hydrothermal treatment of vitreous volcanic tuff indicate that glass-to-smectite alteration occurred by dissolution of the former and precipitation of the latter on preexisting smectite, which acted as nucleation sites. Precipitation seems to be the rate-limiting step in smectite formation. The change of oxygen isotope composition of the finer size fractions is due to glass-water exchange and to smectite formation. The early hydration process of the

coarser fraction of volcanic glass for which oxygen isotope exchange is relatively reduced results in a pattern of decreasing  $\delta^{18}\text{O}$  values.

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