Formation and evolution of weathering products in rhyolitic pyroclastic flow deposit, southern Kyushu, Japan

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Abstract

Weathering reactions of a rhyolitic pyroclastic flow deposit in southern Kyushu, Japan were investigated in order to understand the behavior of elements and the formation and evolution of reaction products. The weathering profile developed in the pyroclastics contains variable amounts of erionite, halloysite and noncrystalline Al-Si-Fe-rich materials with or without noncrystalline Mn-rich material as weathering products. The formation of these products appears to reach depth of more than 10 m below the surface. The mobility of cations in this profile is Na > Ca > K > Si > Fe > Al > Ti > Mn, in which Al, Fe, Mn, and Ti accumulate mostly in the surface horizon during the weathering. The accumulation of these elements is caused by dissolution of volcanic glass, feldspar, and pyroxene, and precipitation of noncrystalline clays enriched in Al, Fe, Mn, and Ti. Aluminum and Si released into solutions from volcanic glass and feldspar tend to combine with each other to produce Al-Si complexes with high reactivity with other metal cations at the initial weathering stages. Fe$^{3+}$ and Mn$^{2+}$ derived mainly from pyroxene are incorporated with the Al-Si complexes and precipitate as Al-Si materials containing Fe and Mn exhibiting irregular aggregates of randomly elongated very fine noncrystalline fibers less than 0.1 μm in length. These noncrystalline fibers tend to crystallize to halloysite by partial development of a domain structure and elimination of Fe and Mn during crystallization processes. This weathering profile characteristically contains erionite crystals exhibiting hexagonal rods and thin needles normally less than 5 μm in length as a major weathering product of the rhyolitic pyroclastic flow deposit. The chemical compositions of erionite crystals show a wide range with negative correlation between numbers of Si and those of Al+Fe$^{3+}+\text{Ti}$ in which Si content increases continuously with depth. These erionite crystals may have been formed in a micro-environment where high pH and high cation activity conditions have been achieved by heterogeneous dissolution of volcanic glass and feldspar.

Key words: crystallization, dissolution, erionite, halloysite, noncrystalline clays, rhyolitic pyroclastic flow deposit, weathering

Introduction

Pyroclastic flow deposits are widely distributed in many areas of the world as surficial deposits of Quaternary age (Heiken and Wohletz, 1985). These surficial deposits always contact with water, which causes various weathering reactions such as dissolution of primary constituents, selective transport of elements, and formation of secondary products. It is well known that these reactions are strongly affected by chemistry and flow rate of the solution, and also by the chemical composition and structure of primary constituents. In addition, biological activity and interaction with organics supplied from the biosphere accelerate these reactions (Barker et al., 1997). There are many studies about formation of crystalline clay minerals by weathering processes (Nagasawa, 1978; Allen and Hajek, 1989; Chamley, 1989), but there is
less information about dissolution of primary minerals in natural weathering conditions and also about formation and transformation processes of secondary noncrystalline precipitates. On the other hand, dissolution mechanisms and its rate of various rock-forming minerals have been extensively investigated under artificial weathering conditions in both open and closed reaction systems (e.g., White and Brantley, 1995). These experimental studies indicated that the dissolution rates of artificial weathering are about one to two orders of magnitude greater than the natural rates (Paces, 1983; Velbel, 1985). The reasons for this discrepancy are considered to be heterogeneous weathering reactions caused by preferential leaching of high-energy sites, incomplete exposure of surface area, and preferential flow through high-permeability channels (Drever and Clow, 1995). The solution compositions under such heterogeneous weathering conditions are not chemically comparable to bulk solution conditions in a micro-environment of parent materials. This also affects the overall weathering reaction involving formation of secondary materials. Consequently, more extensive study about weathering reactions in natural conditions is required for constructing an accurate geochemical weathering model on the earth's surface.

In this study, we investigated the chemical reactions occurring in a weathering profile developed in a pyroclastic flow deposit in southern Kyushu, Japan. This pyroclastic flow deposit provided a good sample for study of weathering involving dissolution of primary materials, transportation of elements, precipitation of secondary materials, and formation of crystalline clay minerals. Here, we examine the chemical transportation and mineralogical trends of bulk samples during weathering, and discuss the various chemical reactions occurring in this weathering profile.

Sample and weathering profile

Rhyolitic pyroclastic flow deposit erupted from the Aira caldera prior to 22,000 y (Aramaki, 1969) forms a widespread, surficial deposit in southern Kyushu, Japan (Fig. 1). The pyroclastic flow deposit consists of massive, nonwelded, fine to coarse ash fragments with no stratigraphic units. It is composed mainly of
volcanic glass (50–60 wt.%), feldspar (30–20 wt.%), quartz (<10 wt.%), pyroxene (<5 wt.%), and less amounts of magnetite (<2 wt.%). The deposit normally contains variable amounts of clay minerals such as halloysite, smectite, and noncrystalline clays, and small amounts of erionite is locally produced as a weathering product. The samples studied here were collected from a weathering profile developed in the deposit at the Korimoto area, Kagoshima city, Japan. This weathering profile is exposed in a road cut along east side of the Korimoto cemetery, where A, B, and C horizons exhibiting brown, yellowish, and white to gray colors are clearly observed. Four samples of weathered pyroclastics were collected from A to C horizons at a depth of about 0.1, 0.5, 3, and 9 m (Fig. 1).

Experimental methods

Sample used in this study

The samples collected from the weathering profile were dried in air, and >2.0 mm size grains, which are composed mainly of rock fragments and pumice blocks, were removed by dry sieving. The sieved samples composing <2.0 mm size grains were used in this study as bulk samples.

Bulk chemical composition

About 10 g of bulk samples were finely powdered in an agate mortar, and about 1 g of the powdered samples were pressed into a disc in a vacuum chamber, and were used for EDX after coating with carbon. EDX was conducted with a HITACHI S-4100 scanning electron microscope equipped with LINKS ISIS EDX operated at an accelerating voltage of 15 kV.

Particle size, and contents of H2O and organic materials

Variations of particle size of the bulk samples were determined by wet sieving and normal sedimentation methods. The contents of H2O and organic materials were obtained by gravimetric methods: weight losses of the bulk samples after heating at 110°C for 1 day were assigned to H2O content, and those after treatment with 30% hydrogen peroxide (H2O2) for 2 hours under 100°C to that of organic materials.

Quantification of constituents

An estimate of the percent of constituents was carried out by internal standard XRD methods using powdered bulk samples mixed with a standard of NaCl. Generally, the weight ratio of a component A to a standard S can be expressed by the following equation:

\[ \frac{W_A}{W_S} = K \frac{I_A}{I_S} \]  

where, \( W_A \) and \( W_S \) are weights of the component A and standard S, respectively. \( I_A \) and \( I_S \) are intensity of XRD reflections of the component A and standard S, respectively. \( K \) is a constant depending on weight ratio of the component A and standard S. To determine the \( K \) factor, volcanic glass obtained from the pyroclastic flow deposit that contained no impurities and NaCl supplied from Wako Pure Chemical Industries Ltd were mixed in a weight ratio of 5 : 1. Similarly, each component, feldspar, quartz, and halloysite were also mixed with NaCl as weight ratio of 5 : 1, and the \( K \) factor of each component was determined. The bulk samples collected from the weathering profile were mixed with the same weight ratio of NaCl as well as the pure samples, and then weight % of each component was calculated. Before mixing with NaCl, all samples were heated at 200°C overnight to remove adsorbed water and to dehydrate completely interlayer water of halloysite.

Measurement of pH

The pH values of samples were measured using two different solutions of deionized, distilled water and a 1 N KCl solution. About 4.0 g of bulk sample was mixed with 100 ml of each solution, and after an hour, the pH of each solution was measured with a glass electrode of a digital pH meter.

Mineralogy of weathering products

Fractions of <50μm size were collected by sedimentation methods, and were used for XRD, TEM-EDX, and SEM-EDX. XRD was done with a RIGAKU RU-200B diffractometer with monochronous CuKα radiation (30 kV, 100 mA) using a sample deposited on a glass slide. SEM was made with a HITACHI S-4100 scanning electron microscope equipped with EDX facilities (Be window) operated at an accelerating voltage of 15 kV using a carbon-coated sample. TEM was carried out with a JEM-2000FX transmission electron microscope equipped with EDX facilities (ultrathin window) operated at an accelerating voltage of 200 kV using a carbon-coated sample deposited on a Cu grid covered with a collodion film.

Constituents of pyroclastic flow deposit

Volcanic glass

The pyroclastic flow deposit contains about 50–60 wt.% of volcanic glass exhibiting fragments of
Table 2. Chemical compositions of bulk samples collected from the weathering profile of the pyroclastic flow deposit.

<table>
<thead>
<tr>
<th></th>
<th>K-1</th>
<th>K-2</th>
<th>K-3</th>
<th>K-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>62.27</td>
<td>68.93</td>
<td>71.12</td>
<td>72.62</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.90</td>
<td>0.66</td>
<td>0.23</td>
<td>0.27</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>22.54</td>
<td>15.56</td>
<td>14.15</td>
<td>11.92</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.22</td>
<td>6.67</td>
<td>5.64</td>
<td>5.33</td>
</tr>
<tr>
<td>MnO</td>
<td>0.37</td>
<td>0.04</td>
<td>0.27</td>
<td>0.20</td>
</tr>
<tr>
<td>CaO</td>
<td>2.83</td>
<td>2.98</td>
<td>3.58</td>
<td>3.77</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.08</td>
<td>2.26</td>
<td>2.23</td>
<td>2.67</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.79</td>
<td>2.90</td>
<td>3.06</td>
<td>3.32</td>
</tr>
<tr>
<td>Total (%)</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Total Fe as Fe₂O₃. The weight % of oxide compounds were normalized by 100% total.

bubble-wall with planar or curviplanar surfaces and sharp edges, angular blocky shape with flat surfaces on which vesicles poorly developed, and irregular shapes of highly vesicular blocks similar to that of large size pumices. Most of the glass grains in each sample are coated with aggregates of very fine particles of Al-Si rich clays produced during weathering, and many etch pits elongated in irregular directions are developed on the surface. The chemical composition of the volcanic glass is given in Table 1.

**Feldspar**

Feldspar is a second most abundant constituent (30–20 wt.%) of the pyroclastic flow deposit. Most of the feldspar grains exhibit angular blocky shapes having flat surfaces and sharp edges with or without various sizes of etch pits depending on the degree of weathering. The surfaces are partly covered by Al-Si rich clays easily removable by sonification. A typical chemical composition of unweathered feldspar grain is listed in Table 1. This agrees to that of labradorite (Ab₃₈An₆₂), but the compositions vary Ab₃₈An₆₂ to Ab₃₁An₆₉ depending on the grains.

**Pyroxene**

The pyroclastic flow deposit contains a small amount of pyroxene grains (<5 wt.%). The chemical compositions (Table 1) varies between En₃₈Fs₃₉ and En₄₀Fs₅₅. Most of the pyroxene grains are greatly weathered and have lens-shaped etch pits aligned with long axes of the grains parallel to the c-axis of the crystal as reported by Berner and Schott (1982). Some grains of pyroxene are covered characteristically with Fe-rich materials precipitated from solution and also with Al-Si rich clays as well as volcanic glass and feldspar.

**Quartz**

The surfaces of quartz grains are smooth, and there is no evidence suggesting that the grains undergo any appreciable degree of weathering.

**Bulk sample of pyroclastic flow deposit**

**Elemental transport**

Weathering of the pyroclastic flow deposit causes dissolution of primary constituents and transport of elements released into solution. The behavior of elements in the weathering profile are different from each other depending mainly on their solubility and reactivity. Chemical compositions of bulk samples are listed in Table 2. Figure 2 shows changes in oxide weight % of major elements in the profile. The important features of behavior of the elements are the apparent enrichment of Al, Fe, Ti, and Mn, and depletion of Si, Ca, Na, and K with decreasing depth. These elemental trends suggest that Al, Fe, Ti, and Mn released from primary materials would accumulate at the upper most surface of the profile as weathering products, whereas Si, Ca, Na, and K may be removed during weathering.

**Particle size, and contents of H₂O and organic materials**

Chemical weathering is generally accompanied by changes in particle size distributions to finer sizes, which is mainly due to the decomposition of coarser primary materials and then precipitation of very fine secondary products. In the weathering profile studied here, <50μm size fractions increase with decreas-
Fig. 3. Variations of particle size with depth (a), and contents of organic materials, H₂O and inorganics of the weathering profile in the pyroclastic flow deposit (b).

Fig. 4. Mineralogical trends with depth of the weathering profile in the pyroclastic flow deposit. The quantification was carried out by internal standard XRD method using bulk samples mixed with standard of NaCl, and the values were normalized by 100% total.

...ing depth, whereas grains between 2 to 0.5 mm slightly decrease in amount (Fig. 3a). Another change with weathering is increase in contents of H₂O and organic materials with decreasing depth (Fig. 3b). The increase in H₂O content is due to formation of weathering products containing water molecules in their structure, and increase of surface area which enables an increase in the amounts of adsorbed water. The organic materials are supplied from the uppermost surface horizon by mainly biological degradation of plant materials and various organisms to high molecular organic substances, so called as “humus” (Oades, 1989). The organic materials are transported gradually to lower horizons with water flow.

Mineralogical abundance

The amounts of four selected major constituents, i.e., volcanic glass, feldspar, quartz, and halloysite, were estimated by the internal standard XRD method using samples mixed with a standard of NaCl. The bulk samples contain variable amounts of weathering products consisting mainly of halloysite which increases in amounts with decreasing depth, and volcanic glass and feldspar decreases. Figure 4 shows weight % of these constituents normalized by 100% total. The standard deviations of these values are less than 5%. This diagram indicates that the sample K-1 contains about 10% of halloysite which decreases gradually with depth. In contrast, volcanic glass increases slightly to about 60% with depth. There is no significant change in the amount of feldspar and quartz through the profile. In this diagram, non-crystalline clays are not included because such materials give no characteristic diffraction peak required for direct quantification, and also of the relative difficulty in obtaining a pure sample as a standard for determination of the K-factor.

pH values

The pH values of water and 1 N KCl solution added to the bulk samples are listed in Table 3. The pH of water appears to be near neutral and decreases with depth. Generally, water in sediments contains variable amount of CO₃²⁻ supplied from air and biological activity of microorganisms, which decreases the pH of the solution to slightly acidic. The pH values of the samples are apparently higher than the expected values of natural solution, indicating that the solution is neutralized by interaction with constituents of the samples such as volcanic glass and feldspar. On the other hand, the pH of KCl solution is almost constant to about 5.5-5.7. These discrepancies of the pH values are caused by cation exchange reactions be-
Table 3. pH values of bulk sample of the pyroclastic flow deposit collected from the weathering profile.

<table>
<thead>
<tr>
<th></th>
<th>K-1</th>
<th>K-2</th>
<th>K-3</th>
<th>K-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (H₂O)</td>
<td>7.48</td>
<td>7.57</td>
<td>6.37</td>
<td>6.40</td>
</tr>
<tr>
<td>pH (KCl)</td>
<td>5.76</td>
<td>5.56</td>
<td>5.73</td>
<td>5.72</td>
</tr>
<tr>
<td>ΔpH</td>
<td>1.72</td>
<td>2.01</td>
<td>0.64</td>
<td>0.68</td>
</tr>
</tbody>
</table>

pH (H₂O) represents pH value of 100ml of water mixed with 4.0g of sample. pH (KCl) is that of 100ml of 1N KCl solution mixed with 4.0g of sample. ΔpH means difference in these values. The measurement of the pH values was made after leaving 1 hr.

tween protons adsorbed on the surface of solids and K ions in the solution.

Mineralogy of weathering products

Clay minerals

All samples collected from the pyroclastic flow deposit contain variable amounts of weathering products consisting mainly of halloysite, noncrystalline clays, and erionite. Figure 5 illustrates XRD profiles of <5μm size fractions in which pronounced reflections of both hydrated (10Å) and dehydrated (7Å) states of halloysite and erionite, and small peaks of quartz and feldspar are observed. Halloysite successively changes in hydration states from hydrated to dehydrated forms with increasing amounts (Fig. 4).

TEM observations revealed that the weathering products are composed mainly of halloysite exhibiting both spherical and tubular habits, irregular aggregates of very fine noncrystalline materials, and small amounts of erionite rods. The amounts of these products vary with samples as observed by changes in intensities of XRD peaks. The amounts of spherical halloysite increase with decreasing depth, but those of noncrystalline materials increase with increasing depth. Figure 6 shows a typical example of the weathering products in sample K-1, which contains spherical halloysite and noncrystalline materials as indicated by arrows h and f, respectively. Most of the spherical halloysite grains in the products exhibit well-developed domain structure less than 0.5μm in diameter composed of curled fringes about 10–15nm in thickness. EDX analyses indicate that the halloysite spheres consist mainly of Si and Al, and characteristically contain small amounts of Fe (Fig. 6 b).

On the other hand, the noncrystalline materials exhibit irregular aggregates of randomly elongated very fine noncrystalline fibers less than 0.1μm in length. The chemical compositions of the noncrystalline fibers are characterized by higher contents of Al and Fe than that of halloysite as shown in Figure 6 b. In addition, TEM revealed that the weathering products contain small amounts of rounded aggregates less than 0.2μm in diameter composed of noncrystalline fibers surrounded by curled fringes of poorly developed domains as indicated by arrows d (Fig. 6 a). The electron diffraction patterns displayed diffuse halo, indicating noncrystalline structure. EDX spectra of the rounded aggregates show large peaks of Al and Si, and a relatively weak peak of Fe, which correspond to intermediate compositions between noncrystalline fibers and spherical halloysite. Similar materials exhibiting irregular aggregates of noncrystalline Al-Si-Fe-rich fibers have been reported as weathering products formed at early weathering stages of volcanic glass (Kawano et al., 1997) and K-feldspar (Tazaki and Fyfe, 1987).

Other fibrous materials that exhibit aggregates of fine fibers and/or curled thin files less than about 0.1 μm in length are present in the sample K-1 (Fig. 7 a). These materials are also noncrystalline for electron diffraction and are enriched in Al, Si, and Fe, but characteristically contain variable amounts of Mn as a
major element (Fig. 7 b).

**Erionite**

Erionite occurs as a major weathering product in the pyroclastic flow deposit as recognized in the XRD profiles of $<5 \mu m$ size fractions (Fig. 5). The reflections of erionite become very weak or disappear on XRD profiles of $<2 \mu m$ size fractions, since most of erionite crystals are larger than 2 $\mu m$. SEM indicates that the erionite crystals normally exhibit hexagonal symmetry of short rods about 2-5 $\mu m$ in length and 1-2 $\mu m$ in thickness (Fig. 8 a). Most of the erionite crystals adhere to the volcanic glass surface perpendicular to the axis of elongation. Figure 8 b shows a typical example of erionite crystals which have grown on the surface of volcanic glass. Some erionite needles less than 2 $\mu m$ in length can be observed by TEM. The average chemical composition of 10 erionite crystals in each sample collected from the profile is given in Table 4 together with numbers of cations calculated on the basis of 72 oxygens. The common features of chemical compositions of the erionite crystals are relatively rich in Si and Fe$^{3+}$ relative to those by other origins reported by Sheppard and Gude (1969). Noticeably, the Si content increases and Al content decreases with depth. Figure 9 shows plots of Al$^{3+}$+Fe$^{3+}$+Ti cations versus Si per unit cell of 40 erionite crystals. This indicates that the relation between numbers of Si and those of Al$^{3+}$+Fe$^{3+}$+Ti shows a good linear correlation, and there is a wide range of chemical variation from 24.4 to 29.9 for numbers of Si. However, Si contents of the crystals are apparently shifted toward higher region with depth. The atomic ratios of Ca-Na-K of erionite crystals in each sample are given in Figure 10. The crystals are rich in K and Ca, and poor in Na, and there is no clear difference in each sample.

**Discussion**

**Elemental transportation**

Chemical compositions of bulk samples from the weathering profile of a pyroclastic flow deposit in the Korimoto area provide clear evidence for elemental transport during weathering. The results obtained from this profile suggest accumulation of Al, Fe, Ti, and Mn at the surface of the profile, and removal of Si, Ca, Na, and K from the same parts. Figure 11 shows the relative mobility index of each element calculated by using the following equation:

$$\mu = 1 - \frac{R}{R_0},$$

where $\mu$ is the relative mobility index, and $R$ and $R_0$ are the element contents in weathered and unweathered horizons, respectively. In this study, element contents of sample K-1 collected from the uppermost horizon were used for $R$, and those of sample K-4 from the deepest horizon were used for $R_0$. An element having positive value of $\mu$ tends to be re-
moved during weathering, whereas that having negative value tends to accumulate in the horizon depending on its $\mu$ value. The order of mobility obtained from this weathering profile is $\text{Na} > \text{Ca} > \text{K} > \text{Si} > \text{Fe} > \text{Al} > \text{Ti} > \text{Mn}$. All these elements have been essentially contained in the primary materials, and are released into the solution during dissolution of the materials by interaction with water. Therefore, the elements accumulated at the surface horizon of the weathering profile would remain as secondary precipitates. The behavior of dissolved elements in the weathering profile are extremely complex and very difficult to estimate quantitatively because the behavior of each element is strongly affected by various factors such as flow rates of solution and their chemical conditions, reactions with other inorganic and organic materials involving cations and substances, and biological accumulation. The flow rate of solution is important for controlling the concentration of elements in solution, which affects thermodynamical formation of secondary precipitates consisting mainly of Al and Fe$^{3+}$. In this profile, the presence of various clays enriched in Al and Fe indicates that the flow rates are sufficiently slow to exceed their solubility limits. The chemical conditions of solution such as pH, Eh, and reactions with organic materials are important to control solubility of elements in solution. In the upper most horizon, it would be assumed that the conditions are near neutral pH, oxidizing, and rich in various organic materials. In these conditions, Al and Ti rapidly precipitate as hydroxides or complexes with Si. For Fe and Mn, these cations tend to be oxidized by $\text{O}_2$ in solution and/or bacterial activity if the cations remain in the surface horizon long enough for complete oxidation (Hariya and Kikuchi, 1964; Emerson et al., 1982), and then precipitate as Fe- and Mn-hydroxides. Another possible behavior of Fe and
Table 4. Average chemical compositions of 10 erionite crystals in samples collected from the weathering profile of the pyroclastic flow deposit.

<table>
<thead>
<tr>
<th></th>
<th>K-1</th>
<th>K-2</th>
<th>K-3</th>
<th>K-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>66.25</td>
<td>69.41</td>
<td>70.03</td>
<td>74.10</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.28</td>
<td>0.44</td>
<td>0.28</td>
<td>0.18</td>
</tr>
<tr>
<td>Ab₂O₅</td>
<td>24.64</td>
<td>20.95</td>
<td>20.80</td>
<td>14.27</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.24</td>
<td>1.67</td>
<td>1.94</td>
<td>1.91</td>
</tr>
<tr>
<td>MnO</td>
<td>0.06</td>
<td>0.12</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>CaO</td>
<td>3.29</td>
<td>3.29</td>
<td>4.08</td>
<td>4.59</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.49</td>
<td>0.44</td>
<td>0.30</td>
<td>0.76</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.75</td>
<td>3.68</td>
<td>2.93</td>
<td>4.15</td>
</tr>
</tbody>
</table>

Total (%): 100.00 100.00 100.00 100.00

Total Fe as Fe₂O₃. The weight % of oxide compounds were normalized by 100% total.

Mn is formation of complexes with precipitates of Al and Si. Fe³⁺ and Mn²⁺ have substantially high solubility limits relative to their oxidized forms, but both divalent cations are rapidly incorporate with Al-Si complexes in solution containing these cations, and form complexes of Al-Si-Fe-Mn.

**Formation of Al-Si-Fe-rich and Mn-rich materials**

During weathering processes of rocks and pyroclastics, dissolution of primary constituents and formation of secondary products proceed simultaneously. Generally, the secondary products formed at early weathering stages are noncrystalline materials which develop to crystallized clay minerals during subsequent weathering reactions (Tazaki and Fye, 1987; Kawano et al., 1997). In the present weathering profile, all samples contain certain amounts of noncrystalline materials enriched in Al, Si, and Fe as a secondary product (Fig. 6). The Al-Si-Fe-rich materials exhibit normally irregular aggregates of very fine fibers whose compositions, especially Fe content, vary considerably from each other. Al and Si ions are the predominant elements in volcanic glass and feldspar, and Fe is a major element of pyroxene. SEM observations showed clear evidence for dissolution of these materials, which indicate that the elements are released into solution. These elements in solution would precipitate as the Al-Fe-Si-rich materials under near neutral pH and oxidizing condition. The solubility limits of Al and Fe³⁺ ions are substantially very low in near neutral solution (Garrels and Christ, 1965), whereas the solubility of Si ions is about five to six order of magnitude higher than that of Al (Stumm and Morgan, 1981). This suggests that Al

![Fig. 9. Relationships between numbers of Al+Fe³⁺+Ti cations and Si per unit cell in erionite crystals formed in the weathering profile. It is noteworthy that these values give a good linear correlation for decrease of Al+Fe³⁺+Ti cations and increase of Si with depth.](image)

![Fig. 10. Triangular diagram of Na-K-Ca showing the chemical compositions of erionite crystals formed in the weathering profile.](image)

and Fe³⁺ easily precipitate as gibbsite and hematite, respectively. However, no evidence was found for the formation of these minerals in this weathering profile. Form experimental reactions between Si and Al ions and between Si and Fe ions, it has been revealed that 1) significant amounts of Si are incorporated into the noncrystalline structure of Al- and Fe-
Fig. 11. Diagram showing relative mobility of elements during weathering. The elements plotted in positive region of mobility index tend to be removed from the profile, whereas those in negative region accumulate during weathering reactions.

hydroxides (Violante and Hung, 1993); 2) Si in the noncrystalline Al- and Fe-hydroxides inhibits their crystallization (Carlson and Schwertmann, 1981; Karim, 1984); and 3) Fe$^{3+}$ is readily incorporated into the structure of aluminosilicate precipitates and nontronite-like noncrystalline Al-Si-Fe-rich materials are formed (Farmer et al., 1991). Furthermore, most Fe originally present in the primary materials is divalent. If Fe$^{2+}$ is oxidized in solution, differential precipitation of Fe-minerals would occur during weathering. However, most noncrystalline materials apparently contain variable amounts of Fe, suggesting that the element is incorporated with Al-Si complexes as divalent forms and is oxidized in their structure. Consequently, the noncrystalline Al-Si-Fe-rich materials in the weathering profile are produced by ionic reaction of Al and Si, and then Fe$^{2+}$ ions incorporate with the Al-Si complexes during weathering processes. The Mn-rich materials also may be produced by reaction of Mn$^{2+}$ ions with these Al-Si-Fe-rich materials.

Formation of halloysite

The weathering profile of pyroclastic flow deposit in the Korimoto area contains variable amounts of halloysite mostly exhibiting a spherical habit with small amount of a tubular one. In natural weathering conditions, spherical halloysite is a common clay mineral formed from volcanic glass, whereas tubular halloysite normally occurs as an alteration product of feldspars (Nagasawa and Miyazaki, 1976). For artificial weathering conditions, spherical halloysite is only produced from volcanic glass (Kawano and Tomita, 1994, 1995), but tubular one is formed from feldspar (Parham, 1969). The relationship between the crystal morphology of halloysite and parent material suggests that the formation mechanisms of these halloysites may be different (Banfield and Eggleton, 1990). TEM observations of clay fractions in the present samples suggest the following plausible formation process of spherical halloysite from noncrystalline Al-Si-Fe-rich materials as follows:

1) Formation of heterogeneous aggregates of Al-Si-Fe-rich noncrystalline fibers by precipitation from solution.

2) Development of small rounded aggregates of fine fibers surrounded by curled fringes of thin domains with decrease in Fe content.

3) Further development of domain texture in rounded aggregates with successive decrease in Fe by partial crystallization to halloysite.

Formation of erionite

Erionite is a common alteration mineral of rhyolitic tuffaceous sediments in saline, alkaline lakes and under diagenetic and hydrothermal environments, but is a rare secondary product in weathering environments (Hay, 1978; Gottardi and Galli, 1985). However, erionite crystals exhibiting hexagonal symmetry of short rods about 2-5 μm in length occurred as a major weathering product of rhyolitic pyroclastic flow deposit in the Korimoto area. Important observations related to its formation are as follows:

1) Most of erionite crystals adhere to the volcanic glass surface together with aggregates of halloysite and noncrystalline Al-Si-Fe-rich materials, indicating that the crystals have grown on the glass surface.

2) The chemical compositions of the crystals showed a linear relationship between numbers of Si and those of Al$^{3+}$ + Ti, and it is clear that Si content of the crystals increases with increasing depth. Therefore the activity of Si in the deeper horizon is likely higher than that in the surface horizon, which is in good agreement with the bulk chemical variation.

3) The pH values of bulk samples are near neutral, suggesting that the pH of solution in the weathering profile would be higher than these values, because the solution of the profile remain in contact with the constituents for longer duration.

4) The pyroclastic flow deposit, which is distributed over an extensive area more than 10,000 km$^2$ (Fig. 1), normally contains halloysite and noncrystalline clays as weathering products. Erionite is not a common weathering product in the pyroclastics, and its occurrence is localized in the Korimoto and some other areas (Chishiki et al., 1992).

Barrows (1980) estimated that formation temperature of erionite formed by burial diagenesis is below 100°C. Aiello and Barrer (1970) obtained synthetic erionite from aluminosilicate gel in solution mixed with NaOH and (CH$_3$)$_3$NOH at 80°C for 7 days. These studies indicate that formation of erionite is favored in alkaline solution with relatively high cation activity. In weathering environments, the chemistry and
pH of solution are controlled by dissolution of constituents of pyroclastics, particularly volcanic glass and feldspar. When solution contact glass and feldspar, hydrolysis of the materials increases the pH of the solution, and the concentrations of dissolved elements increase with increasing contact duration. In the pyroclastic flow deposit, alkaline and high cation activity would be achieved in some local micro-environments such as channels, cavities, and etch pits. It has been shown that the chemical and physical properties of solution in local micro-environments and near surfaces of primary materials differ fundamentally from those of bulk solution (Banfield et al., 1991; Hochella and Banfield, 1995). Thus, erionite crystals in the pyroclastics may have been formed in alkaline and high cation activity conditions in local micro-environments similar to a closed system. The chemical compositions of erionite crystals have a wide range of variations, indicating difference in chemistry of solution in each micro-environment where formation of erionite occurs.

Conclusions

The rhyolitic pyroclastic flow deposit aged 22,000 B.P. Y. in Korimoto area contains halloysite, erionite, and noncrystalline Al-Si-Fe-rich materials as weathering products. Weathering reached to depth of more than 10 m below the surface. Halloysite decreases in amount with depth and erionite is more abundant in the middle depth level. The highly developed etch pits of the surface of volcanic glass, feldspar, and pyroxene suggest that they are major sources for providing various cations into the solution involved in weathering reactions. The relative mobility index of the cations calculated using chemical compositions of bulk samples indicates that the order of mobility in this weathering profile is: Na > Ca > K > Si > Fe > Al > Ti > Mn, in which Al, Fe, Mn, and Ti accumulated mostly in the surface horizon. These elements released into solution precipitate as various weathering products mainly of noncrystalline Al-Si-Fe-rich materials with or without Mn, and thereby they crystallize to halloysite as weathering proceeded. The greatly abundant Al and Si among the released elements produce Al-Si complexes by ionic reaction, and then the noncrystalline Al-Si-Fe-rich materials are formed by incorporation of Fe$^{3+}$ and/or Mn$^{2+}$ with the Al-Si complexes.

The weathering profile also contains erionite crystals exhibiting hexagonal rods and thin needles as a major weathering product. The chemical compositions of erionite crystals show relatively wide range variations with continuous increase in Si content and decrease in Al + Fe$^{3+}$ + Ti with depth. The wide range chemical variations of erionite crystals suggest that the crystals may have been formed in a micro-environment where high pH and high cation activity conditions have been achieved by heterogeneous dissolution of volcanic glass and feldspar. It seems reasonable to assume that the chemical conditions of solution in the micro-environment are significantly different from each other, which result in the chemical variation of erionite crystals.

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References


* in Japanese with English abstract

(要旨)


南九州に分布する流紋岩火砕流堆積物の風化過程での元素の挙動および風化生成物の生成と変化について検討した。風化プロフィルでの陽イオン移動度は Na > Ca > K > Si > Fe > Al > Ti > Mn, 風化生成物はエリオナイト, ハロサイト, 非晶質 Al-Si-Fe 物質, 非晶質 Mn 物質を主体とする, 難移動性を示す Fe および Mn は風化初期段階に生成される, 非晶質 Al-Si 二相体の構造中に取り込まれ, ドメイン構造の発達によるハロサイトへの結晶化過程で溶液中に放出される。一方, エリオナイトの化学組成は表層から深部方向に Si/(Al + Fe²⁺ + Ti) 比が増加するとともに, 風化に伴う陽イオンの移動度をほぼ一致した傾向を示すが, 個々の結晶では著しい組成変動が認められる。このような組成変動は風化プロフィルの中での微環境の化学的条件の違いを反映したものと思われる。