WEATHERING MECHANISM OF SILICATE PHENOCRYSTS IN TEPHRAS, INFERRED FROM SEM OBSERVATIONS OF SURFACE ETCHING

HARUMI SAGARAa and ATSUYUKI INOUEb

a Graduate School of Natural Sciences, Chiba University, Chiba 263-8522
b Department of Earth Sciences, Chiba University, Chiba 263-8522

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ABSTRACT

In the present study we describe the surface etching features of plagioclase, pyroxene, olivine, amphibole, and biotite phenocrysts in tephras from Hachijo-Higashiyama, Daisen, and Niijima volcanoes with progress in weathering. The variations in the size and number of etch pits were quantified by image analysis as a function of depth in tephra column from Hachijo-Higashiyama. In Hachijo-Higashiyama tephras, pyroxene and plagioclase phenocrysts were completely covered with glassy materials and etching did not occur during the early weathering duration of about 10 ky after deposition. After the glassy cover disappeared, etching began selectively at dislocations. The etch-pit shapes are crystallographically controlled on different faces, particularly in plagioclase. The etch-pit density decreased, the size increased with increase in depth of tephra column. This change is an overall result of etch-pit coalescence and neoformation of small etch pits. Etching of phenocrysts is preceded by halloysitization of glass, which results in the increase of saturation levels in porewaters infiltrating through tephra column. Consequently, it is implied that mineral dissolution rates are strongly controlled by the saturation level of porewaters with respect to solute species supplied from rapid dissolution of glasses during chemical weathering of tephras.

Key words: Chemical weathering, Tephra, Silicate Phenocrysts, Etch pit, Saturation level

INTRODUCTION

Chemical weathering, involving dissolution of primary minerals and growth of secondary hydrous minerals associated with increase in time, is essentially a net reaction of various elementary reactions occurred at the interface of mineral and solution phases. Extensive scanning electron microscopic (SEM) examination of both experimentally dissolved and natural mineral surfaces has revealed numerous and ubiquitous crystallographically controlled etch pits (e.g., Wilson, 2004 and references cited therein). The etch-pit formation was considered as evidence for surface-controlled reactions in mineral dissolution (e.g., Berner, 1981). On the other hand, it has been thought that the dislocation etch pit dissolution occurred at specific sites makes a minor contribution to overall dissolution rate of mineral, particularly in undersaturated soil systems (e.g., Blum et al., 1990). Recently, nevertheless, Teng (2004) demonstrated in calcite dissolution experiment that there are three different dissolution modes related to saturation state: near-equilibrium, far-from-equilibrium, and intermediate situations. In near-equilibrium situations, no etch pit forms and dissolution occurs at steps on the mineral surface. At far-from-equilibrium conditions, a sharp increase in etch pit formation occurs and thus there is no significant relationship between dissolution rate and dislocation density. At intermediate saturation levels, however, dissolution takes place primarily at dislocations and along steps. Similar relationships were demonstrated for the dissolution of siltic minerals by Dove et al. (2005). Lasaga and Lüttge (2001; 2003) incorporated the influence of saturation state on etch pit formation into a dissolution rate formulation based on a step wave model. Thereby they united the slow dissolution rates near equilibrium concordantly with the so-called dissolution plateau rates far from equilibrium. Despite the attractive model, there is much to be done to develop and test its concept.

Apart from the above theoretical and experimental progress, White and Brantley (2003) indicated that there are two obstacles which have not yet been overcome for understanding natural mineral weathering rate and mechanism: (1) dissolution rates measured in the laboratory are always several orders of magnitude greater than those measured in natural systems and (2) the dissolution rates in natural systems decrease with time. They attributed the cause of the inconsistencies to be related to the estimation of surface roughness, i.e., the density of reactive sites on ongoing weathering minerals. The mineral dissolution rates are a function of the saturation...
state in soil solution as well as the surface roughness. Brantley et al. (1993) indicated that if the saturation level of soil solutions or the surface roughness are of primary importance determining natural mineral weathering rates, then etching of mineral surfaces should depend on soil depth.

The purpose of this study is to describe etch pits developed on the crystal faces of plagioclase, pyroxene, olivine, amphibole, and biotite phenocrysts in tephra s from Hachijo-Higashiyama, Daisen, and Niijima volcanoes. The special emphasis is paid to elucidate the crystallographic relationship of etch pits developed on different faces and the variation in the size and number of etch pits with depth using chronosequential samples. In the companion paper (Sagara et al., in preparation), dissolution experiments of anorthitic plagioclase monocrystal have been carried out and the morphologies of etch pits artificially formed on several crystal faces have been compared with the natural pit morphologies. We will apply these natural and experimental observations to the improved understanding of reactive surface area evolution related to the saturation state of soil solutions during weathering of tephra s in natural conditions.

STUDY SAMPLES AND THEIR GEOLOGIC SETTINGS

Plagioclase, pyroxene, and olivine from Hachijo-Higashiyama tephra s

Hachijojima Island, located 300km south of Tokyo, consists of two Quaternary volcanoes, Higashiyama and Nishiyama (Fig. 1). Nishiyama is characterized by basaltic eruptions, whereas the volcanic activities of Higashiyama are diagnostic of mainly andesitic to dacitic eruptions, associated with minor basaltic ones. The activities of the latter volcano have ceased at present and the volcanic edifice has been eroded significantly.

A standard columnar section showing the activities of Higashiyama volcano is illustrated in Fig. 2, which was cited from Tsukui et al. (1991, 1993). The authors divided the eruptive history during recent ca. 30 ka into four stages: Pre-Sueyoshi (abbreviated as PS hereafter) (> 30 ka), Sueyoshi (abbreviated as SY) (29–26 ka), Nakanogo (abbreviated as NK) (20–10 ka), and Mitsune (abbreviated as MA) (10–3.5 ka) stages, referring to the reported age data of the marker tephras such as Aira-Tn (AT) ash (26–29 ka after Machida and Arai, 2003) and Kikai-Akahoya (K-Ah) ash (7.3 ka after Machida and Arai, 2003). The AT ash is sandwiched between SY2 and SY3 pumice layers; the K-Ah ash is correlated to the base of Myohoji (MY) pumice layer in Higashiyama.

According to the standard columnar section, we sampled tephra s from 10 sites (A-J) shown in Fig. 1. Since the degree of weathering is generally affected by topographic, hydrologic, and vegetation factors in addition to the chemical composition and physical properties of original materials, we preliminarily checked the degree of weathering in different sites by powder X-ray diffraction (XRD). From the reasons that there are no peculiarities like springs and hydrothermal effects at the sites A and G, and complete chronosequential sampling of

Fig. 1. Location map of Hachijojima Island, Daisen volcano, and Niijima Island, and sampling locations in Hachijo-Higashiyam.
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Fig. 2. Standard columnar section of Hachijo-Higashiyam volcano (after Tsukui et al., 1993).
tephras from OBP to AT is possible there, the tephra samples from the two sites were chosen here as representative of the entire Hachijo-Higashiyaama tephras. No attempt was made in selecting sites to standardize vegetation cover. Especially, plagioclase and pyroxene phenocrysts separated from SY10 to SY6 tephras were used to analyze variations in the size and number of etch pits developed on the crystal faces with progress in weathering. The tephras from SY10 to SY6 are commonly dacitic in composition and contain lots of phenocrysts (Tsukui et al., 1993). The compositions (anorthite contents) of the rim of plagioclase phenocrysts from SY6 to SY10 range from An50 to An70 (labradorite). The Mg# (Mg/Mg+Fe atomic ratio in %) of orthopyroxene, clinopyroxene, and olivine are 52–55, 54–62, and 78–82, respectively (Tsukui et al., 1993).

Recent climate conditions at Hachijo Island are as follows: the mean annual precipitation is 326 cm, the mean annual temperature is 18.2°C, and the mean annual relative humidity is 77% according to the averaged data from 1961–1990 (National Astronomical Observatory, 2000). Several springs and wells are distributed in the flank of Higashiyaama volcano. Machida (1999) reported that the total dissolved solute concentrations of the recharge waters are low in general, from 100–600 μScm⁻¹ as electric conductivities and the pH of the waters are within 7.5–8.0.

**Plagioclase, amphibole, and biotite from Daisen tephras**

Daisen volcano is a large Quaternary composite volcano situated in western Japan on the coast of the Sea of Japan (Fig. 1). According to Tsukui (1984), the eruptive activity of Daisen volcano began in middle Pleistocene and continued until later than ca. 20 ka. The eruptive products are mostly acidic in composition and divided into the older and younger groups based on the mode of activity (Tsukui, 1984). In the present study we examined plagioclase, amphibole, and biotite phenocrysts from HDp (Hidani pumice) to KS-p (Kusatanihara pumice) tephras of the younger group (Fig. 3b). The AT ash (26–29 ka) is intercalated between the HgP (Higashidaisen pumice) and DKp (Kurayoshi pumice). The age of DKp is ≥ 55 ka; those of SKP (Kisuki pumice) and DMP (Matsue pumice) are reported to be 110–115 ka and < 130 ka, respectively (Machida and Arai, 2003). The age of DNP (Namatake pumice) is > 80 ka (Machida and Arai, 2003); the DSP (Sekigane pumice) is intercalated between DKP and DNP. The pumice samples examined all were provided by M. Tsukui. The average An contents of plagioclase phenocrysts from HDp to KS-p range from 38 to 55 (andesine) and they tend to decrease with time (Tsukui, 1984). The compositions of primary amphibole and biotite phenocrysts were not determined because of being subjected to intensive alteration.

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**Fig. 3.** Standard columnar sections of (a) Niiijima volcanoes (after Saito, 2008) and (b) Daisen volcano (simplified from Tsukui, 1984).
Climate conditions at Matsue, located about 40 km west of Daisen volcano, are reported to be 14.3°C of the mean annual temperature and 190 cm of the mean annual precipitation (National Astronomical Observatory, 2000).

**Plagioclase and biotite from Niijima tephra**

For comparison, we also studied four tephras having plagioclase and biotite from Niijima volcanoes (Fig. 1): Mukaiyama (Nj-My, AD 886), Niijimayama (Nj-Nj, ~5.0 ka), Shikineshima (Nj-Sk, ~8.5 ka), and Miyatsukayama (Nj-Mt, ~12.8 ka). The studied samples were provided by K. Saito. The standard columnar section is shown in Fig. 3a. According to Saito (2008), these tephras are dacitic in composition and contain commonly plagioclase and biotite phenocrysts. Cummingtonite accompanies in the Nj-Mt tephra. The compositions of the rim of plagioclase phenocrysts range from An15 to An28 (oligoclase) and the Mg# of biotite from 48 to 56 (Saito, 2008).

No data on the climate conditions are available for Niijima Island, but they are roughly of an intermediate between Hachijojima Island and Daisen in both precipitation and temperature.

**EXPERIMENTAL METHODS**

Phenocrysts in pumices from three volcanic areas were first concentrated by repetition of panning and decantation and then handpicked under the binocular microscope. Separated crystals were examined by XRD for mineral identification. Clay fractions (< 2 μm) of tephra also were separated by decantation and ultrasonication, and x-rayed to determine the alteration products of glasses.

The surface morphologies of phenocrysts were examined by SEM using JEOL JSM-6400 and Hitachi S-2400. The number and size of etch pits developed on pyroxene and plagioclase were measured by analyzing SEM photomicrographs of flat crystal faces that were taken by being inclined as perpendicular as possible to the incident electron beam, using a software of Scion Image (Scion Corporation). Etch pits were defined as regular geometries, closed perimeter depressions on the crystal faces. Irregular-shaped pits were not taken into consideration in the present study. The etch-pit size was represented by the equivalent diameter that is defined as diameter of a circle with the same area as that of the measured etch-pit shape. The measurements were carried out on pyroxenes more than 20 grains and plagioclases more than 40 grains for each tephra in the present study. Data were normalized as the data per unit area using the measured crystal face perimeter.

As will be described below, some of phenocrysts have been still covered by volcanic glasses. The attached glass was removed by a selective dissolution technique with cold fluoboric acid (HBF₄) solution (Luhr, 2001) in order to ascertain the presence of etch pits beneath the glassy cover. In preliminary experiments, glassy materials were almost completely removed by dissolution treatment for 2 hrs. After the selective dissolution by HBF₄ solution was continued for more than 24 hrs, some etch pits were newly formed on the mineral surfaces by HBF₄ treatment. We stop dissolution reaction with HBF₄ solution up to 2 hrs at maximum.

**WEATHERING OF GLASSES**

XRD patterns of the clay fractions from Hachijo-Higashiyama tephras are shown in Fig. 4. Four tephras (OBP, MYP, HHP, and MIP) of the Mitsune stage principally consist of unaltered volcanic glasses, though very small amounts of halloysite are contained in the HHP and MIP. The presence of allophone and imogolite was not clearly identified in the XRD patterns. The weathering features of volcanic glasses are visible under SEM (Fig. 5). Bubble walls of the OBP pumice are wholly smooth, whereas those of MYP to MIP are rough with the alteration products, probably halloysite. The alteration products of tephras from the Nakano stage (NK10 to NK1), consisting of scorias with basaltic composition, are mainly halloysite; the amount is noticeably less than those in the two acidic tephras (Pumice Layer and Rhyolitic Ash) intercalated in the tephras of Nakano stage. Halloysitization becomes more intensive in tephras (SY10 to SY1) from the Sueyoshi stage, and even more intensive in the intercalated AT pumice. Cristobalite is found in tephras below the SY8, together with halloysite. Under SEM, most of glass in the SY10 tephras is replaced by halloysite; spindle-like shaped halloysite aggregates are often observed inside bubbles (Figs. 5f and g). Unaltered glasses having dimple-like pits still remain in the SY10 tephras (e.g., Fig. 5h). Gibbsite, together with halloysite, begins to appear in the PS tephras (> 30 ka), though gibbsite itself was identified from the weathered ash overlying the NK10 (~10 ka). In the present study, the weathered ash is considered as loess involving a part of weathered pyroclastics following the definition of Hayakawa (1995). Generally speaking, weathered ash overlying each tephra contains much more amounts of alteration products like imogolite, halloysite, cristobalite, and/or gibbsite compared to the underlying tephra.

In Daisen tephras, the weathering of glassy part is varied from site to site. As a whole, halloysitization is extensive and becomes intensive from KaP to Hdp with increase in age. Vermiculite, hydrobiotite, interstratified minerals, and gibbsite are common in the clay fractions of the tephras from DKP to Hdp. The former three minerals are probably the alteration products of biotite phenocrysts (see below). Glasses from the Nj-Sk and Nj-Mt of Niijima have altered to halloysite, while they remain intact in the Nj-My and Nj-Nj, concomitant with vermiculitization. The vermiculite also is considered as the alteration product of biotite phenocrysts.

In short, the degree of weathering of volcanic glasses is varied with local topographic and hydrologic conditions in each volcanic area. Apart from the effects of these factors, the weathering features of glassy materials are summarized as follows: (1) halloysitization begins to be clearly detected by XRD from ~7 ka, as exemplified in the MYP of Hachijo-Higashiyama. This age is consistent with previously reported ones (e.g., Inoue, 1996). (2) The extent of halloysitization generally becomes intensive with the age of tephra; in other words, it is a function of the length of time of weathering and/or the depth of burial. Besides, it depends on the composition and physical properties of original materials. For instance, scorias with basaltic composition exhibit resistivity against halloysitization compared to pumices with dacitic to rhyolitic composition. This is due to the lower porosities in scorias than
Fig. 4. XRD patterns of the clay fractions from some Hachijo-Higashiyama tephras. pl: plagioclase, hal: halloysite.
Fig. 5. SEM photomicrographs of glasses from Hachijo-Higashiyama tephras. (a) OBP, (b) MYP, (c) close-up of (b), (d) MIP, (e) SY9, (f) SY8, (g) SY6, and (h) SY2.
Fig. 6. SEM photomicrographs of pyroxenes from Hachijo-Higashiyama tephras. (a) OBP, (b) MIP, (c) SY2, (d) and (e) pyroxene surface after HBF₄-treatment for 2 hrs, (f) and (g) saw-teeth termination of pyroxene from SY8, (h) saw-teeth termination of pyroxene from SY9, (i) and (j) lens-shaped etch pits on the (100) and (110) of pyroxenes. Photos from (k) to (u) shows evolution of etch pits on pyroxenes. (k) and (l) pyroxenes from SY10, (m) and (n) pyroxenes from SY8, (o)-(s) pyroxenes from SY6, (t) and (u) show the etch-pit coalescence and small pit formation on the bottom of enlarged etch pit in SY6 and SY8.
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those in acidic pumices. (3) Gibbsite begins to appear from ~25 ka, as inferred from the data of the SY and PS tephras at Hachijojima and the KsP at Daisen, excluding that from weathered ashes overlying tephras. The age when gibbsite begins to appear in tephras seems to be later than those in soils developed from volcanic ash in humid and temperate climate zones previously summarized by Wada (1977).

WEATHERING OF SILICATE PHENOCRYSTS

Pyroxenes from Hachijo-Higashiyama

Figure 6 shows SEM photographs of pyroxenes from Higashiyama tephra. As described before, Higashiyama tephra comprise two pyroxenes, i.e., orthopyroxene and clinopyroxene. Despite it, we did not distinguish them accurately in the present SEM observations. Pyroxenes from OBP to HHP are completely covered with glass (Fig. 6a). The remnants of attached glassy materials still remain slightly even on the crystalline faces of pyroxenes from SY2 (Fig. 6c). Since the glassy remnants could not be removed by ultrasonication, they were selectively dissolved by HBF₄ solution. It is assured that etching does not proceed until the glassy covers dissolve and the crystal surfaces contact directly with soil solution.

SEM photographs indicate that lens-shaped etch pits elongated to the c axis develop on the {100} and {110} of pyroxene crystals (Figs. 6i and j). In the early stages of etching, etch pits developed on the {100} seem to be skewed compared to those on the {110}. Etching on the (001) and (111) penetrates preferentially downward along the cleavage lines. The peculiar etching results in characteristic saw-teeth or cockscomb terminations (Figs. 6f, g, and h) because materials between the intersecting cleavage planes remain as isolated pinnacles. These etching features are basically similar to those of weathered pyroxenes in crystalline rocks reported previously (Berner and Schott, 1982; Nahon and Colin, 1982). In highly weathered pyroxene crystals (e.g., SY6), small pits with similar shapes newly develop on the flat bottom of enlarged pits (Fig. 6t), and etch-pit coalescence is common (Fig. 6u).

As seen in Figs. 6k to u, etch pit formation progresses with depth or time. Using the SEM photographs, variations in the size of etch pits developed on the (010), (110), and (100) of pyroxenes from SY10, 9, 8, and 6 were quantified by image analysis. The etch-pit size histograms are shown in Fig. 7, where the size is represented by the equivalent diameter that is defined as diameter of a circle with the same area. The figures reveal that the etch-pit size distribution shifts toward larger with depth from SY10 to SY6. The trend is almost similar in the three crystal faces of pyroxenes.

In highly weathered pyroxenes, some alteration products occupy inside of the pit holes (e.g., Figs. 6p, 6s, and 6u). The alteration products could not be assigned by convenient XRD measurements of separated pyroxenes for SEM observations.

Olivine from Hachijo-Higashiyama

Figure 8 shows SEM photographs of olivines from the SY tephra of Hachijo-Higashiyama. Olivines from SY10 and SY9 tephra, though small in amount, remain unaltered associated with relatively smooth crystal faces. Small pits are observed on the crystal surfaces from SY 8; they show elongated pits along the c axis on the (~110), while shallow flat-
Fig. 8. SEM photomicrographs of olivines from Hachijo-Higashiyama tephras. (a)–(d) olivine having small amounts of etch pits from SY8, and (e)–(j) extensively etched olivines from SY6.
Fig. 9. SEM photomicrographs of plagioclases from Hachijo-Higashiyama tephras. (a) HHP, (b) plagioclase completely covered by glasses from MIP, (c) plagioclase having the glassy remnants from MIP, (d) plagioclase having etch pits in the same grain as (c), (e) plagioclase from the Pumice Layer, (f) SY10, (g) and (h) SY6, (i) and (j) represent quadrilateral and sector-shaped etch pits developed on the (010).
bottomed, rectangular-shaped pits develop on the (021) as shown in Figs. 8a–d. The long side of the rectangular etch pit is nearly parallel to the <010>. Small circular pits develop on the flat bottom of rectangular pits on the (021). Development of etching and surface bulk dissolution is remarkable in olivines from SY6 (Figs. 8e–j). The {010} and {110} display irregularly dissolved surfaces along with polygonal pits (Figs. 8g and h). Polygonal pits are generally large and solitary, and they display a rectangular, pit-bottomed shape associated with bulk dissolution textures around the pit hole (Figs. 8i and j). Although Wegner and Christie (1976) reported the development of rectangular dislocation etch pits elongated parallel to the [001] direction on the (010) of olivines by chemical etching, such crystallographic relations were not clearly observed in the natural etch pits developed on olivine phenocrysts from Hachijo-Higashiyama. Despite minor variations, the observed etching features are basically similar to those in olivines artificially dissolved by some etchants (e.g., Horn and Maurette, 1967; Wegner and Christie, 1976; Awad et al., 2000). The alteration products occupied pit holes could not be assigned by convenient XRD measurements.

**Plagioclase from Hachijo-Higashiyama, Daisen, and Niijima**

SEM photographs of plagioclase phenocrysts from Hachijo-Higashiyama tephras are given in Fig. 9. Plagioclase from the Mitsune stage are covered with glassy materials (Figs. 9a, b, and c), similar to pyroxenes. In the same plagioclase grain, etching has begun on the crystal faces without attached glasses (Fig. 9d). The glassy cover has disappeared completely in plagioclases from SY10. In plagioclase from the Pumice Layer with abundant halloysite in the clay fraction, the crystal surfaces are covered by numerous pits compared to those from the adjacent SY10 (Figs. 9e and f).

The pit morphologies of plagioclase are generally polygonal shaped, as being easily distinguished from circular shaped etch pits developed on the surface of glassy materials. The etch-pit shapes differ from face to face in plagioclase. Although the shape depends on the direction of dislocation line issued on the crystal surface, in general, the pits developed on the (010) tend to show a sector shape (Fig. 9j) and asymmetric quadrilateral shapes dominate on the (110) (Fig. 9i). The long side of quadrilateral on the (010) is parallel to the [110] direction. Suzuki et al. (1996) observed crystallographically controlled arrangement of etch pits on the {100} of labradoritc plagioclase by hydrothermal etching. Such arrangement was not clearly observed in the etch pits on Hachijo-Higashiyama plagioclases, except clustering of etch pits along dislocation line. The characteristics in shape described above are quite similar to those of etch pits on anorthite artificially formed by HCl etching (pH4) at room temperature (Sagara, 2005). Jordan et al. (1999) reported similar sector-shaped etch pits developed on the (001) of anorthite by HCl dissolution at 125°C. The etch-pit morphologies observed in the Hachijo-Higashiyama tephras also are similar to those of etch pits developed on the (010) and (001) of albite and oligoclase using HF-H2SO4 solution (Berner and Holdren, 1979).

Figure 10 shows the size distribution of etch pits developed on different faces of plagioclase from SY9 and SY8 of Hachijo-Higashiyama. Measurable etch pits are few in plagioclases

![Fig. 10. Diameter histograms for etch pits developed on different faces of plagioclases from SY9 and SY8 of Hachijo-Higashiyama tephras.](image-url)
from SY10; in those from SY6 etch pits coalesce densely and display complicated textures (Figs. 9f, g, and h). Thereby it was difficult to measure the size of each pit accurately. In comparison between SY9 and SY8, however, it suggests that the pit size tends to increase with depth, similar to in pyroxenes. It is also seen from the figures that the sizes of etch pits developed on the (20–1) are wholly smaller that those on the other faces.

Similar variations in etching were observed in plagioclases from Daisen and Niijima volcanoes. Etching was more intensive in Daisen plagioclases than those from Hachijo-Higashiyama tephras, and glasses still remained even on some plagioclase grains from the DKP tephra (Sagara, 2005). This was the same case as in Niijima plagioclase.

Plagioclase crystals from three volcanoes, separated for SEM observations, did not contain any weathering products.

**Amphibole from Daisen**

Figure 11 shows SEM photographs of amphiboles from Daisen tephras. Amphiboles from Ksp display smooth faces without etch pits, except the cleavage lines (Figs. 11a and b) and those from DKP, having glassy remnants, do not have any etch pits (Figs. 11c and d). Visible pits were firstly recognized on the surfaces of amphiboles from DSP. The numbers of pits tend to increase with age or depth. The pit morphologies are basically similar to those of pyroxenes from Hachijo-Higashiyama, i.e., lens-like shapes elongated to the c axis (Figs. 11f, h, and i) on the (010) and (110), while saw-teeth textures on the (001) and (011). Coalescence of pits is common. These features also are the same as those of etch pits from crystalline rocks reported previously (e.g., Berner and Schott, 1982; Cremene et al., 1988, 1992; Brantley et al., 1993). Nevertheless, development of the saw-teeth textures on the (001) and (011) is not clear in amphiboles from Daisen compared to prolonged weathered ones reported by Proust et al. (2006). Any weathering products were not identified in amphiboles by conventional XRD measurements.

**Biotite from Daisen and Niijima**

Figure 12 shows SEM photographs of biotites from Niijima and Daisen tephras. Biotites from Niijima tephras display a hexagonal euhedral form without any pits on the (001) and {110} (Fig. 12a). Some gold-colored grains, having crumpled basal surface (Fig. 10b), were discernible under the binocular microscope; they have altered to vermiculite by XRD examination (Fig. 13).

Biotites from Daisen tephras are already bleached and do not show euhedral hexagons and rather corroded edge faces (Figs. 12 c–h). On the (001) face of biotite, there are only a few etch pits developed along to dislocations and cracks (Figs. 12e, g, and h). The basal surface is undulated by closer SEM observation (Fig. 12d). Biotites from Daisen have characteristically frayed edges associated with precipitates between the layers. The frayed, corroded edges are the common weathering features of biotite (e.g., White et al., 1998; Murphy et al., 1998; Wilson, 2004). As seen in Fig. 13, most of biotites from Daisen have altered to vermiculite and/or hydrobiotite together with gibbsite.

**WEATHERING MECHANISMS OF PHENOCRYSTS IN TEPHRAS**

Variations in the size and number of etch pits developed on different crystal faces were quantified by image analysis using pyroxene and plagioclase from SY10 to SY6 of Hachijo-Higashiyama (Figs. 7 and 10). For statistic comparison, the logarithmic etch-pit density (the numbers per unit area) and the calculated mean equivalent diameters are plotted as a function of depth from SY10 in Fig. 14. It is obvious, particularly in pyroxenes, that the etch-pit density decreases with depth from SY10 to SY6. This change can be related to the decrease in etch-pit density on quartz surfaces with depth observed through a soil profile of granitic rock (Brantley et al., 1986). They attributed the observed change in quartz to high silica concentrations in soil waters lower in the profile. Hall and Horn (1993) observed that etching of hornblende in soils of glacial deposits decreases rapidly with increasing soil depth, and that etching was faster where atmospheric precipitation was higher and where soil grains were coarser. In contrast, in pyroxene and plagioclase from tephras, the etch-pit density decreases, while the size increases with depth as shown in Fig. 14. Based on our SEM observations, the surface etching (or weathering) of silicate phenocrysts in tephras can be interpreted as follows: after mineral surfaces contacted with soil solutions, etching begins to occur at reactive sites of line dislocations appeared on the crystal faces. An etch pit enlarges and coalesces with the neighbors into larger one with progress in dissolution. With increasing duration of etching (or weathering), mineral dissolution occurs at dislocation core points and along steps, and at the same time small pits newly develop on the bottom of enlarged pits. This style of etching may be established in intermediate saturation conditions of soil solutions infiltrated through tephra column, following Lasaga and Lüttge (2001, 2003), Teng (2004), and Dove et al. (2005). As mentioned previously, halloysitization of glassy materials precedes etch-pit formation on the crystal surfaces of phenocrysts. The preceding glass alteration supplies materials to pore solutions so as to increase the saturation level. Consequently, although the dissolution of phenocrysts in tephras occurs in far-from-equilibrium conditions at the incipient stage of weathering, the undersaturation level in pore waters decreases immediately due to rapid dissolution of glassy materials, and at a steady state the dissolution of mineral surfaces proceeds by both dislocation etch pit dissolution and step wave dissolution. Although our data on sequentially etched crystals is too limited to warrant the calculation of rates, the decrease in dissolution rates occurs more distinctly through tephra chronosequence due to the continual dissolution of glassy materials, compared to those observed previously (Brantley et al., 1986, 1993; Hall and Horn, 1993; White and Brantley, 2003).

**SUMMARY AND CONCLUSIONS**

Chronosequential evolution of dislocation etch pits on the crystal faces of pyroxenes, olivine, plagioclases, amphibole, and biotite has been examined under SEM, using tephras from Hachijo-Higashiyama, Daisen, and Niijima volcanoes. The
Weathering mechanism of silicate phenocrysts in tephra, inferred from SEM observations of surface etching

Fig. 11. SEM photomicrographs of amphiboles from Daisen tephra. (a) and (b) KsP, (c) and (d) DKP, (e) and (f) DSP, (g) and (h) DNP, (i) lens-like etch pits associated with alteration products from DSP, and (j) (001) or (011) face of amphibole having saw-teeth etch textures from DNP.
FIG. 12. EM photomicrographs of biotites from Niijima and Daisen tephras. (a) euhedral shaped biotite without any pits from Niijima (Nj-Sk), (b) crumpled basal face of biotite from Niijima (Nj-Sk), (c) and (d) biotite from Daisen (HgP), (e) and (f) biotite from Daisen (DSP), (g) and (h) biotite from Daisen (DNP), (i) and (j) biotite from Daisen (HdP).
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Fig. 13. XRD patterns of weathered biotites from Niijima and Daisen tephras. pl: plagioclase, gb: gibbsite.
following results and conclusions were obtained:
(1) In Hachijo-Higashiyama tephras, halloysitization of glassy materials was recognized by XRD from tephras of ~7 ka. Etching of phenocrysts did not occur before dissolving the glassy cover, and therefore it was always preceded by the halloysitization of glass in tephras.
(2) In early stages of etching in silicate minerals other than biotite, it occurs at dislocations and makes crystallographically controlled etch pits characteristic on each face of minerals. The size of etch pits increases with increase in depth or age of tephra, while the etch-pit density (the number of etch pits per unit area) tends to decrease. This change was clearly observed for pyroxenes (and probably for plagioclase) from Hachijo-Higashiyama tephras. The characteristic etching features resulted from the both dissolution at dislocations and along steps at prolonged weathering stages. The etching style is related to that occurred at intermediate undersaturation levels in porewaters. In other words, the dissolution rates of minerals in tephra column is strongly controlled by the changes in saturation levels of porewaters, intrinsically depending on rapid dissolution of associated glassy materials, particularly with higher porosities, although our data on sequentially etched crystals is too limited to warrant the calculation of rates.
(3) Biotite has altered to vermiculite, hydrobiotite, and/or interstratified minerals associated with gibbsite. This alteration occurred topotactically as suggested by the SEM observations. On the other hand, other silicates contained small amounts of unidentified alteration products in enlarged pit holes. From the viewpoints of alteration products, biotite is the lowest mineral in terms of the resistivity for chemical weathering because it alters easily to vermiculite due to oxidation and leaching of constituent elements, as pointed out by previous works (e.g., Wilson, 2004).

Fig. 14. Plots of logarithmic etch-pit density (the numbers per unit area) and mean diameter as a function depth from SY10 for pyroxenes (a) and (b), for plagioclases (c) and (d), respectively.
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