

Rates and mechanism of weathering-rind development on andesite gravel in fluvial terrace deposits

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4. Discussion

4.1. Relationship between rock property and weathering time

Relationships between rock properties and weathering time are firstly examined. Quantitative parameters of rock properties applied to more than 20 rock samples were used for the purpose. They are: (1) the apparent thickness of weathering rinds (Table 2), (2) chemistry and the weathering indices calculated from the XRF data (Table 4, 5 and 10), (3) physical properties determined from the PSD measurements (Table 7 and 8) and (4) mechanical properties determined from VHN measurements (Table 9).

4.1.1. Growth of the weathering-rind thickness with time

Figure 39 shows the relationships between time and apparent thickness of the weathering rinds corresponding to the brown layers (Table 2). The red circles show average values and the red bars show the range of one standard deviation. The trend of change in the average values is represented in a red broken line.

The thickness values for the 320-ka and 450-ka rocks tend to be variable: the ranges of the values for 320-ka and 450-ka rocks are *ca.* 1.0-5.3 mm and *ca.* 2.0-5.3 mm, respectively. Despite of such variations among 320-ka and 450-ka rocks, the average thickness of the weathering rinds gradually increases with increasing time. The growth rate gradually decreases with increasing weathering time.

The three black bars represent the ranges of weathering-rind thickness for andesite moraine gravels in western North America (Colman and Pierce, 1981). The data concern weathering-rind thickness through weathering periods less than 300 ka BP. The growth rate of the weathering rinds in North America is smaller than that of the rocks examined in the present study. This suggests that andesite gravels in terrace deposits in Japan have undergone more rapid

weathering under a warmer and more humid environment than in western North America.

4.1.2. Changes in chemical properties with weathering time

Figure 40 shows the relationship between chemical composition in weight percent (Table 6) and weathering time. The raw data for the inner parts and the brown layers are represented in small symbols with light green and orange colours, respectively. The raw data for the white layer are shown by yellow symbols. The average values for the inner parts and the brown layers are represented by large symbols with dark green and red colours, respectively, and the trend of change in the average values are represented by broken lines.

Despite of some scatters of the raw data, changing trends based on the average values of most elements in the inner parts have no variation over 830,000 years. This indicates that chemical compositions of the inner parts have unchanged through the long-term weathering periods. On the other hand, the chemical compositions for the brown layers have changed with weathering time. Three changing patterns are identified as follows. (1) Decrease with time: MnO, MgO, CaO, Na₂O and Sr belong to this type. The decrease is slightly faster in the early stage of weathering (0-320,000 years) than in the late stage (320,000-830,000 years). (2) Increase with time: TiO₂, FeO+Fe₂O₃, Ba, Ga, Nb, V, Zr and ignition loss belong to this type. The increase in the early stage of weathering is fast but that in the late stage is less distinct. (3) No distinct change with time: SiO₂, Al₂O₃, K₂O, P₂O₅, Cu, Mo, Ni, Rb, Pb, Th, U and Y belong to this type. Generally, the contents of Al₂O₃ in weight percent increase with weathering, because Al₂O₃ is an immobile element in most environments. However, such a trend cannot be observed in the present study (Fig. 40), indicating that weathering environment in the study area has been under acid condition. This may have resulted from the influence of Nasu volcano and Takahara volcano.

Figure 41 shows the relationship between weathering time and the

weight per unit volume for each elements (Table 6). The raw data for the inner parts and the brown layers are represented in small symbols with blue and orange colours, respectively. The raw data for the white layer are shown by yellow symbols. The average values for the inner parts and the brown layers are represented by large symbols with purple and red colours, respectively, and their changing trends are represented by broken lines.

The raw values of weight per unit volume for the same age rocks vary depending on samples, which agrees with the chemical composition data. The average weights of most elements in the inner parts tend to be unchanged over 830,000 years. On the other hand, the average weights for the brown layers have changed with weathering time. Three changing patterns are identified as follows. (1) Decrease with time: Most elements (SiO_2 , Al_2O_3 , TiO_2 , $\text{FeO}+\text{Fe}_2\text{O}_3$, MgO , CaO , Na_2O , K_2O , P_2O_5 , Ga, Mo, Nb, Rb, Sr, U and Y) belong to this type. The decrease in their weights during the early stage of weathering is fast but that during the late stage is null or very slow. Although TiO_2 , $\text{FeO}+\text{Fe}_2\text{O}_3$ as well as Al_2O_3 are known as immobile elements, their contents decreased, suggesting that weathering environment in the study area has been under intense acid condition. (2) Increase with time: only ignition loss belongs to this type. The increase in the weight is faster in the early stage of weathering than in the late stage. The increase of ignition loss corresponds to the formation of clay minerals. (3) No distinct change with time: MnO, Ba, Cu, Ni, Pb, Th, V and Zr belong to this type.

From these findings, it can be said that the brown layers are characterized by depletion of most elements. They differ from the zones with strong accumulation of Fe_2O_3 and/or Al_2O_3 often observed in laterite profiles. Although it is difficult to estimate the precise contents of each FeO and Fe_2O_3 , it can be considered that the brown layers have less abundant $\text{FeO}+\text{Fe}_2\text{O}_3$ but more abundant Fe_2O_3 than the inner parts. In other words, a part of the dissolved FeO was oxidized to be Fe_2O_3 , resulting in brown colour at the brown layer.

Table 10 shows five weathering indices calculated from the XRF data: $\text{SiO}_2/\text{Al}_2\text{O}_3$ (Harrassowitz, 1926), $\text{SiO}_2/\text{TiO}_2$ (Ichikuni, 1972), CIA (Chemical Index of Alteration defined as $100 \times \text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$); Nesbitt and Young, 1982), WPI (Weathering Potential Index defined as $100 \times [\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO} - (\text{Ignition loss})] / (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3)$); Reiche, 1943) and PI (Product Index defined as $100 \times \text{SiO}_2 / (\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3)$); Reiche, 1943). $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{TiO}_2$ are the convenient indices to represent the degree of the leaching of SiO_2 , which were widely used in previous studies on chemical weathering. CIA represents the leaching degree of alkali/alkaline earth metals. WPI shows the changes in the contents of major elements including ignition loss, and PI indicates the amount of the formation of clay minerals.

Figure 42 shows these indices versus weathering time. The raw data for the inner parts and the brown layers are represented in small symbols with blue and orange colours, respectively. The raw data for the white layer are shown by yellow symbols. The average values for the inner parts and the brown layers are represented by large symbols with dark blue and red, respectively, and changing trends of the average values are represented by broken lines.

The values of $\text{SiO}_2/\text{Al}_2\text{O}_3$ for the brown layers are similar to those for the inner parts (Fig. 41a). This fact means that Al_2O_3 has been dissolved along with SiO_2 . The values of $\text{SiO}_2/\text{TiO}_2$ for the brown layers tend to be smaller than those for the inner parts (Fig. 42b). The relatively high $\text{SiO}_2/\text{TiO}_2$ value for the brown layer of the 830-ka rock agrees with the presence of Si-concentrated grains near the rock surface, which was detected on the element-concentration map of the EPMA analysis (Fig. 31). $\text{SiO}_2/\text{TiO}_2$ more adequately represents the degree of SiO_2 -dissolution due to weathering than $\text{SiO}_2/\text{Al}_2\text{O}_3$, because Al_2O_3 contents are more influenced by weathering environments than TiO_2 contents at least for a long-term weathering period. The values of CIA for the brown layers increase with increasing weathering

time, whereas those for the inner parts tend to be unchanged (Fig. 42c). This indicates that alkali/alkaline earth metals have been depleted even after the formation of the brown layers.

The values of WPI for the brown layers decrease with time, whereas those for the inner parts unchanged (Fig. 42d). The difference between the brown layers and the inner parts is the largest of all the weathering indices examined in this section, indicating that the brown layers have been weathered intensely. The decrease for the brown layers is fast in the early stage of weathering (0-320,000 years), but that in the late stage (320,000-830,000 years) is less distinct. The PI values for the brown layers tend to be smaller than those for the inner parts (Fig. 42e). The PI values have less difference between the inner parts and the brown layers than the WPI values. This indicates that clay minerals formed in the brown layers are limited in amount, although the brown layers have undergone intense weathering during the long weathering period. Acidic environment caused by the presence of volcanoes probably prevented the formation of clay minerals.

4.1.3. Changes in physical properties with weathering time

Figure 43 shows the relationships between weathering time and pore volumes (V_{α} , V_{β} , V_{γ} , V_{δ} and V_t), $(V_{\alpha}+V_{\beta})/V_t$ and $(V_{\gamma}+V_{\delta})/V_t$. The changes in bulk density and porosity with weathering time are shown in Fig. 44. In these three figures, the raw data for the inner parts are represented by small solid rhombuses of dark blue, those for the white layer are shown by yellow triangles, and those for the brown layers are represented by small solid circles of red colour. The average values for the inner parts and the brown layers are represented by large open rhombuses and circles with red and green, respectively. Their changing trends for the inner parts and the brown layers are represented by red and green broken lines, respectively.

The values of V_{α} , V_{β} , V_{γ} and V_{δ} for the inner parts are notably small and nearly constant over 830 ka (Fig. 43a to 43d). The four values for the

white layer are also small. The four values for the brown layers are much larger than that for the inner parts and they are nearly constant between 320 ka and 830 ka. These facts suggest that the brown layers have been formed with changes in rock structure such as the separation of adjacent micro-phenocrysts in groundmass, resulting in drastic increase in pore volume. The increase in pore volume after the brown-layer formation is much less distinct. The V_t -values for the inner parts are notably small and nearly constant over 830 ka, whereas those for the brown layers are much larger than that for the inner parts and they are nearly constant between 320-ka and 830-ka rocks (Fig. 43e). Figure 43f shows that the values of $(V_\alpha+V_\beta)/V_t$ for the brown layers increase with time. In contrast, the values of $(V_\gamma+V_\delta)/V_t$ for the brown layers decrease with time (Fig. 43g). These facts indicate that the ratio of large pore volume to that of total pore volume increases with time.

The above changes in pore volumes with time for the brown layers agree with the changes in bulk density and porosity (Fig. 44). The bulk density for the brown layers tends to decrease with time but the decrease is much less significant between 320-ka and 830-ka (Fig. 44a). The average value of bulk density for the brown layers of 320-ka, 450-ka and 830-ka rocks is *ca.* 1.3 g/cm³. On the other hand, porosity for the brown layers increases with increasing time and their changes are small between 320-ka and 830-ka (Fig. 44b). The average porosity for the brown layers of 320-ka, 450-ka and 830-ka rocks is *ca.* 37 %.

Both the values of bulk density and porosity for the brown layers (*i.e.*, *ca.* 1.3 g/cm³ and *ca.* 37 %, respectively) are almost the same as those of highly weathered materials: *e.g.*, sandy grus (>1.5 g/cm³ and >40 %, Suzuki *et al.*, 1977; Matsukura *et al.*, 1983), weathered porous rhyolite (*ca.* 1.6 g/cm³ and *ca.* 37 %, Oguchi *et al.*, 1994). Generally, the highly weathered materials have little possibility for further weathering. Thus, andesite gravel examined in this study quickly formed the brown layers with high porosity and low density in the early stage of weathering, and the subsequent changes in the

physical properties are less distinct.

4.1.4. Changes in mechanical properties with weathering time

Figure 45 shows the relationships between weathering time and the rock hardness in terms of the average VHN values (Table 9). The raw data for the inner parts are represented by solid rhombuses of dark blue, and the brown layers are represented by solid circles with red colour. The average values for the inner parts and the brown layers are represented by red open rhombuses and green circles, respectively. The patterns of their changes for the inner parts and the brown layers are represented by broken lines.

Despite of different weathering time, the hardness of the inner part of the rock is nearly constant around $500 \text{ gf}/\mu\text{m}^2$. In contrast, the hardness of the brown layer for 320-ka, 450-ka and 830-ka rocks is less than $100 \text{ gf}/\mu\text{m}^2$. Figure 45 indicates that rock strength rapidly reduces during the early stage of weathering, whereas the reduction after 300 ka is much less distinct. This finding agrees with the decreasing pattern of compressive and tensile strengths of weathered porous rhyolite investigated by Oguchi *et al.* (1994).

4.1.5. Changing rates of rock properties

Using the above results, the changing rates of different rock properties with weathering were compared. The changing rates were represented by the ratio of $P_{\text{each}}/P_{0\text{-ka}}$, where P_{each} is the value of a rock property for each rock and $P_{0\text{-ka}}$ is that for 0-ka rock, assuming that 0-ka rock is completely non-weathered. Rock properties that decrease with weathering time were used for the calculation of the ratio. Chemical properties were represented by 'chemical index of alteration (CIA)' because it shows leaching of alkali/alkaline earth metals with distinct deference between the inner parts and the brown layers. Physical properties were represented by bulk density.

Figure 46 shows the relationships between weathering time and average values of the calculated ratios for the samples from each geomorphic surface.

VHN-ratio decreases most rapidly with weathering time than other properties: VHN-ratio changes by 70-90 % in 830,000 years. CIA-ratio decreases most slowly: CIA-ratio changes by *ca.* 30 % in 830,000 years. The ratio of the values for bulk density decreases *ca.* 40 % in 830,000 years. These evidences show that mechanical properties change most rapidly than other properties and chemical properties change most slowly. This result agrees with the weathering of porous rhyolite investigated by Oguchi *et al.* (1994).

The changes in chemical properties for the porous rhyolite decreased by 20-30 % during 40,000 years (Oguchi *et al.*, 1994). In contrast, the decrease for andesite examined in this study is by 30 % during 830,000 years. These differences indicate that the weathering rate for andesite is much lower than that for porous rhyolite. New pores with wedged shapes have been acceleratively formed in porous rhyolite (Oguchi and Matsukura, 1996). On the other hand, microscopic observations indicate that large pores in the brown layers rounded and pore surfaces are covered with thin coatings of clay and ferric-hydroxide minerals (Fig. 47), because of the rapid alteration and subsequent dissolution of pyroxene microphenocryst. The coatings by clay and ferric-hydroxide minerals are less abundant in porous rhyolite because of less opaque minerals. For these reasons, chemical elements can be dissolved more rapidly from porous rhyolite than andesite during water-rock interaction.

4.2. Changes in rock properties with depth from the rock surface

Detailed changes in rock properties with depth from the rock surface are examined. Colours (L*-, a*- and b*-values), chemistry determined from the ICP analyses, and Vickers microhardness were used for the purpose, because the depth of measurement points is only available for these parameters. The results for the samples 20-B2, 20-B6, 450-B1 and 450-B64 were obtained.

Figure 48a shows the values of the parameters versus the depth from rock

surface for the sample 20-B2 which has both the white and brown layers with a thickness of *ca.* 1 mm and less than 0.1 mm, respectively. Between 5-mm and 10-mm depth, most elements have constant contents. Between 1- and 5-mm depth, the contents of Al_2O_3 , $\text{FeO}+\text{Fe}_2\text{O}_3$, CaO , MgO , MnO and P_2O_5 increase with decreasing depth, whereas those of Na_2O , K_2O , TiO_2 , Zr , Sr , Zn and V decrease with decreasing depth. At the same part, the values of L^* , a^* and b^* tend to be constant. The VHN values are constant at more than 1.5-mm depth. At the white layer between 0.2- and 1.0-mm depth, the contents of Al_2O_3 , $\text{FeO}+\text{Fe}_2\text{O}_3$, CaO , MgO , MnO and P_2O_5 decrease with decreasing depth, whereas those of Na_2O , K_2O , TiO_2 , Zr , Sr , Zn and V increase with decreasing depth. At the outermost part less than 0.2-mm depth corresponding to the brown layer, the contents of $\text{FeO}+\text{Fe}_2\text{O}_3$ increase with decreasing depth. Between 0- and 1.0-mm depth, L^* - and b^* -values increase with decreasing depth, but a^* -value tends to decrease. At the same part, the VHN values decrease with decreasing depth.

Figure 48b shows the values of the parameters versus the depth from rock surface for the sample 20-B6 that has only a thin brown layer with *ca.* 1.0-mm thickness. Between 6- and 10-mm depth, the contents of $\text{FeO}+\text{Fe}_2\text{O}_3$, TiO_2 and V slightly increase with decreasing depth, whereas those of Sr slightly decrease with decreasing depth. Between 2- and 6-mm depth, the contents of Cu and Zn increase with decreasing depth, whereas those of CaO , K_2O and Sr decrease with decreasing depth. Between 2- and 5-mm depth, L^* -values decrease with decreasing depth, whereas a^* - and b^* -values tend to be constant. The contents of Cu and Zn increase with decreasing depth, whereas those of CaO , K_2O and Sr decrease with decreasing depth. The VHN values tend to be constant at more than 3-mm depth but decrease with decreasing depth at less than 3-mm depth. Within less than 2-mm depth, the contents of $\text{FeO}+\text{Fe}_2\text{O}_3$, TiO_2 , K_2O , V and Zr increase with decreasing depth, whereas those of Al_2O_3 , CaO , Na_2O , and Sr decrease with decreasing depth. At the same part, the values of L^* and b^* increase with decreasing depth, whereas

a*-values tend to decrease with decreasing depth.

Figure 48c shows the changes in the values of the parameters with depth for the sample 450-B1 with a *ca.* 3-mm brown layer but no white layers. Between 6- and 15-mm depth, the contents of most elements tend to be constant, but Cu and Zn increase with decreasing depth. Between 2.5- and 6-mm depth, the contents of most elements tend to be constant, but Cu and Zn decrease with decreasing depth. All the values of L*, a*, b* and VHN are constant at more than 3-mm depth. At the brown layer (the part less than 2.5-mm depth), the contents of FeO+Fe₂O₃, TiO₂, K₂O, Ba, V and Zr increase with decreasing depth, whereas those of Al₂O₃, CaO, Na₂O and Sr decrease with decreasing depth. At the same part, the values of L*, a*, b* tend to be large, and VHN values are extremely small, *i.e.*, less than 100 gf/μm².

Figure 48d shows the changes in the values of the parameters with depth for the sample 450-B64 with brown and white layers between *ca.* 0-4 mm and *ca.* 4-10 mm depth, respectively. Between 11- and 22-mm depth, the contents of Sr decrease with decreasing depth. Between 10- and 15-mm, L*-values increase with decreasing depth, whereas a*- and b*-values tend to be constant. At the same part, VHN-values slightly decrease with decreasing depth. Between 7- and 11-mm depth, the contents of FeO+Fe₂O₃, TiO₂, Cu and V increase with decreasing depth. Between 4- and 7-mm depth, the contents of FeO+Fe₂O₃, TiO₂, Co, Zr and Zn increase with decreasing depth, whereas those of Al₂O₃, CaO, Na₂O and Sr decrease with decreasing depth. Between 3.5- and 10-mm depth, L*-values increase with decreasing depth, but a*- and b*-values are nearly constant. At the same part, the VHN values decrease with decreasing depth. Within less than 4-mm depth, the contents of FeO+Fe₂O₃, TiO₂, V and Zr increase with decreasing depth, whereas those of CaO, Na₂O MgO, K₂O and Sr decrease with decreasing depth. The values of L*, a* and b* at the same part are higher than those at the inner part. VHN values are less than 100 gf/μm² between 0- and 4-mm depth.

From the above evidence, the rock properties of the brown layers, white

layers, and the inner parts can be summarized as follows (Fig. 49):

Brown layer: The layer can be observed in all the samples of 320-ka, 450-ka and 830-ka rocks. It has small contents of Sr and alkali/alkaline earth metals, large contents of FeO+Fe₂O₃, TiO₂, Mn, V and Zr, low VHN values, and large L^{*}-, a^{*}- and b-values. The layer corresponds to Zone I of the VHN measurement.

White layer: The layer can be observed between the brown layers and the inner parts of some 320-ka and 450-ka rocks. The contents of Sr, alkali/alkaline earth metals, FeO+Fe₂O₃, TiO₂, Mn, V and Zr as well as L^{*}- and VHN-values tend to remain constant at moderate values. The values of these parameters, however, change rapidly at the boundary with the brown layer. The layer corresponds to the outer part of Zone II of the VHN measurement.

Inner part: The part corresponds to the Zones II and III determined by the VHN measurement. Some rock samples with high porosity lack Zone III. In Zone II, the contents of Sr and alkali/alkaline earth metals as well as VHN values increase with increasing depth. In contrast, the contents of FeO+Fe₂O₃, TiO₂, Mn, V and Zr as well as L^{*}-values decrease with increasing depth. Zone III tends to have large and constant contents of Sr and alkali/alkaline earth metals as well as large VHN values. It also has small contents of FeO+Fe₂O₃, TiO₂, Mn, V and Zr as well as small L^{*}-, a^{*}- and b^{*}-values.

4.3. Definition of weathering rinds

4.3.1. Problems with definition in the previous studies on weathering rinds

The original definition of the weathering rind is 'an outer crust or layer on a rock fragment formed by weathering' (Gary, *et al.*, 1972) or 'a hard and thin weathered layer with Si, Fe or Mn enrichment at surfaces of rock blocks' (Maruyama, 1981). In recent years the definition of the term "weathering rind"

includes the formative process of oxidation with colour alteration: 'oxidation phenomena which stain the parent rock red-yellow when exposed to air or near-surface groundwater for some time' (Anderson and Anderson, 1981; Goudie *et al.*, 1985). Caine (1983) also called the weathering rinds as 'oxidation-hydration rinds'. However, the term "weathering rind" has been used more frequently to represent a coloured weathered zone near the rock surface identified not by chemical analyses but by eye observations (*e.g.*, Chinn, 1981; Watanabe, 1990; Aoki, 1994). As noted before, the identification of such coloured weathering rinds is often difficult because some rocks have more than one-coloured zones near the surface. Andesite rocks investigated in the present study also have both the brown and white layers. Moreover, weathered zone does not always correspond to the zone with altered colours. Therefore, it is necessary to re-define "weathering rind" based on weathering processes discussed in the following section rather than rock colours.

4.3.2. Two zones of weathering rinds determined from weathering processes

Based on the measurements of rock properties in the present study, weathering rinds with two zones can be defined:

Zone A – This zone corresponds to the brown layer, which is characterized by large Fe contents and high a^* - and b^* -values. This zone experienced both oxidization and dissolution. The oxidation of Fe accounted for the brown colour. Ignition loss inferred from the XRF analysis is notably large within this zone, indicating the effects of hydration or hydrolysis. This zone also corresponds to Zone I determined by the VHN measurement.

Zone B – This zone corresponds to Zone II identified from the VHN measurement. It is characterized by dissolution of alkali/alkaline earth metals. The dissolution is more distinct in the white layer than in the inner part of Zone II. The inner border of this zone is located at the place where the amounts of Ca and Sr as well as VHN values start decreasing with decreasing depth.

4.4. Mechanisms and rates of weathering-rind development

4.4.1. Growth mechanism of weathering rinds

Zones A and B have some common characteristics with Chigira's (1990, 1991) oxidized and dissolved zones. The latter two zones were identified for a large-scale weathering profile of sedimentary rocks in mountains under humid temperate climate. Chigira (1990, 1991) emphasized that the dissolved zone occurs below the oxidized zone. Their development is explained by pyrite oxidation by carbonic acid supplied from percolated water, and subsequent dissolution of other minerals caused by sulfuric acid generated from pyrite decomposition. This model assumes one-way downward water flux through the weathering profile.

Zones A and B in this study, however, differ from Chigira's (1990, 1991) oxidized and dissolved zones in that the upper zone (Zone A) underwent not only oxidation but also dissolution, and the formation of Zones A and B needs two-way water flux. In each rock particle of fluvial-terrace deposits, weathering rinds occur in parallel to the rock surface with nearly constant thickness. Thus, the mechanism of weathering-rind formation is related to smaller-scale water flux in and around the rock particles, which is different from the large-scale flux assumed by Chigira (1990, 1991). Gravel in terrace deposits is attacked by underground water percolated into sediments. When rainfall is abundant, subsurface water table rises and the water is supplied toward rock particles. In this case, water flux is directed from outside to inside of a rock. In contrast, during the period of less rainfall, water supply from outside stops, and water flux from inside to outside of a rock can be expected.

These different directions of water flux are responsible for the growth of the two sub-zones of a weathering rind. Based on the results of the mineralogical and chemical properties, a model to explain the mechanism of

the development of *dissolution zone* (whose thickness corresponds to Zones A+B) and *oxidation zone* (whose thickness corresponds to Zone A alone) was constructed as shown in Fig. 50. The growth of the *dissolution zone* is explained as follows: (1) When water is supplied into matrix around a rock particle, water flux toward the inside of the particle takes place; (2) Alkali/alkaline earth metals are dissolved from the rock into percolated water; (3) A decoloured zone with depleted elements is formed near the rock surface; (4) The zone thickens as the front of dissolution moves into the inside of the rock.

The growth of oxidation zone is explained as: (1) When the subsurface water table is low, water flux toward the outside of a rock takes place; (2) Although most dissolved metals move out of the rock with water, Fe^{3+} is precipitated near the rock surface because Fe^{2+} is oxidized to form Fe^{3+} with low solubility in natural water (Ichikuni, 1972, p.75); (3) The outermost zone turns to be brown due to accumulation of ferric oxide/hydroxide minerals and compounds such as Fe_2O_3 (e.g., hematite and maghemite), $\text{FeO}(\text{OH})$ (e.g., goethite and lepidochrocite) and $\text{Fe}(\text{OH})_3$.

4.4.2. Growth rates of weathering rinds

The growth rates of *weathering rinds* are discussed in this section. The former discussion revealed that weathering rinds consist of two zones: the upper zone (Zone A) formed by the combination of oxidation and dissolution, and the lower zone (Zone B) formed by dissolution alone. *Weathering rinds* can be classified into Zone A and Zone A+B in terms of weathering processes, because the thicknesses of Zone A and Zone A+B are equal to those of the zones subjected to oxidation and dissolution, respectively. Although Zones A and B were originally defined based on chemical properties, chemical data sufficient to identify these zones are available for only some selected samples. As noted before, these two zones correspond well to rock-hardness zones determined by VHN measurements. The rock-hardness data are available for

all the samples. The thickness of Zones A and B were, therefore, determined using the VHN data. Zone A occurs between the rock surface and the inner limit of low VHN values (Fig. 51a). Zone B occurs between the inner limit of Zone A and the point where VHN values start decreasing toward the surface of the rock (Fig. 51b).

Both the thicknesses of Zone A+B (L_{A+B}) and that of Zone A (L_A) are used to construct a growth model of weathering rinds for the 0-ka, 20-ka, 320-ka 450-ka and 830-ka rocks. The values of these two thicknesses are listed in Table 11. The relationships between these thicknesses and weathering period are shown in Fig. 52.

In general, the thickness of a weathered zone has often been approximated using a diffusion equation (*e.g.*, Friedman and Long, 1976).

$$L = (D \cdot t)^{1/2} = D^{1/2} \cdot t^{1/2} \quad \dots\dots\dots(5.1)$$

where L is the thickness of weathered zone, D is a diffusion coefficient, and t is weathering periods. This equation was fitted to the data obtained in the present study. The equation for Zone A has a good correlation ($r=0.9288$; Fig. 53a):

$$L_A = 0.1348 \cdot t^{1/2} = (0.0182 \cdot t)^{1/2} \quad \dots\dots\dots(5.2)$$

The equation for Zone A+B, however, has a low correlation ($r=0.4537$; Fig. 53b). These results suggest that not only time but also other factors are responsible for determining the thickness of Zone A+B.

Drever (1997, p.357) have stated that an effective diffusion coefficient (D_{eff}) is related to rock porosity (n):

$$D_{eff} = D / n \quad \dots\dots\dots(5.3)$$

Combining equations (5.3) and (5.1), the following equation is obtained:

$$L = (D_{\text{eff}} \cdot n \cdot t)^{1/2} = D_{\text{eff}}^{1/2} \cdot (n \cdot t)^{1/2} \quad \dots\dots\dots(5.4)$$

In order to examine whether the equation (5.4) holds true for the data of the present study, the relationship between L and $(n \cdot t)^{1/2}$ was examined (Fig. 54). The correlation for Zone A+B has significantly improved ($r=0.8609$; Fig. 54b):

$$L_{\text{A+B}} = 0.2571 (n \cdot t)^{1/2} = (6.61 \times 10^{-2} \cdot n \cdot t)^{1/2} \quad \dots\dots\dots(5.5)$$

The correlation for Zone A, however, became lower than that of the equation (5.2). The improved correlation for Zone A+B probably reflects the variability of diffusion processes operated during dissolution. The influence of porosity on dissolution is more distinct because porosity directly controls the depth of water penetration into a rock. Therefore, the equation (5.1) is adequate to express the growth rate of the thickness of Zone A, and equation (5.4) is useful for the growth rate of the thickness of Zone A+B.

In Figure 55, the equation (5.4) is shown by brown curve, and the equation (5.5) with different rock porosity (n) is shown by the curves with dark colours. The curves for $L_{\text{A+B}}$ indicate that the thicknesses of Zone A and Zone A+B is almost the same when $n < 0.3$. In other words, the thickness of Zone B alone is nearly null if the rock is very dense.