3. Analyses and the Results

Five kinds of properties of the rock samples for each geomorphic surface were examined: (1) mineralogical properties, (2) colours, (3) chemical properties, (4) physical properties, and (5) mechanical properties. Optical observations using a polarizing microscope and X-ray diffraction analysis (XRD) were performed to identify the minerals. *Colours* were quantitatively measured using visible microspectrometer. Major and trace elements were investigated by X-ray fluorescence analysis (XRF), electron-probe microanalysis (EPMA) and inductively coupled plasma analysis (ICP). Physical properties such as bulk density, porosity and pore-size distribution were measured using mercury intrusion porosimetry. Mechanical properties were examined using Vickers microhardness tester.

3.1. Rock texture and mineralogical properties

3.1.1. Naked-eye observation of cut rocks

Cut rock observations by naked eyes have shown that rock samples from each geomorphic surface have the following characteristics. 0-ka rocks are not visibly weathered (Fig. 10). They have white phenocrysts of feldspar and black phenocrysts of pyroxene surrounded by the groundmass with gray colour, although the amounts of phenocrysts vary among on samples. The sample 0-B1 is very dense and has glassy groundmass (Fig. 10c). No samples have weathered layers with altered colour all through the rock surfaces to the inner parts.

20-ka rocks also have the phenocrysts of feldspar and pyroxene surrounded by the gray groundmass (Fig. 11). The sample 20-B2 has glassy groundmass (Fig. 11c), whereas the other samples do not have it. All the 20-ka rocks are slightly weathered: their surfaces have altered layers with brown or

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white colour with an average thickness of *ca.* 0.7 mm. The sample 20-B2 has a whitish gray zone (*white layer*) with a thickness of *ca.* 1 mm (Fig. 11c). This sample also has a very thin brownish coloured layer (less than 0.1-mm thickness) on the surface, which can be recognized not by cut-rock observation but by thawing the surface with an awl.

The inner parts of the 320-ka rocks also have the same texture as 0-ka and 20-ka rocks (Fig. 12). The samples 320-B5 and 320-B20 have abundant vesicles in the inner parts (Figs. 12a and 12c, respectively). All 320-ka rocks have brown weathering rinds (*brown layers*) on the surface with a thickness of 2-4 mm. The rinds have more abundant pores than the inner parts.

The inner parts of the 450-ka rocks also have the same texture as 0-ka, 20-ka and 320-ka rocks (Fig. 13). The sample 450-B1 is very dense and has glassy groundmass (Fig. 13a). The sample 450-B39 has abundant vesicles in the inner parts (Figs. 13d). All 450-ka rocks have brown layers with a thickness of 3-5 mm on the surfaces. They have pores more abundant than the inner parts. The sample 450-B64 has a whitish-gray zone (white layer) between the weathering rind and the inner part of the rocks (Fig. 13e).

The 830-ka rock is pyroxene andesite (Fig. 14). The rock has a brown weathering rind with a thickness of *ca.* 6 mm. The inner part of the rock is quite hard, whereas the weathering rind is brittle. The rinds also have pores more abundant than the inner parts.

3.1.2. *Optical microscope observation*

Optical microscopic photographs of thin sections were taken for rock samples cut perpendicularly to their surfaces (Figs. 15 to 19). The inner parts of almost all rocks have a porphyritic texture with phenocrysts of plagioclase and pyroxene and the groundmass of the same minerals and magnetite (*e.g.*, Figs. 15b and 19). Some samples have glassy groundmass that looks black in microphotographs (*e.g.*, Fig. 15a, 16a, 18a).

The sample 0-B1 (Fig. 15a) is composed of abundant glassy groundmass.

All the 0-ka rocks have fresh textures through rock surface to the inner parts (Fig. 15). No brown weathered layers can be observed. The 20-ka rocks have no marked weathered layers (Fig. 16), although these samples have very thin layers of alteration that can be observed by naked eyes. The sample 20-B2, for example, has abundant glassy groundmass but no phenocrysts (Fig. 16a). The sample 20-B6 has plentiful phenocrysts of feldspar and pyroxene with a maximum size of 0.5 mm.

The 320-ka, 450-ka and 830-ka rock samples have both outermost weathered layers and inner fresh or relatively fresh parts (Figs. 17 to 19). The former layers with black or brown colour under microscope correspond to *brown layers* by naked-eye observation of cut rocks, while the latter parts with pale colours are related to *the inner parts* (*e.g.*, Figs. 12 to 14). Some samples have a semi-weathered part with a pale colour (*e.g.*, Fig. 18d) which corresponds to *white layers* by naked-eye observations of cut rock (Fig. 13d). The boundary between the brown layers and the inner parts or the white layers is sharp. In contrast, there is no definite boundary between white layers and the inner parts (Fig. 18d). The black areas in cross-polarized light and colourless areas in plane-polarized light correspond to pores in rocks. They are more abundant in the brown layers than in the inner part (Figs. 17a, 18b and 18c), which agrees with the naked-eye observations. Micropores or microfractures of some samples are filled with reddish brown materials (*e.g.*, Fig. 18a).

3.1.3. X-ray diffraction analysis

The minerals were identified by X-ray diffraction analysis (XRD). All the samples were first divided into the inner parts and the brown layers. The collected specimens of the fresh or fresh-looking inner parts for all the rocks were ground into material fine enough for analysis of the powdered sample. For the brown layers, the specimens for 320-ka, 450-ka and 830-ka rocks were easily collected using a chisel and a hammer, whereas those for 0-ka and 20-ka

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rocks could not be collected because the layers were too thin. Although hydraulic elutriation was performed on the collected the brown layers, it was impossible to gather clay components because all particles sunk soon. This indicates that the particle sizes of weathered material are larger than silt sizes. Thus, the untreated specimens for the brown layers were ground into material fine enough for the powdered analysis.

Next, the fine powdered samples were analyzed to identify both original rock-forming minerals and clay minerals. The analysis was performed using a X-ray diffractometer of RIGAKU Model RAD-C System. The operating conditions were X-ray target of CuKα, tube voltage of 50 kV and tube current of 20 mA.

Figure 20 shows the X-ray diffraction pattern of the rocks. Main minerals detected are summarized in Table 3. The paragenetic minerals in the inner parts of the rocks are quartz, tridymite, feldspar, pyroxene and magnetite (Fig. 20a to 20e). The most samples from the brown layers mainly consist of kaolin minerals, feldspar, pyroxene and quartz (Fig. 20f to 20i). Moreover, smectite, maghemite and hematite were detected in some samples. Main weathering products are kaolin minerals altered from feldspar and pyroxene, because the ratio of peak intensity of feldspar and pyroxene to that of quartz for the brown layers is much lower than the ratio for the inner parts.

3.2. Colour measurements using a visible microspectrometer

Colour measurements were performed using rock samples 0-B1, 20-B2, 20-B6, 450-B1, 450-B38, 450-B39 and 450-B64. The samples were first cut perpendicularly to the rock surface, then were formed into smaller tablets, and finally polished by #2000 carborundum. Colours from the rock surface to the inner part of the specimens were measured at Japan Atomic Energy Research Institute using a visible microspectrometer with a CCD type diffractometer

and an optical microscope (Olympus; BH-2). The instrument provides the dark field images and visible reflectance spectra corresponding to diffuse reflectance spectra of powdered samples with the wavelength resolution of 1 nm. Calibration was carried out using the emission spectra of a mercury-vapor lamp while $CaCO_3$ powder was used as a reference. To gain intensity high enough for reproducible measurements, the spot diameter and the exposure time for each measurement were set to be 80 μm and 60 second, respectively. Only groundmass was measured because colour changes there are more marked than those in phenocrysts.

The colour measurement yields three values of colour spaces denoted conveniently by L*, a* and b*, which can be calculated from the basic spectral data. The L* a* b* colour system are one of standard methods to describe colour in a quantitative way because they have uniform colour space (Hunt, 1980). The values of L*, a* and b* represent lightness, redness-greenness, and yellowness-blueness, respectively.

Figure 21 shows the L*-, a*- and b*- values plotted against the depth from the rock surface. For 0-ka rock (the sample 0-B1), L*-, a*- and b*-values show no variations through all measurement points from the surface to 5.0-mm depth (Fig. 21a). The values of L* are ca. 40, and those of a* and b* are about null. These three values indicate dark gray colour.

Between the rock surface and 1.0-mm depth of both the samples 20-B2 and 20-B6, L*- and b*- values are higher than those for the inner parts, whereas a*-values do not depend on depth (Figs. 21b and 21c). The values of L* and b* at the surface are ca. 60 and ca. 5, respectively, and they gradually decrease with increasing depth. For 1.0-mm to 5.0-mm depth from the rock surface, a*- and b*- values are almost constant. L*-values also tend to be constant in the sample 20-B2 (Fig. 21b), whereas the sample 20-B6 show gradual change from ca. 50 to ca. 30 (Fig. 21c).

Figures 21d to 21g show the results for 450-ka rocks. The sample 450-B1 has the higher L*-, a*- and b*-values in the brown layer (from the rock

surface to 3.0-mm depth) than in the inner part (Fig. 21d). The values for the brown layer are, from 40 to 50 for L*, from 0 to 6 for a*, and from 10 to 25 for b*. These three values represent brownish colour as a whole. From 3.0-mm depth to the inner parts of this rock, L*-, a*- and b*-values are *ca.* 30, 0, and -5, respectively, which hardly change with depth. All the three values represent darkish gray colour. The sample 450-B39 (Fig. 21f) shows the same changing patterns in L*-, a*-, and b*-values as those in the sample 450-B1. The values for the brown layer (from the rock surface to 4.0-mm depth) are from 55 to 75 for L*, from 2 to 12 for a*, and from 10 to 40 for b*, respectively. The inner parts of this rock, L*-, a*- and b*-values are *ca.* 40, 0, and 0, respectively, with very little change with depth.

The sample 450-B38 also has the high L*-, a*- and b*-values within the brown layer (from the rock surface to 4.0-mm depth) than in the inner part (Fig. 21d). The values for the brown layer are, from 55 to 75 for L*, from 2 to 12 for a*, and from 8 to 40 for b*, which also represent brownish colour. From 4.0-mm depth to the inner parts of this rock, a*- and b*-values are *ca.* 0 and 5, respectively, which hardly change with depth. In contrast, L*-values of the same part decrease with increasing depth, with the values from 40 to 30. The sample 450-B64 (Fig. 21e) shows the similar changing pattern in L*-, a*- and b*-values as those in the sample 450-B38. L*-, a*- and b*-values for the brown layer (from the rock surface to 4.0-mm depth) are from 55 to 65, from 0 to 6 for, and from 10 to 40. The values of a* and b* for the inner parts are *ca.* 0 and *ca.* 10, respectively, which hardly change with depth. L*-values for the white layer (from 4-mm to 10-mm depth) are constant with *ca.* 50, showing whitish gray colour. The values for the inner part (more than 10-mm) decrease with increasing depth.

Figure 22 shows the spectral data of 450-ka rocks for selected points with marked colours. The points are indicated by arrows in Fig 21. In the sample 450-B1 (Fig. 22a), the spectral curves for 9.0-mm and 4.4-mm depth from the rock surface have a higher degree of absorbance without absorption

bands (broad changes in absorbance), which points to the dark colour without chroma. The spectral curve for 2.4-mm depth for the same rock has two-absorption bands around 420 nm and 450-500 nm in wavelength, which represents yellowish brown colour. The former absorption band indicates the existence of jarosite ($KFe_3(SO_4)_2(OH)_6$), and the latter band corresponds to FeO(OH)-minerals (e.g., goethite and lepidochrocite) (Hunt and Ashley, 1979; Nakashima et al., 1992), although the amounts of these minerals are very small. The spectral curve for 0.4-mm depth has no absorption band around 420-nm wavelength, whereas that of 450-500 nm is distinct. A bulge near 550-nm wavelength indicates reddish brown colour and the existence of Fe_2O_3-minerals (e.g., hematite and maghemite) (Hunt and Ashley, 1979; Nakashima et al., 1992).

The spectral curve for 14.5-mm depth of the sample 450-B64 (Fig. 22b) shows higher degree of absorbance without absorption bands, representing dark gray colour. The curve for of 8.5-mm depth has the absorption band of 450-500 nm wavelength, showing slightly yellowish gray colour and the existence of FeO(OH)-minerals. The spectral curve for 4.2-mm depth shows lower absorbance than that of 8.5-mm depth. This point has pale gray colour that is the lightest of the four points. The spectral curve for 1.6-mm depth has two absorbance bands at 420 nm and 450-500 nm in wavelength. This represents yellowish brown colour and the existence of jarosite and FeO(OH)-minerals. The lack of Fe_2O_3-minerals suggests that the brown layer of the sample 450-B64 tends to preserve more water than that of the sample 450-B1.

3.3. Physical properties

3.3.1. Mercury intrusion porosimetry

It is technically difficult to obtain bulk density, porosity and other physical properties for weathering rinds from the common method using cored

rock samples because weathering rinds are thin. A mercury intrusion porosimetry, however, provides a method to investigated physical properties related to pores of rocks from the measurement of pore-size distribution (called as PSD hereafter). The method was devised by Washburn (1921) who assumed that pores are *open pores* with cylindrical shape.

$$D = 4\gamma \cdot \cos\theta / P$$

Where γ is surface tension of mercury (*ca.* 484 dyne/cm), θ is contact angle between mercury and solid (about 130) and P is a pressure of mercury intrusion.

In the present study, the porosimetry AUTO-PORE #9200 manufactured by Micromeritics Co., USA. was used. Although this apparatus reports PSD-values for a range from 0.003 μm to 360 μm in pore diameter, only the diameters of $10^{-2.5}$-$10^{1.5}$μm (0.003-33 μm) are reliable (*e.g.*, Yamashita and Suzuki, 1986). The PSD for this range was measured for the brown layers of 320-ka, 450-ka and 830-ka rocks as well as the inner parts of 0-ka, 20-ka, 320-ka 450-ka and 830-ka rocks.

Figures 23 to 26 show the resultant histograms from PSD measurements. The list of the original data is shown in Appendix. Pores are divided into four grades following the criteria of Suzuki and Matsukura (1992): $10^{1.5}$ μm$\geq D_\alpha>$ $10^{0.5}$ μm, $10^{0.5}$ μm$\geq D_\beta>10^{-0.5}$ μm, $10^{-0.5}$ μm$\geq D_\gamma>10^{-1.5}$ μm, and $10^{-1.5}$ μm $\geq D_\delta>10^{-2.5}$ μm. The pore volume for these four grades are denoted as V_α, V_β, V_γ and V_δ, respectively. A sum of V_α to V_δ is called as total pore volume and is denoted as V_t. The values of V_α, V_β, V_γ, V_δ and V_t for the rock samples are summarized in Table 4.

Figure 23 shows histograms for the inner parts of 0-ka rocks. Each column in the histogram belongs D_α to D_δ for all the samples have less than *ca.* 1.0 mm³/g in pore volume. The values of V_α and V_β for all the samples are always smaller than V_γ and V_δ. Especially, the samples 0-B1, 0-B37 and 0-A20 have the smaller values of V_α and V_β than the sample 0-A6. These differences

in pore volume (V_α, V_β, V_γ and V_δ) for different samples are ascribed to original varieties in physical rock properties.

Figure 24 shows the result of 20-ka rocks. The values of V_α and V_β for all the samples are always smaller than V_γ and V_δ, which is a common characteristic to the 0-ka rocks. Especially, the samples 20-A1, 20-A3 and 20-B2 have the smaller values of V_α and V_β than the sample 20-A16 and 20-B6. Such varieties in pore volume among 20-ka rocks are larger than those among 0-ka rocks.

Figure 25 shows the results for 320-ka rocks. Pore volume for the inner parts of 320-ka rocks are also various depending on samples. The varieties are larger than those for 20-ka rocks. The values of V_α, V_β, V_γ and V_δ for the brown layers are more than ten times as large as those for the the inner parts. The volume of pores with diameters from 10^0 μm to 10^{-1} μm is nearly equivalent to the total pore volume. These results show that the pore diameters with large pore volume tend to increase with the progress of weathering.

Figure 26 shows the results for the 450-ka rocks. They have pore-size distribution similar to 320-ka rocks: (1) pore volumes for the inner parts show marked variety depending on samples; (2) the volume of pores with 10^0-10^{-1} μm diameters is nearly equivalent to the total pore volume.

Figure 27 shows the results for the 830-ka rock (The sample 830-A1). The values of V_α, V_β, V_γ and V_δ for the brown layers are more abundant than those for the inner part, which is a common characteristic to 320-ka and 450-ka rocks. The volume of pores with 10^0-10^{-1} μm diameter for the brown layer is smaller than that for 320-ka or 450-ka rocks. On the other hand, the volume of pores with 10^{-1}-10^0 μm diameter for the brown layer is larger than that of 320-ka and 450-ka rocks. These results indicate that the pore diameters with large pore volume, even in the brown layers, tend to increase with the progress of weathering.

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3.3.2. Bulk density and porosity calculated from PSD data

The PSD measurement also yields the values of total pore volume (V_t) and bulk density. Thus, porosity can be calculated by multiplying the above two values. Table 5 shows bulk density and the calculated porosity. The inner parts of all the rocks have the large bulk density of *ca.* 2.4-2.5 g/cm^3 in average. In contrast, the bulk density for the brown layers of 320-ka, 450-ka and 830-ka rocks are *ca.* 1.2-1.4 g/cm^3 in average.

On the other hand, porosity for the brown layers is larger than that for the inner parts because of much larger pore volume. The inner parts of all the rocks have a porosity of *ca.* 2-5 % in average, and the brown layers of 320-ka, 450-ka and 830-ka rocks have a porosity of *ca.* 30-40 % in average.

3.4. Chemical properties

3.4.1. X-ray fluorescence analysis

Chemical composition as bulk samples was determined by X-ray fluorescence analysis (XRF). Samples were collected from the brown layers of 320-ka, 450-ka and 830-ka rocks as well as the inner parts of 0-ka, 20-ka, 320-ka, 450-ka and 830-ka rocks. The brown layers of 0-ka and 20-ka rocks could not be collected because they were very thin. The collected samples were ground into powders fine enough for analysis. Then the powdered samples were mixed with the binder of wax in the proportion of 30:1. The mixed powders were put into aluminum rings and pressed for one minute with 25-t load to make tablet-like pellets with 3-cm diameter and 2-mm height.

The apparatus used for the analysis is the X-ray fluorescence spectrometer of RIGAKU model 3270, with the operating conditions of tube voltage and tube currents of 50kV and 50 mA, respectively. Analyzed elements are ten major elements (SiO_2, TiO_2, Al_2O_3, $FeO+Fe_2O_3$, MnO, MgO, CaO, Na_2O, K_2O and P_2O_5) and fourteen trace elements (Ba, Cu, Ga, Mo, Nb, Ni, Pb, Rb, Sr, Th,

U. V. Y and Zr). Calibration was performed using pellets for 26 standard-rock samples of Geological Survey of Japan (JG-1a, JG-2, JG-3, JA-1, JA-2, JA-3, JR-1, JR-2, JR-3, JB-1a, JB-2, JB-3, JGb-1, JGb-2, JP-1, JF-1, JF-2, JSD-1, JSD-2, JSL-1, JSL-2, JCh-1, JLK-1, JLS-1 and JDO-1), their composites (*e.g.*, JCh-1: JG-2, 1:1), and the doped composites with some trace elements (chemical reagents). The methods for removal of matrix effects were modified after Sugisaki *et al.*, (1977, 1981), Nakada (1987), and Nakada *et al.*, (1985).

The results are shown in Table 6. SiO_2-values for the inner parts of most rocks range from 50 to 71 %. Na_2O, CaO, MgO and Sr of the inner parts are richer than those of the brown layers. On the other hand, the amounts of $FeO+Fe_2O_3$, TiO_2, Al_2O_3, V, Zr and ignition loss for the inner parts are smaller than those for the brown layers. Figure 28 shows the values of the elements in the brown layers versus those in the inner parts. The proportion of the contents of Na_2O, CaO, MgO and Sr for the brown layers to those for the inner parts is 0.03:1 in minimum. On the other hand, the proportion of the contents of ignition loss and $FeO+Fe_2O_3$ for the brown layers to that for the inner parts is 10:1 and 5:1 in maximum, respectively. There is little difference in total- and SiO_2- values between the brown layers and the inner parts.

To estimate absolute contents of chemical elements (*i.e.*, weights in unit volume), the percentage of chemical elements was multiplied with bulk density Table 7. The unit is g/cm^3 for major elements and mg/cm^3 for trace elements. The values for the brown layers versus those for the inner parts are shown in Fig. 29. Most elements have the smaller values for the brown layers than for the inner parts. The proportion of the contents of Na_2O, K_2O, CaO, MgO and Sr for the brown layers to those for the inner parts is 0.01:1 in minimum. The proportion of the total-, SiO_2- and Al_2O_3-values for the brown layers to those for the inner parts are in the range between 0.1:1 and 1:1.

3.4.2. Electron-probe microanalysis

The present paper examined weathering processes occurred within small

rock gravel. Thus, it is important to examine differences in chemical properties within a small area. However, the investigation of the differences by XRF analysis for small area is technically difficult. Therefore, electron-probe microanalysis (EPMA) was conducted to examine aerial variation (qualitative mapping) and linear variation (line analysis) of major elements within each layer. The analysis was carried out using JEOL JXA-8621; the electron probe was operated at 25 kV and the electron beam was focused to $ca.$ 10 μm in diameter. Samples with thick and distinct weathering rinds (450-B1, 450-B64 and 830-A1) were analyzed using polished thin sections cut normal to rock surfaces.

Figures 30 and 31 show the coloured composition maps of nine elements: Si, Ti, Al, Fe, Ca, Mg. Na, K and Mn. The maps cover the zone from the inner parts to surface of the rocks. Colour steps on the right of the figure indicate the relative content of each element: white step (right) corresponds to larger quantities and the black step (left) corresponds to pore space. The amounts of most elements for the sample 450-B1 are small in the brown layer (the part between $ca.$ 3.0-mm depth and the rock surface) and large in the inner part (Fig. 30). The phenocryst enriched in Si, Al, Na and Ca is plagioclase. The contents of Si, K, Na, Mg, Ca and Mn in the brown layer are smaller than those in the inner part. Among these elements, Na, Mg, Ca and Mn were highly dissolved within the brown layer. Especially, Ca was much more leached out than other elements. The contents of Al are also small in the brown layer, except for the outermost zone with a thickness of 0.5 mm. The contents of Fe and Ti are large in the brown layer except for pores represented in black colour.

For the sample 830-A1, the amounts of most elements are also small in the brown layer (the part between $ca.$ 6.0-mm depth and the rock surface) and large in the inner part (Fig. 31). The contents of Si and Al are small within the brown layer, but they are large at the outermost zone of 2-mm thickness. The grains enriched in Si are thought to be secondary accumulated minerals. The

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contents of Ti are small in the brown layer and large in the inner part. The contents of Fe within the groundmass of the brown layer is smaller than those of the inner part, but it is large within the outermost zone of $ca.$ 3-mm thickness. Other elements (K, Na, Mg, Ca and Mn) for this sample show the same changes as those for the sample 450-B1: the contents of them for the brown layer are smaller than those for the inner part, and especially, Ca was much more leached out.

Figure 32 shows the results of line analyses for the samples 450-B1 and 450-B64. The sample 450-B64 has the white layer, while 450-B1 does not have it. The three representative elements (Si, Fe and Ca) were examined. The results of the sample 450-B1 (Fig. 32a) show that (1) Si is more decreased within the brown layer than within the inner part, (2) Ca is completely leached out in the brown layer of 3-mm thickness, and (3) Fe has higher values within the brown layer than within the inner part. These results correspond to the analyses of map data shown in Fig. 30. The results of the sample 450-B64 (Fig. 32b) show that (1) Si decreases more in the brown layer than in the inner part, (2) Ca decreases in the brown layer with 4-mm thickness, but it tends to increase from there to the inner part, and (3) Fe shows little changes throughout the inner part and the brown layer.

3.4.3. Inductively coupled plasma analysis

Inductively coupled plasma analysis (ICP) was performed on the samples 20-B2, 20-B6, 450-B1, 450-B10, 450-B12 and 450-B64, to quantity changes in chemical properties through the inner parts to the brown layers. The rock samples were cut perpendicularly to rock surfaces and then powdered materials were collected using a micro-drill. The drilling was conducted at four or five points between rock surfaces and the inner parts with a few-millimeter intervals. The powdered material of 50-mg for each point was put into liquid mixed acid with 1-ml HF, 0.5-ml HNO_3 and 0.2-ml $HClO_4$. The soluted samples were investigated using ICP analyzer ICAP-757, Jaerelash $Co.$

Ltd. Calibration was performed using three standard solutions of 5%-HNO₃ and two standard rocks of Geological Survey of Japan (JA-2 and JA-3). Nine major elements (TiO_2, Al_2O_3, $FeO+Fe_2O_3$, MnO, MgO, CaO, Na_2O, K_2O and P_2O_5) and twelve trace elements (As, Ba, Co, Cr, Cu, Li, Ni, Pb, Sr, V, Zn and Zr) were analyzed.

The results for the six samples are listed in Table 8. Figure 33a shows the results of the sample 20-B2. The rock sample has both the white layer and the brown layer with a thickness of *ca.* 1 mm and less than 0.1 mm, respectively. Between 10- to 15-mm depth from the rock surface, the contents of Ni, Cr and Cu decrease with decreasing depth. In contrast, the contents of Al_2O_3, $FeO+Fe_2O_3$, CaO, MgO, MnO, P_2O_5 and Pb tend to be constant if depth is more than 5 mm, but they increase with decreasing depth between 1- and 5-mm depth. The contents of Na_2O, K_2O, TiO_2, Zr, Sr, Zn and V decrease with decreasing depth at the same part. At the white layer between 0.2- and 1.0-mm depth, the contents of Al_2O_3, $FeO+Fe_2O_3$, CaO, MgO, MnO and P_2O_5 decrease with decreasing depth. In contrast, the contents of Na_2O, K_2O, TiO_2, Zr, Sr, Zn and V at the same part increase with decreasing depth. At the outermost part less than 0.2-mm depth corresponding to the brown layer, the contents of $FeO+Fe_2O_3$ increase with decreasing depth. The contents of Ba, As and Li show no significant changes throughout 0- to 15-mm depth.

Figure 33b shows the results for the sample 20-B6 which has only a thin brown layer with *ca.* 1.0-mm thickness. The contents of Cr increase with decreasing depth between 2- and 30-mm depth. Between 6- and 10-mm depth, the contents of $FeO+Fe_2O_3$, TiO_2, V and Cr increase with decreasing depth, whereas those of Sr decrease with decreasing depth. Between 2- and 6-mm depth, the contents of Cu and Zn increase with decreasing depth, whereas those of CaO and K_2O decrease with decreasing depth. The amounts of most elements within less than 2-mm depth change more abruptly than those within the inner zones: $FeO+Fe_2O_3$, TiO_2, K_2O, V and Zr increase with decreasing depth, whereas Al_2O_3, CaO, Na_2O, Cr, Ni, and Sr decrease. The contents of Ba

and As show no significant changes throughout 0- to 35-mm depth.

Figure 33c shows the results for the sample 450-B1 with *ca.* 3-mm brown layers but no white layers. The rock sample has quite large density (ρ=2.61 g/cm^3, shown in Table 5). Between 15- and 26-mm depth, the contents of Cr and Ni increase with decreasing depth, whereas those of Pb decrease with decreasing depth. Between 6- and 15-mm depth, the contents of Ni then decrease with decreasing depth. At the same part, the contents of Al_2O_3, Fe_2O_3 and V decrease slightly with decreasing depth. Between 2.5- and 6-mm depth, the contents of these three elements increase with decreasing depth at 6-mm depth, whereas those of Cu and Zn decrease with decreasing depth at the same part. At the brown layer (the part less than 2.5-mm depth), the contents of $FeO+Fe_2O_3$, TiO_2, K_2O, Ba, V, Zr and Li increase with decreasing depth, whereas those of CaO, Na_2O, MnO, Ni and Sr decrease with decreasing depth. The contents of Al_2O_3 also decrease with decreasing depth within the brown layer. The contents of P_2O_5, Co and As do not change significantly.

Figure 33d shows the results for sample 450-B10 with *ca.* 3-mm brown layers but no white layers. The rock sample has also quite large density (ρ=2.68 g/cm^3, shown in Table 5). Between 0- and 15-mm depth, the contents of Cr decrease with decreasing depth, whereas those of Pb tend to increase with decreasing depth. The contents of other elements have no marked changes in the part more than 3-mm depth. At the brown layer (the part less than 3-mm depth), the contents of $FeO+Fe_2O_3$, TiO_2, V, Zr, Li and Pb increase with decreasing depth. In contrast, the contents of Al_2O_3, CaO, Na_2O, MnO, Cr, Ni and Sr decrease with decreasing depth within the brown layer. The contents of K_2O, P_2O_5, Ba, and As do not change significantly.

Figure 33e shows the results for the sample 450-B12 with *ca.* 4-mm brown layers but no white layers. The rock sample has small density (ρ=2.39 g/cm^3, shown in Table 5). Between 10- and 24-mm depth, the contents of Cr and Ni decrease with decreasing depth. The contents of other elements have

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no marked changes in the part more than 10-mm depth. Between 6- and 10-mm depth, the contents of most elements (Al_2O_3, $FeO+Fe_2O_3$, CaO, Na_2O, K_2O, TiO_2, V, Sr, and Pb) decrease with decreasing depth. Between 0- and 6-mm depth, the contents of $FeO+Fe_2O_3$, TiO_2, K_2O, V and Pb increase with decreasing depth and those of CaO, Na_2O, Cr and Sr still decrease with decreasing depth. The contents of Ba, Zr and Zn increase with decreasing depth at the same part. The contents of $FeO+Fe_2O_3$, TiO_2, V, Zr and Zn within the brown layer (less than 4-mm depth) are much more abundant than those within the inner part. On the other hand, the contents of CaO and Sr within the brown layer are much less than those within the inner part. The contents of MnO, P_2O_5, Co, Li and As show little changes throughout 0- to 24-mm depth.

Figure 33f shows the results for the sample 450-B64 with the brown layers and white layers between $ca.$ 0-4 mm and $ca.$ 4-10 mm depth, respectively. The rock sample has small density ($\rho=2.40$ g/cm^3, shown in Table 5) as well as the sample 450-B12. Between 11- and 22-mm depth, the contents of Ca, Cr, Ni, Sr and Pb decrease with decreasing depth, whereas those of Li increase with decreasing depth. Between 7- and 11-mm depth, the contents of $FeO+Fe_2O_3$, TiO_2, MnO, Cu and V increase with decreasing depth. The contents of Cr and Pb are abundant within the white layer (between 11- and 4-mm depth). Between 4- and 7-mm depth, the contents of $FeO+Fe_2O_3$, TiO_2, Co, Zr and Zn increase with decreasing depth, whereas those of Al_2O_3, CaO, Na_2O and Sr decrease with decreasing depth. Within the brown layer (less than 4-mm depth), the contents of $FeO+Fe_2O_3$, TiO_2, V and Zr increase with decreasing depth, whereas those of Al_2O_3, Cr, Ni and alkali/alkaline earth minerals (CaO, Na_2O MgO, K_2O and Sr) decrease with decreasing depth. The contents of P_2O_5 and As show little changes throughout 0- to 21-mm depth.

Four element groups can be identified from the above results: (1) TiO_2, $FeO+Fe_2O_3$, V and Zr are more abundant in the brown layers than in the inner parts; (2) Al_2O_3 and alkali/alkaline earth metals (especially Ca and Sr) are less abundant in the brown layers than in the inner parts; (3) heavy metals such as

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Ni, Cr and Cu have been markedly depleted from the deepest zone, although the amounts of these elements in the inner parts are originally variable depending on measurement points; (4) P_2O_5, As, Ba, Co and Li tend to have constant amounts irrespective of change in depth.

3.5. Mechanical properties based on Vickers microhardness

It is technically difficult for the small area of the brown layers and the inner parts to obtain commonly used rock-strength parameters such as uniaxial strength and tensile strength. Vickers hardness tester conquers this difficulty. The hardness measured by the equipment (Vickers Hardness Number: VHN) is defined as the load applied to an indenter divided by the contact area of the impression (e.g., Nakhla, 1956; Young and Millman, 1964). The Vickers indenter is a square-based diamond pyramid with an included angle of $136°$ between opposite faces, so that a perfect indentation is seen as a square with equal diagonals. The superficial area of the indentation can be expressed in terms of the length of the diagonal d (in millimeters) as $d^2/2 \sin 68°$. The VHN-value, the ratio of load L (in kilogram force, kgf) to the area of indentation, is given by $VHN = L \times 2 \sin 68°/d^2 = 1.8544 \ L/d^2$ (kgf/mm^2).

The microhardness equipment used for the present study is the *Shimadzu Microhardness Tester (M-type)*. The load of 0.2, 0.5, or 1.0 kgf/mm^2 was employed for about 15 seconds in order to obtain available data, which makes indentations of diagonal lengths of up to 0.02 mm (20 μm). Measurements for microhardness were carried out using rock specimens. The rock samples, which are the same as for the PSD measurement, were cut normal to the rock surface with a thickness of 5-10 mm. They were polished by #800 carborundum on the cut surfaces. Measurement was performed from the rock surface to the inner parts of each rock sample along a line, perpendicularly to the rock surface. Measurement points were set every 0.2 or 0.5 mm intervals.

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The results of the VHN measurement are shown in Figs. 34 to 38. Based on the changing patterns of the VHN values, three zones were identified as follows. (1) Zone I is a part with small VHN values from 10 $gf/\mu m^2$ to 80 $gf/\mu m^2$. (2) Zone II is a part with abrupt or gradual increase in VHN values with increasing depth, in which VHN values vary from *ca.* 100 $gf/\mu m^2$ to *ca.* 500 $gf/\mu m^2$. (3) Zone III has large and constant VHN values of *ca.* 500 $gf/\mu m^2$. Zone I corresponds to the brown layer (from 0 mm to 2-3 mm) of 320-ka, 450-ka and 830-ka rocks. Zone II occurs in the rock samples of 20-ka, 320-ka, 450-ka and 830-ka. It is assumed that 0-ka rocks have no Zone II despite of small VHN values at very small depth, because the low values are probably caused not by weathering but by the Zone I and *edge effect* (Hutchison, 1974). Zone III occurs at the innermost part of all the rock samples. Table 9 is the list of the average VHN values for these three zones of each rock sample.

Figure 34 shows the VHN profiles for the 0-ka rocks. As noted above, all the 0-ka rocks have only Zone III. The range of the VHN values is from *ca.* 400 $gf/\mu m^2$ to *ca.* 600 $gf/\mu m^2$ (Table 9) with an average of 502 $gf/\mu m^2$.

Figure 35 shows the results for 20-ka rocks. All the rock samples have Zones II and III but have no Zone I. The range of the VHN values for Zone III is from *ca.* 450 $gf/\mu m^2$ to *ca.* 550 $gf/\mu m^2$ with an average of 504 $gf/\mu m^2$ (Table 9). The VHN values for the samples 20-A1 and 20-A3 decrease with decreasing depth between 0- and 3.5-mm depth (Fig. 35a and 35b). The values for the samples 20-A16 and 20-B2 decrease with decreasing depth at 0-2 mm and 0-2.5 mm, respectively. Thus, it can be said that the 20-ka rocks have Zone II with a thickness of 2-3.5 mm. The average VHN value for Zone II of these rocks is 331 $gf/\mu m^2$ (Table 9).

Figure 36 shows the results for 320-ka rocks. The samples 320-B10 and 320-B22 has all the Zones I, II and III (Fig. 36b and 36d), whereas the samples 320-B5 and 320-B20 lack Zone III (Fig. 36a and 36c). The thickness of Zone I for all the 320-ka rocks is 2-3 mm. The thickness of Zone II is 3 mm for the samples with all three zones and more than 10 mm for the samples without

Zone III. The average VHN values for Zone I, II and III are 47 gf/μm^2, 311 gf/μm^2 and 531 gf/μm^2, respectively (Table 9).

The VHN profiles for 450-ka rocks are shown in Fig. 37. The samples 450-B1, 450-B10, 450-B37, 450-B38 and 450-C1 have Zones I, II and III (Figs. 37a to 37d, 37f). In contrast, the samples 450-B39 and 450-B64 lack Zone III (Figs. 37e and 37f). The thickness of Zone I for all the 450-ka rocks is 2-3 mm. The thickness of Zone II is *ca.* 0.5 mm for the samples with all zones and more than 10 mm for the samples without Zone III. The average VHN values for Zone I, II and III are 29 gf/μm^2, 289 gf/μm^2 and 503 gf/μm^2, respectively (Table 9).

Figure 38 shows the VHN profile for the sample 830-A1. The sample has all the three zones: Zone I with 4-mm thickness, Zone II with 2-mm thickness, and Zone III. The average VHN values for Zone I, II and III are 79 gf/μm^2, 433 gf/μm^2 and 485 gf/μm^2, respectively (Table 9).

3.6. Summary

The measured rock properties of different age rocks are summarized as follows:

(1) The 0-ka rocks have no layers of altered colour at the surface. The 20-ka rocks have the white layers less than 1-mm thickness and the very thin brown layers. All the 320-ka, 450-ka and 830-ka rocks have the brown layers with a thickness of 3-6 mm and some of them have the white layer between the brown layer and the inner part.

(2) The brown layers contain kaolin minerals and small amounts of smectite, maghemite and hematite. The peaks of feldspar and pyroxene on XRD patterns are high in the inner parts but low in the brown layers. These phenomena suggest that the secondary altered minerals such as kaolin minerals were mostly originated from feldspar and pyroxene.

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(3) The brown layers have low contents of Na_2O, CaO, Sr, Cr, Cu, Ni and Pb. In contrast, they have high contents of TiO_2, $FeO+Fe_2O_3$, V and Zr. EPMA mapping data show that the 830-ka rock has secondary concentrated grains at the rock surface.

(4) The brown layers have small values of total pore volume, bulk density, and porosity. They have extremely low VHN-values.