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Chemical and Mineralogical Properties of Tephras and Mobility of Chemical Elements in Tephra-Derived Soils

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Abstract

The SiO_2 content of tephras was closely correlated with the contents of other major elements except for the K_2O content in Japan tephras, which varied considerably with the volcanic zones where the volcanoes were located. Volcanic glass was abundant in rhyolitic and basaltic tephras and the contents of heavy minerals and plagioclase were high in dacitic, andesitic and basaltic andesitic tephras. Although the heavy mineral assemblage was correlated with the rock types of tephras and volcanic zones in the Japan tephras, these correlations were not clear in the New Zealand tephras. The composition of volcanic glass in andesitic, dacitic and rhyolitic tephras was felsic and non-colored glass with refractive indices about 1.50 was observed. In the mafic tephras, the composition of glass was intermediate and mafic and the colored glass with indices greater than 1.52 was observed. The stability sequence of the primary minerals in tephra-derived soils under temperate and humid climate conditions was graded as follows: volcanic glass < plagioclase = olivine < augite < hyperthene $\leqq$ common hornblende $\leqq$ ferromagnetic minerals. The mobility sequence of the major elements in tephra-derived soils under these climate conditions was considered to be as follows: Cao, Na_2O > SiO_2 > MgO, K_2O > Al_2O_3, Fe_2O_3.

Discipline: Soil, fertilizers and plant nutrition
Additional key words: volcanic glass, primary minerals, volcanic ash, Andosols

Introduction

The eruption of the circum-Pacific volcanic belt which appears like a ring of fire has led to the deposition of a large volume of tephras over the lands in these areas in the Quaternary. Tephras including volcanic ash, pumice, scoria and pyroclastic flow are one of the most important parent materials of the soils in Japan, New Zealand, Philippines, Indonesia and North to South America situated in the circum-Pacific volcanic zone.

Tephras, especially wide-spread pyroclastic fall, impart special characteristics to the soils formed from them. Investigations of the chemical and mineralogical properties of tephras and mobility of chemical elements in tephra-derived soils are, therefore, important for studies on the chemical and mineralogical characteristics and the fertility of tephra-derived soils.

Materials and methods

The total chemical composition of fresh tephras and tephra-derived soils was determined by X-ray emission spectroscopy (XES) or wet analysis, and that of volcanic glasses by electron probe microanalyzer (EPMA). The refractive indices of volcanic glasses were determined by the Beck line methods and the morphology was observed with a polarized microscope and scanning electron microscope (SEM). The primary mineral composition was determined under a polarized microscope using the 0.1 to 0.2 mm fraction after ultrasonic treatment and separation of light and heavy mineral fractions by a solution with a specific gravity of 2.96. The degree of weathering of primary minerals was determined under a polarized microscope, based on etching degrees with the following scores: I (fresh), II (low degree of etching), III (medium degree of etching) and IV (high degree of etching).

Results and discussion

1) Chemical composition of tephras

Japan and New Zealand are representative volcanic countries in the world, and Andosols cover large areas of these countries. However, petrographic provinces with a significant reflection on the chemical and mineralogical properties of volcanic products are different between Japan and New Zealand[1]. In Japan, there are petrographic provinces with high alumina basalt and alkali basalt contents, while the tholeliite petrographic province in Japan is lacking in New Zealand[1]. It is important to investigate the properties of tephras in these countries because

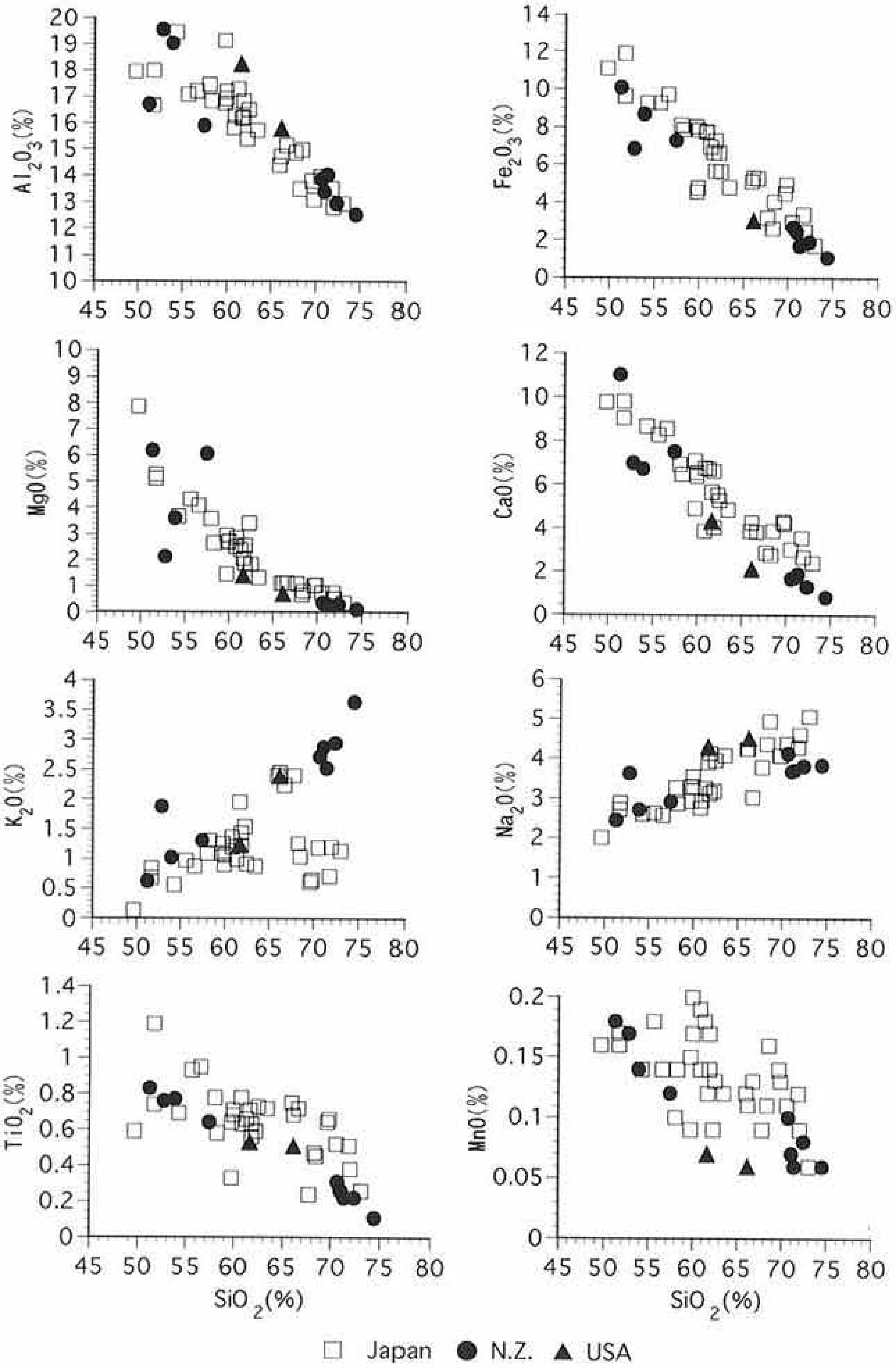

Fig. 1. Contents of major elements in relation to silica in tephras

tephras easily undergo a weathering process and release chemical elements affecting the fertility of tephra-derived soils.

Shoji et al.[8] classified tephras into 5 rock types on the basis of silica content, as follows; rhyolite (70 to 100% SiO_2), dacite (62 to 70% SiO_2), andesite (58 to 62% SiO_2), basaltic andesite (53.5 to 58% SiO_2) and basalt (45 to 53.5% SiO_2).

Fig. 1 shows the analytical data of 33 samples of Japan tephras including the 26 samples reported by Shoji et al.[8], 9 New Zealand samples and 2 USA samples[10]. Correlation equations between SiO_2 content (x) and contents of other elements (y) of tephra samples of Japan and New Zealand are as follows:

Japan tephras (n = 33): Al_2O_3% $y = -0.250x + 31.52$ $r = -0.882^{***}$, Fe_2O_3% $y = -0.385x + 30.34$ $r = -0.924^{***}$, MgO% $y = -0.247x + 17.78$

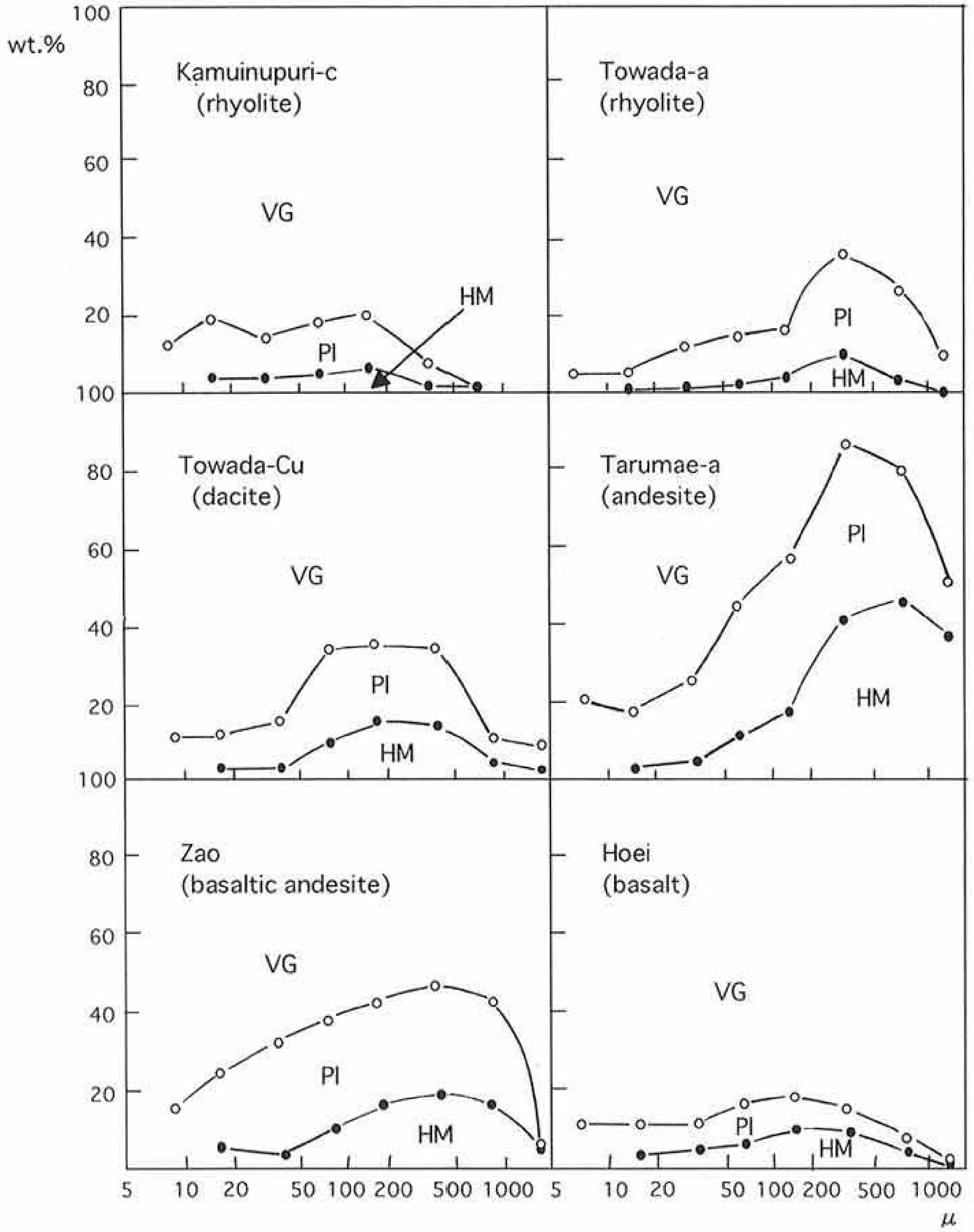

Fig. 2. Primary mineral composition of fraction of each size
VG: Volcanic glass, Pl: Plagioclase, HM: Heavy minerals.

Table 1. Relationships between rock types and heavy mineral assemblage[a)]

	Rhyolite	Dacite	Andesite	Basaltic andesite	Basalt	Total
Olivine			7		10	17 (15%)
Pyroxene	4	12	31	6		53 (47%)
Pyroxene·hornblende		17	11			28 (25%)
Hornblende	1	13				14 (13%)
Total	5 (4%)	42 (38%)	49 (44%)	6 (5%)	10 (9%)	112 (100%)

a): Figure shows the number of samples.

$r = -0.916^{***}$, CaO% $y = -0.324x + 25.80$ $r = -0.926^{***}$, Na_2O% $y = 0.107x - 3.139$ $r = 0.862^{***}$, K_2O% $y = 0.030x - 0.701$ $r = 0.340$, TiO_2% $y = -0.018x + 1.790$ $r = -0.579^{***}$, MnO% $y = -0.0029x + 0.315$ $r = -0.536^{***}$.

New Zealand tephras ($n = 9$): Al_2O_3% $y = -0.248x + 31.16$ $r = -0.923^{***}$, Fe_2O_3% $y = -0.345x + 26.79$ $r = -0.976^{***}$, MgO% $y = -0.220x + 16.20$ $r = -0.844^{***}$, CaO% $y = -0.364x + 27.66$ $r = -0.959^{***}$, Na_2O% $y = 0.049x + 0.330$ $r = 0.812^{***}$, K_2O% $y = 0.096x - 3.981$ $r = 0.926^{***}$, TiO_2% $y = -0.029x + 2.325$ $r = -0.996^{***}$, MnO% $y = -0.0045x + 0.397$ $r = -0.950^{***}$.

The SiO_2 content of the tephras was closely correlated with the contents of all the major elements except for K_2O in the Japan tephras and with the contents of all the elements in the New Zealand tephras. The K_2O content in the Japan tephras was closely correlated with the petrographic provinces (volcanic zone), being lowest in the Nasu volcanic zone (tholeiite petrographic province), intermediate in the Chokai volcanic zone (high alumina basalt petrographic province) and highest in the Daisen volcanic zone (alkali basalt petrographic province)[14)], whose volcanic zones are located in parallel to the Japan trench. The potassium contents in the tephras belonging to the tholeiite petrographic province were low, even though the chemical composition of the tephras was felsic.

2) *Mineralogy of tephras*

Fig. 2 shows the contents of volcanic glass, plagioclase, and heavy minerals in 6 tephras with different rock types[11)]. The contents of light minerals which were dominated by volcanic glass were much higher than those of heavy minerals in all the samples. Especially, volcanic glass was overwhelmingly abundant in rhyolitic and basaltic tephras. On the other hand, the contents of heavy minerals and plagioclase were higher in intermediate tephras composed of dacite, andesite and basaltic andesite. Compared with the contents of heavy minerals in fractions with different sizes, the contents were higher in the 0.1 to 0.5 mm fraction and lower in the fraction finer than 0.05 mm.

Table 1 shows the relationship between heavy mineral assemblage and rock types of tephras and tephra-derived soils in Tohoku, Japan[16)]. The andesitic and dacitic samples accounted for the larger part of 112 samples while the samples of other rock types were not conspicuous.

Based on the heavy mineral composition, tephras and tephra-derived soils were divided into 4 types: olivine type, pyroxene type, pyroxene-hornblende type and hornblende type[16)]. As shown in Table 1, the pyroxene type accounted for almost half of all the samples. Olivine type was not observed in felsic samples. Hornblende type was not observed in andesitic to basaltic samples and pyroxene-hornblende type was not detected in mafic samples. These results indicated that the heavy mineral composition could be used to estimate the rock types, namely the characteristics of chemical elements in tephra-derived soils of Japan. However, the correlation between the heavy mineral composition and the rock types was not clear in the New Zealand tephras[10)].

As for the correlation between the heavy mineral assemblage of tephras and volcanic zone of Japan, hornblende and biotite were detected in the tephras of the Daisen volcanic zone, but not in the tephras of the Nasu volcanic zone. Hornblende was detected, but biotite was absent in the tephras of the Chokai volcanic zone which is located between the Nasu volcanic zone and Daisen volcanic zone.

3) *Volcanic glass in tephras*

Since tephras were produced under the rapid cooling of magma, volcanic glass is the dominant primary mineral in tephras. Volcanic glass is also considered

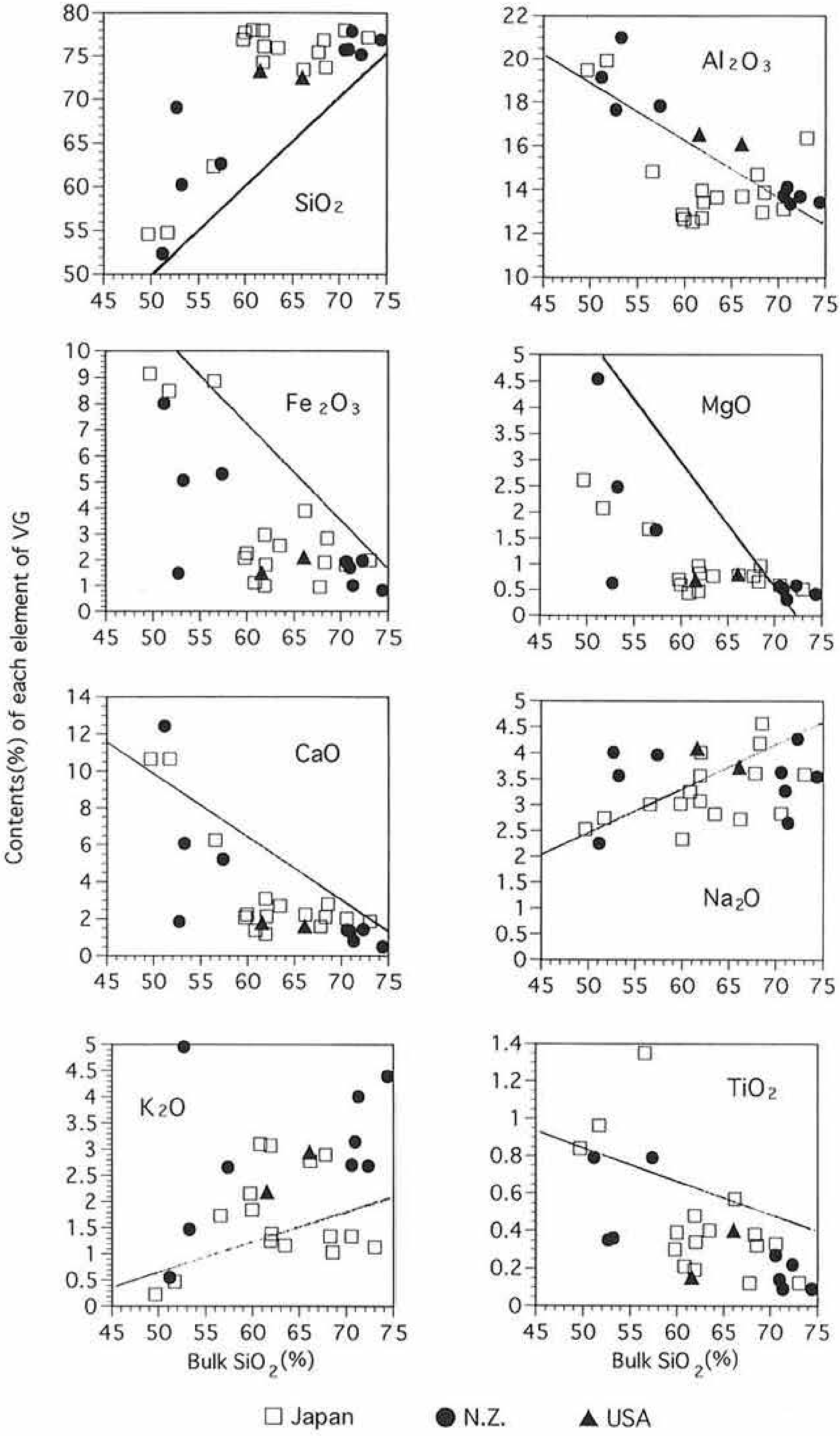

Fig. 3. Relationship between bulk SiO_2(%) and the content of each element in volcanic glass

to be the least resistant mineral to weathering. These facts indicate that volcanic glass is the most important primary mineral as parent material of tephra-derived soils.

Fig. 3 shows the relationship between the silica content of Japan tephras and New Zealand tephras and the content of each chemical element of the volcanic glass[10,14]. The straight lines in this figure indicate the correlation equations between the bulk silica content and the contents of other elments in the Japan tephras, given by Shoji et al.[8].

The silica contents of volcanic glass in the rhyolitic, dacitic and andesitic tephras ranged from 73 to 78% and these volcanic glasses were non-colored, while the silica contents of volcanic glasses in the basaltic andesitic and basaltic tephras ranged from 60 to 70% and 50 to 55%, respectively and these volcanic glasses were colored. The deviations from the regression line of the silica content of tephras on that of volcanic glasses were greatest in andesitic tephras and small in rhyolitic and basaltic tephras. The chemical composition of non-colored volcanic glasses in the rhyolitic, dacitic and andesitic tephras was very similar to the chemical composition of the rhyolitic tephras shown in Fig. 1. Therefore, the deviations from the regression lines of Al_2O_3, Fe_2O_3, MgO, CaO and TiO_2 were also greatest in the andesitic tephras and small in the rhyolitic and basaltic tephras. These deviations may account for the fact that the content of crystalline minerals such as heavy minerals and plagioclase was largest in the andesitic tephras and lowest in the rhyolitic and basaltic tephras as shown in Fig. 2.

Since the greater part of Na_2O and K_2O in the tephras is contained in volcanic glasses, the deviations from the regression line were very small in the tephras of all rock types.

Determination of the refractive indices of volcanic glasses is simple and is very useful for estimating their chemical composition. The values of the indices of non-colored volcanic glass in the rhyolitic, dacitic and andesitic tephras ranged between 1.48 and 1.52, while those of colored volcanic glasses ranged between 1.51 and 1.57 in the basaltic andesitic tephras and were higher than 1.55 in the basaltic tephras[14].

The morphology of volcanic glasses in the tephras was divided into 4 types, namely spongy, fibrous, platy and berry types[14]. Non-colored volcanic glass consisted of one or some of these types, whereas colored volcanic glass consisted of only the berry type.

4) Stability of primary minerals

The release of chemical elements from the primary minerals with the progression of weathering is closely related to the stability of primary minerals to chemical weathering. Fig. 4 shows the relationships between the rates of stages III and IV of etching,

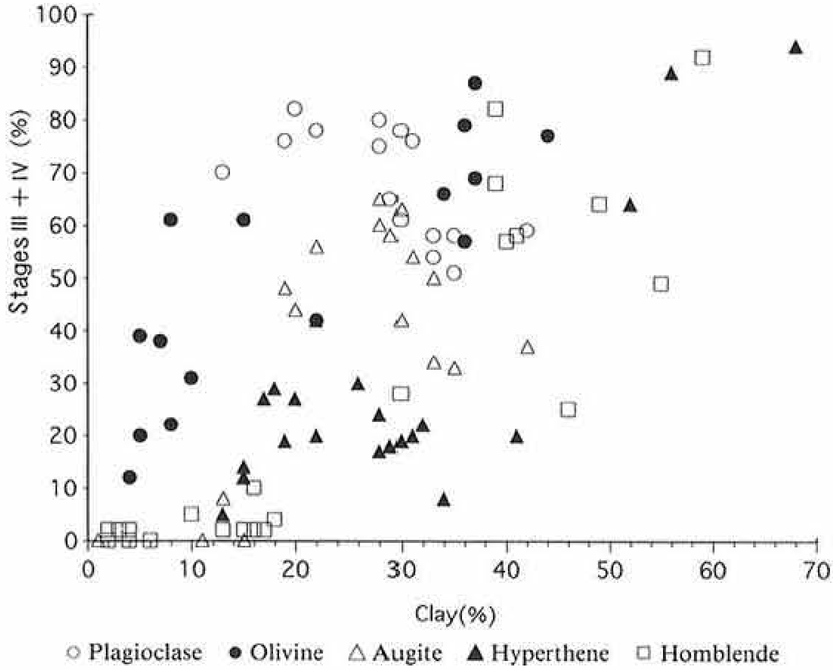

Fig. 4. Correlation between the clay content and higher degree of etching of primary minerals

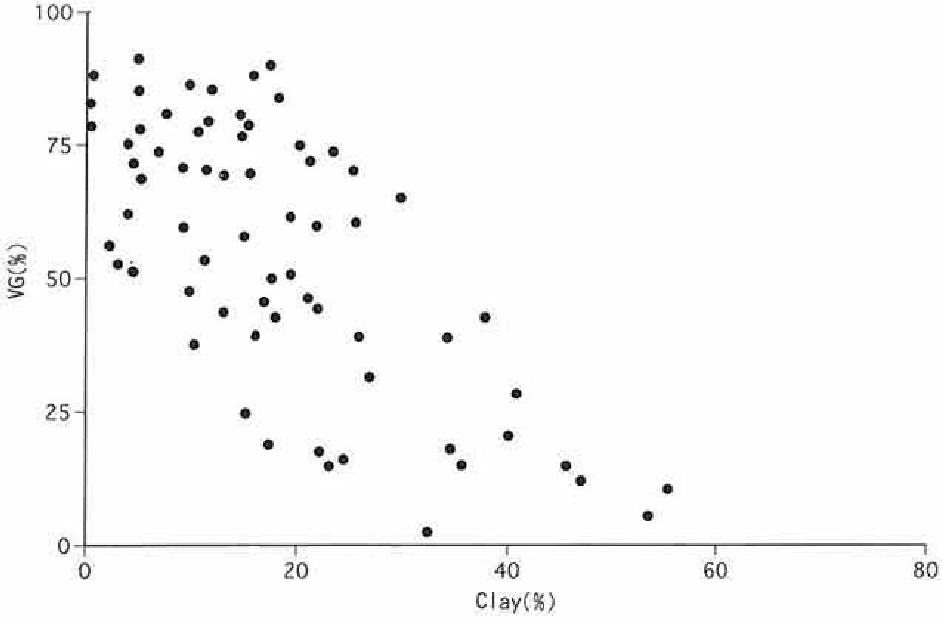

Fig. 5. Correlation between clay contents and volcanic glass contents

which correspond to highly weathered stages, and the clay contents of tephra-derived soils in Tohoku and Kanto, Japan[6,9].

Plagioclase, which is the second most abundant component of tephras next to volcanic glass and is therefore an important primary mineral in tephras, was most susceptible to weathering in the primary crystalline minerals. Olivine was as susceptible as plagioclase to weathering. Augite underwent rapid weathering over 20% of clay, while hyperthene was much more resistant than augite to weathering. Common hornblende was the most resistant among these minerals. Ferromagnetic minerals such as ilmenite and titanomagnetite were more resistant than common hornblende except for the easy weathering of titanomagnetite under poorly drained soil conditions[15].

Fig. 5 shows the relationship between the volcanic glass contents in the light mineral fraction of 0.1 to 0.2 mm size and the clay content in tephra-derived soils of Tohoku, Japan[17]. The volcanic glass content rapidly decreased with the progression of weathering.

Based on the results obtained, the stability sequence of primary minerals in tephras with weathering was determined and the major primary minerals concerned with the source of supply of chemical elements in the tephra were arranged as follows:

Stability sequence; volcanic glass < plagioclase = olivine < augite < hyperthene $\leqq$ common hornblende $\leqq$ ferromagnetic minerals.

Source of supply of chemical elements; SiO_2: volcanic glass $\gg$ plagioclase $\gg$ quartz. Al_2O_3: volcanic glass $\gg$ plagioclase. Fe_2O_3: volcanic glass, ferromagnetic minerals and pyroxenes in rhyolitic to basaltic andesitic tephras and volcanic glass in basaltic tephras. MgO: volcanic glass > pyroxenes in rhyolitic to basaltic andesitic tephras and volcanic glass in basaltic tephras. CaO: volcanic glass and plagioclase. Na_2O: volcanic glass $\gg$ plagioclase. K_2O: volcanic glass.

5) Mobility of chemical elements

It has been generally recognized that not only soil formation, but also soil properties are markedly influenced by the rock types of tephras[12,13]. Fig. 6 shows the relationships between the clay contents and the weight ratio of each element to Al_2O_3 in tephra-derived soils in Tohoku, Japan. Since Al_2O_3 is the most immobile element during the weathering of parent materials[3,5], the ratios of each element can be used for determining accurately the mobility of the chemical elements. The rock types of soil samples were determined by the V-Zn belt method[7].

It appeared that both CaO and Na_2O were highly mobile and leached out rapidly in tephra-derived soils under temperate and humid climate conditions. SiO_2 was leached out gradually. Though Fe_2O_3 is reported to be more mobile than Al_2O_3[3,5], the mobility of these elements did not differ appreciably in tephra-derived soils under these climate conditions as described by Kurashima et al.[2]).

The mobility of MgO and K_2O was more complicated. The equation of the relation between the clay contents(x) and $MgO/Al_2O_3 \times 100$(y) in samples of each rock type was derived as follows:

$y = 0.002x + 0.094$, $r = 0.009$ in rhyolitic and dacitic samples. $y = -0.002x + 0.188$, $r = -0.077$ in andesitic samples. $y = -0.003x + 0.26$, $r = -0.774$*** in basaltic andesitic and basaltic samples.

The equation of the relation between the clay contents(x) and $K_2O/Al_2O_3 \times 100$(y) in samples of each rocktype was derived as follows:

$y = -0.008x + 0.091$, $r = -0.461$*** in rhyolitic and dacitic samples. $y = -0.0001x + 0.065$, $r = -0.095$ in andesitic samples. $y = -0.004x + 0.035$,

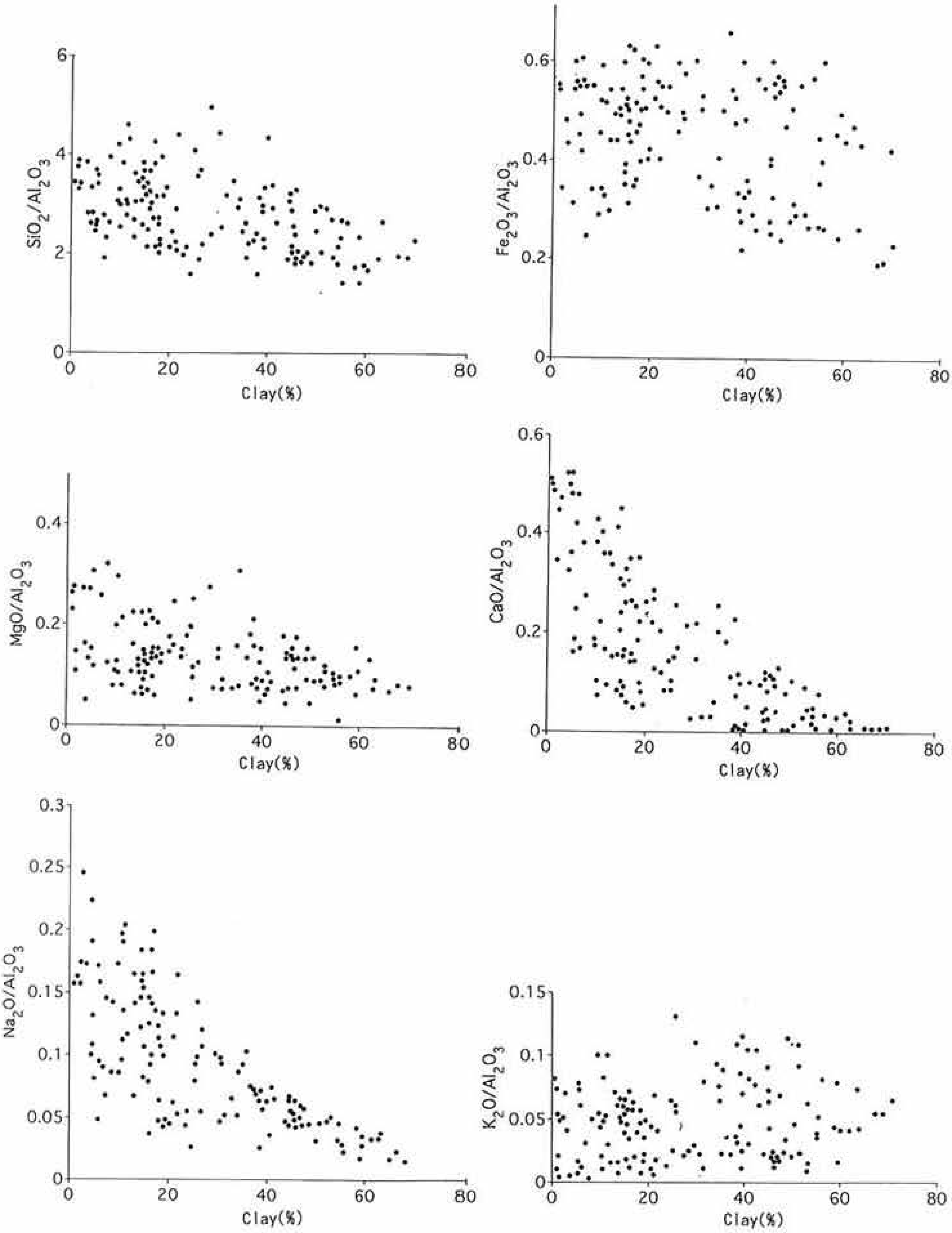

Fig. 6. Correlation between clay contents and weight ratio of each element to Al_2O_3 of soil samples

r = -0.404^{***} in basaltic andesitic and basaltic samples.

MgO and K_2O in mafic samples, in which allophane was the predominant clay mineral[8], and K_2O in felsic samples were gradually lost with the progression of weathering, but there were no relationships between the clay contents and the mobility of these elements in other samples. K_2O accumulated in the top layers of non-allophanic Andosols where 2:1 layer silicate clay predominated and only a small amount of MgO was removed by leaching[2]. On the other hand, MgO was gradually leached out and there was no relationship between the clay contents and K_2O content in allophanic Andosols where allophane predominated in the clay fraction[4].

The mobility sequence of the major elements in the tephra-derived soils under the temperate and humid climate conditions was proposed as follows: CaO, $Na_2O > SiO_2 > MgO$, $K_2O > Al_2O_3$, Fe_2O_3.

References

1) Kuno, S. (1976): Volcanic rocks. Iwanami, Tokyo [In Japanese].
2) Kurashima, K. et al. (1981): Mobilities and related factors of chemical elements in the topsoils of Andosols in Tohoku, Japan. 1. Mobility sequence of major chemical elements. *Soil Sci.*, **132**, 300-307.
3) Loughnan, F. C. (1969): Chemical weathering of the silicate minerals. American Elsevier, New York, 27-66.
4) Nanzyo, M. (1993): Chemical characteristics of volcanic ash soils. *In* Volcanic ash soils. Elsevier Amsterdam, 145-188.
5) Polynov, B. B. (1937): The cycle of weathering. Thomas Murby, London (translated by A. Muir), 160-164.
6) Shoji, S. et al. (1974): Soils formed from andesitic and basaltic volcanic ashes. 1. The nature of the parent ashes and soil formation. *Tohoku J. Agric. Res.*, **25**, 104-112.
7) Shoji, S. et al. (1975): Relationships between the geochemistry of ferromagnetic component and the chemical properties of air-born pyroclastic materials. *J. Jpn. Assoc. Mineral. Petrol. Econ. Geol.*, **70**, 12-24.
8) Shoji, S. et al. (1975): Chemical and mineralogical studies of volcanic ashes. 1. Chemical composition of volcanic ashes and their classification. *Soil Sci. Plant Nutr.*, **21**, 311-318.
9) Yamada, I. (1978): Thesis for Ph. D degree submitted of Tohoku Univ. [In Japanese].
10) Yamada, I. (1988): Tephra as parent matetial. *In* Proc. of the 9th Int. Soil Classification Workshop. eds. Kinloch, D. I. et al., 509-519.
11) Yamada, I. & Shoji, S. (1975): Relationships between particle size and mineral composition of volcanic ashes. *Tohoku J. Agric. Res.*, **26**, 7-10.
12) Yamada, I. & Shoji, S. (1975): Soils formed from andesitic and basaltic volcanic ashes. 2. Soil properties and fertilities problems. *Tohoku J. Agric. Res.*, **26**, 102-116.
13) Yamada, I. & Shoji, S. (1980): Fertility of Andosols from basaltic and dacitic volcanic ashes. *Tohoku J. Agric. Res.*, **31**, 149-155.
14) Yamada, I. & Shoji, S. (1983): Parent materials of the important Ando soils of Tohoku district. 2. Chemical and morphological properties of volcanic glasses and relationships between the chemical and mineralogical properties of tephras and volcanic zones. *J. Soil Sci. Plant Nutr., Jpn.*, **54**, 311-318 [In Japanese with English summary].
15) Yamada, I. & Shoji, S. (1987): Weathering of titanomagnetite in a recent rhyolitic ash in Miyagi Prefecture, Japan. *Soil Sci. Plant Nutr.*, **33**, 493-499.
16) Yamada, I. et al. (1980): Parent materials of the important Ando soils of Tohoku district. 1. Rock types and primary mineral composition. *J. Soil Sci. Manure, Jpn.*, **51**, 193-202 [In Japanese with English summary].
17) Yamada, I. et al. (1986): Chemical weathering of Ando soils in Tohoku, Japan. *Abst. 1986 Meeting Jpn. Soc. Soil Sci. Plant Nutr.*, **32**, 23.

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