# DIFFERENTIAL WEATHERING OF VOLCANIC ASH AND PUMICE, RESULTING IN FORMATION OF HYDRATED HALLOYSITE[1]

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Abstract

The discovery of differential weathering of volcanic ash and pumice on a slope of Mt. Aso made it possible to study the quantitative aspects of the temperate, humid weathering of volcanic materials and the resulting formation of clay minerals. Mineral fractionation was made on relatively fresh and weathered portions. The results indicate that the relative stability of primary minerals to weathering increases in the following order:

volcanic glass < feldspar ≦ hypersthene-augite < magnetite,
(andesine-labradorite)
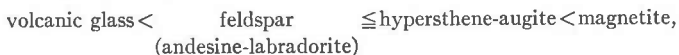
and that the dominating weathering sequence is

volcanic glass, feldspar→allophane→hydrated halloysite.

The differential weathering resulted in sporadic formation of hydrated halloysite, whereas the remaining portion remained at an allophanic stage.

Chemical analysis of the corresponding portions has shown that the process is a desilication together with remarkable loss of bases. Al and Fe remain essentially static in the system.

X-ray, differential thermal analyses and electron microscopic observations were carried out with the respective clay fractions. The allophanes exhibit rather high silica-alumina ratios, nearly two. On the other hand, the hydrated halloysites reach their dehydroxylation peak at lower temperatures and resist dehydration more strongly than do typical hydrated halloysites of hydrothermal origin. The amount of "excess hydrogen" is remarkably high in the allophanes, and may have a bearing on the stability of 1:1 layer structure.

The pH and concentrations of Si and Al were determined by placing the respective portions in acid and alkaline solutions. The results indicate that the formation of clay minerals is proceeding in the range of pH 5.3–5.4 under an ample supply of Si in either allophanic or halloysitic portions. Field observations together with laboratory analyses suggest that some differences in leaching and biotic activities act as causes of the differential weathering.

Introduction

As products of volcanism that extended from the Pleistocene to the present, volcanic ash and pumice deposits cover many hillsides and plains over some 3,000,000 hectares of Japan, commonly interstratified with buried soil layers. Extensive studies have been carried out on these volcanic formations to identify clay minerals and to deduce a weathering sequence of the minerals under temperate, humid conditions (*e.g.,* Kanno, 1959; Sudo, 1959; Tsuchiya and Kurabayashi, 1958; Aomine

[1] As to the nomenclature of halloysite minerals, the recommendations made by MacEwan (1947) and Brindley (1961) will be followed in this article.

and Jackson *cited in* Aomine, 1957). A process of alteration:

volcanic glass, feldspar→allophane→hydrated halloysite→metahalloysite
(+gibbsite)
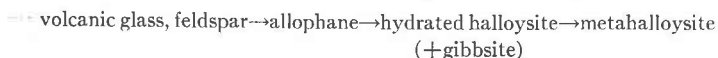
has been generally regarded as a most probable westhering sequence leading to the formation of hydrated halloysite. A similar conclusion was also drawn from studies on weathering of volcanic ash in New Zealand (Fieldes and Swindale, 1954; Fieldes, 1955). An implicit assumption in these studies is that chemical weathering of volcanic materials increases with depth, which constitutes a measure of the weathering time since deposition. This might be correct at a megascopic level, but other factors often overshadow its effect as illustrated in the profile described here (Table 1).

A discovery of differential weathering of volcanic ash and pumice,

TABLE 1. PROFILE DESCRIPTION

Depth (cm)	Parent material	Color[1]	Clay minerals[2]		Water-soluble SiO_2 (mg/100g oven-dry matter)[3]
			Allophane	Hydrated halloysite	
0– 30	Volcanic ash	bk.	+	−	9.1
30– 80	Volcanic ash	br.	+++	−	28.3
80– 90	Volcanic ash	y. gr.	+	−	—
90–140	Volcanic ash	dk. br.	+++	?	—
140–190	Volcanic ash	bk.	+++	+	25.5
190–220	Volcanic ash	dk. br.	+++	+	31.5
220–270	Volcanic ash	bk.	+	+++	29.8
270–440	Volcanic ash	lt. br.	++	−	28.4
440–450	Volcanic ash	lt. br.	++	−	22.4
450–510	Volcanic ash	lt. br.	++	−	25.2
510–570	Volcanic ash	dk. gr. br.	?	++	18.1
570–580	Volcanic ash	dk. gr. br.	?	++	12.7
580–630	Volcanic ash	dk. gr. br.	?	++	12.9
630–680 (VA)	Volcanic ash	br.	+	−	13.6
630–680 (VH)	Volcanic ash	br. y.	+	+++	19.4
680–695	Volcanic ash	y. br.	?	+++	17.5
695–765 (PA)	Pumice	red, y.	++	−	23.9
695–765 (PH)	Pumice	y.	+	+++	20.9
765–795	Volcanic ash (+pumice)	dk. br.	?	+++	26.7

[1] bk, black; br; brown; y; yellow; dk, dark; lt, light; gr, grayish; red, reddish; y, yellowish.

[2] Estimation by differential thermal analysis (Analyst; T. Higashi).

[3] Determination by N. Yoshinaga (Solid water ratio, 1:10).

however, has made possible another approach to the problem, based on quantitative information on the mineralogy and chemistry of mineral transformations. Differential weathering is defined as the process by which different sections of a rock mass weather at different rates (Leet and Judson, p. 93, 1960). Unequal rates of weathering are caused by local variations either in the composition of the rock itself or in the intensity of weathering. The differential weathering of pumice deposits was first found by the senior author at Choyo, Aso County,[1] and later by several investigators at several localities in Japan (Kuwano and Matsui, 1957; Kanno, 1959). In these deposits it was found that hydrated halloysite forms locally, while the remaining portion still remains at an allophanic stage of weathering. Since there seems no apparent variation in the composition of the parent materials from one section to another, these provide excellent samples to study the quantitative aspects of mineral transformations in these volcanic materials. In addition to their close relationship in genesis, allophane and hydrated halloysite as weathering products are interesting, in general, in view of their probable transition in crystal chemistry as constituting endmembers of low crystallinity in the kaolin group minerals.

OCCURRENCE

The profile studied consists of a series of volcanic ash and pumice deposits, located at Tochinoki on a western slope of the central cone of Mt. Aso. As shown in Table 1, formation of hydrated halloysite tends to proceed as a function of depth, but evidently there are a few exceptions indicating that the rate of its formation is also affected by some factors other than mere weathering time, such as differences of source materials in texture, chemical and mineralogical composition, and in the period of surface weathering.

Differential weathering occurs in a volcanic ash layer at a depth of 630 to 680 cm (Fig. 1) and also in a pumice layer at a depth of 695 to 765 cm (Fig. 2). These layers consist of two portions which are quite different in appearance and texture; materials in the first portion are apparently less weathered and are more brownish or reddish (Table 1), whereas the second portion consists of yellowish white clay masses which vary in size and shape from tiny granules as small as a grain of pumice to a large block as shown in Fig. 2. Also there is a tendency for the latter to form as veins either parallel with the underlying contact (Fig. 2), or vertically along a channel (Fig. 1), which is possibly a vestige of plant root that provided a passage for water. The appearance of brownish

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[1] Read at Annual Meeting of the Society of the Science of Soil and Manure, Japan, April, 1954.
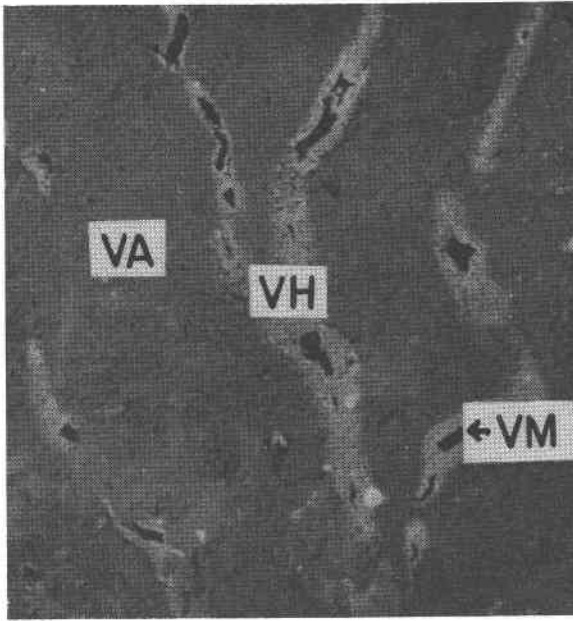
Fig. 1. Differential weathering in a volcanic ash layer at Choyo, Aso County, Kumamoto Prefecture. VA: relatively fresh, allophanic portion; VH: relatively weathered, halloysitic portion; VM: manganese oxide concretions. Width of section is 5 inches.

black to black materials in spherical forms or in streaks is another megascopic characteristic of the white clay portions.

In this article, for convenience of description, VA and PA will denote the relatively fresh (allophanic) portions of the volcanic ash and pumice layers respectively, whereas VH and PH will denote the corresponding weathered (halloysitic) portions, respectively (Figs. 1 and 2); VM will denote the brownish black to black (manganese oxide) concretions appeared in VH (Fig. 1).

LABORATORY ANALYSES

Mineral fractionation

Samples taken from VA, VH, PA and PH were air-dried, crushed lightly with a wooden pestle and passed through a 2-mm sieve. Fractionation was carried out in duplicate with 10 g of each sample, resulting in size and mineral fractions as summarized in Table 2. Extractable iron and aluminum oxides, and silica along with organic matter were removed by treatment with sodium dithionite-citrate-bicarbonate and with sodium carbonate (Jackson, p. 47–95, 1956). Size-fractionation was
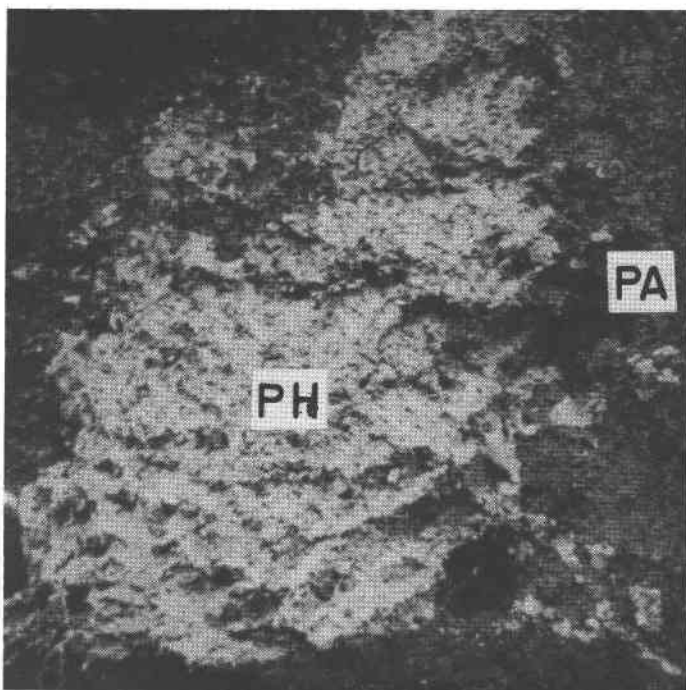
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Fig. 2. Differential weathering in a pumice layer at Choyo, Aso County, Kumamoto Prefecture. PA: relatively fresh, allophanic portion; PH: relatively weathered, halloysitic portion. Width of section is 16 inches.

carried out by sieving ($>200\mu$) and by repeated sedimentation of dispersed materials ($<200\mu$). Specific gravity separations at 2.60 and 2.80 were made with 0.5 g of $>20\mu$ fractions by means of a simple pointed centrifuge tube using tetrabromoethane-benzene mixtures. Electromagnetic separation was further carried out with heavy fractions.

Mineralogical analyses

(a) Clay minerals

Minerals falling into $<20\mu$ fractions were identified by means of x-ray diffraction and differential thermal analyses. The main constituents of these fractions are allophane and hydrated halloysite (Table 2). There was no detectable 2:1 minerals that could be identified from x-ray patterns of oriented specimens preheated at 550° C. and boiled in 0.5 N NaOH (Hashimoto and Jackson, 1960). Allophane and volcanic glass are here defined simply as an x-ray amorphous material in $<2\mu$ and $>2\mu$ fractions respectively, because differentiation of allophane from

TABLE 2. MINERAL CONSTITUENTS AND THEIR SIZE DISTRIBUTION
(% OVEN-DRY BASIS)

Size fraction	Magnetite	Hyp.-Aug.[1]	Feld.[2]	Glass-Allo.[3]	H.H.[4]	Total
			VA			
<2μ	—	—	0	7.3	0	7.3
2–5	—	—	0.3	6.4	0	6.7
5–20	—	—	1.1	7.1	0	8.2
20–200	1.65	8.3	14.1	30.8	0	54.9
>200	0.31	3.3	8.0	9.5	0	21.1
Total	1.96	11.6	23.5	61.1	0	98.2[5]
			VH			
<2μ	—	—	0	9.5	22.0	31.5
2–5	—	—	0.8	6.3	7.6	14.7
5–20	—	—	0.7	4.0	8.9	13.6
20–200	2.23	9.6	7.4	6.1	5.3	30.6
>200	0.32	2.6	1.4	1.2	0.9	6.4
Total	2.55	12.2	10.3	27.1	44.7	96.8[5]
			PA			
<2μ	—	—	0	7.2	0	7.2
2–5	—	—	0	15.0	0	15.0
5–20	—	—	0	12.2	0	12.2
20–200	0.83	1.55	4.4	13.2	0	20.0
>200	0.24	2.45	20.3	18.6	0	41.6
Total	1.07	4.00	24.7	66.2	0	96.0[5]
			PH			
<2μ	—	—	0	8.1	27.0	35.1
2–5	—	—	0	2.9	9.9	12.8
5–20	—	—	0.5	2.1	7.0	9.6
20–200	1.33	2.30	10.6	0.5	4.7	19.4
>200	0.21	1.16	9.8	7.3	0	18.5
Total	1.54	3.46	20.9	20.9	48.6	95.4[5]

[1] Hypersthene-augite:

VA-VH . . . Hyp.:Aug.=8:2; PA-PH . . . Hyp.:Aug.=5:5.

[2] Feldspar: andesine-labradorite.

[3] Volcanic glass (acidic)—allophane:

VA-VH . . . Includes transparent, colorless to dark brown species; $n=1.51$, ca. 95%; $n=1.515$, ca. 5%, and rock fragments.

PA-PH . . . Includes transparent, colorless to dark brown species; $n=1.52$, and pumice fragments.

[4] Hydrated halloysite.

[5] Does not include silica, alumina and iron oxide dissolved during segregation treatments.

volcanic glass is not feasible. The amount of hydrated halloysite was estimated by means of x-ray diffraction analysis using quartz as an internal standard and a Yoake halloysite of hydrothermal origin (Aomine and Higashi, 1956) as a reference halloysite, in which the diffraction maxima at 4.44 Å of halloysite (02, 11) and 4.21 Å of quartz were compared. A small amount of feldspar in some fractions $(2-20\mu)$ was also estimated by means of x-ray analysis; a PH fraction of $20-200\mu$ and s.g. 2.60-2.80 was used after grinding, as a reference material for feldspar. The remaining portion of each fraction was allocated to allophane or volcanic glass according to particle size.

Differential weathering was most conspicuous in the species and contents of clay minerals; no hydrated halloysite was detected in VA and PA, whereas allophane was a common constituent throughout the weathered materials (Table 2). X-ray diffraction patterns and differential thermal curves of the clay fractions are summarized in Tables 3 and 4, respectively. Detailed examination of these data reveals that the hydrated halloysites as weathering products are possibly intermediate between typical allophane and hydrated halloysite; their diffraction intensity ratio of $(001)/(02, 11)$ is relatively high, and dehydroxylation as well as recrystallization occurs at lower temperatures in comparison with

TABLE 3. X-RAY ANALYSIS DATA FOR CLAY FRACTIONS $(<2\mu)$ IN WEATHERED VOLCANIC ASH AND PUMICES

VA		VH		PA		PH	
dÅ	I	dÅ	I	dÅ	I	dÅ	I
		10.0	45			10.0	30
		4.40[1]	18			4.40[1]	17
3.5	6	3.30	10	3.3	6	3.33	7
3.21[2]	4						
		2.51	7			2.51	6
		1.48	4			1.48	4

$I_{(10.0A)}/I_{(4.40A)}$

VH		PH		Hydrothermal hydrated halloysite (Yoake)	
2.5	1.2[3]	1.8	0.9[3]	1.1	0[3]

[1] Low-angle termination for (02, 11) diffraction.

[2] Due to the presence of weathered feldspar.

[3] After standing at R.H. 35% for 2 weeks.

TABLE 4. DIFFERENTIAL THERMAL PEAKS FOR CLAY FRACTIONS ($<2\mu$)
IN WEATHERED VOLCANIC ASH AND PUMICES (° C.)

Reaction	VA	VH	PA	PH	Hydrothermal hydrated halloysite	
					Yoake[1]	Joshin[2]
Dehydration	155	150	155	150	130	135
Dehydroxylation	—	530	—	530	570	570
Rearrangement	950	940	920	940	960	970

[1] Aomine and Higashi (1956).
[2] Sudo and Takahashi (1956).

hydrothermal hydrated halloysites. Similar relationships between x-ray and differential thermal analyses data were obtained for halloysitic clays altered from glassy tuffs by Sudo and Takahashi (1956) and interpreted in terms of a low degree of crystallinity of these hydrated halloysites. Another indication of their poor crystallinity is that the halloysitic clays in VH and PH tend to resist dehydration more strongly; the 10.1 Å diffraction remains after allowing the samples for two to three weeks at R.H. 35 per cent, whereas those of hydrothermal origin dehydrate readily under the same condition. Generally, the stability of water complexes of kaolin minerals from kaolinite to halloysite has been shown to increase with increasing randomness of stacking of their structural layers (Wada, 1961).

The clay fractions of VH and PH were estimated to contain 70 and 77 per cent of hydrated halloysite, respectively. Since its crystallinity has been indicated to be low, these estimates can be considered probably as the lowest ones.

The allophane derived from the volcanic ash exhibits finely fibrous forms (Fig. 3), such as those reported in some Ando soils (Aomine and Yoshinaga, 1955), whereas allophane from pumice is in ordinary rounded forms. The size of the latter particles does not exceed 70 mμ in diameter in a well-dispersed state. On the other hand, spherules of 200 to 250 mμ in diameter, associated with very thin, curled laths (Fig. 4), predominate in both the VH and PH clay fractions. The presence of a small amount of allophane as indicated by means of x-ray analysis is confirmed by the less common appearance of fine granules and fibrous materials. Concentric striations appeared on nearly all the spherules parallel with somewhat polyhedral outlines, suggesting that these are largely aggregates of curled laths of hydrated halloysite. Similar observations were made on
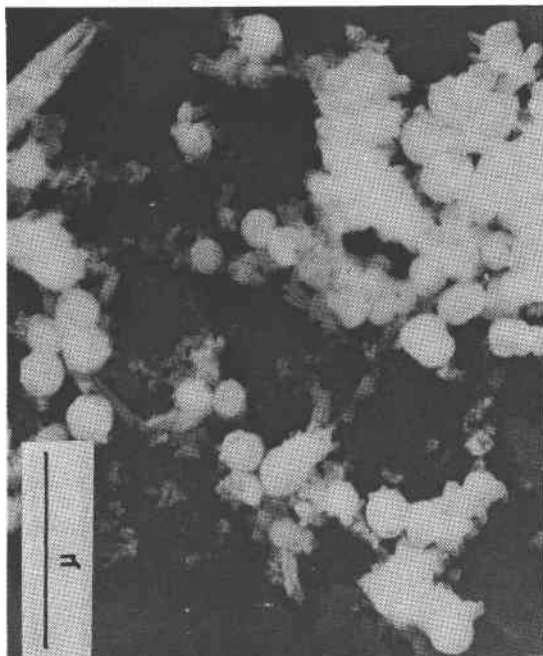
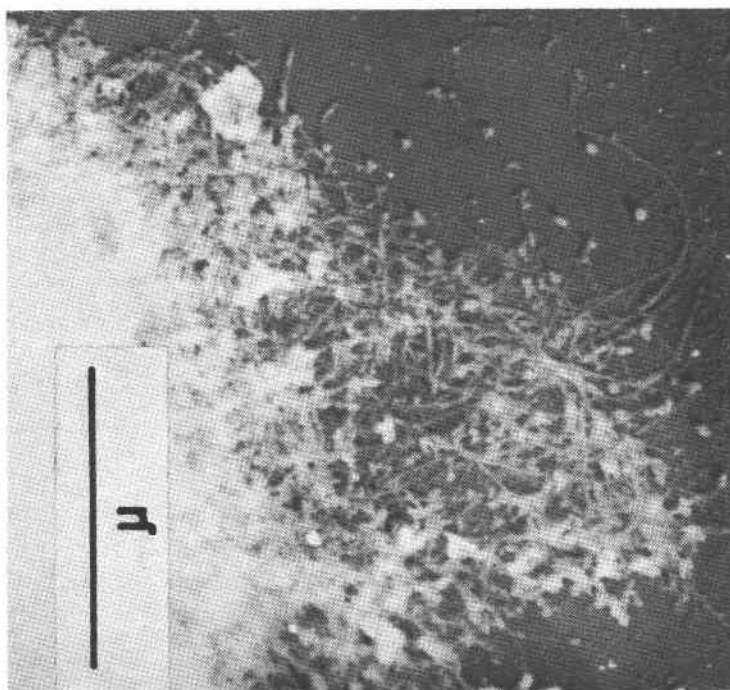Fig. 4. Electron micrograph of VH clay fraction (by T. Higashi).

Fig. 3. Electron micrograph of VA clay fraction (by T. Higashi).

some hydrated halloysites derived from volcanic materials by Birrel *et al.* (1955). Sudo and Takahashi (1956) and Sudo (1959) studied this structure in detail and treated it as a morphological transition in the process of crystallization of allophane to hydrated halloysite. Bates (1958) published a replica of similar spherules but described them as allophane.

(b) Primary minerals

A brief description of minerals in the lighter fractions is given in the footnote to Table 2. In cases where the separations of glass from feldspar were achieved with difficulty the percentages of these minerals were checked by microscopic counting and x-ray diffraction analysis. The latter method also permitted a check of the presence of hydrated halloysite in some lighter fractions (Table 2). Its persistence in "large size fractions," after dispersion treatments in fractionation, suggests that hydrated halloysite forms *in situ*, remaining as a kind of pseudomorph after volcanic glass or feldspar rather than forming secondary aggregates. Actually, microscopic observation of thin sections indicated that original glass fragments were filled with a number of fine granules. The approximate index of refraction of these halloysites, after drying at 105° C., is 1.53–1.55.

The weights of the heavy non-magnetic and magnetic fractions were taken as the amount of hypersthene plus augite, and of magnetite, respectively.

A similarity in the relative proportions of some primary minerals, such as magnetite, hypersthene, augite and feldspar may give further confirmation of the similarity of parent material in either VA and VH or PA and PH. The mineral compositions as a whole are indicative of an andesitic origin of these materials.

Chemical analyses

(a) Chemical analysis of bulk samples and clay fractions

Two 0.5 g samples were used for chemical analysis. The weight loss between 110° C. and 950° C. was taken as H_2O (+). In one of two samples SiO_2 was determined gravimetrically after fusion with Na_2CO_3; CaO and MgO were determined titrimetrically with EDTA. In the other sample, decomposed with a $HF-H_2SO_4$ mixture, Al_2O_3 and Fe_2O_3, TiO_2, MnO, and P_2O_5 were determined colorimetrically using "Ferron," H_2O_2, periodate and vanadomolybdate, respectively; K_2O and Na_2O were determined by means of flame photometry.

Chemical compositions of the bulk samples are shown in Table 5. The results indicate that the process of differential weathering as a whole is desilication together with the loss of bases, provided Al remained

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TABLE 5. CHEMICAL COMPOSITION OF WEATHERED VOLCANIC ASH AND
PUMICES (% OVEN-DRY BASIS)

	VA	VH	VM	PA	PH
SiO_2	49.99	43.14	35.61	51.80	45.70
Al_2O_3	20.62	26.03	26.28	22.91	28.20
Fe_2O_3	8.75	10.99	9.88	5.89	6.93
TiO_2	1.31	1.44	0.72	1.13	1.43
MnO	0.10	0.11	6.79	0.09	0.13
P_2O_5	0.41	0.27	—	0.23	0.17
CaO	4.68	2.13	—	3.42	2.70
MgO	2.88	2.63	—	0.98	0.89
K_2O	1.45	0.78	—	1.79	0.75
Na_2O	2.80	1.08	—	2.90	1.71
H_2O (+)	6.99	11.35	—	8.78	10.35
Total	99.98	99.95	—	99.92	98.96

constant during weathering. This is a common assumption in determining gain or loss of some elements in the weathering of silicate rocks and is also valid for the present systems as will be shown later.

In addition the results of chemical analysis seem to be in accord with those from the mineralogical analysis; the higher contents of Fe_2O_3 and MgO in the weathered volcanic ash as compared to those in the pumices reflect the higher content of mafic minerals in the former (Table 2). The fact that the amount of H_2O (+) is generally great even in VA and PA indicates that internal weathering occurs to a considerable extent in volcanic glass.

A high MnO content in VM evidently indicates that manganese oxides cause the brownish to black color in the concretions found in the halloysitic portions (Figs. 1 and 2). Since x-ray diffraction analysis of these concretions failed to detect any crystalline manganese oxides and revealed merely the presence of hydrated halloysite, they seem to be clay aggregates cemented together mainly by amorphous manganese oxides.

The chemical compositions of clay fractions ($<2\mu$) of the weathered volcanic ash and pumices are shown in Table 6. The relative proportion of framework elements, Si and Al, is very close to that for ideal kaolin minerals and is not much different between the corresponding allophanic and halloysitic fractions. The high Na_2O content of these clay fractions resulted from a treatment in 2% Na_2CO_3 at a pH of 10.5 in their preparation for study. The fact that the CEC of allophane is largely affected by past acid or alkali treatments has been described by Aomine and Jackson (1959) and interpreted in terms of the development of negative charge

through increasing dissociation of H^+ from Si-OH groups of allophane with increasing pH. On the basis of similar reasoning, it is likely that the poorly crystallized "end-members" of hydrated halloysite exhibit high CEC in an alkaline solution. Thus the figures may give estimates for CEC as well as for the amount of dissociable H^+ at pH 10.5 in the form of Si-OH.

Relatively high Fe_2O_3 contents in VH and PH fractions may be subject to question. Advanced weathering in these portions and the immobility of Fe as a whole should result in its accumulation in their finer fractions. However, Fe in these fractions was no longer dissolved by further deferration treatments (Jackson, p. 47, 1956), indicating that Fe is not in ordinary "free iron oxides." Whether some octahedral Fe^{3+} ions are present in the hydrated halloysites or whether Fe forms principally a separate phase as the result of segregation during the course of crystallization of hydrated halloysite is an interesting problem itself, but it remains to be solved in further works.

(b) Determination of pH, concentrations of Al and Si in acid and alkaline salt solutions

The pH and concentrations of Si and Al were determined by placing VA and VH in acid and slightly alkaline solutions. Each of five to six

TABLE 6. CHEMICAL COMPOSITION OF CLAY FRACTIONS ($<2\mu$) OF WEATHERED VOLCANIC ASH AND PUMICES (% OVEN-DRY BASIS)

	VA	VH	PA	PH
SiO_2	37.57	42.17	38.54	41.23
Al_2O_3	33.80	33.89	33.36	34.02
Fe_2O_3	2.21	3.84	1.30	4.22
TiO_2	1.34	0.94	1.88	1.02
MnO	tr.	tr.	tr.	tr.
P_2O_5	0.38	0.06	0.56	0.25
CaO	0.12	0.10	0.09	0.03
MgO	0.20	0.14	0.15	0.03
K_2O	0.32	0.33	0.19	0.18
Na_2O[1]	7.09	3.36	7.46	4.79
H_2O (+)	16.52	14.58	16.36	14.55
Total	99.55	99.41	99.89	100.32
Na[1] (me/100g)	229	108	241	154
CEC at pH 7.0[2]	—	—	67	39

[1] Na saturated at pH 10.5 in a hot 2% Na_2CO_3 solution.

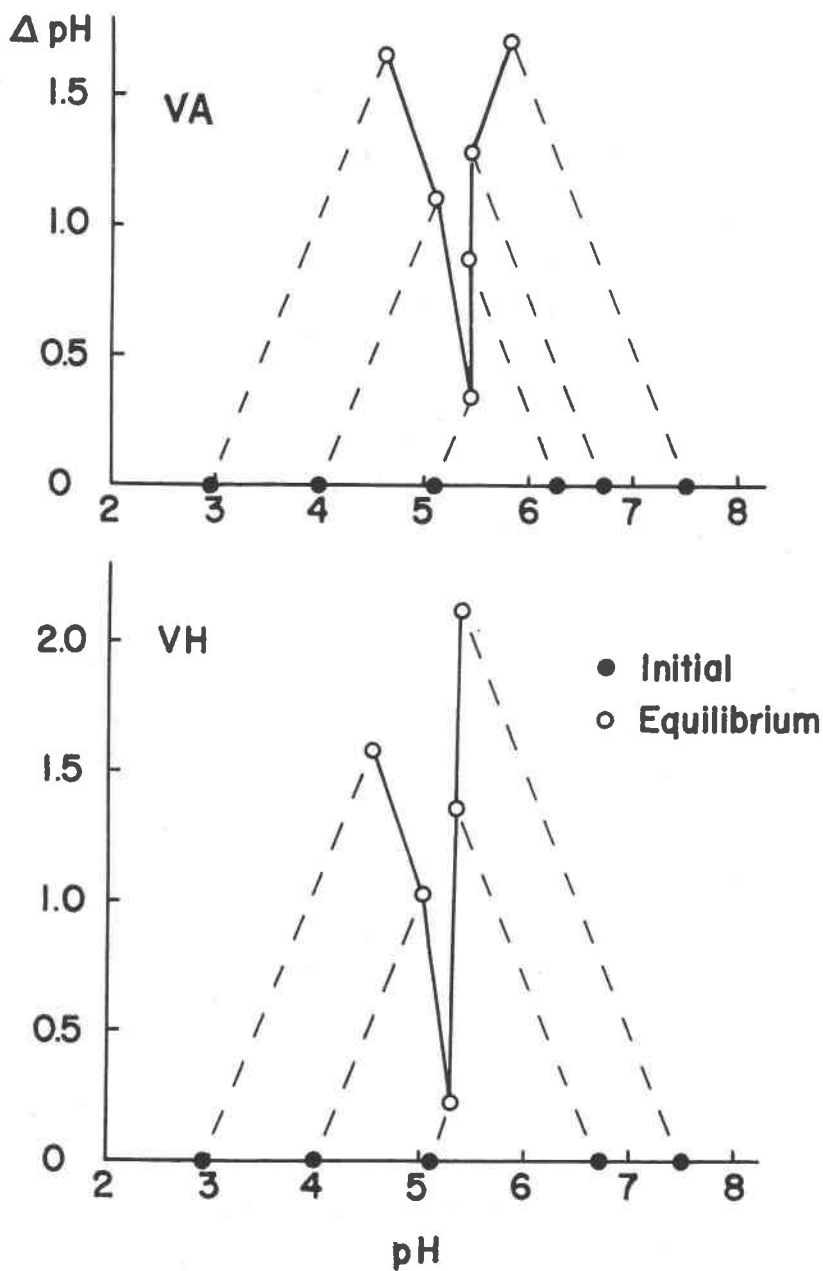[2] Wada, (1959).

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FIG. 5. Changes in pH values of VA and VH suspensions in
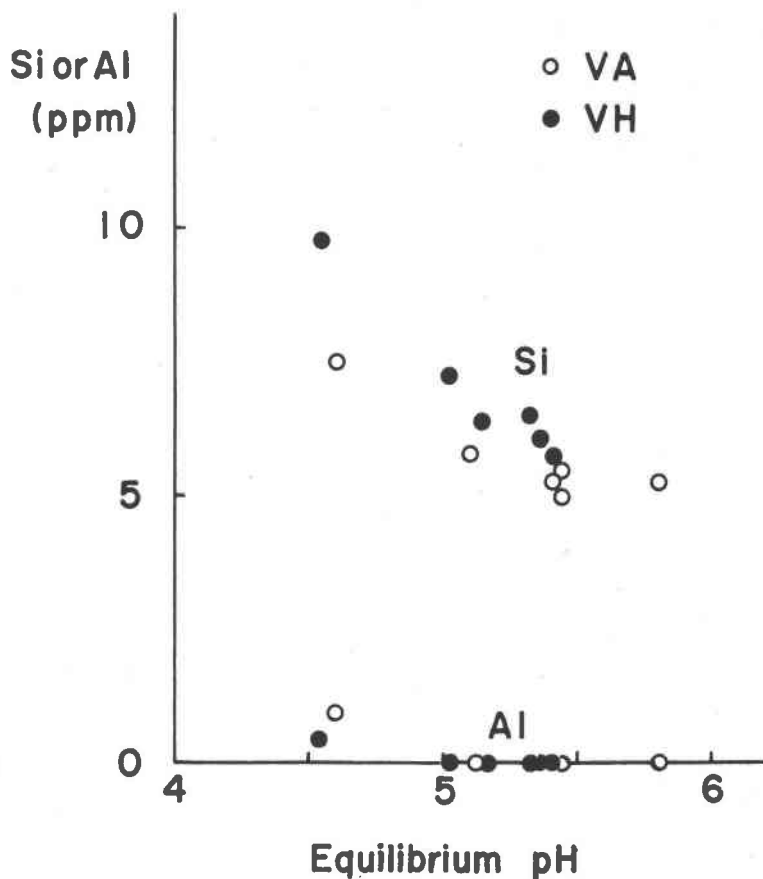0.05 N NaCl solution after shaking 24 hours.

Fig. 6. Concentrations of Si and Al in VA and VH suspensions
in 0.05 N NaCl solution after shaking 24 hours.

10 g samples of the air-dried materials was placed in 100 ml of 0.05 NaCl solutions, the pH values of which were adjusted with HCl and NaOH in the range of pH 3 to 7.5. After 24 hours shaking on a reciprocating shaker, the pH values, Si and Al, were determined with supernatants obtained by centrifugation.

The shift of pH values upon suspending VA and VH samples in dilute, acid and alkaline NaCl solutions is shown in Fig. 5. No change would be expected at pH 5.3–5.4 in either VA or VH systems. The reaction involved is neither simple dissolution nor ion exchange on clay surface; in suspensions more acid than pH 5.3, simultaneous determination of Si and Al in the supernatant shows that Si and Al dissolve to an appreciable extent (Fig. 6). The upward shift of pH values may occur as the result

of dissolution of Al as well as OH release through anion-exchange reaction of allophanic components (Wada and Ataka, 1958). In suspensions more alkaline than pH 5.4, the downward shift of pH values may be interpreted as an effect of dominating H^+ release through cation-exchange reaction. In any event, the dip in the curves suggests that the formation of clay minerals proceeds in the range of pH 5.3 to 5.4 in both allophanic or halloysitic portions.
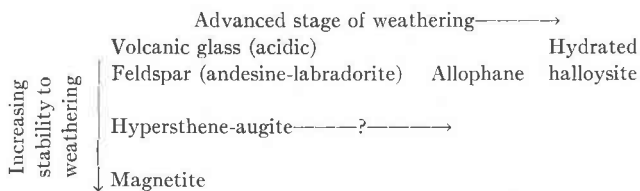
The dissolution of Si and Al suggests that pH 5.3 to 5.4 nearly corresponds to the extreme acid pH of the minimum solubility range of the elements in the present weathering systems, in which the behavior of Si is modified by the presence of Al. In pure water systems, the solubility of Si is almost constant up to pH 8, and then increases abruptly with pH (Alexander *et al.* 1954).

In conclusion, it seems important to bear in mind that essentially there is no significant difference in chemical conditions prevailing in VA and VH for clay formation.

DISCUSSION

Weathering sequence

Differential weathering that appeared in the mineral composition was evaluated by assuming that magnetite is most resistant to weathering in the systems (Fig. 7). On the basis of the rate of loss or gain of each of the various minerals, one might deduce the following weathering sequences of the minerals:

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                          Advanced stage of weathering————→
                      Volcanic glass (acidic)                      Hydrated
         ┌────┐     │ Feldspar (andesine-labradorite)   Allophane  halloysite
Increasing │    │     │
stability to │   weathering │
weathering │    │     │ Hypersthene-augite————?————→
         └────┘     │
                    ↓ Magnetite
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The weathering sequences of the primary minerals involved has been discussed by various investigators (reviewed in Jackson and Sherman, 1953). Those pertinent to the present system may be cited as follows in the order of increasing stability to weathering:

1) *Basic volcanic glass*, olivine, *hypersthene*, biotite, *augite*, amphibole, anorthite, epidotite, bytownite, *andesine*, oligoclase, muscovite, garnet, orthoclase etc. (Marel, cited in Jackson and Sherman, 1953)

2) Olivine, *augite*, *hypersthene—volcanic glass (basic)*, zeolite—biotite, muscovite—*volcanic glass (acidic)*, *feldspar*—quartz (Fieldes and Swindale, 1954).

The present results deserve attention with respect to the following points:

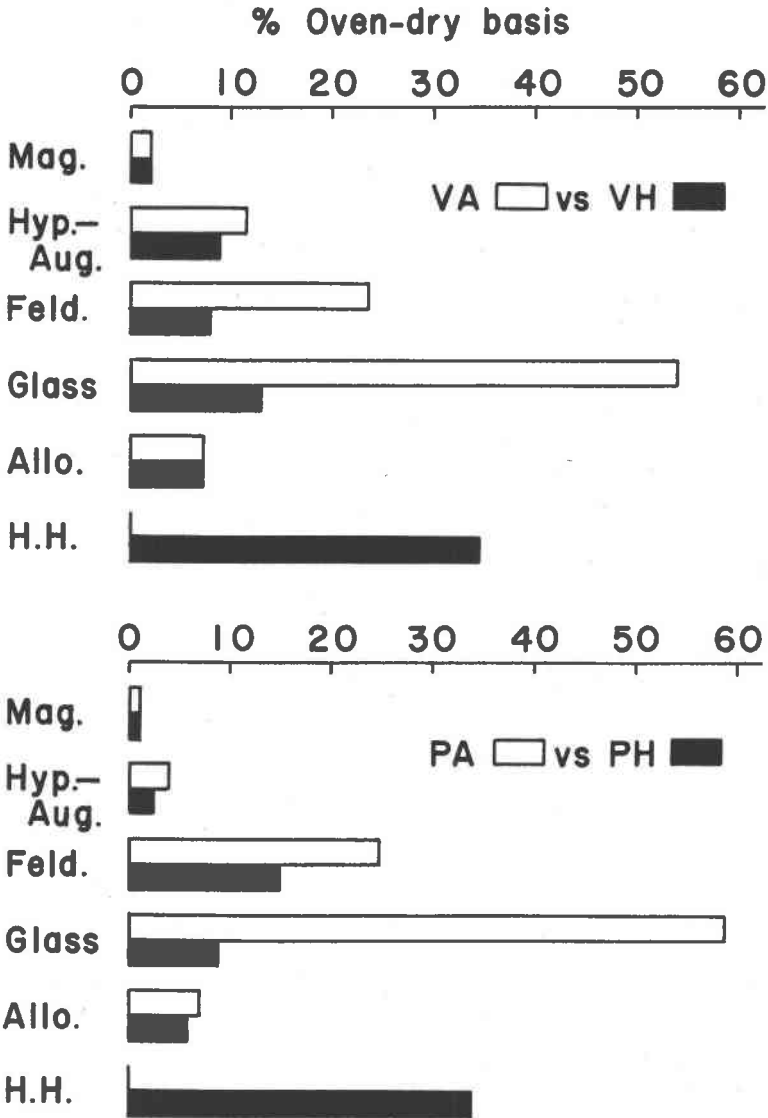1) Although Fieldes and Swindale (1954) tentatively approximated

FIG. 7. Changes in mineralogical composition upon differential weathering.

volcanic glass with feldspar, the relative stability of acidic volcanic glass to weathering remains undetermined. In view of the present results, however, it is evident that acidic volcanic glass weathers much faster than feldspar and even faster than either hypersthene or augite. The least stability of basic volcanic glass has already been indicated by Marel.
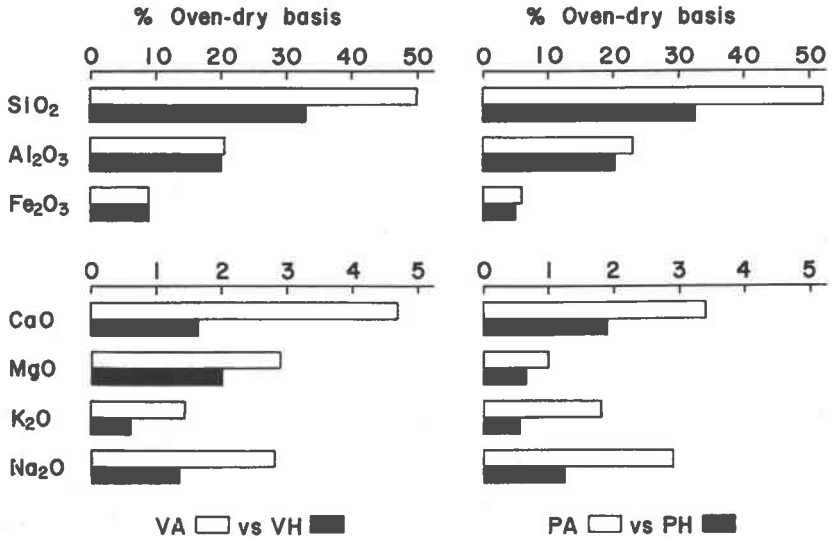
Fɪɢ. 8. Changes in chemical composition upon differential weathering.

This illustrates that the amorphous nature of volcanic glass, either basic or acidic, dominates the situation.
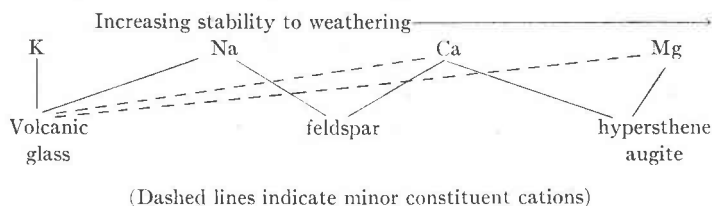
2) Usually hypersthene and augite are supposed to weather much faster than feldspar. The percentage loss of the respective minerals, however, indicates that the rate of weathering is higher in feldspar or not much different, even when the feldspar is not extremely calcic.

With regard to the secondary minerals the results support the common view that hydrated halloysite represents a more advanced stage of weathering than does allophane under temperate, humid conditions. Under tropical, humid conditions, however, the allophanic stage has not been demonstrated in the weathering transition from primary to kaolin minerals whereas the presence of another allophane was noted as an intermediate product between halloysite or kaolinite and gibbsite (Tamura *et al.*, 1953, 1955; Bates, 1960).

The changes in chemical composition during differential weathering can be evaluated on the basis of the chemical analysis of the materials as a whole (Table 5), assuming again that magnetite remains essentially constant in the system. In Fig. 8 it is evident that the process as a whole is desilication together with the remarkable loss of bases. Al and Fe remained essentially constant. A close interrelationship between chemical and mineralogical weatherings can be seen in the following orders of the percentage loss of the bases and their source minerals:

VA—VH $Na_2O > CaO > K_2O > MgO$
         (70)   (65)   (59)   (30)
         volcanic > feldspar > hypersthene
           glass   augite
           (75)   (66)   (19)

PA—PH $K_2O > Na_2O > CaO > MgO$
         (70)   (58)   (44)   (36)
         volcanic > feldspar = hypersthene
           glass   augite
           (84)   (40)   (40)

The general trend may be well understood by relating each of the metallic cations to its source minerals and also to their stabilities to weathering, as postulated by mineralogical analyses:

Increasing stability to weathering⟶

K   Na   Ca   Mg

Volcanic   feldspar   hypersthene
glass   augite

(Dashed lines indicate minor constituent cations)

Apparently, there seems no fixation of released cations in the secondary clay minerals. The rate of loss of K in the VA—VH system is slightly lower than that of Na and Ca. Slight K fixation together with Mg in their clay fractions (Table 6) may suggest the presence of some 2:1 layer minerals. However the presence of such minerals was not positively confirmed by x-ray analysis.

Structural chemistry of allophane and hydrated halloysite

Although numerous studies have identified allophane and hydrated halloysite in weathered volcanic materials, their structural chemistry has not received similar attention. At present the main interest is that there are rather sharp differences between the two in crystal structure and morphology but not in chemical composition.

The number of the cations in a structure unit corresponding to a unit cell of halloysite was calculated from the chemical analyses on the basis of 18 oxygens, neglecting small amounts of P, Ca, Mg and K. All H evolved as H_2O (+) was assumed to be present in the form of (OH) and all Na to be equivalent to dissociable H^+ from (OH). Allowance for the presence of allophane in the VH and PH clay fractions was made according to the x-ray data and by assuming that the chemical composition of each of the allophanes in VH and PH is the same as that of allophane in the corresponding VA and PA portions.

TABLE 7. CATIONS PER STRUCTURE UNIT OF 18 OXYGENS

	Allophane		Halloysite	
	VA	PA	VH	PH
Si	3.39	3.48	3.96	3.77
Al	3.59	3.55	3.59	3.60
Fe	0.15	0.09	0.30	0.34
H	9.93	9.87	8.22	8.34
H^+	1.23	1.31	0.32	0.69

Table 7 gives the number of the cations resulting from this calculation. In comparison with the ideal composition of kaolinite, both Si and (Al+Fe) contents appear considerably lower in allophane, whereas the H content is considerably in excess of 8.0, even in hydrated halloysites.

According to the procedure adopted by Bates (1959), structural formulas were calculated on the basis of 18 oxygens and by adding "excess" H to the tetrahedral sheet as $(H_4)^{4+}$ along with excess O. The resulting formulas (Table 8) indicate that the transition from allophane to hydrated halloysite is continuous. The deficiency of Si, both absolute as well as relative to (Al+Fe), and the excess of H together with associated O may result in an unstable configuration of the tetrahedral sheets, and, in turn, of the 1:1 layer structure in allophane. The two factors might be related to each other. Bates (1959) pointed out that the presence of "excess" H is important in determining the morphology of 1:1 layer minerals. This is based on the study of analyses of halloysite and chrysotile that contain significantly more H_2O (+) than those of their platy counterparts. The effect of these elements was interpreted as weakening interlayer bonds to the extent that misfit of the sheets produced tubes or curved laths rather than plates. In view of the present result, the amount

TABLE 8. STRUCTURAL FORMULAS

Allophane

VA $O_{6.79}Si_{3.39}Al_{0.10}Fe_{0.07}(H_4)_{1.01}O_{2.27}$ $O_{1.78}(OH)_{1.78}Al_{3.49}Fe_{0.08}(OH)_{5.36}$

PA $O_{6.84}Si_{3.48}Al_{0.03}Fe_{0.05}(H_4)_{1.02}O_{2.28}$ $O_{1.77}(OH)_{1.78}Al_{3.52}Fe_{0.04}(OH)_{5.34}$

Halloysite

VH $O_{6.25}Si_{3.96}Al_{0.00}Fe_{0.00}(H_4)_{0.19}O_{2.05}$ $O_{1.95}(OH)_{1.94}Al_{3.59}Fe_{0.30}(OH)_{5.84}$

PH $O_{6.37}Si_{3.77}Al_{0.00}Fe_{0.15}(H_4)_{0.36}O_{2.12}$ $O_{1.89}(OH)_{1.90}Al_{3.60}Fe_{0.19}(OH)_{5.69}$

Ideal formula

$O_{6.00}Si_{4.00}Al_{0.00}Fe_{0.00}(H_4)_{0.00}O_{2.00}$ $O_{2.00}(OH)_{2.00}Al_{4.00}Fe_{0.00}(OH)_{6.00}$
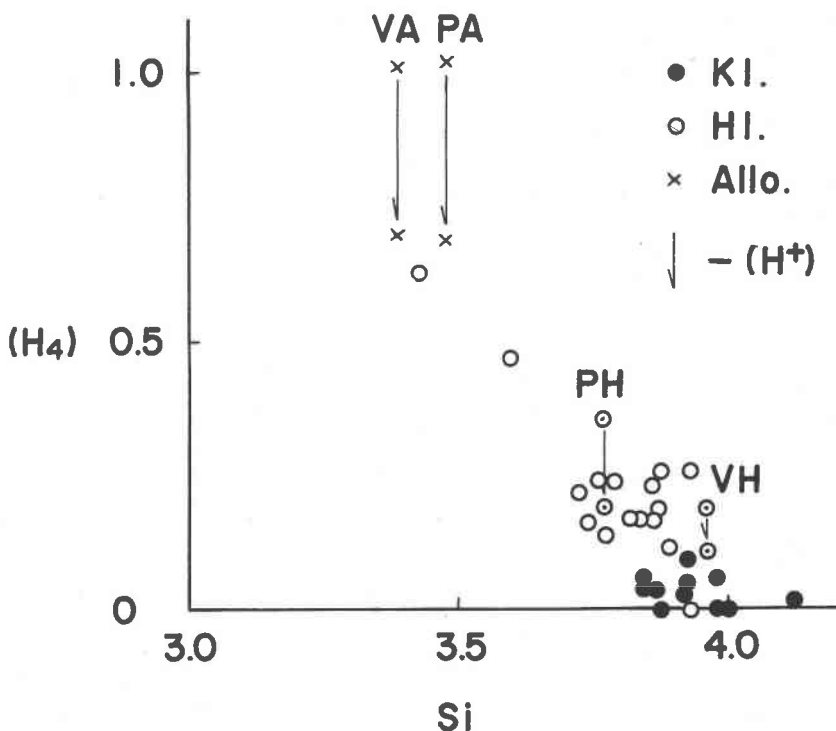
Fig. 9. Relationship between H and Si contents of kaolin
minerals per structure unit of 18 oxygens.

of H, together with that of associated O, may also be an important factor
in determining the stability of a 1:1 layer structure in the transition
from allophane to hydrated halloysite.

The assignment of "excess" H as $(H_4)^{4+}$ in the tetrahedral sheet is
merely a tentative one for this can result in some interesting relation-
ships between scattered facts:

1) The large increase of CEC of these clays in an alkaline solution (Table 6) was inter-
preted as the dissociation of H in the bonding of Si-OH (Wada and Ataka, 1958; Aomine
and Jackson, 1959).[1] The amount of this H, together with associated O, may have a bearing
on the stability of the tetrahedral sheet. The transition from allophane to hydrated halloy-
site is in the direction of decreasing amount of this dissociable H^+.

2) By assuming that the remaining "excess" H replaces Si as (H_4), forming $(OH)_4$
tetrahedra as suggested by McConnell (1950), calculation shows that the sum of the
number of $(Si+H_4)$ approaches that of Si in the ideal formula (Fig. 9). This alone proves

[1] Another explanation for development of cation-exchange site in silica-alumina gel was
proposed by Milliken *et al.* (1950). They assumed 4 coordination of Al instead of 6 at
higher pH, and claimed the Al in 4 coordinated state to act as an acid. This possibility is
not taken into consideration at present because of the lack of the actual configuration data.

neither the presence of discrete $(OH)^4$ nor 1:1 replacement of SiO_4 with $(OH)_4$, but these relationships can be seen more generally in the chemical transition from kaolinite to halloysite and possibly to allophane in the present samples (Fig. 9). The plots are made according to the data calculated by Bates (1959), except for the present samples. There seems a general tendency to increase 1:1 replacement of Si with (H_4), with increasing randomness of crystal structure in kaolin minerals. The stable regions of respective species could be designated using the number of (H_4) as a parameter.

3) The fact that the stability of the interlayer water of kaolin minerals increases toward the poorly crystalline end-members (Wada, 1961) supports the presence of some H at the surface of tetrahedral sheet of hydrated halloysite. Since dissociable H^+ was already replaced with Na^+ in the present samples, the extra stability in bonding between interlayer water and silicate layers might be ascribed at least partly to the presence of H in the form of $(OH)_4$ at the surface of the tetrahedral silica sheet.

The adoption of the interpretations presented here must await further evidences. If these views are correct, however, the chemical transition from allophane to halloysite to kaolinite can be regarded as a continuous process of dehydroxylation through condensation and replacement with SiO_4, which results in higher crystallinity of these minerals. Indeed this seems the direction of post-depositional weathering of volcanic materials under temperate, humid conditions. Although the presence of kaolinite was not known, the appearance of halloysite in dehydrated form was reported by Tsuchiya and Kurabayashi (1959) in some older volcanic ash formation in Kanto district.

The mechanism and environmental conditions for clay formation

From the foregoing the steps of the mechanism leading to the formation of hydrated halloysite may be depicted as follows:

1) Partial hydration of volcanic glass or feldspar leading to alteration of O linkage to OH and resulting in release of some Si and metallic cations.

2) Rearrangement of the remaining Al and Si together with associated O, OH, H_2O, *in situ*, forming a separate entity or remaining pseudomorphous after the original minerals. Prevailing chemical conditions adjust the composition of the resulting silica-alumina system.

3) Formation of a gibbsite-like structure with some adsorbed SiO_4 tetrahedra.

4) Replacement of OH groups by O on further addition of SiO_4 tetrahedra or on the condenstation resulting in dehydroxylation.

5) Re-orientation of SiO_4 tetrahedra.

The allophanic clays and volcanic glass in VA and PA—the latter was hydrated to a considerable extent (Table 5)—represent steps 2 to 3, whereas differential weathering has brought about formation of hydrated halloysite, probably through completion of steps 1 to 5.

Differential weathering is caused by local variations in the composition of parent materials or in the nature and intensity of weathering. Mineralogical analyses as well as field observations exclude the possibility that the former factor contributes to any appreciable extent to the

present situation. Kuwano and Matsui (1957) and Kanno (1959) suggested that stagnant, underground water plays an important part in the similar occurrence of hydrated halloysite in some pumice layers, through resilication and crystallization of allophane, apparently corresponding to step 5. Indeed the amount of Si relative to Al is slightly higher in hydrated halloysite than in allophane (Table 6; Kuwano and Matsui, 1957), and the appearance of Mn oxide concretions in halloysitic portions suggests that the water regime might have a bearing on the formation of hydrated halloysite. However, Si concentrations determined with VA and VH suspensions indicate that there is an ample supply of Si throughout the layers (Fig. 6). Furthermore, there seems no definite relationship between the formation of hydrated halloysite and water-soluble Si throughout the profile (Table 1). Determination of suspension pH also suggests that the prevailing chemical conditions are not essentially different between the corresponding portions. On the other hand, a complete breakdown of the original mineral structure should precede resilication in the formation of secondary minerals. There are rather remarkable differences in the contents of some primary minerals as well as of some metallic cations between VA and VH or PA and PH. In conclusion, it seems evident that the resilication is a necessary process leading to the formation of hydrated halloysite from allophane, but it may not cause the differential weathering. Instead, repeated renewal of fresh water, in place of the stagnation of Si-rich water, is likely the most important factor in the differential weathering and promotes the reactions in steps 1 and 2 through removal of released bases.

High permeability of most of the volcanic ash and pumice deposits in the profile and rather plentiful rainfall (annual precipitation 2923 mm vs. annual average temperature 9.1° C., Wadachi, 1958) assure that these weathering products are nearly water-saturated and that vertical movement of water occurs with great efficiency. However, there is still an indication that some difference in leaching activity might relate to the difference in the clay formation in these peculiar layers. As already described in the field occurrence, the formation of hydrated halloysite took place locally along a vertical channel, or horizontally along a boundary with an underlying, less permeable layer. In either case the leaching activity would be significantly higher in these places than in other parts and continuous for a longer period after deposition.

In connection with this, the presence of brownish black to black manganese oxide concretions is also another indication of the extra leaching activity; the transportation of Mn, together with Fe and Al in smaller amounts, occurs for some distance along with formation of hydrated halloysite. In addition, it has been known that humic complexes and micro-

organisms are important in the transportation of this element, through chelation and oxidation to higher oxides (Leeper and Swaby, 1940; Leeper, 1947; Rankama and Sahama, p. 647, 1950). *Vice versa*, the observed accumulation of Mn together with Fe and Al in the halloysitic portions might indicate that some biotic effects contribute to some extent to the observed difference in weathering. Corroborative evidence for this concept was obtained upon removal of extractable iron oxides with sodium dithionite-citrate-bicarbonate (Jackson, p. 47, 1956); the color of the extract due to the presence of some organic matter is much stronger in the halloysitic portions than in the corresponding allophanic portions, although the nature and properties of this organic matter are not yet clear. The rapid segregation of Mn from the reaction system may help crystallization of hydrated halloysite from the decomposition products of primary minerals.

CONCLUSIONS

The differential weathering of volcanic ash and pumice has resulted in local formation of hydrated halloysite, whereas the remaining portion still remains at an allophanic stage of weathering. The morphological and structural characteristics together with the chemical composition of the respective clay fractions indicate that these species represent intermediates between typical allophane and hydrated halloysite. Chemically, the weathering is a process of desilication together with a remarkable loss of bases. Aluminum and iron remain essentially static during weathering. The chemical transition from allophane to hydrated halloysite can be regarded as a continuous process of dehydroxylation through condensation and replacement with silica tetrahedra.

The cause of the differential weathering is still not evident. The major chemical conditions, such as pH, Si and Al concentrations of the systems, may not differ significantly between allophanic and halloysitic portions. However the mode of the occurrence of the latter clay together with corroborative analytical evidence suggests that local variations in leaching activity associated with some biotic effects contribute largely to the differential formation of hydrated halloysite.

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