

## EFFECT OF $\text{SiO}_2/\text{Al}_2\text{O}_3$ RATIO ON THE THERMAL REACTIONS OF ALLOPHANE

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**Abstract**—Differences were found in the differential thermal analysis curves and in the temperatures of new-phase development between allophanes of high (1.91–1.99) and low (1.47–1.53)  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. The endothermic peak due to continuous dehydration and dehydroxylation was at higher temperatures (153°–185°C) for allophanes with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios and at lower temperatures (148°–165°C) for those with low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. The temperature of the exothermic peak was lower and the height affected more by the exchangeable cation content for allophanes with high ratios than for those with low ratios. New phases did not develop in allophanes having high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios even after they were heated to 1000°C, above the temperature of the exothermic peak. In contrast, a symptomatic development of new phases was noted in allophanes with low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios at 900°C, below the temperature of the exothermic peak. The effect of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in the thermal behavior of allophane strongly suggests that differences in the structure are closely associated with the chemical composition of this material.

**Key Words**—Allophane, Dehydration, Dehydroxylation, DTA, Silica/alumina ratio, Thermal reactions.

### INTRODUCTION

In differential thermal analysis (DTA), allophane generally shows a broad endothermic peak between 100° and 300°C and an exothermic peak between 800° and 1000°C due to continuous dehydration and dehydroxylation, and to the formation or nucleation of mullite and/or gamma-alumina, respectively (Mitchell *et al.*, 1964; Wada and Harward, 1974; Fieldes and Claridge, 1975; Wada, 1977). The DTA curve has been shown to be susceptible to various factors. Thus, Fieldes (1955) differentiated "Allophane B" from "Allophane A" in New Zealand volcanic ash soils on the basis of the lack, or appearance of an exothermic peak near 900°C. Fieldes (1957) further mentioned that the endothermic peak of "Allophane B" tended to be lower in temperature than that of "Allophane A." Miyauchi and Aomine (1966) indicated that the exothermic peak of allophane varied in temperature, height, and area with exchangeable cation. The exothermic reaction also was observed to be affected by the method of separation or pretreatment of the material (Miyazawa, 1966; Campbell *et al.*, 1968). For amorphous silicoaluminas synthesized as analogues of allophane, the shape of the exothermic peak was correlated with their  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (Wada, 1977). As allophanes have a wide range of chemical composition, ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.0$  to 2.0; Yoshinaga, 1966; Wada and Yoshinaga, 1969; Henmi and Wada, 1976), their thermal behavior can be expected to be influenced by the chemical composition.

The present investigation is concerned with the effect of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio on the DTA curve of allophane and on the temperature at which new phases develop.

### MATERIALS AND METHODS

Fine clay fractions (<0.2  $\mu\text{m}$ ) were separated by centrifugation from weathered volcanic ash and pumice

from Japan (Table 1). Before the separation, the ash and pumice were repeatedly treated with  $\text{H}_2\text{O}_2$  to remove organic matter, gently pulverized, and dispersed by sonification at 20 kHz. X-ray powder diffraction analysis (XRD) and infrared spectroscopy (IR) showed that the fine clay separates were typical allophanes. Electron optical observation affirmed that the clays were virtually "pure" allophane and that they appeared as various size aggregates with irregular shape. Many small particles, probably consisting of hollow spherules in three dimensions, were seen as ring shapes with diameters of 35 to 50 Å in electron micrographs (see also, Kitagawa, 1971; Wada *et al.*, 1972; Henmi and Wada, 1976; Wada and Wada, 1977; Shoji and Saigusa, 1977). Only small amounts of imogolite fibers (Yoshinaga *et al.*, 1968; Wada *et al.*, 1970) were recognized in the clays; imogolite is commonly admixed in allophanes from weathered volcanic ash and pumice (Henmi and Wada, 1976). The clays were treated with sodium dithionite-citrate-bicarbonate (Mehra and Jackson, 1960) and 2%  $\text{Na}_2\text{CO}_3$  (Jackson, 1956a) and washed with 1 N NaCl solution to exchange the clay with Na. The Na-saturated product was dialyzed against distilled water until the solution was free of Cl ion. H-clay was prepared from the Na-clay by treating it with a H-form ion-exchange resin (IR-120). Part of the Na-clay was dissolved completely with 0.15 M sodium oxalate-oxalic acid mixture (pH 3.5) at 90°C (Higashi and Ikeda, 1974; Henmi and Wada, 1976; Wada and Wada, 1976). The Si and Al in the resulting solution were determined using an atomic absorption spectrophotometer (Hitachi 508) by the method of Henmi and Wada (1976).

DTA was carried out using an automatic recording instrument with chromel-alumel thermocouples (Rigaku Thermoflex 8001). The sample (100 mg) was loosely packed in a platinum holder after being freeze-dried and

Table 1. Sample descriptions.

Sample <sup>1</sup>	$\text{SiO}_2/\text{Al}_2\text{O}_3$ <sup>2</sup>	Locality and origin
Ki-P	1.47	Kitakami, Iwate; pumice
Ky-P	1.53	Kurayoshi, Tottori; pumice
PA-P	1.99	Choyo, Kumamoto; pumice
VA	1.91	Choyo, Kumamoto; volcanic ash

<sup>1</sup> Henmi (1977).

<sup>2</sup> Molar ratio of the  $<0.2\text{-}\mu\text{m}$  fraction treated with sodium dithionite-citrate-bicarbonate and 2%  $\text{Na}_2\text{CO}_3$ .

stored over a saturated solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , according to the method of Mackenzie and Mitchell (1970). Calcined  $\text{Al}_2\text{O}_3$  was used as a reference material. A heating rate of  $20^\circ\text{C}/\text{min}$  was employed in a static atmosphere (air). Silver nitrate standard was used to calibrate the furnace temperature of the instrument (Jackson, 1956b). The temperatures of the endothermic and exothermic peaks were estimated from the positions of the top or bottom of the peak on the chart.

XRD was carried out using  $\text{CuK}\alpha$  radiation (30 kV, 10 mA) for the freeze-dried clays after they had been heated for 5 hr to  $1200^\circ\text{C}$  at  $100^\circ\text{C}$  increments to determine the temperature at which mullite formed.

## RESULTS AND DISCUSSION

The samples listed in Table 1 range in  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios from 1.47 to 1.99 and fall into two groups with low ( $\sim 1.5$ ) and high ( $\sim 1.9$ )  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. The DTA curves are characteristic of allophane and show a broad endotherm and an exotherm in the temperature ranges  $150\text{--}187^\circ\text{C}$  and  $946\text{--}977^\circ\text{C}$ , respectively. Figure 1 shows the temperature of endothermic and exothermic peaks plotted against the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of the clays. Evidently these temperatures are influenced by the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios as well as by the nature of the exchangeable cation.

### Endothermic peak

The endothermic peak temperatures are always higher for H-clays than for Na-clays. Higher endothermic peak temperatures appear in both the H- and Na-clays with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios, but the increase is smaller for Na-clays. The order with decreasing temperature is as follows: H-clay with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios  $>$  H-clay with low ratios  $>$  Na-clay with high ratios  $>$  Na-clay with low ratios. This order corresponds to the surface acid strength of allophane (Henmi, 1977) because with stronger surface acidity, water is probably more strongly adsorbed as a base on the allophane surface. It is inferred that water and hydroxyls are more strongly bonded in allophane with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios than in those with low ratios. Barshad (1965) showed that the temperature of the endotherm due to dehydration of montmorillonite and vermiculite varied

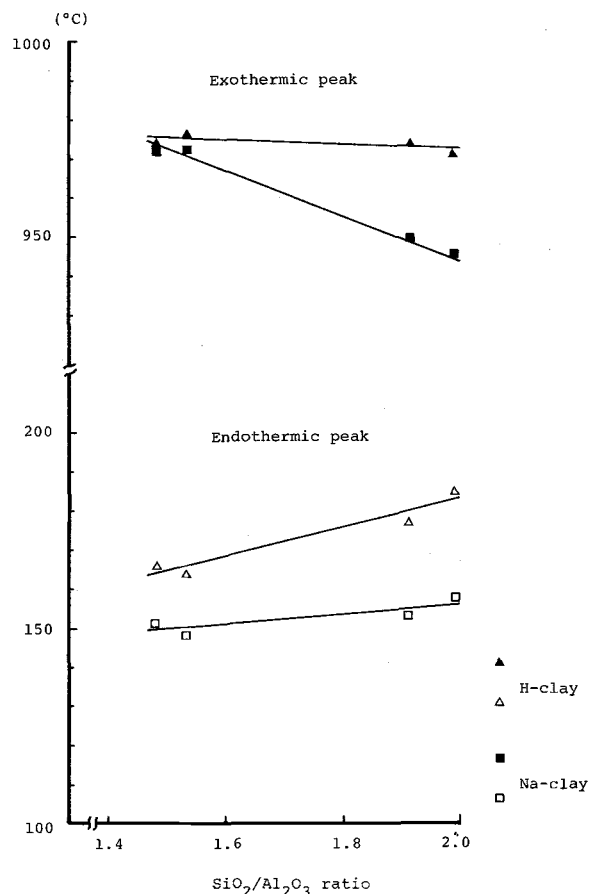


Figure 1. Effect of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio on the temperature of endothermic and exothermic peaks for H- and Na-exchanged allophanes.

with exchangeable cation. The temperature variation for montmorillonite has been attributed to differences in the hydration energies of different cations (Mackenzie, 1970). Therefore, the difference in endothermic peak temperature between the H- and Na-allophanes can be explained by the different hydration energies of the cations.

### Exothermic peak

The temperature of the exothermic peak for allophanes with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios is higher for H-clays than for Na-clays. This is consistent with the results of Miyauchi and Aomine (1966). As seen in Figure 1, however, exothermic peak temperatures are almost the same for H- and Na-clays having low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. The temperature of the exothermic reaction is also dependent on the chemical composition, if allophane is treated with NaCl instead of a H-ion exchange resin. H-ion saturation results in a nearly constant temperature ( $\sim 975^\circ\text{C}$ ) for the allophane exotherm, irrespective of its  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio.

Table 2. Exothermic peak height of H- and Na-allophanes.<sup>1</sup>

Clay	Na-clay $I_{Na}$	H-clay $I_H$	$I_H/I_{Na}$
Ki-P	42	43	1.02
Ky-P	51	90	1.76
PA-P	15	118	7.83
VA	35	108	3.09

<sup>1</sup> In terms of  $\Delta$  e.m.f. ( $\mu$ V). I = peak intensity.

The exothermic peak heights listed in Table 2 in terms of differential electromotive force ( $\Delta$  e.m.f.) vary with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and with exchangeable cation. Stronger peaks (42–51  $\mu$ V) are associated with Na-clays having low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios than those having high ratios (15–35  $\mu$ V). The intensity of the exothermic peak was correlated with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio for allophane from a stream-bed deposit below Silica Spring outlet on Mt. Ruapehu of New Zealand by Wells *et al.* (1977) who also reported that the peak decreased in sharpness (intensity) with an increase in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. This observation was also made for the Na-clays studied in the present investigation. On the other hand, stronger exothermic peaks (108–118  $\mu$ V) were noted for H-clays with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios than for those with low ratios (43–90  $\mu$ V). Thus, exchanging  $\text{Na}^+$  for  $\text{H}^+$  causes a considerable reduction in the intensity of the exothermic peak for all samples (Table 2). Miyauchi and Aomine (1966) also showed that the height of exothermic peak was greater for allophane saturated with  $\text{H}^+$  than with  $\text{Na}^+$ . The ratio of the exothermic peak height for H-clays to that for Na-clays differs from one clay to another, indicating that among allophanes of different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios, peak height enhancement is more pronounced for clays with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (3.09 to 7.83) than for those with low ratios (1.02 to 1.76).

#### New-phase-development

The correlation between the chemical composition and the temperature at which new phases develop is given in Table 3. Only data for H-clays are compared because the temperature of exothermic peak of H-clays is essentially unaffected by the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, although the peak heights vary with the ratios (Figure 1, Table 2). The temperature at which mullite was detected by XRD is regarded as the new-phase-development temperature. This temperature is different for clays with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios and with low ratios. New phases developed in all the clays after heating to 1200°C. Although the temperature of the exothermic peak of H-clays is between 970° and 977°C, new phases were not detected in clays with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios until they had been heated to >1000°C. However, a symptomatic development of new phases was noted in clays with low ratios at temperatures below the exothermic peak. The results indicate that crystallization

Table 3. Detection of mullite in heated fine clays by X-ray powder diffraction analysis.

Clay <sup>1</sup>	Temperature (°C)				
	400	800	900	1000	1200
Ki-P	–	–	±	+	+
Ky-P	–	–	±	+	+
PA-P	–	–	–	–	+
VA	–	–	–	–	+

<sup>1</sup> H-clay. + = detected, ± = symptomatic, – = not detected.

to mullite is easier from allophanes with low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios than from those with high ratios, wherein a  $\text{SiO}_2$  component may inhibit the crystallization of mullite or growth of its crystal size. Ossaka (1962) noted that mullite crystallized as low as 840°C, before the exothermic peak appeared, from two materials having  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 0.14 and 1.04, which were referred to as “precipitated allophane” in view of their occurrence as stream deposits (Ossaka, 1960, 1961).

#### Interpretation

The experimental results discussed above indicate that the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio influences the thermal behavior of allophane and suggest that structural differences are closely associated with chemical composition. Henmi and Wada (1976) noted differences in the amount of Al in 4-fold coordination ( $\text{Al}^{\text{IV}}$ ) among allophanes of different chemical composition, and other workers have assigned Al to both 4- and 6-fold coordinations on the basis of X-ray fluorescence spectroscopic results (Egawa, 1964; Udagawa *et al.*, 1969; Okada *et al.*, 1975). Henmi and Wada (1976) noted that with higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, more  $\text{Al}^{\text{IV}}$  is present, leading to the expectation that the negative charge due to the presence of tetrahedral Al increases with an increase in the ratio. In fact, the cation-exchange capacity (CEC) measured at pH 7 is higher for allophanes with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (~1.9) than those with low ratios (~1.3) (unpublished data from this laboratory). It is, therefore, reasonable to suggest that the variation in CEC with chemical composition is partly responsible for the differences in thermal behavior among allophanes of different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. The effects of the nature of the exchangeable cation on the DTA curve are greater for allophanes with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios than those with low ratios (Figure 1, Table 2). This fact can be explained by the higher CEC, and therefore, the greater amount of exchangeable cations in allophanes with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios compared with those with low ratios.

Brindley and Fancher (1969) proposed that allophane has a defect kaolinite structure wherein O is replaced by OH, thereby placing H on the outer edge of the layer, or by replacing Si by 4H so as to produce vacancies.

The variation in thermal behavior with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios suggests that differences in the nature or the extent of the defects in the proposed structure exist for allophanes of different chemical compositions. Tables 2 and 3 show that both the intensity of the exothermic peak and the temperature at which mullite was detected were higher for H-clays with high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios than those with low ratios. This may be explained by a smaller defect structure of kaolinite, namely better crystallinity or longer range order in the structure of allophanes with high ratios than those with low ratios. The strength of adsorbed water or structural OH supports the hypothesis that allophane with high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios are less poorly crystalline than allophane with low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios.

Properties, such as surface acidity, that are intimately connected with the structure were reported to be dependent on the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (Henmi, 1977). Different structure models have been proposed for allophanes having SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 1 and 2 (Okada *et al.*, 1975; Wada, 1978). The differences in such properties and structures among allophanes of different chemical compositions might be discernible by means of ordinary mineralogical analyses, such as XRD and IR, although these differences would not be large in comparison with the differences found between allophane and other related clay minerals, such as imogolite and halloysite. These differences might be useful in dividing allophane into subspecies.

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**Резюме**—Были обнаружены различия в кривых дифференциального термического анализа и в температурах развития новой фазы между аллофанами высоких (1,91–1,99) и низких (1,47–1,53) отношений  $\text{SiO}_2/\text{Al}_2\text{O}_3$ . Эндотермический пик из-за постоянной дегидратации и дегидроксилирования наблюдался при высоких температурах (153°–185°C) для аллофанов с высокими отношениями  $\text{SiO}_2/\text{Al}_2\text{O}_3$  и при низких температурах (148°–165°C) для аллофанов с низкими отношениями  $\text{SiO}_2/\text{Al}_2\text{O}_3$ . Для аллофанов с высокими отношениями температура эндотермического пика была ниже и высота более обусловлена содержанием обменных катионов, чем для аллофанов с низкими отношениями. Новые фазы не развились в аллофанах с высокими отношениями  $\text{SiO}_2/\text{Al}_2\text{O}_3$  даже после подогрева до 1000°C, выше температуры экзотермического пика. Наоборот, симптоматическое развитие новых фаз было замечено в аллофанах с низкими отношениями  $\text{SiO}_2/\text{Al}_2\text{O}_3$  при 900°C, ниже температуры экзотермического пика. Влияние отношения  $\text{SiO}_2/\text{Al}_2\text{O}_3$  на термическое поведение аллофанов указывает на то, что различия в структуре тесно связаны с химическим составом этого материала. [N. R.]

**Resümee**—Bei den DTA-Kurven und bei den Bildungstemperaturen neuer Phasen wurden Unterschiede zwischen Allophanen mit hohen (1,91 bis 1,99) und niedrigen (1,47 bis 1,53)  $\text{SiO}_2/\text{Al}_2\text{O}_3$ -Verhältnissen gefunden. Der endotherme Peak, verursacht durch die ständige Dehydrierung und Dehydroxylierung, war für Allophane mit hohem  $\text{SiO}_2/\text{Al}_2\text{O}_3$ -Verhältnis bei höheren Temperaturen (153° bis 195°C). Für Allophane mit niedrigem  $\text{SiO}_2/\text{Al}_2\text{O}_3$ -Verhältnis war er bei niedrigeren Temperaturen (148° bis 165°C). Bei Allophanen mit großen Verhältniszahlen war die Temperatur des endothermen Peaks niedriger, und die Höhe mehr durch die austauschbaren Kationen beeinflusst, als bei solchen mit kleinen Verhältniszahlen. In Allophanen mit hohem  $\text{SiO}_2/\text{Al}_2\text{O}_3$ -Verhältnissen wurden keine neuen Phasen gebildet, selbst wenn sie auf über 1000°C, über die Temperatur des exothermen Peaks, erhitzt wurden. Im Gegensatz dazu wurde bei Allophanen mit niedrigen  $\text{SiO}_2/\text{Al}_2\text{O}_3$ -Verhältnissen die symptomatische Bildung neuer Phasen bei 900°C, unter der Temperatur des exothermen Peaks, beobachtet. Die Wirkung des  $\text{SiO}_2/\text{Al}_2\text{O}_3$ -Verhältnisses auf das thermische Verhalten von Allophan legt die Annahme nahe, daß Unterschiede in der Struktur eng mit der chemischen Zusammensetzung dieses Materials zusammenhängen. [U. W.]

**Résumé**—Des différences ont été trouvées dans les courbes d'analyse thermique différentielle et dans les températures de développement de nouvelle phase entre les allophanes aux proportions hautes (1,91–1,99) et basses (1,47–1,53) de  $\text{SiO}_2/\text{Al}_2\text{O}_3$ . Le sommet endothermique dû à la déshydratation et à la déshydroxylation continues était à des températures plus hautes (153°–185°C) pour des allophanes avec des proportions élevées de  $\text{SiO}_2/\text{Al}_2\text{O}_3$  et à de plus basses températures (148°–165°C) pour celles avec les proportions les plus basses. De nouvelles phases ne sont pas développées dans les allophanes ayant des proportions élevées de  $\text{SiO}_2/\text{Al}_2\text{O}_3$ , même après échauffement à 1000°C, au-delà de la température du sommet exothermique. Par contraste, un développement symptomatique de nouvelles phases a été noté dans les allophanes ayant de basses proportions de  $\text{SiO}_2/\text{Al}_2\text{O}_3$  à 900°C, en dessous de la température du sommet exothermique. L'effet de la proportion de  $\text{SiO}_2/\text{Al}_2\text{O}_3$  dans le comportement thermal de l'allophane suggère fortement que les différences dans la structure sont associées de près avec la composition chimique de ce matériel. [D. J.]