

## EFFECT OF $\text{SiO}_2/\text{Al}_2\text{O}_3$ RATIO ON THE THERMAL REACTIONS OF ALLOPHANE. II. INFRARED AND X-RAY POWDER DIFFRACTION DATA

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**Abstract**—Allophanes with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios from 1.38 to 1.92 were heated at temperatures up to 500°C, and the changes induced were investigated by means of infrared spectroscopy (IR) and X-ray powder diffraction (XRD). Heat treatment caused the IR absorption band near 1000  $\text{cm}^{-1}$  due to Si–O stretching to shift towards higher frequencies, and the band near 450  $\text{cm}^{-1}$  due to O–Si–O bending to increase markedly in intensity. These results are probably due to condensation of SiO tetrahedra, following breakdown of Si–O–Al linkages and dehydroxylation of SiOH groups. Concurrent intensity increase of the IR absorption at about 700  $\text{cm}^{-1}$  suggested an increase in the amount of 4-coordinated Al in the heated materials. ‘Imogolite structures’ were decomposed progressively at higher temperatures and were almost absent at about 400°C, as indicated by the weakening and disappearance of the IR band at 348  $\text{cm}^{-1}$  and of the XRD reflections at 2.25 and 1.40 Å. The XRD reflection at 3.3–3.45 Å shifted to about 3.6 Å, probably as a result of thermal condensation of the silica component. The observed thermal changes were much greater for samples with low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (1.38–1.51) than for those with high ratios (1.81–1.92), indicating a lower thermal stability for the former materials. Thus, the thermal stability of allophanes appears to be related to the content of ‘imogolite structures’ and to the polymerization status of the silica component.

**Key Words**—Allophane, Imogolite, Infrared spectroscopy, Silica/alumina ratio, Thermal stability, X-ray powder diffraction.

### INTRODUCTION

Allophane consists principally of varying proportions of silica, alumina, and water (van Olphen, 1971). Although  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios range from 1 to 2 for samples from weathered pyroclastic deposits, materials containing both more and less aluminum are also known (Wada and Harward, 1974). Significant differences have also been reported in properties such as surface acidity, amount of Al in 4-fold coordination, IR absorption behavior, and phosphate retention, between allophanes with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (Henmi and Wada, 1976; Henmi, 1977; Parfitt *et al.*, 1980). Such differences strongly suggest that allophane exhibits structural variations which are associated with chemical composition (Parfitt and Henmi, 1980).

In Part I of this study, Henmi (1980) found significant differences in the differential thermal analysis (DTA) curves and in the temperature of new-phase development between two groups of allophanes with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios of 1.91–1.99 and 1.47–1.53. The purpose of this paper is to examine differences in thermal stability among allophanes with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios by means of X-ray powder diffraction and infrared techniques.

### MATERIALS AND METHODS

Allophane clays (<0.4  $\mu\text{m}$ ) separated from the same ash and pumice samples used in Part I of the study

(Henmi, 1980) were used along with a clay sample obtained from pumice from Kakino, Kumamoto Prefecture. The Kakino pumice was collected at an escarpment where the pumice bed, about 3 m thick, is overlain by a 4-m thick series of weathered ash layers. The pumice bed is severely weathered but contains no gel films of imogolite, in contrast with those from Kitakami (Wada and Matsubara, 1969) or Kurayoshi (Yoshinaga and Yamaguchi, 1970) where gel films are abundant. The ash and pumice samples were treated with  $\text{H}_2\text{O}_2$ , followed by treatment with buffered dithionite and 2%  $\text{Na}_2\text{CO}_3$  (Jackson, 1973), and then dispersed in water of pH 10.5 (NaOH) with the aid of sonification. Clay fractions (<2  $\mu\text{m}$ ) were first collected by sedimentation, and then <0.4- $\mu\text{m}$  fractions were separated by centrifuge. The <0.4- $\mu\text{m}$  fractions were air-dried after successive washings with 0.5 M NaCl, ethanol, and acetone.

The air-dried samples were heated for 5–6 hr at 100°C intervals up to 500°C in a thermostated furnace, cooled in a desiccator containing saturated  $\text{Mg}(\text{NO}_3)_2$  solution (RH ~ 55%), and examined by IR and XRD. IR spectra were recorded on a Hitachi 295 spectrometer using 1-mg samples in 13-mm diameter KBr discs (200 mg). XRD patterns were obtained using 300-mg samples randomly oriented in an Al cell (Klug and Alexander, 1954, p. 300–302) with a Rigakudenki D-3F apparatus ( $\text{CuK}\alpha$  with Ni filter; 40 kV and 15 ma).

Table 1. Elemental composition of allophane samples.<sup>1</sup>

	KnP	PA	VA	KyP	KiP
SiO <sub>2</sub>	41.29	40.56	39.97	36.98	34.80
Al <sub>2</sub> O <sub>3</sub>	36.55	37.38	37.57	41.71	42.85
Fe <sub>2</sub> O <sub>3</sub>	1.08	1.19	1.33	0.58	0.50
TiO <sub>2</sub>	1.18	1.08	1.05	0.71	0.47
P <sub>2</sub> O <sub>5</sub>	0.15	0.18	0.27	0.41	0.25
MnO	nil	nil	nil	nil	nil
CaO	0.14	0.32	0.20	0.07	0.40
MgO	0.14	0.68	0.35	0.10	0.55
K <sub>2</sub> O	0.02	0.04	0.05	0.01	0.04
Na <sub>2</sub> O	5.44	4.17	3.50	0.42	2.70
H <sub>2</sub> O(+)	13.91	14.49	15.17	19.55	17.59
Total	99.90	100.09	99.46	100.54	100.15
SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub> <sup>2</sup>	1.92	1.84	1.81	1.51	1.38
H <sub>2</sub> O/ Al <sub>2</sub> O <sub>3</sub> <sup>2</sup>	2.16	2.20	2.29	2.66	2.33

<sup>1</sup> Na-saturated <0.4- $\mu$ m clays treated with buffered dithionite and 2% Na<sub>2</sub>CO<sub>3</sub> (Jackson, 1973). Percent on the oven dry basis. Analysis by the Na<sub>2</sub>CO<sub>3</sub>-fusion method.

<sup>2</sup> Molar ratios.

## RESULTS AND DISCUSSION

### Description of starting materials

The clay samples were examined for purity by XRD, DTA, IR, and transmission electron microscopy (TEM). The results showed that all samples were typical allophanes. Less than 0.5% imogolite tubes could be seen by TEM. The composition and the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios (Table 1) of four samples (KiP, KyP, VA, and PA) were somewhat different from those reported previously for clay fractions from the same sources (Aomine and Wada, 1962; Yoshinaga, 1966; Henmi and Wada, 1976; Henmi, 1980). This is presumably due to differences in sample preparation, particle size, or analytical procedure. The samples fall into two groups with respect to SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio: one group with low ratios, 1.38–1.51 (KiP and KyP), and the other with high ratios, 1.81–1.92 (VA, PA, and KnP).

### Infrared spectroscopy

The IR spectra of unheated samples were generally similar to each other and to those reported elsewhere for allophanes, with five major absorption bands near 3400, 1640, 1000, 560, and 450 cm<sup>-1</sup> (cf. Brown *et al.*, 1978). A small but distinct difference was noticed, however, in the absorption maximum near 1000 cm<sup>-1</sup> due to Si–O stretching between samples with high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios (985–995 cm<sup>-1</sup>) and low ratios (962–970 cm<sup>-1</sup>) (Figures 1 and 2a). The difference indicates a variation in the degree of polymerization of the silica in allophanes, i.e., a higher degree of polymerization in those with high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios (cf. Mitchell *et al.*, 1964).

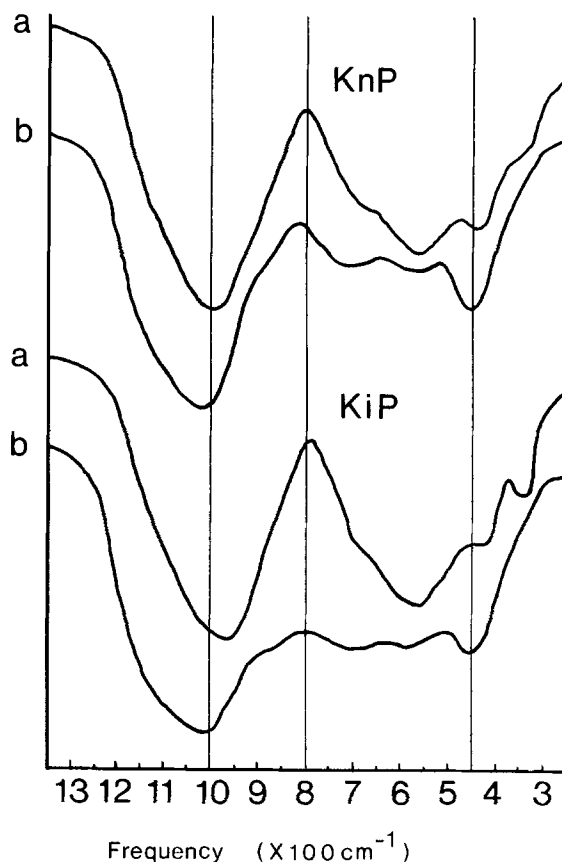


Figure 1. IR spectra in the 250–1350 cm<sup>-1</sup> region of KiP and KnP. Unheated (a) and heated at 500°C (b).

The absorption maximum at about 1000 cm<sup>-1</sup> shifted towards higher frequencies with increasing heating temperature (Figures 1 and 2a) which can be ascribed to condensation of the SiO tetrahedra, following the breakdown of Si–O–Al linkages (Egashira and Aomine, 1974) and the dehydroxylation of SiOH groups. The condensation was further supported by a concurrent, marked increase in intensity of the absorption near 450 cm<sup>-1</sup> (Figure 1), which is assignable to O–Si–O bending of condensed silicates (Moenke, 1974). The absorption band near 450 cm<sup>-1</sup> also showed a high-frequency shift (Figure 2b), which can be attributed to condensation of the silica component because it occurred in parallel with that of the Si–O stretching band near 1000 cm<sup>-1</sup> (Figure 2a). Figure 2a shows that the shift of the absorption maximum near 1000 cm<sup>-1</sup> was much more rapid in samples with low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios than in those with high ratios; this was particularly so at temperatures below 300°C, indicating a much higher rate of thermal condensation of the silica in the former samples. Differences in the condensation rate are even more apparent in the ratio of the absorbances at 1100 and 940 cm<sup>-1</sup> between the two groups of samples (Fig-

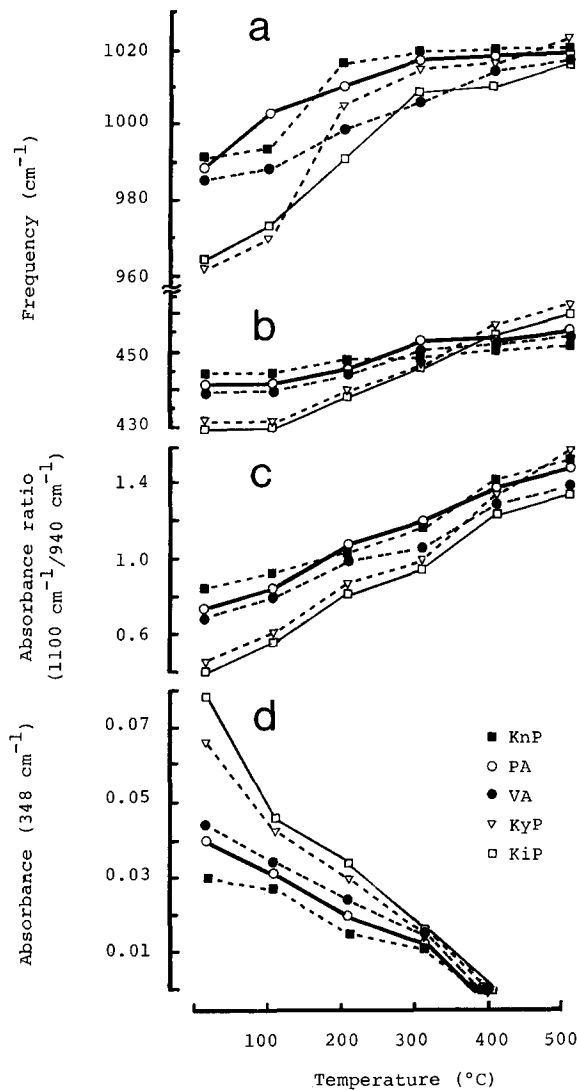


Figure 2. Effects of heat treatment on IR spectra of allophane samples. Shift of the absorption maximum near  $1000\text{ cm}^{-1}$  (a) and  $450\text{ cm}^{-1}$  (b), ratio of the absorption intensity at  $1100\text{ cm}^{-1}$  to that at  $940\text{ cm}^{-1}$  (c), and the absorption intensity at  $348\text{ cm}^{-1}$  (d).

ure 2c). The ratio may be taken as an index of polymerization of the silica in allophane because highly polymerized silicates such as quartz show an absorption due to Si–O stretching around  $1100\text{ cm}^{-1}$  (Moenke, 1974), whereas ortho- and pyrosilicates absorb in the range  $900\text{--}970\text{ cm}^{-1}$  (Farmer, 1964). The ratio of absorbances ( $1100\text{ cm}^{-1}/940\text{ cm}^{-1}$ ) increased steadily with heating temperature, but at a higher rate for samples with low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. The above observations suggest that the thermal stability varies between allophanes with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios, and that the stability is higher for those allophanes with higher ratios. The term thermal stability is used here to denote

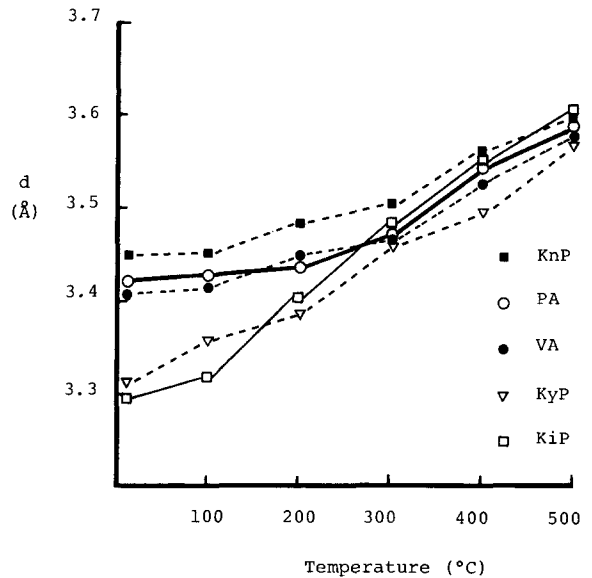


Figure 3. Shift of the  $3.3\text{--}3.45\text{ \AA}$  XRD reflection by heating. For symbols of the samples see Figure 2.

the susceptibility to thermal condensation of the silica component.

The heat treatment also caused a marked increase in the intensity of the IR absorption near  $700\text{ cm}^{-1}$ , which is due to Al in 4-fold coordination ( $\text{Al}^{\text{IV}}$ ) (V. C. Farmer, Macauley Institute for Soil Research, Craigiebuckler, Aberdeen, Scotland, personal communication); the resulting IR spectra in the frequency range below  $1400\text{ cm}^{-1}$  resembled those of aluminosilicate precipitates prepared by Farmer *et al.* (1979) from alkaline solutions containing orthosilicic acid and sodium aluminate with Si:Al ratios of 1.0–2.0 (Figure 1). These authors regarded the precipitates as having a feldspathoid structure, incorporating a condensed tetrahedral aluminosilicate anion (Farmer *et al.*, 1979). It seems, therefore, that heating caused the allophanes to transform into a feldspathoidal material in which some of the Al was incorporated in tetrahedral coordination in the condensed silicate framework. That the proportion of  $\text{Al}^{\text{IV}}$  relative to  $\text{Al}^{\text{VI}}$  in allophane increases by heating up to  $700^\circ\text{C}$  was shown by Udagawa *et al.* (1969).

The intensity of the absorption band at  $348\text{ cm}^{-1}$  decreased with increasing heating temperature (Figure 2d). This band was assigned to an imogolite-like structural component in allophane (Farmer *et al.*, 1977). Figure 2d indicates more ‘imogolite structures’ in allophanes with lower  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios than in those with higher ratios, and shows that this component was completely destroyed by heating to  $400^\circ\text{C}$ . Heating pure specimens of imogolite showed that the absorption band at  $348\text{ cm}^{-1}$  still persisted at temperatures above  $400^\circ\text{C}$  (but below  $500^\circ\text{C}$ , not shown), indicating that ‘imogolite structures’ are thermally less stable than

well-crystallized, tubular imogolite. The more rapid decrease of the absorbance, particularly below 300°C, for samples with low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios suggests that the thermal stability of allophane is associated with the amount of 'imogolite structures' present (see also Figure 2a). Thus, the lower the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of allophane, the higher the proportion of 'imogolite structures' present and the lower the thermal stability. Figure 2d also shows that 'imogolite structures' are more stable in allophanes with higher SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios than in those with lower ratios, but this is probably due to a 'sheltering effect' of the more polymerized silicate framework in the former materials. It may therefore be considered that the thermal stability of allophane depends also on the polymerization status of the silica component.

#### *X-ray powder diffraction analysis*

The unheated samples exhibited three broad diffraction bands with maxima at 3.3–3.45, 2.25, and 1.40 Å, with relative intensities of strong, medium, and weak, respectively (patterns not shown). Similar features were reported by Yoshinaga and Aomine (1962). The latter two bands correspond in position to 63 (2.25 Å) and 06 (1.40 Å) reflections of imogolite and may be ascribed to the 'imogolite structures' (Farmer *et al.*, 1977). Actually, the intensity of both bands, particularly that of the 1.40-Å band, was greater in samples with low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios than in those with high ratios, and the bands decreased in intensity as the heating temperature rose and disappeared almost completely after heating at 400°C (results not shown). This behavior corresponds closely to that of the IR absorption band at 348 cm<sup>-1</sup> (Figure 2d), and indicates that heat treatment caused the allophane to become more poorly ordered as suggested by a weakening and disappearance of XRD and IR absorption bands, indicating a certain initial degree of structural order.

On the other hand, heat treatment only shifted the position of the diffraction band at 3.3–3.45 Å to higher spacing (3.6 Å), with virtually no change in intensity, at least up to 500°C (Figure 3). The diffraction patterns as a whole became similar to those of synthetic silica gels which display only a broad band at 3.7–3.8 Å (patterns not shown). This similarity with diffraction patterns of vitreous materials, such as silicate glass (Klug and Alexander, 1954, p. 585–633) and silica gels, suggests that the diffraction band at 3.3–3.45 Å arises from an interference between neighboring SiO tetrahedra. Thus, its thermal shift can be attributed to a change in the bonding environment of these tetrahedra. The shift of the spacing was obviously dependent on the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the samples in the same manner as has been noted for thermal change in the IR spectra (Figures 1 and 2). The shift, therefore, is considered to be associated with polymerization of the silica component.

## CONCLUSIONS

Heat treatment of allophanes caused significant structural changes through condensation of SiO tetrahedra, probably arising from a breakdown of Si–O–Al linkages and a dehydroxylation of SiOH groups. The extent of such thermal transformations was apparently dependent on the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of allophanes: the lower the ratio, the greater was the extent of transformation. The thermal stability of allophane, in terms of its susceptibility to condensation of the silica component, is therefore a function of the relative alumina content which forms 'imogolite structures,' and of the polymerization status of the silica component in its structure.

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**Резюме**—Аллофаны с молярным соотношением  $\text{SiO}_2/\text{Al}_2\text{O}_3$  в диапазоне от 1,38 до 1,92 нагревались в температурах до 500°C. Перемены, вызванные этим нагревом, исследовались при помощи инфракрасной спектроскопии (IR) и порошковой рентгеновской дифракции (XRD). Нагрев образцов вызывал сдвиг полосы абсорбции IR в по близости 1000  $\text{cm}^{-1}$ , принадлежащей к Si–O растягивающему колебанию, к более высоким частотам, и заметное увеличение интенсивности полосы около 450  $\text{cm}^{-1}$ , принадлежащей O–Si–O изгибающему колебанию. Эти результаты были вызваны вероятно конденсацией тетраэдров SiO после разрыва связи Si–O–Al и дегидроксилирования групп SiOH. Одновременное увеличение интенсивности абсорбции IR в по близости 700  $\text{cm}^{-1}$  указывало на увеличение количества 4-координированных Al в нагретых образцах. "Имоголитовые структуры" раскладывались постепенно в повышенных температурах и почти отсутствовали при 400°C, на что указывало ослабление и исчезновение полос IR при 348  $\text{cm}^{-1}$  и отражений XRD при 2,25 и 1,40 Å. Сдвиг отражения XRD от 3,3–3,45 Å до около 3,6 Å есть, вероятно, результатом тепловой конденсации кремниевого компонента. Наблюдаемые тепловые перемены были более интенсивные для образцов с низкими соотношениями  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (1,38–1,51), чем для образцов с высокими соотношениями (1,81–1,92), что указывает на более иную тепловую устойчивость первых. Таким образом тепловая устойчивость аллофанов кажется быть связанной с количеством "имоголитовых структур" и с полимеризацией кремниевого компонента. [E.C.]

**Resümee**—Allophane mit molaren  $\text{SiO}_2/\text{Al}_2\text{O}_3$ -Verhältnissen von 1,38–1,92 wurden auf Temperaturen bis zu 500°C erhitzt. Die daraus resultierenden Veränderungen wurden mittels Infrarotspektroskopie (IR) und Röntgenpulverdiffraktometrie (XRD) untersucht. Die Hitzebehandlung verursachte eine IR-Absorptionsbande bei 1000  $\text{cm}^{-1}$ , die auf eine Verschiebung der Si–O-Streckschwingung nach höheren Frequenzen zurückzuführen ist. Weiters nahm die Bande bei etwa 450  $\text{cm}^{-1}$ , die durch eine O–Si–O-Deformationsschwingung hervorgerufen wird, beträchtlich an Intensität zu. Diese Ergebnisse werden wahrscheinlich durch eine dichtere Packung der SiO-Tetraeder verursacht, die dem Zusammenbrechen von Si–O–Al-Bindungen und einer Dehydroxylierung der SiOH-Gruppen folgt. Eine gleichzeitige Intensitätszunahme der IR-Absorption bei etwa 700  $\text{cm}^{-1}$  deutete auf eine mengenmäßige Zunahme von 4-koordiniertem Al in den erhitzten Substanzen hin. "Imogolit-Strukturen" wurden bei höheren Temperaturen in zunehmendem Maße zersetzt und fehlten bei etwa 400°C nahezu vollständig. Dies ging aus der Schwächung und dem Verschwinden der IR-Bande bei 348  $\text{cm}^{-1}$  und aus den XRD-Reflexen bei 2,25 und 1,40 Å hervor. Der XRD-Reflex bei 3,3–3,45 Å verschob sich nach etwa 3,6 Å, was wahrscheinlich durch eine dichtere Packung der Siliziumdioxid-Komponente auf thermischem Wege zurückzuführen ist. Die beobachteten thermischen Veränderungen waren bei Proben mit niedrigen  $\text{SiO}_2/\text{Al}_2\text{O}_3$ -Verhältnissen (1,38–1,51) viel größer als bei Proben mit hohen Verhältnissen (1,81–1,92). Dies deutet auf eine geringere thermische Stabilität der ersten Proben hin. Aus diesem Grund scheint die thermische Stabilität der Allophane mit dem Gehalt an "Imogolit-Strukturen" und mit dem Polymerisationszustand der Siliziumdioxid-Komponente zusammenzuhängen. [U.W.]

**Résumé**—Des allophanes ayant des proportions molaires  $\text{SiO}_2/\text{Al}_2\text{O}_3$  de 1,38 à 1,92 ont été chauffés à des températures jusqu'à 500°C, et les changements induits ont été investigués au moyen de spectroscopie infrarouge (IR) et de diffraction poudrée aux rayons-X (XRD). Le traitement à la chaleur a causé la bande d'adsorption IR près de 1000  $\text{cm}^{-1}$  à cause de l'étirement Si–O de s'approcher de plus hautes fréquences, et la bande près de 450  $\text{cm}^{-1}$  à cause du pliage de O–Si–O d'intensifier de manière marquée. Ces résultats sont probablement dus à la condensation de tétraèdres SiO, suivant la dissolution des liens Si–O–Al et la déshydroxylation des groupes SiOH. Un accroissement concourant d'intensité de l'adsorption IR à à peu près 700  $\text{cm}^{-1}$  a suggéré un accroissement de la quantité d'Al coordonné-4 dans les matériaux échauffés. Des "structures imogolites" ont été progressivement décomposées à de plus hautes températures et étaient presque absentes à peu près 400°C, tel que l'ont montré l'affaiblissement et la disparition de la bande IR à 348  $\text{cm}^{-1}$  et les réflexions XRD à 2,25 et 1,40 Å. La réflexion XRD à 3,3–3,45 Å s'est rapprochée de 3,6 Å, probablement un résultat de la condensation thermique du composé silice. Les changements thermiques observés étaient beaucoup plus importants pour les échantillons ayant des proportions  $\text{SiO}_2/\text{Al}_2\text{O}_3$  basses (1,38–1,51) que pour ceux ayant des proportions élevées (1,81–1,92), indiquant une stabilité thermique plus basse pour les premiers matériaux. Ainsi, il semble que la stabilité thermique des allophanes est apparentée au contenu des "structures imogolites" et au statut de polymérisation du composé silice. [D.J.]