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THE STRUCTURE AND THERMAL TRANSFORMATIONS OF ALLOPHANES STUDIED BY ^{29}Si AND ^{27}Al HIGH RESOLUTION SOLID-STATE NMR

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Abstract—Examination of two volcanic and two precipitated allophanes by solid-state NMR, thermal analysis and X-ray powder diffraction shows three of the samples to contain structural features similar to both tubular imogolite and defect layer-lattice aluminosilicates such as kaolinite. The fourth allophane, a precipitated sample from New Zealand, had no imogolite-like features and contained tetrahedral as well as octahedral aluminum. The imogolite-like units in allophane are less stable thermally than tubular imogolite. The NMR spectra and their changes on heating can be accounted for by a structural model in which a two-sheet, kaolinite-like structure containing defects (holes in the tetrahedral sheet) is curved into a sphere in which imogolite-like orthosilicate units are anchored into the octahedral sheet and fit into the tetrahedral defects. Computer simulation shows that the model is crystallographically sound, and accounts for all the known facts, including the spherical morphology, the solid-state NMR spectra and the thermal dehydroxylation behavior of all except the New Zealand allophane, which is of a different structural type.

Key Words—Allophane, Imogolite, Dehydroxylation, Crystal structure, Nuclear magnetic resonance, Thermal treatment, X-ray powder diffraction.

INTRODUCTION

Allophanes are by definition very poorly crystalline hydrous aluminosilicate phases. They occur as a major component of soils derived from volcanic ash, and, less commonly, as naturally precipitated gels. The SiO_2/Al_2O_3 molar ratio of allophanes can vary from about 1:1 (as in the more crystalline tubular form imogolite (MacKenzie *et al.*, 1989), to about 2:1 (Wada, 1967). The total water content of allophanes from various sources is about 35.5 to 37.5 wt.%. This water is composed of both structural (hydroxyl) water and hydration water, the relative proportions of which are difficult to distinguish, since, by contrast with imogolite, the respective thermogravimetric weight losses overlap. Kitagawa (1974) estimated the relative proportions of hydroxyl and hydration water to be about 10–11 wt.% and about 23 wt.%, respectively.

Since the X-ray powder pattern of allophane contains only a few weak, diffuse bands, speculation about its possible structural organization has been based more on other evidence (IR spectroscopy, chemical composition, cation exchange reactions, bulk density, etc.). Several models for the structural unit of allophane have been proposed on the basis of such evidence. An early model (Wada, 1967) consisted of hydroxy-aluminum chains, corner-sharing oxygens with a tetrahedral silica chain (Figure 1A and 1B).

Alternatively, a variety of layer-lattice structures related to kaolinite has been proposed for allophane. Udagawa *et al.* (1970) reported that an intermediate spinel is formed from allophane during its thermal transformation to mullite, from which they deduced a kaolinite-like allophane structure (Figure 1C) containing elements of a structure previously suggested by Fripiat *et al.* (1965). Attempts to computer-simulate this structure emphasize its schematic nature. Several other structures derived by introducing various types of defects into kaolinite were investigated by Brindley and Fancher (1970), who demonstrated that a variety of common allophane compositions could be generated by removing some of the tetrahedral Si atoms, compensated for by the addition of protons to the adjacent oxygens (Fig. 1D). In both this structure and the model of Udagawa *et al.* (1970), all the Al is considered to be 6-coordinated. Early X-ray fluorescence measurements (Udagawa *et al.*, 1970) appeared to indicate the occurrence of up to 40% of the Al in tetrahedral sites, but this result is probably an artifact since $AlPO_4$ was inappropriately used as the tetrahedral calibration material. Okada *et al.* (1975) have modified the Brindley/Fancher structures for the 1:1 and 2:1 end-members to allow for the presence of tetrahedral Al (Figure 1E and 1F). In these models, which do not take account of the charge balance, the 1:1 end-member contains too many vacancies in the octahedral sheet to allow a continuous kaolinite-like octahedral sheet to be maintained. Wada (1979) has shown that charge balance can be achieved in such a structure if defects are postulated in both the octahedral and tetrahedral sheets, and the tetrahedral Al is coordinated to a water molecule, forming a Brønsted acid site.

Another school of thought (Parfitt *et al.*, 1980) suggests that allophane has a similar structural unit to

tubular imogolite, which is based on a gibbsite-like hydroxy-aluminum sheet (MacKenzie *et al.*, 1989). Where the SiO_2/Al_2O_3 ratio is approximately one, the structure is considered to contain imogolite-like isolated SiO_4 units, whereas in allophanes of SiO_2/Al_2O_3 ratio of about two, the additional silicate units are thought to be condensed at one or both sides of the gibbsite sheet (Parfitt *et al.*, 1980). Materials of intermediate SiO_2/Al_2O_3 ratio would have structures intermediate between these two types. Such imogolite-like structures should not contain tetrahedral aluminum.

High-resolution solid-state ^{29}Si and ^{27}Al NMR can provide structural information about poorly crystalline phases, especially when used in conjunction with thermal studies as in the case of imogolite (MacKenzie *et al.*, 1989). Previous solid-state NMR studies of natural allophanes (Goodman *et al.*, 1985; Shimizu *et al.*, 1985) indicated ^{29}Si spectra containing a sharp imogolite-like peak at about -79 ppm, superimposed on a broad, higher-field hump ascribed to polymerized silicon species. An allophane from Silica Springs, New Zealand, showed only this latter, broad ^{29}Si feature, centered at about -89 ppm. The ^{27}Al spectra of most natural allophanes so far investigated (Goodman *et al.*, 1985; Shimizu *et al.*, 1985) show predominantly octahedral Al, with only a small tetrahedral component, the intensity of which appears to be in direct proportion to the size of the broad silicon resonance.

The aim of this work is to study the changes in the ^{29}Si and ^{27}Al NMR spectra occurring in several natural allophanes during heating, and, by comparison with similar results found for imogolite, to deduce structural information which may indicate which, if any, of the proposed allophane structures is the more likely.

EXPERIMENTAL

The following well-characterized natural allophanes of different origin and composition were studied: (1) two naturally precipitated allophanes, one from Derbyshire, England (MacKenzie, 1970), the other from Silica Springs, New Zealand (Wells *et al.*, 1977), the latter of size fraction <2 μm, (2) two Japanese allophanes of different SiO_2/Al_2O_3 molar ratios, separated from weathered pumice from Kitakami, Iwate (designated sample Ki-P), and from Choyo, Kumamoto (designated VA). These samples, kindly supplied by Dr. K. Wada, had been deferrated by dithionate-citrate-bicarbonate treatment, followed by treatment with a hot 2% solution of sodium carbonate to remove adsorbed citrate. The samples were saturated with Na, then dialysed and freeze-dried. This deferration, which was necessary because the presence of paramagnetic species interferes with the solid-state NMR experiments, was kept as mild as possible to avoid modifying the allophane structure. While some degree of chemically-induced structure modification cannot be completely ruled out, X-ray powder diffraction and thermal analysis of both treated and untreated materials indicates negligible difference between the two. Furthermore, a ^{57}Fe Mössbauer spectroscopic study of samples Ki-P and VA before deferration (MacKenzie and Cardile, 1988) indicates that the iron is present as a surface oxyhydroxide layer, suggesting that if the deferration conditions are kept sufficiently mild, iron removal should be achieved without structural disruption.

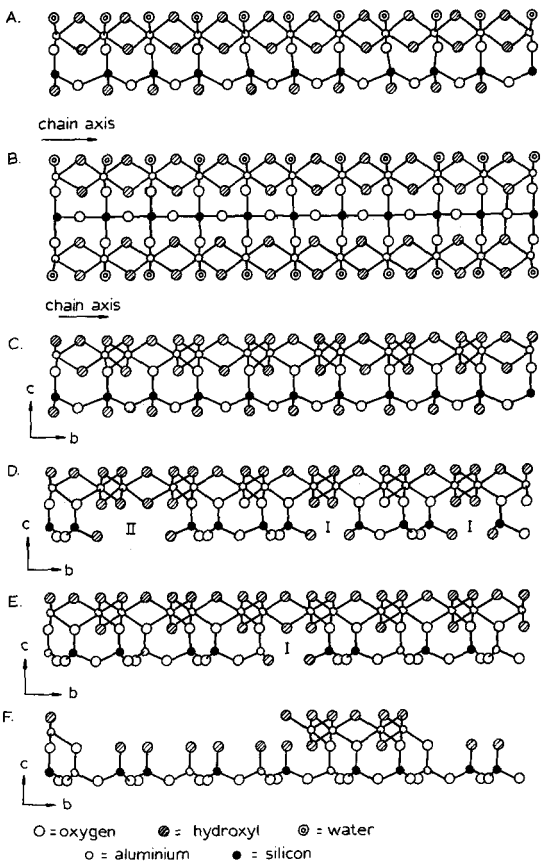

Figure 1. Computer-generated structures of previously-proposed allophane structural models. (A) "Chain" structure of $2SiO_2:Al_2O_3$ allophane, after Wada (1967). (B) "Chain" structure of $SiO_2:Al_2O_3$ allophane, after Wada (1967). (C) Sheet structure, after Udagawa *et al.* (1970). (D) Sheet structure based on defect-containing kaolinite, after Brindley and Fancher (1970). I and II denote the loss of one and two silicons, respectively (type 1 and 2 defects). (E) Sheet structure of $SiO:Al_2O_3$, after Okada *et al.* (1975). I denotes a type 1 Brindley-Fancher defect. (F) Sheet structure of $2SiO_2:Al_2O_3$, after Okada *et al.* (1975).

X-ray powder diffraction indicates that all these allophanes, with the exception of Silica Springs, have three weak, broad diffraction bands corresponding to the strongest maxima listed by Brown (1980). Silica Springs allophane shows only the broad band centered at about 3.4 Å. The chemical analyses of all the allophanes are shown in Table 1.

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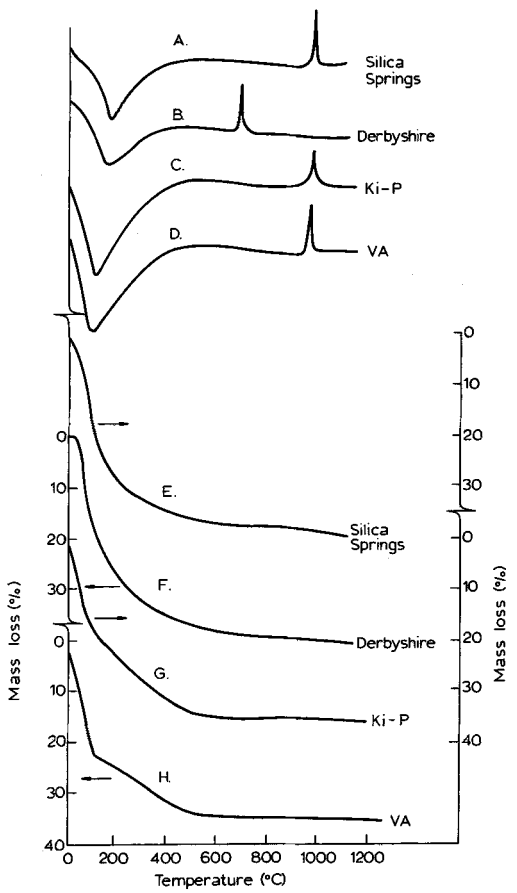

Figure 2. DTA traces (A–D) and TGA traces (E–H) of the allophanes of this study. Heating rate 10°C/min in air.

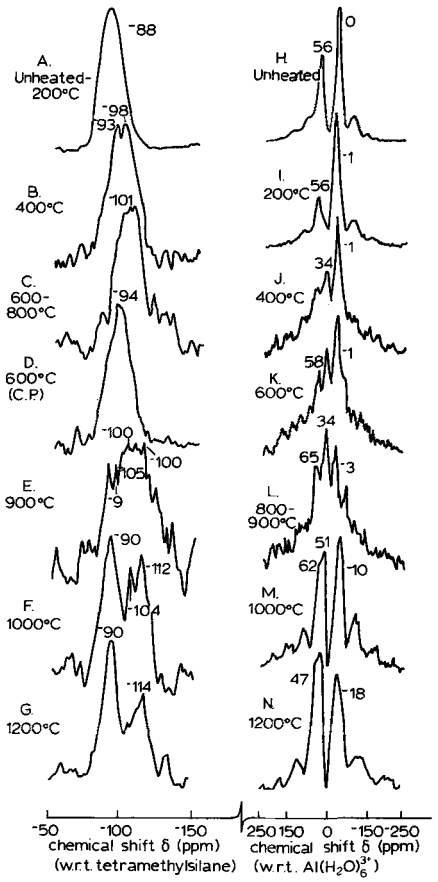

Figure 3. Typical solid-state NMR spectra of Silica Springs allophane; unheated, and heated to the indicated temperatures. A–G, ^{29}Si spectra, H–N, ^{27}Al spectra.

Thermal analyses of all samples were carried out as described by MacKenzie *et al.* (1989), and the results were used to determine the heating temperature in a series of sequential isothermal heating experiments.

Table 1. Chemical analyses of allophanes.

Element	Derbyshire	Silica Springs	Ki-P	VA
SiO_2	17.75	23.45	26.72	31.22
Al_2O_3	32.63	34.77	34.98	30.64
TiO_2	—	0.04	0.26	0.60
Fe_2O_3	0.15	0.11	0.24	0.76
MgO	0.17	0.01	0.03	0.18
CaO	2.73	0.02	0.08	0.22
MnO	0.10	—	—	0.01
Na_2O	0.03	—	0.01	0.13
K_2O	0.04	0.03	0.33	0.08
PbO	2.53	—	—	—
F	5.90	—	—	—
ZnO	0.30	—	—	—
H_2O	37.70	40.58	36.41	35.49
Total	100.03	99.01	99.06	99.33
SiO_2/Al_2O_3	0.93	1.15	1.30	1.73

After each 15 min heat treatment, the samples were cooled in a desiccator to prevent rehydration, and examined by X-ray powder diffraction and high-resolution solid-state MAS NMR (see MacKenzie *et al.*, 1989).

RESULTS AND DISCUSSION

The thermal analysis traces of all four samples contain similar features typical of allophane (Figure 2). The endothermic weight-loss of about 36% due to water removal extends over a temperature range of almost 500°C, but only in the two Japanese allophanes do they show any indication of proceeding in more than one stage, and, even in these samples, the distinction between hydration and structural water is much less well-defined than in imogolite (MacKenzie *et al.*, 1989). As in imogolite, the formation of mullite (nominally $3Al_2O_3 \cdot 2SiO_2$) at higher temperatures is accompanied by a sharp DTA exotherm at about 1000°C. An exception is the Derbyshire allophane, in which crystallization occurs at a lower temperature, probably as a result of the mineralizing action of the fluoride impurity (Berezowski and MacKenzie, 1985).

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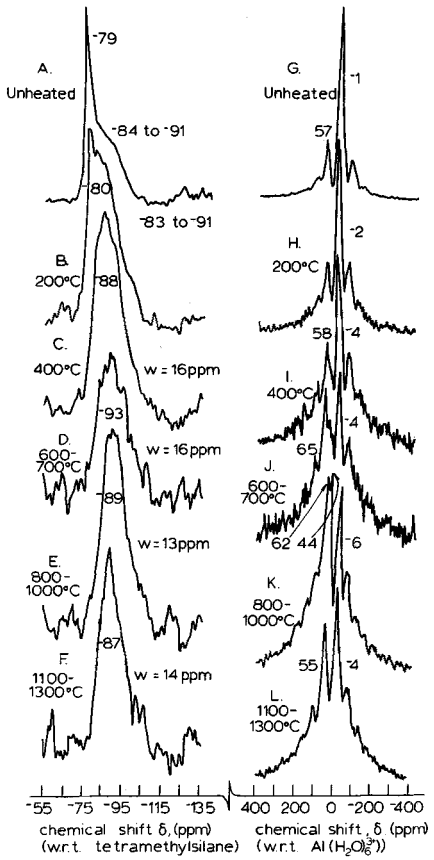

Figure 4. Typical solid-state NMR spectra of Derbyshire allophane; unheated, and heated to the indicated temperatures. A–F, ^{29}Si spectra, G–L, ^{27}Al spectra.

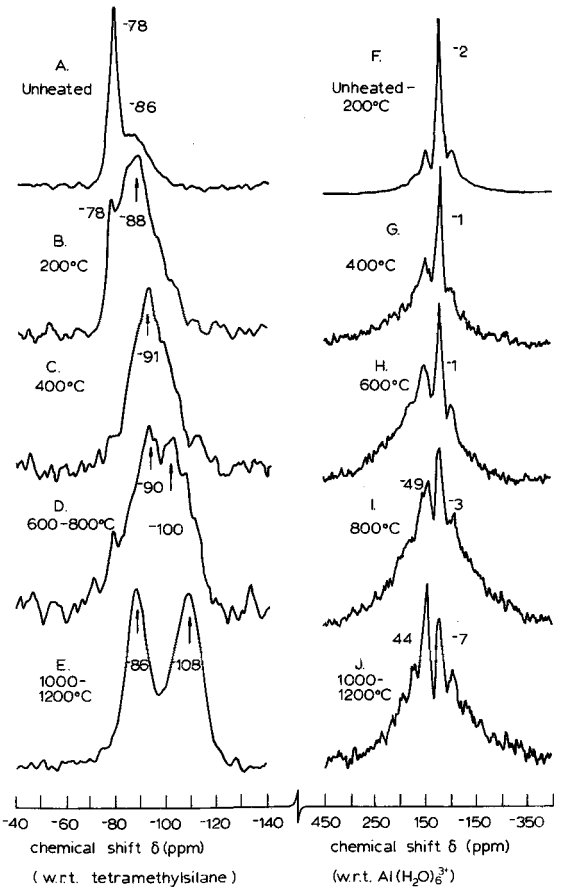

Figure 5. Typical solid-state NMR spectra of Ki-P allophane; unheated, and heated to the indicated temperatures. A–E, ^{29}Si spectra, F–J, ^{27}Al spectra.

X-ray powder diffraction shows that heating produces similar structural changes in all four allophanes, although in the Derbyshire material two additional high-temperature phases, corundum (α-Al_2O_3) and anorthite ($CaAl_2Si_2O_8$), appear above 1000°C. In all the allophanes, the loss of water below about 500°C results in the loss of all the broad diffraction bands except that centered at about 3.4 Å, which broadens still further and shifts to about 4.1 Å. The exothermic DTA peak at about 1000°C corresponds with the appearance of a well-defined mullite X-ray pattern. This is preceded in the Silica Springs and Ki-P samples by small, ill-defined X-ray peaks which appear 200–400°C below the exotherm temperature and correspond to the major mullite peaks at about 3.4 and 2.2 Å. The composition of the mullites formed at 1200°C, estimated from accurate measurements of the cell volume using the relationship of Cameron (1977), are 63.7, 65.1, 61.3 and 52.6 mol % of Al_2O_3 for Silica Springs, Derbyshire, Ki-P and VA allophanes, respectively.

Solid-state ^{29}Si and ^{27}Al MAS NMR spectra of the four allophanes heated to various temperatures for 15 min are shown in Figures 3–6.

The ^{29}Si spectra of the unheated minerals confirm previously published observations (Goodman *et al.*, 1985; Barron *et al.*, 1982) of a sharp imogolite-like peak at −78 to −79 ppm, superimposed on a broader feature centered at about −86 ppm, except in the Silica Springs sample, in which the imogolite-like resonance is absent. Similar ^{29}Si NMR spectra have been published for synthetic aluminosilicates (Wilson *et al.*, 1988) in which the sharp resonance at −79 ppm is ascribed to "protoimogolite." In this instance one hydroxyl group is bonded directly to each silicon, whereas the broad resonance centered at about −90 ppm is ascribed to a range of silicons coordinated to varying numbers of aluminums. The mean chemical shift of this resonance has led to the suggestion that the number of coordinated aluminums is predominantly 1 to 2 (Wilson *et al.*, 1986), although the similarity of this chemical shift to that of spherical halloysite (−93 ppm) and other 1:1 layer aluminosilicates such as kaolinite (−91 to −92 ppm) has been cited as evidence for the presence of a rudimentary 1:1 layer structure (Wada *et al.*, 1988).

The ^{27}Al NMR spectra of the unheated minerals

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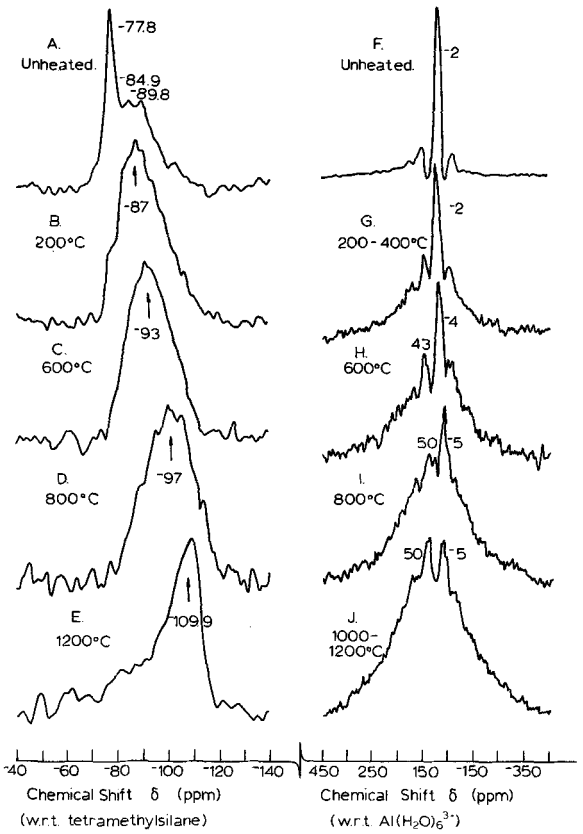

Figure 6. Typical solid-state NMR spectra of VA allophane; unheated, and heated to the indicated temperatures. A–E, ^{29}Si spectra, F–J, ^{27}Al spectra.

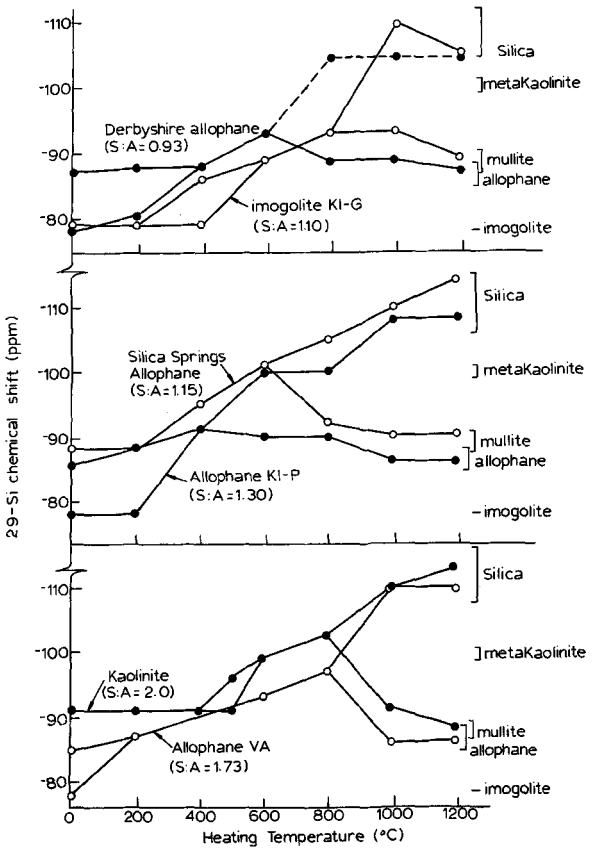

Figure 7. Changes in the ^{29}Si chemical shift of the various allophanes as a function of heating temperature, compared with imogolite and kaolinite.

(Figures 3–6) all show a major resonance close to 0 ppm corresponding to octahedral aluminum. In the Silica Springs sample, a significant tetrahedral resonance also occurs at 56 ppm. Similar tetrahedral resonances may also occur in the other allophanes, but at much lower intensities. The observation of significant tetrahedral Al in the sample containing no protoimogolite is consistent with previous findings (Goodman *et al.*, 1985).

On heating to 200°C, the sharp ^{29}Si protoimogolite resonance decreases in all the samples in which it was originally present (Figures 4B, 5B, 6B), but without an obvious increase in the relative intensity of the tetrahedral Al resonance (Figures 4H, 5F, 6G), as would be expected if the removal of protoimogolite-type hydroxyl groups resulted in the formation of material identical to Silica Springs allophane. When Silica Springs allophane is heated to 200°C, a marked *decrease* in tetrahedral Al is found (Figure 3I). Further heating until all the water has been lost (>600°C) results in progressive changes in the ^{29}Si chemical shifts, as summarized in Figure 7.

Several points emerge from Figure 7: (1) after the loss of the sharp imogolite-type resonance at −78 ppm on heating to >200°C, the chemical shift of the broad allophane resonance progressively moves upfield during dehydroxylation. This eventually splits into two resolvable resonances, the chemical shift of one becoming progressively like that of the principal ^{29}Si resonance of mullite (−86 to −90 ppm, Brown *et al.*, 1985). The chemical shift of the other resonance (−108 to −113 ppm) is characteristic of uncombined silica, shown by X-ray diffraction to be largely X-ray amorphous. The relative intensity of the uncombined silica resonance is consistent with the silica content of the starting material, being greatest in the highest-silica sample VA (Figure 6E), and smallest in the lowest-silica Derbyshire allophane (Figure 4F). The ^{29}Si resonances of anorthite, the secondary product phase formed in Derbyshire allophane, occur at −83 to −89 ppm (Lippma *et al.*, 1980; Kirkpatrick *et al.*, 1985), and would thus fall under the envelope of the broad mullite peak centered at −87 ppm in this sample (Figure 4F). (2) The chemical shift of allophane dehydroxylate, below the temperature at which silica separates, seems to be related to the silica : alumina ratio (S:A)

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of the starting material. Where S:A ≈ 1, the chemical shift of the dehydroxylate is about −90 to −92 ppm, similar to the chemical shift of imogolite dehydroxylate shown for comparison in Figure 7. In allophane VA (S:A = 1.73), the chemical shift of the dehydroxylate (−97 ppm) more closely approaches that of metakaolinite (S:A = 2), also plotted for comparison in Figure 7. Silica Springs allophane (S:A = 1.15) with a dehydroxylate chemical shift of approximately −100 ppm, is an exception, behaving more like metakaolinite than like imogolite or other allophanes of comparable S:A ratios.

Detection of those silicon atoms in close proximity to protons was carried out by making cross-polarization (CP) measurements on the unheated and partially dehydrated samples, but the very short relaxation times $T_{1\rho}H$ (about 1–6 ms) made it difficult to deduce reliable correction factors for quantitation of the CP Si signal intensity. Nevertheless, as expected, the CP signal intensity decreases in all samples in an approximately similar manner to the weight-loss curves (Figure 2). The chemical shifts of the CP ^{29}Si resonances are similar at each temperature to those of the gated-decoupling (non-CP) spectra for all allophanes except Silica Springs. The CP spectrum of this material retains the characteristic chemical shift of the fully hydrated samples, even after heating at 600°C (Figure 3D), whereas the gated-decoupling spectrum of the same sample (Figure 3C) consists of a broad resonance with a chemical shift typical of a dehydroxylated phase. This suggests that in all the samples other than Silica Springs, the environment of all the silicon atoms changes similarly during dehydroxylation. In the Silica Springs allophane, the effects of dehydroxylation are more localized, being reflected by only those silicons in proximity to a hydroxylated species. In this respect, the CP silicon atoms in the Silica Springs allophane behave more like those of pyrophyllite (MacKenzie *et al.*, 1985b), whereas the CP silicons in the other allophanes behave more like those in kaolinite (MacKenzie *et al.*, 1985a).

Thermal dehydroxylation reduces the total intensity of all the ^{27}Al NMR spectra of all samples, as plotted in Figure 8, in which the Al intensity is expressed as a percentage of total Al determined for the unheated samples by chemical analysis and corrected for the measured weight loss at each measurement temperature.

Identical Al intensity behavior has been found in heated imogolite (MacKenzie *et al.*, 1989), and in other aluminosilicate minerals such as metakaolinite (MacKenzie *et al.*, 1985a), pyrophyllite dehydroxylate (MacKenzie *et al.*, 1985b) and montmorillonite dehydroxylate (Brown *et al.*, 1987). The decrease in ^{27}Al signal intensity on dehydroxylation has been ascribed in these papers to electric field gradients set up by crystallographic distortions and/or defect formation

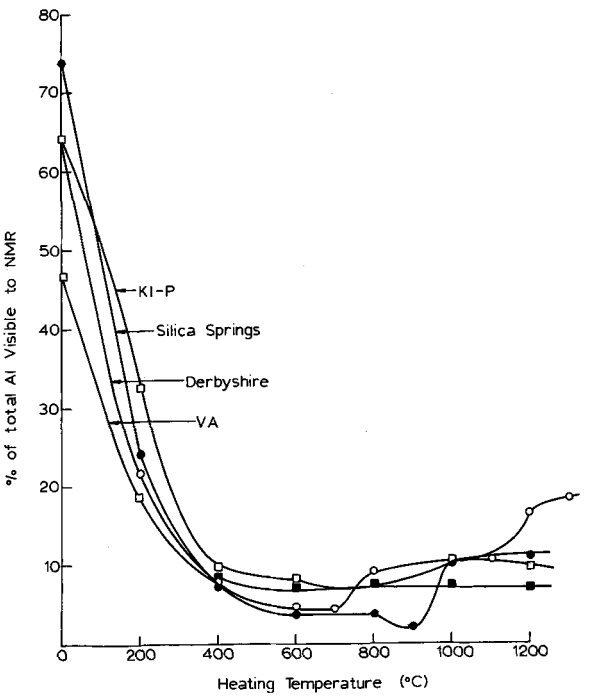

Figure 8. Change in the percentage of NMR-visible Al in the various allophanes as a function of heating temperature.

accompanying dehydroxylation, which broaden the signal from the quadrupolar ^{27}Al nuclei beyond detection. A similar explanation seems reasonable for allophane and imogolite.

As dehydroxylation progresses, the proportion of non-octahedral ^{27}Al resonance detected by NMR increases in all the samples. In the two precipitated allophanes, two non-octahedral resonances can clearly be distinguished (Figures 3K, 4K), and a corresponding splitting may also be present in the Japanese allophanes Ki-P and VA (Figures 5I, 6I). These ^{27}Al spectra are very similar to those of dehydroxylated imogolite (Mackenzie *et al.*, 1989), and for layer-lattice aluminosilicate dehydroxylates derived from pyrophyllite (MacKenzie *et al.*, 1985b) and kaolinite (MacKenzie *et al.*, 1985a). On heating to higher temperatures, the ^{27}Al spectra indicate a combination of octahedral and tetrahedral Al such as found in the ^{27}Al NMR spectrum of mullite (Brown *et al.*, 1985). The relative intensity of the octahedral resonance is greatest in the Derbyshire allophane (Figure 4L) due to the presence in that material of corundum, α-A_2O_3, in which the aluminum is 6-coordinate.

IMPLICATIONS FOR THE STRUCTURE OF ALLOPHANES

To be fully satisfactory, any proposed structural model for allophane must take account of the foregoing NMR results, and fulfill the following requirements: (1) It must contain structural units of the type found

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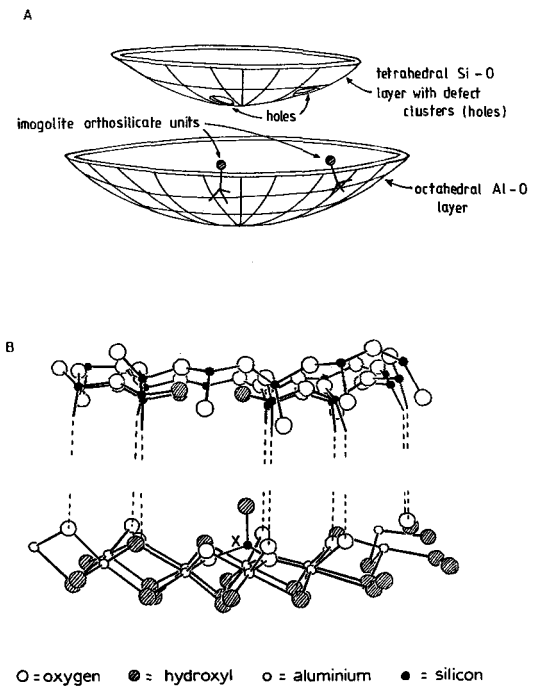

Figure 9. (A) Schematic diagram of the conceptual model of allophane, showing a hemispherical slice only, the Si-O and Al-O sheets separated for clarity. (B) Computer-generated diagram of curved cross-section of sphere wall, with the Si-O and Al-O sheets separated for clarity. The one imogolite unit shown here is marked X.

in imogolite (characterized by a sharp ^{29}Si resonance at −78 ppm), but in a form which is comparatively thermally unstable (decomposing at about 200°C). (2) It must also contain a structural unit which gives rise to the broad ^{29}Si NMR band centered at about −86 ppm. This resonance is very similar to that found in dehydroxylated imogolite, for which a layer structure has been postulated (MacKenzie *et al.*, 1989). (3) It must be able to account for silica/alumina ratios ranging from 1:1 to 2:1, and take account of the spherical morphology of the allophane particles. (4) It must be capable of dehydroxylating to a structure giving rise to a broad ^{29}Si NMR resonance which is normally at about −90 ppm (as in imogolite dehydroxylate), but which can range to about −100 ppm (as in metakaolinite). (5) Ideally, it should also be capable of accounting for features of the ^{27}Al NMR spectra such as the observation of two non-octahedral resonances in the dehydroxylated phase.

The following structural proposals may not apply to Silica Springs allophane, the anomalous behavior of which suggests that it is of a different structural type.

DEVELOPMENT OF A STRUCTURAL MODEL

The present model is based on a defect kaolinite-type layer structure, since a number of compositional and structural features can be accounted for in terms of such structures (Brindley and Fancher, 1970). The isolated orthosilicate units characteristic of imogolite are assumed to be associated with the gibbsite sheet, as in imogolite. They may be inserted either from the alumina side of the kaolinite layer structure, or from the silica side, through the gaps formed by the extended clusters of silicon defects (Brindley and Fancher, 1970). The ease with which the imogolite units dehydroxylate suggests that these hydroxyls are in close proximity to others, such as those which occur at the perimeter of the defect clusters in the tetrahedral sheet. On this reasoning the imogolite units are inserted into the octahedral sheet with their hydroxyls protruding through the gaps in the tetrahedral sheet, as shown schematically in Figure 9A.

To take account of the spherical particle morphology, the kaolinite layer structure was curved, such that the octahedral (gibbsite) sheet is outermost and the defect-containing tetrahedral sheet innermost. Although the mismatch in the b-dimensions of the octahedral and tetrahedral sheets of the kaolinite structure (8.64 Å and ≥9.16 Å, respectively) suggests logically that the tetrahedral sheet might be outermost, this conformation results in the apertures of the octahedral sheet being too large to accommodate the imogolite units. By curving the kaolinite layer structure in the opposite way, the size of these apertures is reduced, although further adjustment of the adjacent oxygens is required for a proper match to the imogolite units (see below).

To curve the kaolinite layer structure, an extended structural segment was created in the a–b plane by amalgamating several adjacent kaolinite unit cells, and a reference point was defined, which becomes the center of the new spherical unit. The perpendicular distance h above the a–b plane which passes through this reference point was then determined for each atom in the structure, and the atoms were then repositioned along the spherical radius in such a way that the radial distance from the reference point is h. If x, y and z are the orthogonal coordinates (in Å) of the planar kaolinite layer structure, where the z coordinates are perpendicular to the plane of the sheet, the corresponding spherical coordinates $\bar{x}$, $\bar{y}$ and $\bar{z}$ are given by:

$$\bar{x} = z \sin[(x^2 + y^2/r)^{1/2}]/[1 + (y/x)^2]^{1/2} \quad (1)$$

$$\bar{y} = y\bar{x}/x \quad (2)$$

$$\bar{z} = z \cos[(x^2 + y^2)/r]^{1/2} \quad (3)$$

where the x and y coordinates are such that the plane of the Al sheet is 25 Å from the origin, i.e., the spherical radius r is taken as 25 Å, a typical dimension for allophane. The spherical coordinates are then used to generate the curved structure.

First attempts to computer-model this structure resulted in a curved sheet structure with a mean tetrahedral angle θ which predicted a satisfactory ^{29}Si NMR

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chemical shift δ (−86 to −89 ppm) when substituted into the empirical relationship:

$$\delta = -176.65 - 55.821 \sec\theta \ldots \quad (4)$$

Eq. (1) has been shown to predict ^{29}Si chemical shifts to within 2 ppm in other aluminosilicates of known structure, and has also been applied to imogolite (MacKenzie *et al.*, 1989).

However, the process of curving the kaolinite layer structure has two undesirable consequences for the structure: (1) The mean Si-O bond lengths are shortened to 1.466 Å, by comparison with about 1.6 Å in the planar structure, and (2) although the aperture in the gibbsite sheet is contracted by the curving process, it is still too large to accommodate the imogolite unit. (In imogolite, the triangle joining the three bonding oxygens of this aperture has a side length of 2.7 Å, whereas in the curved sheet structure this dimension is about 3.1 Å.)

The undesirable contraction in the Si-O bond lengths in (1) above can be counteracted by expanding the kaolinite layer structure by 13% in the a–b plane before applying the curving process. Both the mean Si-O bond lengths and the calculated ^{29}Si chemical shift are then correct (1.6 Å and −89 ppm, respectively), but this procedure does nothing to correct the aperture in the gibbsite sheet [(2) above]. This problem can be overcome by moving these particular oxygen atoms closer together, and simultaneously adjusting the positions of the aluminum atoms in the next coordination sphere to maintain the correct mean tetrahedral angle of the inserted imogolite orthosilicate unit (124.5°, corresponding to a chemical shift of −78 ppm). Thus, the calculated ^{29}Si chemical shifts of both the sheet and orthosilicate units in this structure are consistent with the observed shifts, and the Si-O bond lengths are also correct. The coordination of the aluminums adjacent to the imogolite orthosilicate units is extremely distorted from octahedral symmetry; the *cis* Al-O angles range from 63.8° to 111.2°, while the *trans* Al-O angles range from 160.0° to 169.6° (cf., 90° and 180°, respectively, for true octahedral symmetry). By analogy with similarly distorted Al sites in other minerals, these atoms would not be expected to give rise to a ^{27}Al NMR signal (MacKenzie *et al.*, 1985a). This is again consistent with observation because only 47–64% of the total Al is NMR-visible in the unheated samples other than anomalous Silica Springs allophane (Figure 8). The remaining Al atoms are therefore in sites too distorted to be NMR-visible, which are most likely to correspond to the sites adjacent to the imogolite orthosilicates. A computer-generated view of a portion of this structure is shown in Figure 9B, in which the Si-O and Al-O sheets are separated for clarity.

Although the size of the silicon defects in the tetrahedral sheet, into which the hydroxyl associated with the imogolite unit protrudes (Figure 9), can vary from one silicon up to several (Brindley and Fancher, 1970), there is only one position of the imogolite unit with respect to the defect in which the imogolite hydroxyl is in suitable proximity to a tetrahedral sheet hydroxyl to permit dehydroxylation. A consequence of this disposition of the imogolite orthosilicate unit to the tetrahedral sheet defect is the sharing of one of the oxygens of the gibbsite sheet between one silicon each from the imogolite unit and from the tetrahedral sheet, as well as the two aluminums from the gibbsite sheet. Although this situation could be avoided if the imogolite unit is located elsewhere is relation to the defect, computer simulation shows that the resulting configuration would dehydroxylate only upon structural disintegration, and is inconsistent with the experimental observation that the imogolite units are the first to undergo thermal reaction below 200°C. A computer-generated model of the structure which embodies all these features is shown in Figure 10.

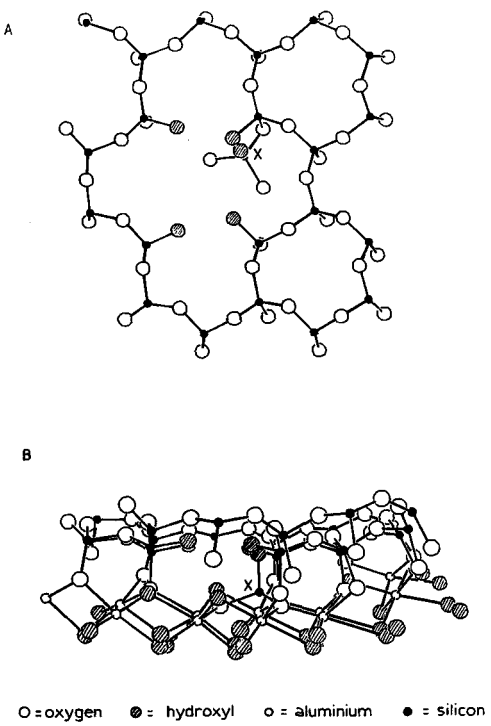

Figure 10. (A) Computer-generated diagram of Si-O sheet of proposed allophane structure. Plan view from center of the spherical particle, showing a Si defect cluster (hole) with an inserted imogolite unit, marked X. (B) Computer-generated diagram of curved cross-section of sphere wall. Imogolite unit marked X.

On heating this structure, the imogolite unit hydroxyls should readily condense at low temperature with the hydroxyls of the tetrahedral sheet defects because the close proximity of these hydroxyls (0.5–1 Å) will make them extremely labile. The loss of the imogolite ^{29}Si NMR resonance at −78 ppm upon low-tem-

perature dehydroxylation is consistent with a readjustment of the positions of the atoms in proximity to the imogolite unit, namely the Al and O atoms bonded both to the imogolite unit and to the neighboring non-imogolite SiO_4 units. Small changes in the position of these atoms can be shown by calculation to shift the ^{29}Si imogolite resonance upfield, to coincide with the broad envelope of the ^{29}Si resonances arising from the layer-lattice silicons. This curved layer-lattice should subsequently dehydroxylate following the sequence established for kaolinite (MacKenzie *et al.*, 1985a), which gives rise to a silicate structure consistent with the observed ^{29}Si NMR spectra of allophane dehydroxylate and provides an explanation for the two non-octahedral ^{27}Al NMR resonances observed both in allophane dehydroxylate and metakaolinite.

The allophane structure proposed above fulfills all the requirements, including full consistency with the NMR results and the dehydroxylation behavior of all the present allophanes (except the Silica Springs sample).

CONCLUSIONS

1. Similarities between the ^{29}Si and ^{27}Al solid-state NMR spectra of two volcanic Japanese allophanes and one precipitated English allophane, and the spectra of imogolite and layer-lattice aluminosilicates such as kaolinite, suggest the presence of common structural features consisting of imogolite-like orthosilicate units and a range of layer-lattice-like structures. A fourth sample (a precipitated New Zealand allophane) contains no imogolite-like units and significant amounts of both tetrahedral and octahedral aluminum.
2. Changes in the solid-state NMR spectra of the allophanes on heating are similar to those found in heated tubular imogolite, except that in allophane the imogolite units are considerably less thermally stable, dehydroxylating at 400°C lower than in tubular imogolite. Heating the New Zealand allophane at 200°C results in a decrease in the tetrahedral aluminum content. Subsequent changes in the ^{29}Si and ^{27}Al spectra on heating are broadly similar to those of imogolite and layer-lattice aluminosilicates such as kaolinite, but the details depend on the silica : alumina ratio.
3. These results for the three allophanes containing imogolite-like units can be accounted for in terms of a structural model consisting of a two-sheet, kaolinite-like structure containing defects (holes in the tetrahedral sheet) which is curved into a sphere. The imogolite-like units are anchored in the octahedral sheet and fit into the defects in the tetrahedral sheet. Computer simulation of this model shows that it is crystallographically sound, having sensible bond lengths and bond angles consistent with the NMR spectra. Such a model also accounts for the spherical particle morphology and the observed dehydroxylation behavior of allophanes containing imogolite-like units.

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