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THE STRUCTURE AND THERMAL REACTIONS OF NATURAL IRON-CONTAINING ALLOPHANES STUDIED BY 57-Fe MÖSSBAUER SPECTROSCOPY

K.J.D. MACKENZIE and C.M. CARDILE
Chemistry Division, DSIR, Private Bag, Petone (New Zealand)

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ABSTRACT

Thermal analysis, X-ray diffraction and Mössbauer spectroscopy have been used to investigate the environment of the iron in four Japanese allophanes, and the changes occurring during dehydration. In the unheated minerals, the iron occurs as a surface coating of poorly crystalline ferrihydrite which appears to be strongly bound to the aluminosilicate substrate. The removal of this oxide coating should be possible by mild chemical treatment without disruption of the allophane structure. On dehydration, the iron sites become progressively more distorted, and although the strongly bound surface oxide still persists, some of the iron has moved into sites which are not magnetically ordered at 4.2 K. By about 1000 ° C, virtually all of the iron has moved into the structural sites of the mullite which is formed at that temperature.

INTRODUCTION

Allophane is a poorly-crystalline hydrous aluminosilicate phase which can form naturally either as a precipitate in streams of appropriate dissolved mineral content (as in Derbyshire, U.K. [1] or Silica Springs, New Zealand [2]), or, more commonly, as a component of soils derived from volcanic ash [3]. By virtue of its origin, soil allophane commonly has appreciable iron content; whether this iron plays any structural role is at present unclear, although McBride et al. [4] have suggested that there is little structural participation of iron in synthetic aluminosilicate gels. A practical consequence of the presence of structural iron arises when natural allophanes have to be chemically deferrated, as is necessary for structural studies by techniques such as high-resolution solid-state 29-Si and 27-Al nuclear magnetic resonance [5], for which a low iron content is essential. The prospect of removing the iron chemically without significant structural damage is clearly better if the iron itself is non-structural. A further matter of interest is the way in which the chemical environment of the iron changes during thermal dehydration, since dehydration/rehydration phenomena are important in determining the characteristics of allophanic soils.

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In the present work, Mössbauer spectroscopy, coupled with X-ray powder diffraction and thermal analysis methods, was used to investigate the behaviour of the iron in four well-characterized Japanese allophanes derived from weathered pumices.

EXPERIMENTAL

The four allophanes were: (i) sample Ki-P, from Kitakami, Iwate, $SiO_2/Al_2O_3 = 1.12$, (ii) sample Ku-P, from Kurayoshi, Tottori, $SiO_2/Al_2O_3 = 1.38$, (iii) sample PA-P, from Choyo, Kumamoto, $SiO_2/Al_2O_3 = 1.67$, (iv) sample VA, also from Choyo, Kumamoto, $SiO_2/Al_2O_3 = 1.68$.

The iron contents of these samples, expressed as wt% Fe_2O_3, are 6.7, 9.1, 13.0 and 9.1% respectively. All these samples and their method of separation and purification are described in detail elsewhere [6]. X-ray powder diffraction showed the broad, characteristic bands of allophane, with one or two sharper reflections superimposed, which were, however, too weak to be unambiguously identified. These additional weak reflections, which were not present in sample VA, were lost from samples heated to 200 ° C.

Thermal analyses were carried out in air at 10 ° C min^{-1} using a Stanton TG770 thermobalance and a Stone model 202 differential thermal analyser (DTA). Mössbauer spectroscopy and X-ray diffraction was carried out on samples heated in air for 15 min at successively higher temperatures in a platinum-lined boat inserted in an electric tube furnace. The Mössbauer spectra were obtained at room temperature using an Elscint AME-50 spectrometer, the 4.2 K spectra being recorded at Monash University. A 57-Co/Rh source was used for all spectra, and the quoted isomer shifts (IS) are referenced with respect to soft iron metal. The spectra were computer-fitted to Lorentzian lineshapes, using the χ^2 test to determine the best fit to the experimental data points. X-ray powder diffraction was carried out using a computer controlled Philips PW1700 diffractometer with Co $K\alpha$ radiation and a graphite monochromator.

RESULTS AND DISCUSSION

The TG and DTA curves of all four samples are similar (Fig. 1), showing an endothermic weight-loss starting at ambient temperature and ending at about 600 ° C, reflecting the gradual removal of gel water from the structure. Throughout this dehydration process, the X-ray diffraction patterns are unchanged, except for the loss at < 200 ° C of the one or two weak peaks of an unidentified phase, and a gradual loss of intensity and merging of the characteristic broad allophane diffraction bands. After dehydration is complete, all the samples remain X-ray amorphous until crystallization of

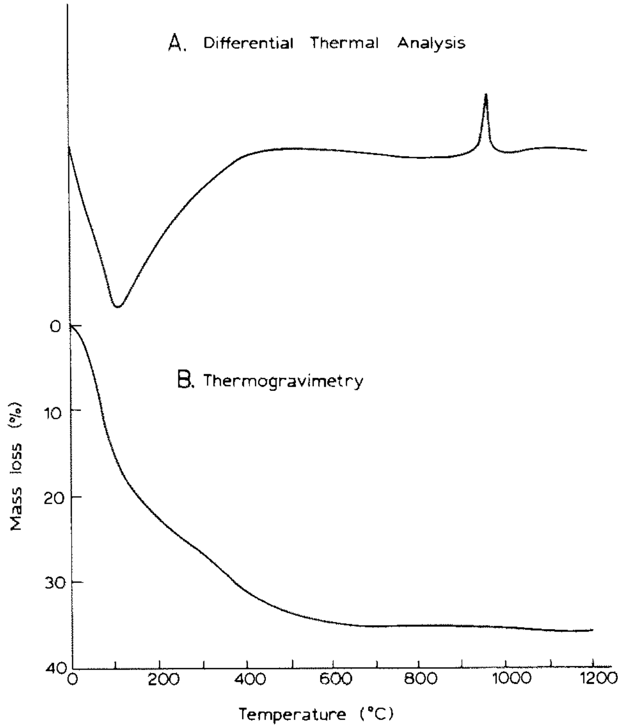

Fig. 1. Typical thermal analysis curves for Japanese allophane (sample Ki-P). Heating rate 10 °C min^{-1}, atmosphere air.

mullite ($3Al_2O_3 \cdot 2SiO_2$) at about 1000 °C, as indicated by a sharp exothermic DTA peak at this temperature (Fig. 1). The X-ray pattern of the newly-formed mullite grows out of diffuse X-ray bands centred at about 2.4 and 1.99 Å, which could correspond to a transitional form of Al_2O_3, but cannot be confidently identified from the present data.

Concomitantly with the appearance of mullite, a weak, broad X-ray band appears, centred at about 4.3 Å; this is probably due to amorphous silica, since on further heating it is converted to a sharp cristobalite peak. The more silica-rich samples VA and PA-P produce significantly more intense cristobalite peaks.

Typical room-temperature Mössbauer spectra of the unheated allophanes are shown in Fig. 2. All the allophanes except VA have spectra as in Fig. 2, which can be fitted with doublets of typical Fe^{3+} parameters (isomer shift, $IS = 0.31$–0.40 mm s^{-1}, quadrupole splitting, $QS = 0.56$–0.62 and 0.89–1.01 mm s^{-1}). A significantly poorer fit, judged by the χ^2 values, is obtained with only one doublet, whereas the inclusion of a third doublet gives little improvement. Allophane VA contains in addition to the Fe^{3+} doublets, a small Fe^{2+} component ($IS = 0.96$, $QS = 2.62$ mm s^{-1}). The resolution of two Fe^{3+} doublets does not necessarily indicate the presence of only two

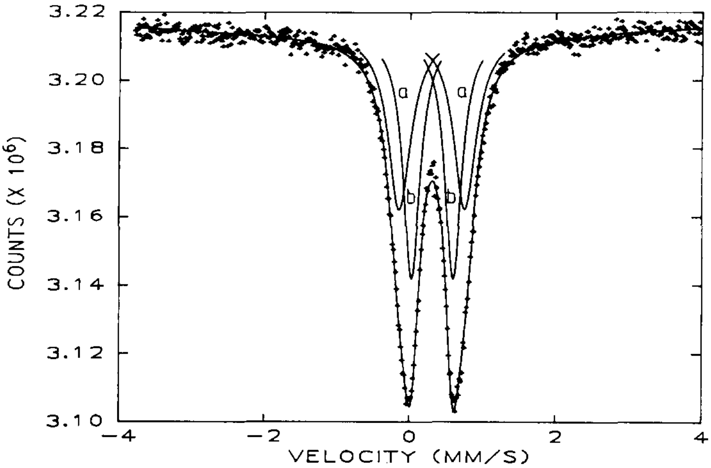

Fig. 2. Typical room-temperature Mössbauer spectrum of unheated Japanese allophane (sample Ku-P).

sites; the Mössbauer spectrum of the poorly crystalline hydrous ferric oxide ferrihydride similarly is best fitted by only two doublets having parameters almost identical to the present allophane parameters [7,8]. These results ($IS = 0.35$–0.36 and 0.33–0.34 mm s^{-1}, $QS = 0.54$–0.56 and 0.89–0.93 mm s^{-1}) [7,8] have been interpreted as representing the best statistical description of a system containing a continuous range of iron environments [7]. A similar interpretation could hold for the present samples, in view of their similar gel-like nature, microcrystallinity and lack of short-range order. The similarity between the present unheated parameters and those of ferrihydride [7] suggests that the iron in the present allophanes may occur in a phase similar to ferrihydride, possibly located on the surface of the allophane particles rather than substituting for Al^{3+} in the aluminosilicate unit.

To investigate this point in more detail, the Mössbauer spectra of the allophanes were determined at 77 and 4.2 K. At 77 K, the spectra are unsplit (Fig. 3A), whereas at 4.2 K, a magnetically-split sextet spectrum was found for the unheated samples (Fig. 3B).

The isomer shifts and effective fields (B_{eff}) at 4.2 K are 0.47–0.51 mm s^{-1} and 43.3–43.9 T respectively. Attempts to fit a small additional central doublet component to the 4.2 K spectra gave a slight improvement in χ^2, but the quality of the data is such that the addition of a central doublet is probably not justified.

Comparison of the parameters at 4.2 K with those reported for other iron oxides (Table 1) indicates that the present B_{eff} values are significantly smaller than those of any other iron oxide phase, with the exception of lepidocrocite. However, similar magnetically-split parameters have recently been found by Murad and Schwertmann for iron-containing soils from

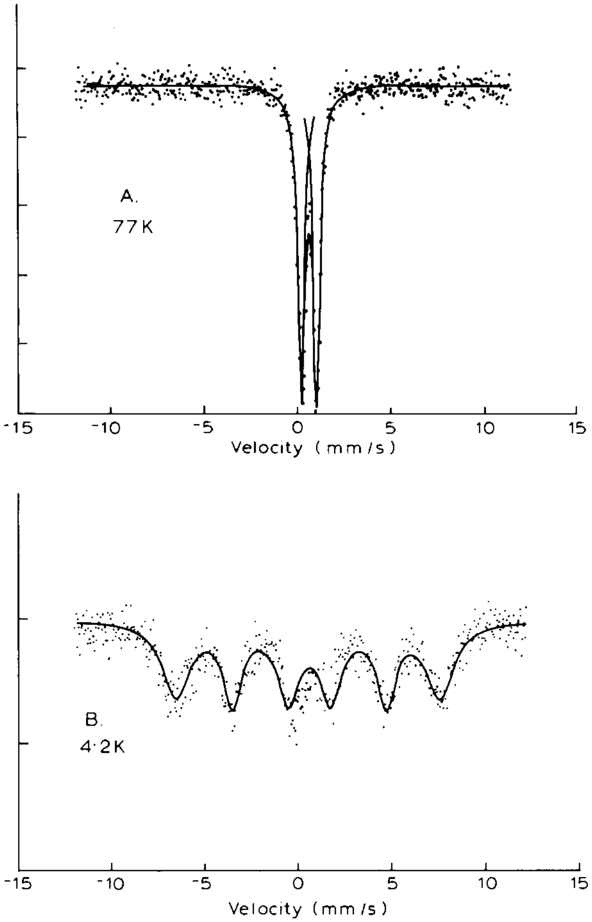

Fig. 3. Typical low-temperature Mössbauer spectra of unheated Japanese allophane (sample PA-P).

TABLE 1

Mössbauer parameters of magnetically ordered spectra in allophane and iron oxides

Compound	Temperature (K)	B_{eff} (T)	Reference
Allophane	4.2	43.3–43.9	this work
Haematite, α-Fe_2O_3	4.2	54.0	8
Haematite with 10 mol% Al substitution	298	50.7–51.0	9
Maghaemite, γ-Fe_2O_3	77	51.6–51.9	10
Goethite, α-FeOOH	4.2	50.5	8
Goethite with 10 mol% Al substitution	4.2	50.0	11
Akaganéite, β-FeOOH	4.2	47.3–48.6	8
Lepidocrocite, γ-FeOOH	4.2	45.5	8
Ferrihydrite	4.2	50.0	8

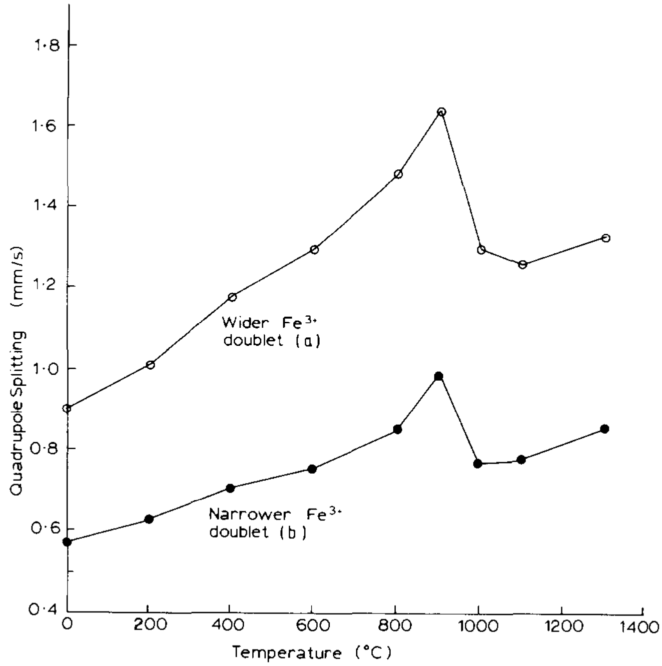

Fig. 4. Typical changes in the *QS* values of the room-temperature Mössbauer spectra of Japanese allophane (sample Ku-P) after heating to various temperatures for 15 min in air.

Marion Island in which a low effective field (47.9 T) is attributed to chemical interaction between a very poorly crystalline ferrihydrite and the surface of the soil mineral on which it is deposited [12]. A similar explanation could also account for the Mössbauer parameters found for the present 4.2 K spectra of unheated allophanes.

The room-temperature Mössbauer spectra of samples heated to progressively higher temperatures continue to be fitted satisfactorily by two Fe^{3+} doublets, the *QS* values of which progressively increase during dehydration, up to the crystallization temperature (Fig. 4). Throughout this temperature range, the isomer shifts remain reasonably constant, but the linewidths of both resonances increase, consistent with increasing disorder. The Fe^{2+} resonance in sample VA does not survive heating above 400 ° C. No discontinuity is observed in the Mössbauer parameters at about 600 ° C (the temperature by which the samples are fully dehydrated), suggesting a smooth transition from a ferrihydrite-like material to its dehydrated form (haematite of a particle size which is too small or finely-dispersed to be magnetically split at room temperature). The Mössbauer parameters of two-line haematite are reported by Van der Kraan as consisting of two partly overlapping doublets of similar *IS* and *QS* values to ferrihydride [13]. However, the *QS* value of two-line haematite is reported to increase with decreasing particle size [14], and can range between 0.44 and 0.98 mm s^{-1}.

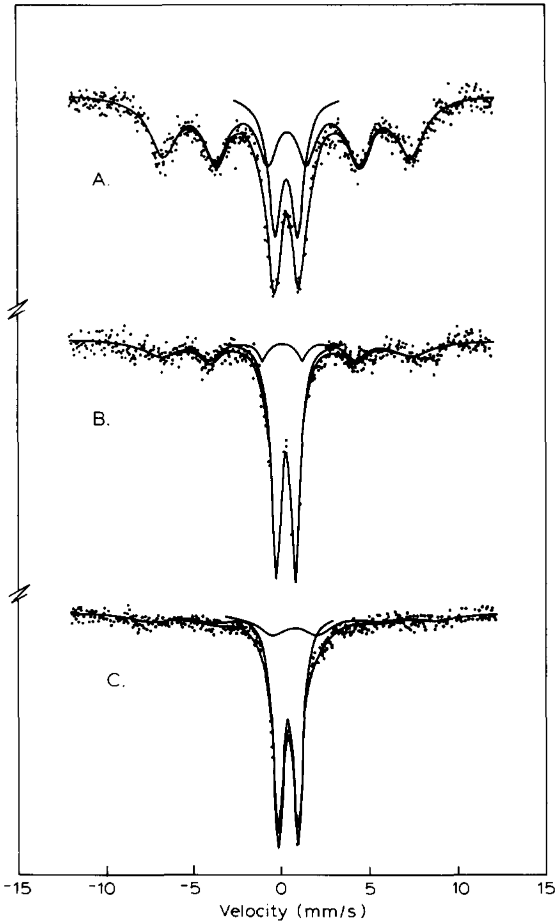

Fig. 5. Typical 4.2 K Mössbauer spectra of heated Japanese allophane (sample PA-P), and, for comparison, mullite from Taupiri clay (described in ref. 15). A. Allophane fully dehydrated at 600 °C for 15 min in air. B. Allophane heated to 1300 °C for 15 min in air. C. Mullite.

Since the present *QS* values tend, as heating progresses, towards larger splittings than the above range, these parameters probably reflect increasing distortion as dehydration proceeds.

The 4.2 K Mössbauer spectrum of allophane fully dehydrated by heating to 600 °C is shown in Fig. 5A. This spectrum consists of a magnetically-split sextet attributable to dehydrated surface iron oxide, together with a clearly-resolved central doublet. The parameters of the sextet ($IS = 0.48$ mm s^{-1}, $B_{eff} = 44.0$ T) are virtually unchanged from those found for the undehydrated mineral, suggesting the persistence of oxide–substrate interactions even after dehydration. The parameters of the central doublet ($IS = 0.45$, $QS = 1.31$ mm s^{-1}) are similar to those of the wider resonance observed at room temperature in dehydrated samples, but the absence of magnetic ordering suggests that this species (which represents about 29% of the total iron) has become incorporated in the structure to a greater degree than the magnetically-ordered oxide.

Crystallization to mullite at about 1000 ° C results in a sharp decrease in the room-temperature *QS* values of both resonances (Fig. 4), which, over the range 1000–1300 ° C assume the values: major resonance, $IS = 0.32–0.36$, $QS = 1.11–1.49$ mm s^{-1}; minor resonance, $IS = 0.29–0.38$, $QS = 0.66–0.92$ mm s^{-1}. These parameters compare well with those previously reported for a range of iron-substituted mullites [15] (major resonance, $IS = 0.28–0.37$, $QS = 1.17–1.30$ mm s^{-1}; minor resonance, $IS = 0.28–0.38$, $QS = 0.63–0.92$ mm s^{-1}). These results suggest that at the temperature at which the allophane structure transforms to mullite, the iron enters fully into structural sites in the product.

Support for this concept is found in the 4.2 K spectrum of allophane fired at 1300 ° C (Fig. 5B), which indicates that the bulk of the iron is present in a central doublet, with $IS = 0.41$, $QS = 1.09$ mm s^{-1}. A similar spectrum was obtained at 4.2 K for a well-characterized mullite [15] prepared from an iron-containing fireclay (Fig. 5C), for which the parameters of the central doublet ($IS = 0.42$, $QS = 1.12$ mm s^{-1}) are virtually identical with those of the fired allophane. This suggests that the environment of the iron in fired allophane is the same as in the well-characterized mullite, in which sample it is fully structural.

CONCLUSIONS

The iron in four Japanese allophanes is present as a hydrated iron oxide similar to poorly crystalline ferrihydrite on the surface of the allophane particles. Mössbauer spectroscopy indicates that on cooling to 4.2 K, magnetic ordering occurs, but the effective field (B_{eff}) is considerably smaller than that of ferrihydrite. This result may indicate a stronger degree of binding between the ferrihydrite and the aluminosilicate substrate, as has been suggested for soils from Marion Island [12]. Nevertheless, the occurrence of the iron as a non-structural surface oxide should facilitate its removal by chemical methods which are sufficiently mild not to cause structural disruption.

On heating, the allophanes progressively lose their hydration water, becoming fully dehydrated by about 600 ° C. Room-temperature Mössbauer spectroscopy indicates that dehydration is accompanied by increases in linewidth and quadrupole splitting, suggesting that the iron sites are becoming progressively more distorted during dehydration. Fully dehydrated allophane has a 4.2 K Mössbauer spectrum which indicates that about 70% of the iron is present in a magnetically-ordered surface oxide phase, which, judging from its effective field, is still strongly interacting with the substrate.

The remaining 29% of the iron has moved into sites which are not magnetically ordered even at 4.2 K.

On heating to about 1000 °C, an exothermic structural rearrangement occurs, with the formation of mullite, $3Al_2O_3 \cdot 2SiO_2$. Crystallization is accompanied by an abrupt decrease in the linewidth and quadrupole splitting. Both the room-temperature and 4.2 K Mössbauer spectra are identical with the spectra of well-characterized iron-containing mullite, suggesting that on crystallization, the iron is essentially fully incorporated into the crystalline phase.

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