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Identification of iron-containing impurities in natural kaolinites using the Mössbauer effect

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SUMMARY. Two clay samples originating in the kaolinized granite area near St. Austell, Cornwall, have been examined by Mössbauer spectroscopy. The iron-containing impurity in the sample with a red discoloration (sample A) has, by measurement of the hyperfine magnetic field, been identified as hematite. In the case of sample B, which was yellow in colour, preliminary Mössbauer work indicated β-FeOOH as the impurity, but detailed measurements of hyperfine field and Néel temperature, when compared with similar results for a synthetic β-FeOOH sample, suggested otherwise. X-ray and chemical work suggested that the iron-containing phase in sample B is goethite, α-FeOOH in which some substitution of Al^{+3} for Fe^{3+} has occurred; the Mössbauer data are consistent with this conclusion. Both clay samples exhibited superparamagnetic behaviour and this has been utilized to obtain rough estimates of the mean radius of the particles of the iron-containing impurity. These were 117 Å for the α-Fe_2O_3 in sample A and 270 Å for aluminian α-FeOOH in sample B.

It has been established by Malden and Meads (1967) by Mössbauer experiments on a natural kaolinite purified by magnetic separation that Fe^{3+} substitutes, almost certainly in the octahedral cation site, in the kaolinite lattice. It is important to distinguish this situation from another that commonly exists, namely the occurrence of iron in separable impurities in the clay, usually in mica, or as oxides and oxy-hydroxides of iron. The experiments here described illustrate the usefulness of Mössbauer work in the identification of impurities of the latter type. Some recent Mossbauer experiments by Janot *et al.* (1973) on kaolinites of tropical soil origin have yielded results that are generally similar to those reported here, but the measurements were restricted to two temperatures, 85 K and 300 K. As will be shown, more information regarding the iron-rich impurity phase can be obtained by experiments at a number of intermediate temperatures.

The association of iron hydroxides with the surfaces of kaolinite particles has been studied by chemical, X-ray, and electron microscopic methods by Greenland and Oades (1968). Under certain circumstances the iron compound may be rather poorly crystallized.

Sample description and preparation. Two samples of kaolinite from a clay pit in the St. Austell area of Cornwall were studied: both showed coloration, sample A having a red tint and sample B a yellow tint. Each clay contained about 2 % by weight of iron oxides, measured as Fe_2O_3. In the case of sample B, detailed Mössbauer experiments proved necessary, and, in order to do these in a reasonable time it was necessary to increase the concentration of the iron-bearing phase in the clay by converting the kaolinite fraction to sodalite in boiling 10 % w/v sodium hydroxide solution and then dissolving the sodalite in acid at $pH = 2$. Comparison of Mössbauer spectra before and after this procedure suggested little or no change in the iron-oxide phase. A sample of β-FeOOH, needed for comparison of magnetic properties, was prepared by hydrolysis of ferric chloride solution using the technique described by Wolf *et al.* (1967).

Instrumentation and technique. The details of the precision velocity-generator employed in the Mössbauer spectrometer used in this work have been given by Clark *et al.* (1967). Hogg and Meads (1970) have described the application of the spectrometer to the study of minerals. In the present work the spectra can be resolved into a six-absorption-line component associated with antiferromagnetically ordered material and a quadrupole doublet associated with a paramagnetic or superparamagnetic fraction.

The spectra were recorded on a 400-channel analyser. For each scan of the 400 channels counts were recorded in the first 200 channels with positive source acceleration and in the second 200 channels with negative acceleration. A computer program permitted the summation of the two mirror-image spectra so obtained.

To improve the statistical definition, all the spectra have been moving-averaged over three channels. In this process the contents of channels N, $N+1$, and $N+2$ were summed and the total placed in channel $N+2$. When this procedure is employed channel-correlation effects sometimes give rise to fluctuations in the spectra, which must be carefully distinguished from genuine absorption resonances. This procedure leads to some artificial broadening of the resonance lines in addition to the genuine line-broadening and asymmetry effects discussed below. The use of a simple Lorentzian line-fitting procedure is inappropriate and was not attempted. Approximate relative area measurements required for estimates of particle size were obtained directly from plotted spectra by visual methods.

Detailed information concerning the iron content of the absorbers is not available but it is small enough for absorber-thickness effects to be negligible.

Many of the spectra exhibit the simultaneous occurrence of doublet and six-line components in which the area ratio of the two components is temperature-dependent. This is attributed to superparamagnetic behaviour characteristic of small, highly dispersed particles of magnetically ordered material.

Identification of the iron-containing component in sample A. Figs. 1(*a*) and (*b*) show, respectively, the Mössbauer spectra of Sample A at room temperature and 77 K. The room-temperature spectrum shows clear evidence of a doublet component. From the positions of the outermost lines of the magnetic spectrum, hyperfine field values of 497 ± 10 kOe and 533 ± 5 kOe respectively were estimated for the above two temperatures. These values are a little lower than those (518 and 542 kOe) given by Kündig *et al.* (1966) for α-Fe_2O_3 but the agreement is close enough to say, with reasonable confidence, that the oxide phase present is hematite. X-ray analysis confirms the presence of hematite. This is also supported by the colour of the clay. The possibility that the low values for the hyperfine field are significant and due to Al^{3+} substitution in the α-Fe_2O_3 is discussed below. Gangas *et al.* (1973) obtain similar results from Mössbauer experiments on small, iron-containing particles in soil and interpret them in terms of a dependence of hyperfine field on particle size.

Identification of the iron-containing component of sample B and discussion of Al^{3+} *substitution in samples A and B.* Figs. 2(*a* to *g*) show the Mössbauer spectra of the ferruginous residue from sample B at temperatures ranging from room temperature to 77 K. It is apparent that the material had become paramagnetic at room temperature since the magnetic spectrum has completely disappeared. The hyperfine field at 77 K is 478±5 kOe and agrees well with published values for β-FeOOH, which range from 466 to 490 kOe (Rossiter *et al.*, 1965; Takada *et al.*, 1964; Johnson, 1969; Vorznyuk and Dubinin, 1973). β-FeOOH has a Néel temperature of about 290 K. Whilst it is tempting to identify the sample B residue as β-FeOOH (see Gangas *et al.*, 1973), X-ray examination indicates the presence of goethite, α-FeOOH; it was therefore decided to attempt a measurement of the Néel temperature of the sample B residue, but this could not be done by direct determination of the temperature at which the six-line spectrum collapsed into a single line, owing to the obscuring presence of the superparamagnetic component over a wide temperature range. The Néel temperature can however be quite accurately measured on the assumption that the hyperfine magnetic field and sub-lattice magnetization vary with temperature in the manner predicted by the Curie–Weiss molecular field model. In this case, the hyperfine field H_e may be obtained at any temperature T below the Néel temperature θ by eliminating x from the equations $H_e/H_{\mathrm{sat}} = B_s(x)$ and $H_e/H_{\mathrm{sat}} = [(S+1)/3S]\,(T/\theta)x$, where $B_s(x)$ is the Brillouin function corresponding to spin S, defined by $B_s(x) = [(2S+1)/2S] \coth \{[(2S+1)/2S]x\} - (1/2S) \coth \{[1/2S]x\}$. $S = 5/2$ for high-spin Fe^{3+}. H_{sat} is the saturation hyperfine field at $T = 0$.

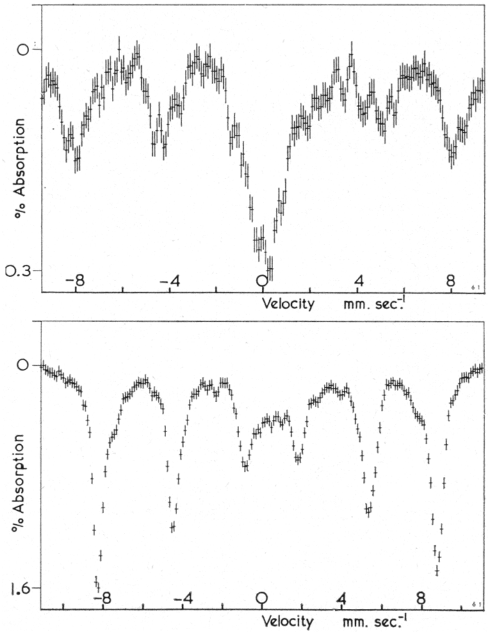

FIG. 1. Moving-averaged Mössbauer spectra of sample A (red) clay, (*a*) at room temperature, (*b*) at 77 K.

The results of computer solution of the above simultaneous equations leads to curves of H_e v. T like those of fig. 3.

Fig. 3 shows the hyperfine fields, measured as a function of temperature, for the

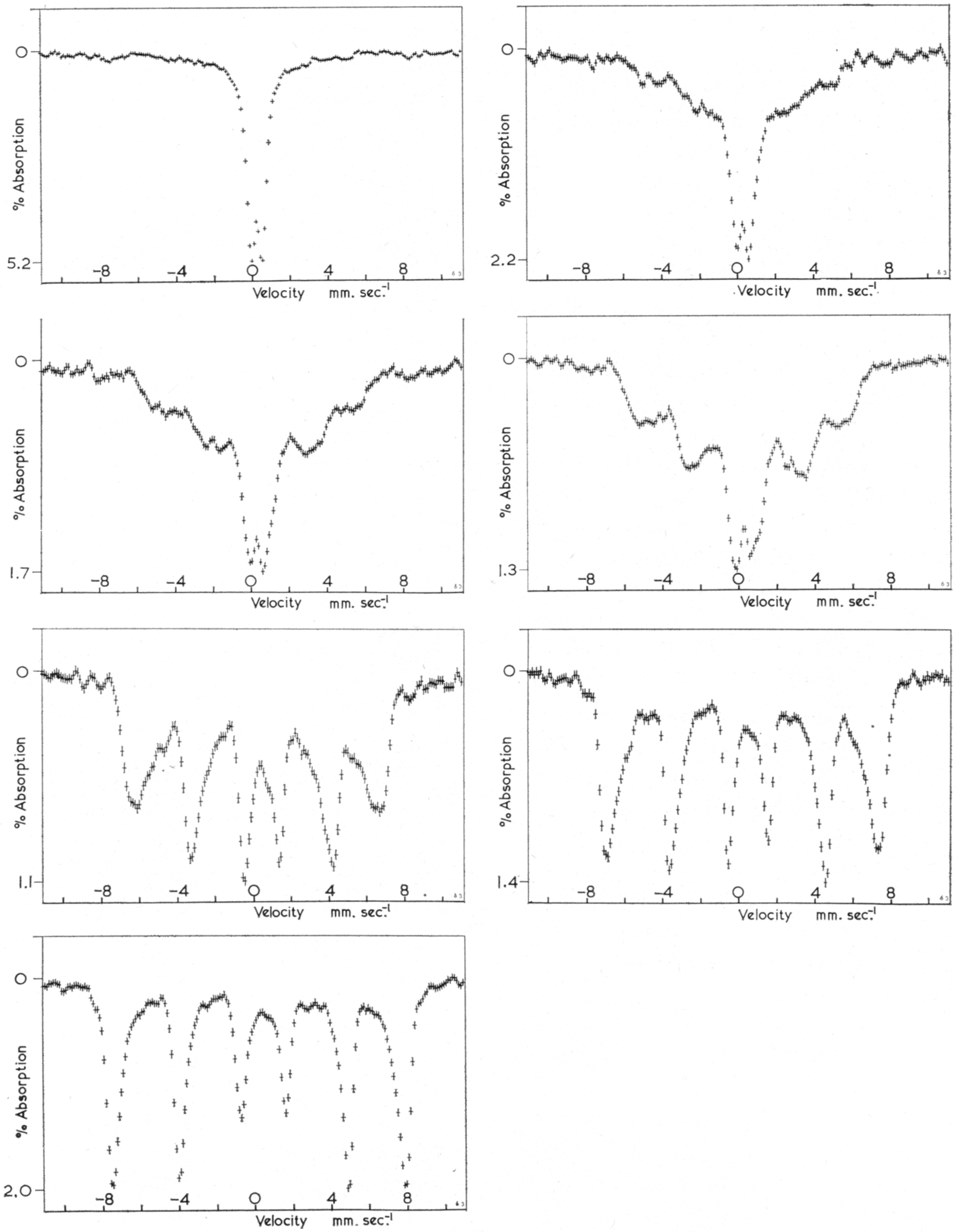

FIG. 2. Moving-averaged Mössbauer spectra of the iron-rich residue from sample B (yellow) (*a*) at room temperature, (*b*) at 270 K, (*c*) at 260 K, (*d*) at 250 K, (*e*) at 200 K, (*f*) at 150 K, (*g*) at 77 K.

sample B residue and for a sample of synthetic β-FeOOH, fitted to appropriate molecular field curves, computed from the above equations. It is clear that the two samples differ significantly both in the value of H_{sat} (sample B, 485 ± 10 kOe; β-FeOOH, 470 ± 10 kOe) and in Néel temperature θ (sample B, 332 ± 5 K; β-FeOOH, 296 ± 5 K). There is, however, conflict between the X-ray evidence that the sample B residue contains goethite and the reported Néel temperature (403 K) and hyperfine field (504 kOe at 77 K) of goethite (Forsyth *et al.*, 1968). It appeared that this conflict of evidence might be resolved by assuming that sample B contains goethite, in which some Fe^{3+} ions have been replaced by Al^{3+}. This substitution is well-known in natural goethites; see Norrish and Taylor (1961), Solymar (1969), Jonas and Solymar (1970, 1971). The Mössbauer results for sample B may be understood if sufficient substitution has occurred to modify the magnetic properties, lowering the hyperfine field and Néel temperature.

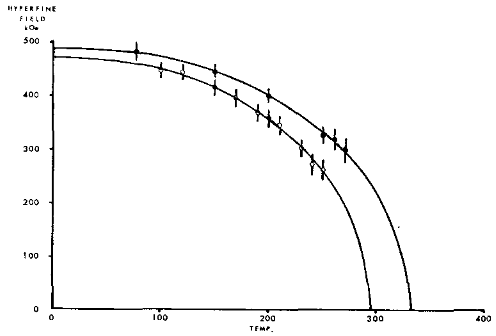

FIG. 3. Hyperfine field *v*. temperature for sample B residue and for β-FeOOH. ● represents data for sample B residue and ○, data for β-FeOOH. The upper theoretical curve is for $\theta = 332$ K, $H_{\text{sat}} = 485$ kOe and $S = 5/2$. The lower theoretical curve is for $\theta = 296$ K, $H_{\text{sat}} = 470$ kOe and $S = 5/2$.

Samples A and B and a reference kaolinite were treated with sodium dithionite solution at pH 2·8 and subsequently washed with 0·05 *N* hydrochloric acid. This procedure would be expected to remove a portion of the free iron oxides. The quantities of iron and aluminium (measured as oxides) going into solution per 100 gm of sample were as follows: Reference kaolinite, 48 mg Al_2O_3; 24 mg Fe_2O_3; sample A, 124 mg Al_2O_3; 124 mg Fe_2O_3; sample B, 96 mg Al_2O_3; 74 mg Fe_2O_3.

Although it may be unwise to interpret this data quantitatively, the fact that substantial solution of aluminium as well as iron occurs suggests close association of these two elements in the impurities.

The Mössbauer results for sample B can be understood if the iron-bearing phase is goethite in which sufficient substitution of Al^{3+} for Fe^{3+} has occurred to modify the magnetic properties, causing a lowering of hyperfine field and Néel temperature.

It was noted earlier that the hyperfine field values obtained at room and liquid nitrogen temperatures for the hematite residue of sample A are somewhat lower than the values obtained by Kündig *et al.* (1966). The possibility of Al^{3+} substitution for Fe^{3+} in this case also arises. The work of Muan (1958) indicates that about 10 wt % substitution of Al^{3+} for Fe^{3+} in hematite may be obtained by quenching the appropriate fired oxide mixture from about 1300 °C. A recent Mössbauer experiment by one of the authors on a synthetic sample prepared by the above method and estimated to contain 11·8 wt % Al_2O_3 gave a value of H_e at room temperature of 505 ± 2 kOe. A sample of pure hematite gave 514 ± 2 kOe. A corresponding change in lattice parameter a to 5·392 Å from 5·423 Å was observed from the powder X-ray diffraction spectrum. Most earlier Mössbauer measurements on the Al_2O_3–Fe_2O_3 mixed-oxide system have concentrated attention on the Al-rich end (Bhide and Date, 1968; Korecz *et al.*, 1972; Kalyamin *et al.*, 1973); this evidence suggests that Fe^{3+} substitutes in Al_2O_3 up to $\approx$ 10 atoms % but that at higher concentrations a second phase with Mössbauer parameters similar to those of pure α-Fe_2O_3 is present, but the experiments on this phase were not extended over a wide enough range of temperatures to establish whether Al^{3+} is present in it. However, Srivastava and Sharma (1972) have studied the effect of magnetic dilution by Al on the Morin phase transition in hematite and, incidentally, investigated the effect of Al substitution on the hyperfine field and Néel temperature, for concentrations up to 10·2 wt % Al_2O_3. The results showed no significant change in H_e at room temperature (in contrast to the result reported above) but showed a change in Néel temperature from 955 K to 859 K as the concentration of Al_2O_3 is increased from zero to 10·2 %.

It is intended to extend the Mössbauer measurements on sample A to higher temperatures to enable determination of the Néel temperature and, hence, an estimate of the aluminium concentration. Routine X-ray measurements on sample A did not reveal any difference in lattice parameter between the sample and pure hematite, but the sensitivity was limited by line broadening due to the small particle sizes involved.

The assumption by Gangas *et al.* (1973) that there is a dependence of hyperfine field on particle size is not supported by the work of Vorznyuk and Dubinin (1973) who have examined the Mössbauer spectra of fine β-FeOOH particles. Over ranges of particle size for which a significant portion of material is superparamagnetic, they found no change in the hyperfine field of the antiferromagnetic fraction.

The Mössbauer spectra displayed in fig. 2 show evidence of line broadening and asymmetry at temperatures fairly near the ordering temperature of the antiferromagnetic phase where the hyperfine field differs substantially from its saturation value. These effects have not been analysed in detail. They are typical of situations in which the magnetic environment of ^{57}Fe nuclei is fluctuating. This could occur because of the random substitution of Al^{3+} for Fe^{3+} and possibly due to the proximity of crystal surfaces in particles of small size. The hyperfine fields at lower temperatures nearer magnetic saturation are well defined.

Particle size estimation. For small particles of magnetically ordered material, which can be treated as single domains, the relaxation time τ_0 for change of the magnetization direction is given by $\tau_0 = (1/af)\exp(2\,Kv/kT)$ (see Kündig *et al.*, 1966); a is the number of directions into which the magnetization vector may pass—two in the case of simple reversal; K is the magnetic anisotropy constant; v is the particle volume, and f is the Larmor frequency of the magnetization vector M in an effective magnetic field equal to $2\,Kv/|M|$.

The value τ_n of the Larmor precession time of the nuclear magnetic moment of ^{57}Fe in a typical hyperfine field of 500 kOe is about $2{\cdot}5\times10^{-8}$ sec. In a Mössbauer experiment on ordered material with particle size such that $\tau_0 \gg \tau_n$ a six-line hyperfine field will be observed, but for $\tau_0 \ll \tau_n$ the hyperfine field averages to zero over the

Larmor precession time and only a single line or quadrupole doublet will be seen. In intermediate ranges of τ_0 both types of spectrum will be superimposed and it is possible to estimate roughly the mean particle size by measurement of the temperature at which both components of the spectrum are of equal intensity.

Kündig *et al.* (1966) have studied fine particles of α-Fe_2O_3 dispersed on silica gel. Using their values for the appropriate parameters in the formula for τ_0 and assuming equality of the doublet and magnetic hyperfine component in sample A at about 350 K a mean particle radius for hematite in this material of 117 Å is deduced. Shinjo (1966) has reported work on goethite and using his parameters and equality of components at 270 K the mean particle radius for α-FeOOH in sample B appears to be about 270 Å. In view of the uncertainties of the parameters used, both these estimates are approximate.

Conclusions. Mössbauer experiments on two iron-containing clays indicate the presence of α-Fe_2O_3 and aluminian α-FeOOH as impurities, respectively. Aluminium substitution in the hematite may also occur. Both impurities exhibit superparamagnetic behaviour, and a study of the temperature-dependance of the doublet and six-line components of the Mössbauer spectra has provided rough estimates of particle sizes. These results illustrate the usefulness of Mössbauer spectroscopy in the identification of separable iron-bearing impurities in minerals. However, it is to be noted that the occurrence of superparamagnetic behaviour in particles of iron oxides and hydroxides dispersed in diamagnetic host materials could lead to confusion and possibly error of identification if spectra are not obtained over a wide range of temperature.

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