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^{57}Fe Mössbauer Studies of Hectorite Exchanged with Fe(II) and Fe(III)

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Abstract

Mössbauer parameters for hectorite saturated with iron(III) are compared with those for a more lightly loaded ^{57}Fe(III) clay. The significantly greater width at half height of the resonance from the ^{57}Fe(III) clay is interpreted to reflect the greater heterogeneity of sites occupied by the six coordinate iron(III) in that case. An iron(II) exchanged hectorite, which had undergone some oxidation, was examined by Mössbauer spectroscopy. The iron(III) resonances were detectable both at 298 and 77 K, but iron(II) was detected only at 77 K. Reasons for this are discussed and the postulate of a 'frozen' matrix at 77 K favoured.

The above clays were heated under nitrogen to 400 °C and the measured Mössbauer parameters are discussed. For the heavily loaded clays only iron(III) resonances were seen; the mechanism of oxidation of the iron(II) is discussed. Remarkably, for the lightly loaded ^{57}Fe clay some iron(II) was detected after thermal treatment.

Introduction

^{57}Fe Mössbauer spectroscopy is a well established technique for the study of iron containing minerals [1], but in the context of clay chemistry it is generally used to study structural iron. Some recent studies have demonstrated the usefulness of the technique in characterising the iron species present on sorbent surfaces [2]. To extend work on the nature of sorbed ions such as cobalt(II) and nickel(II) [3, 4] we chose to study iron sorbed on hectorite. Since hectorite has a very low proportion of structural iron, the observed Mössbauer spectra from the iron exchanged clay should yield direct information on the sorbed species. Some experiments involved enrichment with ^{57}Fe, and in others the effect of heat on the sorbed species was investigated.

Experimental

Mössbauer Spectroscopy

^{57}Fe Mössbauer spectra were recorded with a constant acceleration spectrometer at 298 and 77 K using a ^{57}Co–Pd source. The drive velocity was calibrated relative to metallic iron foil. All the spectra were computer fitted (ICL 1904S; HARRIS 800) using the Gaussian non-linear regression method [5]; this program presents the spectra with each point represented by an error bar, a fact to consider when using the figures in this paper. The chemical isomer shift data are reported relative to metallic iron.

Discs of powdered sample were enclosed in cellotape and rigidly held by thin card. For Mössbauer analysis in an oxygen free environment, samples were enclosed in a matrix of araldite under nitrogen prior to introduction to the spectrometer. Spectra at 80 K were obtained by the use of an Oxford Instruments cryostat.

Preparation of Fe^{3+} Hectorite

A sample of hectorite (obtained from Hector, CA, U.S.A. and exchanged to the sodium form) (1.5 g) was dispersed in a 0.1 M solution of iron(III) chloride (75 cm^3), previously adjusted to pH 1.0 using 1 M HCl, and stirred for three days prior to filtering. The clay was then washed with 2 aliquots of 0.005 M HCl (25 cm^3) and dried in air at room temperature. Prior to Mössbauer examination the clay was crushed to a fine powder in an agate mortar. The Fe(III) hectorite was a sandy colour and atomic absorption analysis of the supernatant iron solution revealed an uptake of 54 meq. Fe(III) 100 g^{-1} clay.

Preparation of Fe^{2+} Hectorite

A sample of hectorite (1.5 g) was added to a 0.1 M solution of iron(II) chloride (75 cm^3), previously adjusted to pH 1.4 using 1 M HCl, and stirred for three days (all stages were carried out under nitrogen). The suspension was filtered in a nitrogen

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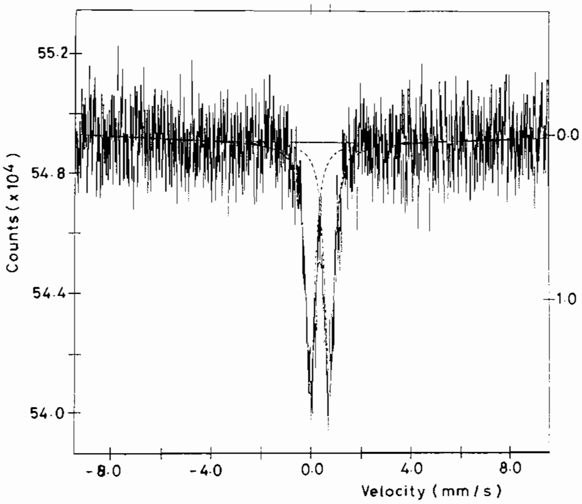

Fig. 1. Room temperature Mössbauer spectrum of Fe^{3+} hectorite.

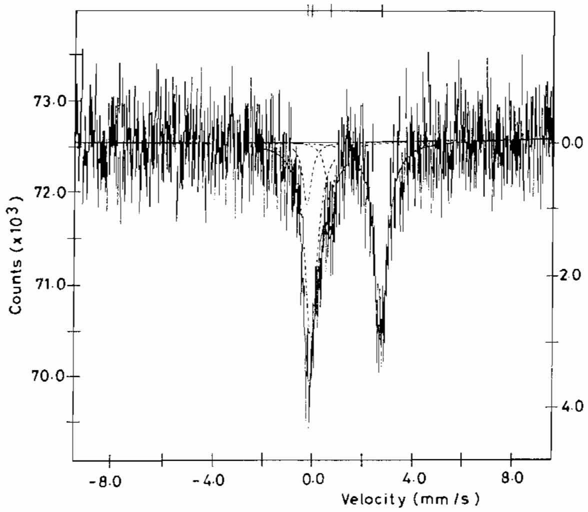

Fig. 2. Mössbauer spectrum of Fe^{2+} hectorite taken at 80 K.

filled glove box, washed with 2 aliquots of 0.005 M HCl, and dried over saturated sodium acetate trihydrate (relative humidity = 76%) under nitrogen. The yellow Fe(II) hectorite contained 50 meq. Fe(II) 100 g^{-1} clay.

The spectra of Fe(III) hectorite at room temperature (Fig. 1), and of Fe(II) hectorite at 80 K (Fig. 2) are given.

Preparation of $^{57}Fe^{3+}$ Hectorite

A portion of hectorite (4.0 g) was covered with a 0.0083 M solution of $^{57}FeCl_2$ (40 cm^3) (prepared by dissolution of ^{57}Fe foil (95%, AERE Harwell) in HCl) at a pH of 1.2 under nitrogen. The procedure then followed that above for Fe(II) hectorite, however it proved necessary to store the product for a considerable period prior to measurement of the Mössbauer spectrum, by which time complete oxidation to the trivalent state had occurred. The white product was examined at room temperature and at 80 K.

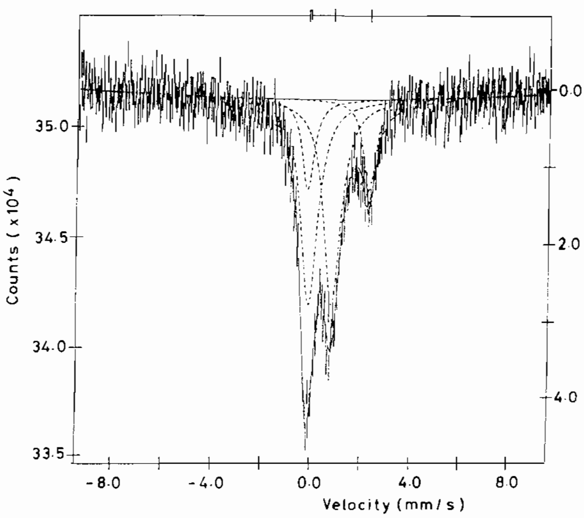

Fig. 3. Room temperature Mössbauer spectrum of $^{57}Fe^{3+}$ hectorite heated to 400 °C.

Thermal Treatment of Iron Exchanged Hectorite

The Fe(III), Fe(II), and ^{57}Fe(III) hectorite samples in porcelain crucibles were heated separately in a furnace at 400 °C under nitrogen (see ref. 6 for experimental design). The samples were allowed to cool under nitrogen for 3 h and then immediately cast into araldite discs for Mössbauer examination. Spectra were recorded at both room temperature and 80 K. A sample spectrum is shown in Fig. 3.

The hectorite sample used in this work was subjected to XRF analysis with the following results: Fe_2O_3, 0.10; MnO, 0.01; TiO_2, 0.02; CaO, 0.52; K_2O, 0.07; S, 0.01; P_2O_5, 0.03; SiO_2, 58.52; Al_2O_3, 0.21; MgO, 27.05; Na_2O, 1.78; H_2O, 6.90 (110 °C), 2.90 (1100 °C)%.

A summary of the Mössbauer parameters (chemical isomer shift and quadrupole splitting) for all the specimens examined is given in Table 1.

Discussion

Prior to examination of the iron exchanged clay, hectorite itself was examined by Mössbauer spectroscopy. Only after a week accumulating counts was a weak Fe(III) resonance seen. This is consistent with the very low iron content. It was quite clear that with the much shorter accumulation times used for the exchanged clays no contribution to the spectrum from structural iron would be obtained.

TABLE 1. Mössbauer parameters recorded from iron-exchanged hectorite

Sample	Temperature of Mössbauer measurement (K)	δ (mm s^{-1})	Δ (mm s^{-1})	Γ	χ^2
Fe^{3+} hectorite	298	0.33 (0.01)	0.76 (0.01)	0.44 (0.02)	520
Fe^{3+} hectorite heated to 400 °C	298	0.32 (0.02)	0.91 (0.02)	0.45 (0.04)	553
	80	0.44 (0.02)	0.98 (0.02)	0.63 (0.03)	466
Fe^{2+} hectorite	298	0.05 (0.04)	0.78 (0.04)	0.35 (0.08)	500
	80	0.14 (0.05) (18%)	0.93 (0.05)	0.41 (0.09)	489
		1.25 (0.02) (82%)	2.80 (0.02)	0.59 (0.04)	
Fe^{2+} hectorite heated to 400 °C	298	0.31 (0.01)	0.99 (0.01)	0.61 (0.02)	514
	80	0.38 (0.01)	1.01 (0.01)	0.70 (0.03)	558
$^{57}Fe^{3+}$ hectorite	298	0.33 (0.01)	0.74 (0.01)	0.69 (0.01)	542
$^{57}Fe^{3+}$ hectorite heated to 400 °C	298	0.31 (0.03) (76%)	0.93 (0.03)	0.82 (0.03)	532
		1.00 (0.04) (24%)	2.47 (0.04)	0.59 (0.05)	

Standard deviation from computer fits shown in brackets. Relative percentages of iron in different oxidation states estimated assuming the recoil free fractions to be the same.

TABLE 2. Mössbauer parameters for Fe^{3+} sorbed onto montmorillonite and hectorite (+/− 0.02 mm s^{-1})

Sorbent	δ (mm s^{-1})	Δ (mm s^{-1})	Reference
Montmorillonite	0.25	0.70	7
Montmorillonite	0.37	0.63	8
Hectorite	0.37	0.60	8
Montmorillonite	0.49	0.55	9

The iron(III) exchanged hectorite (Fig. 1) contained only iron(III) on exchange sites. Both δ and Δ are characteristic of octahedrally coordinated high spin iron(III) and the values (Table 1) are in close agreement with other literature data for smectite clays (Table 2).

The ^{57}Fe hectorite gave a single quadrupole split resonance (Table 1) with very similar parameters to those observed for the 'normal' iron(III). No evidence for iron(II) was obtained even at 80 K, implying the ready oxidation of exchanged $^{57}Fe^{2+}$ to $^{57}Fe^{3+}$ prior to analysis. The loading of the ^{57}Fe clay was very much less than that of the saturated iron(III) hectorite, hence it may be concluded from the similarity in observed parameters that the immediate environment of the iron(III) is similar in the two cases. There is however one interesting difference between the two sets of data. Thus the linewidth of the low loaded ^{57}Fe clay is greater (0.69 mm s^{-1}) than that of the saturated iron(III) clay (0.44 mm s^{-1}). Line broadening can arise from a thick absorber sample, but this effect can be eliminated if the absorbers contain less than 10 mg cm^{-2} of iron as was the case for all samples studied here. Johnston and Cardile [10], in their study of calcium and potassium saturated nontronites, have pointed out that interlayer cations can influence the electric field gradient experienced by structural iron atoms in octahedral and tetrahedral sites and there is, we argue, no reason why reverse effects should not occur. Thus the more lightly loaded ^{57}Fe clay will have iron(III) ions more randomly distributed, in a heterogeneity of 'FeO_6' sites in the interlayer region with the consequence that both next nearest neighbour (other interlayer ions) and more distant (structural ions) interactions will be more random than in the saturated clay, thus giving rise to a distribution of electric field gradients (e.f.g.s). We believe that this result is consistent with the recently published views of Cardile and Johnston [11] that iron(III) Mössbauer spectra of clay minerals are the average of a range of marginally different sites. In the present case it must be remembered that the iron(III) arose from oxidation of iron(II); it is conceivable that this fact might also contribute to the greater observed linewidth.

The sample of Fe^{2+} (normal isotopic composition) treated hectorite gave an iron(III) doublet in the room temperature spectrum (Table 1) which from the observed parameters seems to arise from a tetrahedral site [1]. No Fe(II) resonance was seen at room temperature, but on cooling to 80 K the iron(II) resonance comprised 82% of the observed intensity (Fig. 2). Thus, despite handling precautions, some iron(II) was oxidised to iron(III). This problem has also been experienced by others [8, 9] although in those cases the oxidised iron was located entirely in octahedral sites. Presumably the mechanism of oxidation of the iron(II) will influence to some extent the final environment of the iron(III); we therefore considered the possibility that the observed iron(III) species might contain an oxo-bridge, Fe–O–Fe, however the observed chemical isomer shift did not correspond in any way to values quoted for such oxo-bridged species in the literature [12, 13]. Thus we can only speculate that the oxidative mechanism results in the iron(III) being drawn into the ditrigonal holes, the fourth coordination position being satisfied with OH or H_2O. It must be conceded that if only 9 meq. of the total exchanged iron (50 meq.) is iron(III) (as roughly estimated from the 90 K spectrum), then the structural iron content of the hectorite may be comparable (XRF estimated Fe_2O_3 to be 0.1%); however, even after one week accumulating counts, the sodium hectorite gave only a very weak iron(III) doublet consistent with a little structural iron in octahedral sites, thus we are of the opinion that the iron(III) component of the spectrum under discussion does indeed originate from the exchanged iron. The fact that the Fe(II) resonance only becomes significant at low temperature is more readily explained. Thus it is probable that the interlayer $[Fe(H_2O)_6]^{2+}$ ions are tumbling in a pseudo solution type environment and that the recoil free fraction is low (the higher charge on the Fe(III) species will result in a stronger interaction with the silicate and a more 'rigid' interlayer structure). At 80 K the iron(II) will be in a frozen matrix and the recoil free fraction will be greater. These conclusions are consistent with two earlier studies, thus Delgass *et al.* [14], using both organic and inorganic exchangers concluded that the iron(II) was trapped in a frozen water matrix at 80 K: further their values for the Mössbauer parameters for an iron(II) exchanged zeolite at 80 K ($\delta = 1.5$ mm s^{-1}, $\Delta = 3.1$ mm s^{-1}) were in good agreement with those of Dezsi *et al.* [15] for Fe(II) in frozen water. More comprehensively, Banin *et al.* [16] studied a mixed Fe(II)/Fe(III) montmorillonite and showed that the iron(II) signal was undetectable above 250 K and underwent an abrupt transition at 210 K the temperature observed by Anderson and Tice [17] to correspond to an exotherm attributed to the freezing of the interlayer water.

Although the above explanation accounts for the increase in recoil free fraction at 80 K, it does not account for the fact that a range of parameters have been observed for iron(II) on smectites and silica (Table 3).

The considerable range of parameters in Table 3 imply that the Fe(II) resonance is quite sensitive to the nature of the sorbent and its state of hydration. A particularly important factor is likely to be the charge on the clay surface, thus the sample of hectorite used in this investigation had an ion exchange capacity of 58 meq. 100 g^{-1} whereas a sample of Hector hectorite examined under the auspices of the Clay Mineral Society afforded a value of 43.9 meq. 100 g^{-1}. Hence significant variations in surface charge occur from one specimen to another and the iron(II) resonance appears more sensitive to this variation than the iron(III) resonance (although inspection of Table 2 reveals that for iron(III) also there is some variation, sample to sample). We propose therefore that at 80 K differing strengths of interaction with the clay surface give rise to differing degrees of distortion from true octahedral symmetry, and consequently to differing Mössbauer parameters.

TABLE 3. Mössbauer parameters of iron(II) exchanged onto various sorbents

Sorbent	δ (mm s^{-1})	Δ (mm s^{-1})	Reference
Montmorillonite	1.04	3.12	16
Montmorillonite	1.29	3.52	7
Montmorillonite	1.38	3.36	8
Hectorite	1.38	3.37	8
Montmorillonite	1.40	3.36	9
Silica	1.25	2.59	9

Thermally Treated Iron Hectorite Samples

Heating the iron exchanged clays to 400 °C should remove interlayer water [18], the distance between tetrahedral sheets in adjacent layers will be small, but distorted 'octahedral' holes will exist into which cations may migrate. The major source of distortion will be a mismatch of ditrigonal oxygen atoms in the two layers.

The oxidation state and chemical isomer shift of iron(III) hectorite were unaltered on heating, but an increase in the quadrupole splitting suggested a more distorted environment than that experienced in the unheated clay. Cooling to 80 K revealed no new resonance. The slight increase in δ may be attributed to the second order Doppler shift. Heating the iron(II) hectorite to 400 °C converts all the iron to the 3+ state, and the parameters are very similar to those for the heat treated iron(III) clay. If the room temperature spectra are compared, it seems that the quadrupole splitting for the 'Fe(II)' clay is greater, as is the linewidth, than for the 'Fe(III)' clay. However when the 80 K spectra are compared these differences do not seem real. Thus any differences in iron(III) sites for the unheated clays have been removed by the thermal treatment and in both cases the iron occupies a distorted six coordinate site. The fact that total oxidation of the iron(II) clay occurred despite the fact that heating was carried out under nitrogen implies that hydroxyl groups were implicated in the redox reaction [19]

$$Fe^{2+} + OH^- \longrightarrow Fe^{3+} + O^{2-} + [H]$$

clearly a different mechanism to that which gave rise to the iron(III) in the unheated sample.

Perhaps the most interesting observation is the fact that thermal treatment of the ^{57}Fe clay, which (see above) initially contained no iron(II), produces a specimen for which some 24% of the resonant intensity arises from iron(II) (Fig. 3). The observation is not without precedent since the heating of both montmorillonite and vermiculite to 300 °C in an inert atmosphere has led to partial reduction of the iron(III) [20]. In those cases the iron was structural rather than exchanged, this observation indicates that similar chemical paths are open to the exchanged ions. The mechanistic origin of the iron(II) is not clear. Natural clays may contain small quantities of organic matter which could provide a reducing agent, however it seems improbable that a sufficient quantity was present in this case. It is also possible (perhaps even probable) that water or hydroxyl groups are implicated, in which case hydrogen peroxide is the likely product. This is an interesting observation which could reasonably form the basis of a separate study. The Mössbauer parameters for the ^{57}Fe(II) are distinct from those of the unheated clay containing iron(II) of natural isotopic abundance and the fact that a spectrum is observed at room temperature indicates that the Fe^{2+} ions are held in a rigid lattice; the parameters suggest that the rhombic distortion of the iron(II) is greater in the heated ^{57}Fe clay (smaller quadrupole splitting of 2.47 mm s^{-1}) than in the unheated Fe(II) clay ($\Delta = 2.80$ mm s^{-1}) [1].

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