

THE MÖSSBAUER SPECTRUM OF ILLITE

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ABSTRACT: Eight illites were studied by Mössbauer spectroscopy at room temperature and 4.2 K. On the basis of their Fe contents, these illites can be divided into an Fe-rich (>5 wt% Fe) and an Fe-poor (<1 to ~3 wt% Fe) group. Mössbauer spectroscopy showed that the Fe-rich illites had lower proportions of divalent Fe than their Fe-poor counterparts. Slow paramagnetic relaxation was observed in the Fe-poor illites and must be accounted for when fitting the spectra. Two samples contained iron oxides that were superparamagnetic and thus, although contributing to the Fe³⁺ doublets, escaped detection at room temperature. Structural Fe³⁺ had a temperature-independent quadrupole splitting that was lower for the Fe-rich illites (0.59 mm/s) than that of the Fe-poor illites (0.73 mm/s). The Fe²⁺ quadrupole splittings were higher at 4.2 K than at room temperature, but the Fe-rich illites again had lower Fe²⁺ quadrupole splittings both at room temperature (2.69 vs. 2.88 mm/s) and at 4.2 K (2.96 mm/s vs. 3.08 mm/s). Distinction of Fe sites in the illites with *cis*- and *trans*-OH coordination was not possible. The presence of tetrahedral Fe³⁺ was observed only in the most Fe-rich sample (8.4 wt% Fe).

Definitions of illite vary from that given originally by Grim *et al.* (1937), which was quite general (“the clay mineral constituent of argillaceous sediments belonging to the mica group”), to such that are more recent and specific. While the above definition would also include Fe-rich micaceous minerals such as glauconite and celadonite, a more specific definition describes illite as a clay-sized, non-expanding, dioctahedral, aluminous potassium mica-like mineral (Środoń & Eberl, 1984). The present paper is concerned with illite as identified by the latter definition. Bailey *et al.* (1984) gave a representative formula for such illites as $K_{0.75}(Al_{1.75}R^{2+}_{0.25})(Si_{3.5}Al_{0.5})O_{10}-(OH)_2$. In micas, the octahedral sites have two pairs of hydroxyls in *cis* (M1) and one pair in *trans* (M2) arrangement per formula unit, but in dioctahedral micas the vacant site is always located in M1. By analogy with muscovite, illite may occur as $1M$ or $2M_1$, less frequently as $3T$, and very rarely as $2M_2$ polytype. Disordered stacking sequences, termed $1M_d$, give rise to broadened or missing X-ray diffraction lines. The width at half-height of the first basal peak at ~1.0 nm, termed the Kubler index, is often used to

characterize illite crystallinity (Kubler, 1964). A comprehensive description of illite compositions, structures and modes of formation has been given by Środoń & Eberl (1984).

Illite is a very common constituent of soils, clays and shales; it is also the main source of alkalis in clays. The presence of illite in clays used for the production of structural clay products such as bricks and tiles can have a profound effect on the necessary firing temperature and on the properties (e.g. colour) of the final product. Although not apparent from the above formula, illites invariably contain some Fe. This Fe can serve as a probe for the environment in which it is bound using ⁵⁷Fe Mössbauer spectroscopy, which enables a determination of the coordination, a (usually) quantitative distinction between Fe²⁺ and Fe³⁺, and an assessment of the site distortion to be made.

Straightforward interpretations of ⁵⁷Fe Mössbauer spectra of any substance are only possible if the samples contain no other Fe-bearing components which mask the resonances, or if such components can be removed without affecting the material in question. However, as for many other clay minerals, it is virtually impossible to obtain monomineralic illites. As pointed out by Wentworth (1970), much of the published information on illites consequently suffers from poor sample

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purity or inadequate characterization of sample mineralogy. It is obvious that the presence of even minor amounts of ancillary minerals rich in Fe, e.g. iron oxides, iron sulphides or Fe-rich phyllosilicates, will complicate the acquisition of valid data. This problem becomes particularly evident when Fe-poor illites are studied. Recent Mössbauer work on illitic clays by Goodman & Nadeau (1988) and Wagner *et al.* (1988, 1990) has shown that the presence of such ancillary constituents may render the study of illitic clays of little relevance to the parameters of illite *sensu stricto*. Possible remedial measures are the removal of undesired components by particle-size fractionation (provided different particle-size fractions differ sufficiently in mineralogy) or by selective dissolution (e.g. of iron oxides with oxalate or dithionite). Taking spectra at different temperatures can be useful if this leads to a divergence of parameters (e.g. if some components order magnetically at low temperatures). Particular care must nevertheless be taken to avoid misinterpretation of results in such complex cases (Murad & Wagner, 1989). Furthermore, problems may arise due to the fact that illites are frequently interstratified to some extent with smectites (I-S) or inseparable mixtures of illite with I-S. In their review of illite mineralogy, Śródoń & Eberl (1984) found eight standard 'illites' to be such mixtures, and stated that only one genuinely pure illite had been described to date.

The earliest Mössbauer spectrum of illite was published by Weaver *et al.* (1967). The studied sample, which was not further characterized as to composition or purity, produced a predominant quadrupole doublet due to octahedral Fe³⁺ and a weaker Fe²⁺ doublet. Raclavský *et al.* (1975) fitted the Mössbauer spectrum of an illite with two Fe³⁺ doublets only, but the spectrum was taken in too narrow a velocity range to allow observation of the high-velocity peak of a possible Fe²⁺ doublet. Coey (1980) took Mössbauer spectra of four not further characterized illites, and emphasized the variability of these spectra. Ward's illite #36, from Morris, Illinois, has been used in several Mössbauer studies at room temperature. Malathi *et al.* (1969) indicated that this sample contains pyrite, sericite and limonite as impurities, and described the Mössbauer spectrum of this as consisting of one paramagnetic Fe³⁺ doublet. Ericsson *et al.* (1977) fitted a spectrum of illite #36 with two Fe³⁺ doublets and one Fe²⁺

doublet. Finally, Michael & McWhinnie (1989) fitted a spectrum of the same illite with one Fe³⁺ doublet and two Fe²⁺ doublets. The Mössbauer spectrum of another illite (Ward's #35, which has also been reported to contain some pyrite), taken by Ericsson *et al.* (1977), was fitted with two Fe³⁺ doublets and Fe²⁺ doublets each. Russell & Montano (1978), in contrast, fitted spectra of this sample taken at room temperature, 78 K and 4.2 K with only two doublets, one each for Fe²⁺ and Fe³⁺. Saporoschenko *et al.* (1980) took room-temperature Mössbauer spectra of four samples which they characterized as consisting of "primarily illite", but the possible presence of pyrite was alluded to. Two of these samples (Grundite and Fithian) are probably identical to #36 and #35, respectively. The spectrum of the Fithian sample was fitted with two Fe³⁺ and one Fe²⁺ doublet, whereas the other spectra were fitted with two Fe²⁺ and one Fe³⁺ doublets. Johnston & Cardile (1987) fitted the room-temperature Mössbauer spectrum of an Fe-rich illite from South Australia with five doublets, two of which were each assigned to Fe³⁺ and Fe²⁺, and one to Fe³⁺ in tetrahedral coordination. Ericsson *et al.* (1977), Saporoschenko *et al.* (1980) and Johnston & Cardile (1987) assigned the Fe³⁺ doublet with the smaller quadrupole splitting to the *cis* position and that with the larger quadrupole splitting to the *trans* position.

It is obvious that no general agreement exists on an appropriate fitting model for the Mössbauer spectra of illite. It must be borne in mind that the fitting procedure itself is a mathematical activity. The parameters resulting from any fit, however, must be both mathematically acceptable (χ^2 minimization) and physically significant. There is a certain arbitrariness in some of the models outlined above that, rather than being based on an *a priori* physical model, involve only a χ^2 minimization using multiple doublets that are subsequently assigned to possible structural features to validate the fitting model. The possible contributions from ancillary Fe-bearing minerals to the Mössbauer spectra of some samples have also been occasionally ignored.

A further complication may arise in illites with low Fe concentrations of a few percent or less. For ⁵⁷Fe, relaxation of the electronic spin is generally faster than the lifetime of the excited Mössbauer state (141 ns). In Fe-poor (i.e. magnetically dilute) materials, interactions between the Fe

atoms may, however, be so weak that the electronic relaxation rate is slowed down to an extent where it leads to a static magnetic field at the nucleus (slow paramagnetic relaxation). This phenomenon causes the development of several magnetic fields, including high fields of up to 55 T between 4.2 and 77 K, and is therefore readily observed at low temperatures. Slow paramagnetic relaxation may, however, persist up to room temperature, then leading to the development of low magnetic fields of ~ 5 T. Due to the inherently poor peak-to-background ratio, the resulting Mössbauer pattern cannot be resolved, but will rather contribute to a background that partly overlaps the non-relaxing Fe^{3+} components. Slow paramagnetic relaxation has, for example, been described for kaolinites from a variety of localities (Fysh *et al.*, 1983; Murad & Wagner, 1991; St. Pierre *et al.*, 1992). The possibility of slow paramagnetic relaxation has not been taken into consideration in previous Mössbauer work on illites.

MATERIALS AND METHODS

Eight illites were selected on the basis of mineralogical purity and coverage of a wide range of Fe contents (0.8–8.4 wt% Fe). To complement the illite data, two microcrystalline muscovites were also included in this study. Information on provenance, iron content, degree of structural order and published work on the samples is given in Table 1. In some cases ancillary iron oxides were removed by extraction with Na dithionite (Mehra & Jackson, 1960; Holmgren, 1967), but limited sample quantities precluded such a treatment for all samples.

X-ray diffraction (XRD) was performed using Co- $K\alpha$ radiation on a Philips PW1820 instrument equipped with a sample spinner and a diffracted-beam graphite monochromator. Oriented powder samples were step-scanned in steps of $0.02^\circ 2\theta$, generally for 20 s per step. To obtain precise half-widths and d values, selected peaks were computer-fitted with a combination of

TABLE 1. General characteristics of samples.

Sample	Provenance	Mineralogy ¹	K.I. ²	Fe_t^3	Reference
OECD#5 <2 μm	Le Puy France	II , Fs	0.74	5.18	Olphen & Fripiat (1979)
Muloorina <2 μm	Lake Eyre Australia	II	0.90	8.41	Norrish & Pickering (1983)
26 X-Y	Brives France	II	0.83		Środoń (unpublished) ⁴
Eldorado 0.07–2 μm	Saskatchewan Canada	II , Pt, Hm	0.52	5.28	Kodama & Dean (1980)
57wT <2 μm	Regensburg Germany	II , Q, Fs	0.59	2.70	Knorr (1984)
L-2A-2 ⁵ <0.2 μm	Central Poland	II , Ct	0.86	~ 1.74	Środoń & Eberl (1984), Środoń ⁴
RM5 ⁵ <2 μm	Silverton Colorado, USA	II	0.65	0.88	Eberl <i>et al.</i> (1987)
NP 548	Upper Silesia Poland	II , Ct, Kt, Fh	0.64	0.80	Środoń & Eberl (1984)

¹ II = illite, Ct = chlorite, Kt = kaolinite, Q = quartz, Fs = feldspar, Fh = ferrihydrite, Hm = hematite, Pt = pyrite/marcasite. Predominant constituents are given in bold type.

² 'Crystallinity index' after Kubler (1964).

³ Total Fe (%).

⁴ Personal communication.

⁵ Dithionite-treated sample.

Gaussian and Lorentzian lines (Voigt profile). Relative abundances of clay minerals in samples of complex mineralogy were estimated from the areas of the first basal peaks fitted in this manner multiplied by calibration coefficients given by Laves & Jähn (1972). The presence of minor amounts of phyllosilicates other than illite could usually be determined down to $\leq 1\%$ by this method. Profiles of the first basal peak at 1.0 nm were determined by fitting the XRD data after correction for the increase in count rate at low diffraction angles due to the Lorentz-polarization (Lp) factor (Stanjek & Friedrich, 1986). The existence of shoulders on the low-angle side of the 1.0 nm peak of some samples, which indicates interstratification with smectite (Stern *et al.*, 1991), was more distinct on XRD data that had been corrected in this manner. Improved determination of the degree of structural order of the illites (Kubler, 1964) was possible after subtraction of the contributions from these shoulders.

Thermal analyses (DTA and TG) were carried out up to 1000°C on batches of 50–65 mg using a Linseis instrument operated at a heating rate of 10°C/min. Digital registration allowed subsequent computer-processing of the data.

For Mössbauer spectroscopy a $^{57}\text{Co}/\text{Rh}$ source with an activity of about 20 mCi was oscillated in a sinusoidal mode. To eliminate possible effects of texture, the samples were fused with 3–4 parts of benzophenone at 50–60°C and the resulting mixture gently ground by hand in an agate mortar. Material corresponding to between 60 and 350 mg illite was placed in plastic holders with an area of 2 cm², giving Fe concentrations between 0.4 and 3.3 mg/cm² which led to relative absorptions between about 0.3 and 8%. The transmitted radiation was recorded with a proportional counter and stored in a 1024 channel analyser. Spectra of all samples were taken at room temperature, and at 4.2 K, cooling both source and absorber in a bath cryostat. A 6 μm thick Fe foil was used for velocity calibration. Spectra were collected in different velocity ranges between ± 4 and ± 11 mm/s until sufficiently good statistics (between about 4×10^6 and 31×10^6 counts per channel) had been attained. The mirror halves of the spectra were folded and Lorentzian line fits carried out on a CDC Cyber 2000V computer. Corresponding lines of doublets were generally constrained to have equal widths, and corresponding lines of sextets to have equal

widths and intensities. Spectra were plotted as measured (i.e. relative to the source), whereas isomer shifts have been recalculated relative to the centroid of the room-temperature spectrum of metallic iron.

RESULTS

The clay fraction (<2 μm) of the OECD #5 illite (termed 'OECD') from Le Puy, France was chosen as reference material for Mössbauer spectroscopy under different conditions and for a (yet unpublished) subsequent study of the firing behaviour of illite. The sample has a relatively high structural Fe content of 5.18 wt% and an iron oxide content of <0.1% (Olphen & Fripiat, 1979). X-ray diffraction indicates the sample to consist of a relatively pure, poorly-crystallized $2M_1$ illite. Minor amounts of associated K feldspar would not contribute to the Mössbauer spectra. The Lp-corrected XRD diagram shows a broad band with an average spacing of 1.10 nm bordering the 002 illite peak at 1.00 nm (Fig.1).

To study the possible influence of sample texture and adsorbed water, room-temperature Mössbauer spectra of the OECD illite were taken in the velocity range ± 6 mm/s on specimens that had been (a) fused with benzophenone and subsequently ground, (b) packed into the sample holder without provisions to enhance or eliminate texture, (c) as (b) but dried for 48 h at 100°C, and (d) sedimented from an aqueous suspension into the sample holder. Fits in which the doublet line areas were not constrained to be equal showed the area ratios of the high-velocity and low-velocity peaks to deviate from the ideal value of 1.00 for a random powder sample by only $2 \pm 1\%$ for (a), (b) and (c), indicating insignificant textural effects. For sample (d) the deviation amounted to 6%.

An overnight treatment of the OECD illite with cold Na dithionite (Holmgren, 1967) changed neither the Mössbauer parameters nor the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio.

Parameters of a two-doublet fit to the room-temperature spectrum of the sample of OECD illite that had been fused with benzophenone were a quadrupole splitting $\Delta = 0.61$ mm/s and an isomer shift $\delta = 0.36$, and $\Delta = 2.63$ mm/s, $\delta = 1.11$ mm/s, in accord with Fe^{3+} and Fe^{2+} in octahedral coordination. Although the line-width of the Fe^{3+} doublet ensuing from this fit was

rather high (0.51 mm/s), the relatively low χ^2 -value of 1.5 supported the visual observation that the fit was of an acceptable quality (Fig. 2, top).

Fitting the same spectrum with two Fe^{3+} and one Fe^{2+} doublet lowered χ^2 to 1.1 and reduced the line-widths of the Fe^{3+} doublets to 0.43 and 0.41 mm/s. The Fe^{3+} parameters derived from this fit are $\Delta_1 = 0.43$ mm/s, $\delta_1 = 0.35$ mm/s, and $\Delta_2 = 0.80$, $\delta_2 = 0.35$ mm/s. However, as pointed out in the introduction, random distribution of cations could cause possible different parameters for the *cis* and *trans* sites in illites to be smeared out to an extent that the ideal parameters would become obscured. Such an effect can be expected to be particularly pronounced for a sample of poor crystallinity such as the OECD illite.

In a third approach, the spectrum was fitted with a distribution of quadrupole doublets for the Fe^{3+} resonance (no satisfactory parameters could be obtained for an Fe^{2+} doublet distribution because of the minor proportion of Fe^{2+} , and therefore only one doublet was used to fit this component). The high half-width of 0.89 mm/s of the Fe^{3+} distribution, a symmetric distribution of quadrupole-splitting probabilities, and a low χ^2 of 1.0 validate this fit (Fig. 2, centre). The Fe^{3+} quadrupole distribution was relatively symmetric

with a splitting of maximum probability of 0.59 ± 0.01 mm/s (Fig 2, bottom), and the isomer shift was 0.350 ± 0.002 mm/s. These parameters compare quite well with those given above for the two-doublet fit.

The other Fe-rich illites are Muloorina, 26 X-Y and Eldorado. The Muloorina sample is a very Fe-rich, poorly-ordered $1M_d$ illite from a lacustrine clay in South Australia (Norrish & Pickering, 1983) studied by Johnston & Cardile (1987). When fitted with one Fe^{3+} and Fe^{2+} doublet, the spectrum showed a distinct bulge on the left side of the low-velocity peak, indicating the presence of an additional component. An additional doublet, which yields parameters that are typical for tetrahedrally-coordinated Fe^{3+} ($\Delta = 0.56$ mm/s and $\delta/\text{Fe} = 0.17$ mm/s), significantly improved the fit (Fig. 3a). The 26 X-Y sample also consists essentially of a poorly-crystalline $1M_d$ illite from a lacustrine environment. The Mössbauer parameters of this sample are similar to those of the OECD illite (Tables 2 and 3). Eldorado (Fig. 4b) is a $1M$ illite from a mudstone that has ~5% of its Fe content in ancillary pyrite and/or marcasite (Kodama & Dean, 1980). Both pyrite and marcasite have Fe^{2+} in low-spin configuration, and their Mössbauer parameters will more or less overlap

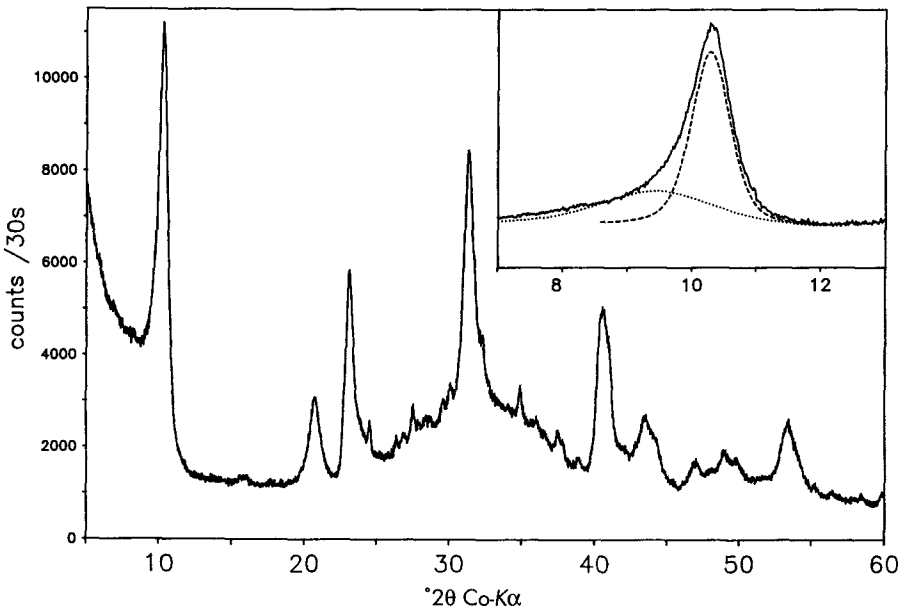


FIG 1. X-ray diffraction diagram of the $<2 \mu\text{m}$ fraction of the OECD #5 illite. The inset shows the $7\text{--}13^\circ 2\theta$ (Co-K α) range of the Lp-corrected XRD data fitted with two Voigt lines: the broken line is the fit to the 002 illite peak at 1.00 nm and the dotted line that to the subsidiary band at ~ 1.10 nm.

the illite Fe^{3+} resonance. At room temperature, pyrite has $\Delta = 0.611$ mm/s and $\delta/\text{Fe} = 0.313$ mm/s, and marcasite $\Delta = 0.503$ mm/s and $\delta/\text{Fe} = 0.277$ mm/s (Evans *et al.*, 1982). For the Eldorado sample, a two-doublet fit gives average parameters for Fe^{3+} in illite plus Fe^{2+} in pyrite and/or marcasite of $\Delta = 0.664$, $\delta/\text{Fe} = 0.367$ mm/s. Subtraction of the contribution of the sulphides to the spectrum yields Fe^{3+} parameters $\Delta_{\text{illite}} = 0.667$ mm/s and $\delta/\text{Fe} = 0.370$ mm/s if corrected for pyrite, and $\Delta_{\text{illite}} = 0.672$ mm/s and $\delta/\text{Fe} = 0.372$ mm/s if corrected for marcasite. The high-velocity Fe^{2+} peak of illite is not affected by the presence of the sulphides.

At 4.2 K, none of the Fe-rich illites revealed magnetic components indicative of slow paramagnetic relaxation. An influence of this can therefore also be ruled out at room temperature.

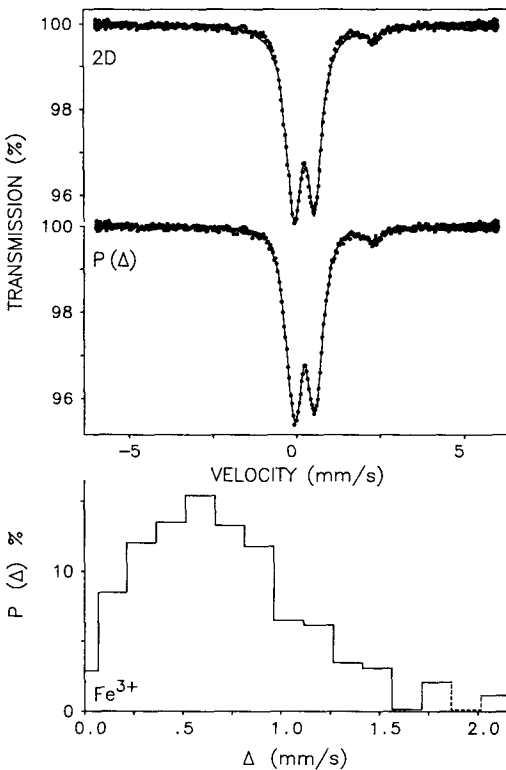


FIG. 2. Mössbauer spectrum of the OECD #5 illite at room temperature fitted with one Lorentzian doublet each for Fe^{3+} and Fe^{2+} (top) and a distribution of Lorentzian doublets for Fe^{3+} plus one doublet for Fe^{2+} (centre). The distribution of Fe^{3+} quadrupole splittings derived from the latter fit is shown at the bottom.

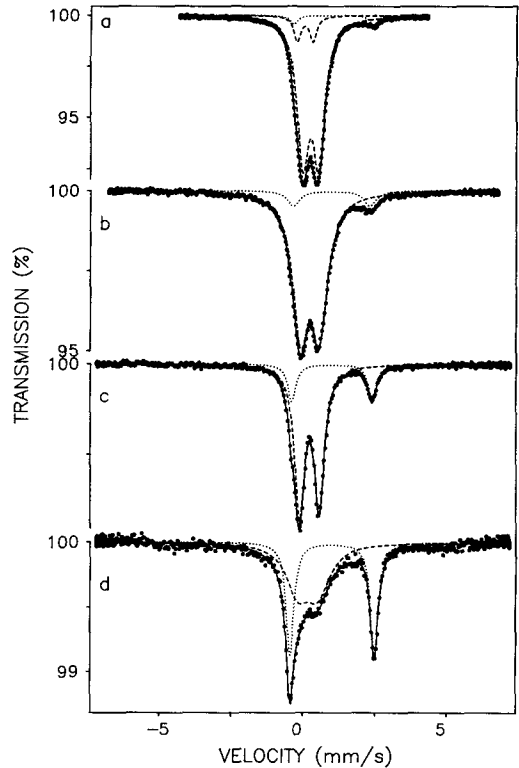


FIG. 3. Room-temperature Mössbauer spectra of the (a) Muloorina, (b) Eldorado, (c) NP 548 and (d) RM5 illites. Non-relaxing Fe^{3+} components are indicated with broken lines and Fe^{2+} components with dotted lines.

The 4.2 K spectra of the OECD, Muloorina (Fig. 4a) and 26 X-Y illites consisted of an Fe^{3+} and an Fe^{2+} doublet, but showed no magnetic order. The parameters of the Fe^{3+} doublet had not changed significantly from those observed at room temperature, whereas the quadrupole splittings of the Fe^{2+} doublets had increased noticeably. The Eldorado sample, however, had 17% of its spectral area at 4.2 K in a magnetic component that can be attributed to hematite (Fig. 4b). The sum of relative areas of this and the remaining paramagnetic Fe^{3+} component (75%) add up to the relative Fe^{3+} area at room temperature (91.5%), i.e. 16% of the latter Fe^{3+} area do not result from illite but from superparamagnetic hematite.

Mössbauer spectra of all of the Fe-poor illites taken at 4.2 K showed the existence of magnetic components that can be attributed to slow paramagnetic relaxation (Fig. 4c,d). To account for

TABLE 2. Room-temperature Mössbauer parameters of samples. For the sake of consistency, parameters are given for two-doublet fits (except for the Muloorina illite).

Sample	OECD#5 ¹	Muloorina ²	26 X-Y	Eldorado	57wT	L-2A-2	RM5	NP 548 ³
Δ_3^4	0.614(2)	0.557(1)	0.600(1)	0.670(3) ⁵	0.77(1)	0.715(5)	0.72(2)	0.696(1)
δ_3/Fe	0.360(1)	0.369(1)	0.369(1)	0.371(1) ⁵	0.318(8)	0.373(3)	0.30(1)	0.353(1)
FWHM ₃	0.549(3)	0.516(2)	0.553(2)	0.679(3)	0.77(1)	0.71(1)	0.99(4)	0.421(2)
A ₃	0.945(5)	0.866(5)	0.939(3)	0.915(4) ⁵	0.63(2)	0.71(1)	0.53(2)	0.821(4)
Δ_2^4	2.61(1)	2.79(1)	2.671(9)	2.68(1)	2.87(1)	2.876(6)	2.959(4)	2.817(5)
δ_2/Fe	1.124(7)	1.157(5)	1.130(4)	1.112(7)	1.178(5)	1.155(3)	1.149(2)	1.137(3)
FWHM ₂	0.32(2)	0.33(1)	0.32(1)	0.53(2)	0.46(2)	0.38(1)	0.331(7)	0.354(8)
A ₂	0.055(3)	0.038(1)	0.061(2)	0.085(3)	0.30(1)	0.21(1)	0.437(8)	0.179(3)

Errors in the last digit are given in parentheses.

δ/Fe : isomer shift w.r.t. metallic iron, Δ : quadrupole splitting, FWHM: full width at half maximum, A: relative area.

Because parameters of spectral components ensuing from paramagnetic relaxation are not included in the Table, the sum of relative areas may add up to less than unity.

¹ Average of measurements on sample (a) fused with benzophenone, (b) prepared with no provisions to control texture, (c) dried at 100°C, and (d) sedimented into the sample holder.

² The sample contains 5% tetrahedral Fe³⁺.

³ The Mössbauer spectrum taken at 4.2 K shows that the sample contains ferrihydrite.

⁴ Subscripts: ₃: paramagnetic Fe³⁺, ₂: paramagnetic Fe²⁺.

⁵ Corrected for the presence of 5% pyrite and/or marcasite.

TABLE 3. Mössbauer parameters of samples at 4.2 K. Parameters are given for doublet components only.

Sample	OECD#5	Muloorina	26 X-Y	Eldorado	57wT	L-2A-2	RM5	NP 548 ¹
Δ_3^2	0.630(1)	0.566(1) ³	0.601(2)	0.670(3)	0.72(1)	0.711(7)	0.77(1)	0.607(3)
δ_3/Fe	0.349(1)	0.376(1) ³	0.347(2)	0.351(2)	0.311(7)	0.335(4)	0.320(7)	0.289(2)
FWHM ₃	0.613(2)	0.551(1) ³	0.628(4)	0.715(6)	0.78(2)	0.68(1)	0.79(2)	0.300(4)
A ₃	0.926(2)	0.888(4) ³	0.880(5)	0.750(3)	0.71(2)	0.78(1)	0.55(1)	0.146(1)
Δ_2^2	2.96(1)	3.056(9)	2.94(4)	2.88(2)	3.080(6)	3.028(7)	3.123(3)	3.075(7)
δ_2/Fe	1.125(7)	1.174(5)	1.14(2)	1.11(1)	1.149(3)	1.140(4)	1.147(1)	1.149(4)
FWHM ₂	0.56(2)	0.31(1)	1.05(6)	0.66(4)	0.29(1)	0.32(1)	0.272(4)	0.40(1)
A ₂	0.074(2)	0.035(1)	0.120(5)	0.079(4)	0.29(1)	0.225(7)	0.451(7)	0.089(2)

Errors in the last digit are given in parentheses.

δ/Fe : isomer shift w.r.t. metallic iron, Δ : quadrupole splitting, FWHM: full width at half maximum, A: relative area.

Because parameters of spectral components ensuing from paramagnetic relaxation are not included in the Table, the sum of relative areas may add up to less than unity.

¹ Sample contains ferrihydrite.

² Subscripts: ₃: paramagnetic Fe³⁺, ₂: paramagnetic Fe²⁺.

³ Octahedral plus tetrahedral Fe³⁺.

this, fits of the room-temperature spectra of these samples were carried out to include also a magnetic component with a low magnetic field. Sample NP 548 (Fig. 3c), a 1M illite from an altered tonstein, has the lowest Fe content of all samples studied. This sample contains 2% chlorite and possibly traces of kaolinite. Moreover, a spectrum taken at 4.2 K showed that ~75% of the

Fe content of this sample is not located in the illite structure, but in an associated ferrihydrite (Fig. 4c). The Fe³⁺ component of the room-temperature spectrum of NP 548 must therefore be excluded from the discussion, because it reflects the parameters of ferrihydrite rather than those of illite. The Fe²⁺ parameters observed at room temperature will not be affected by ferrihydrite,

but the associated chlorite could contribute to the Mössbauer spectra. Sample RM5 (Fig. 3d, 4d) is a pure, hydrothermal illite ("sericite") from the Silverton Caldera, Colorado, with an Fe content almost as low as that of NP 548. Sample L-2A-2 is a diagenetic filamentous 1M illite from SW Poland. It contains about twice as much Fe as RM5 and is also quite pure, with only a minor amount of ancillary chlorite (~0.5%). The last sample from this group, 57wT, is an illitic clay from a mylonitized granite. This sample contains some quartz and feldspar but these would not interfere with the Mössbauer measurements.

All four Fe-poor illites had significant proportions (20–45%) of their Fe in the divalent state. These illites had similar Fe^{2+} Mössbauer parameters at room temperature and higher but again similar Fe^{2+} quadrupole splittings at 4.2 K. The three last mentioned samples had similar parameters for Fe^{3+} at 4.2 K (Tables 2 and 3).

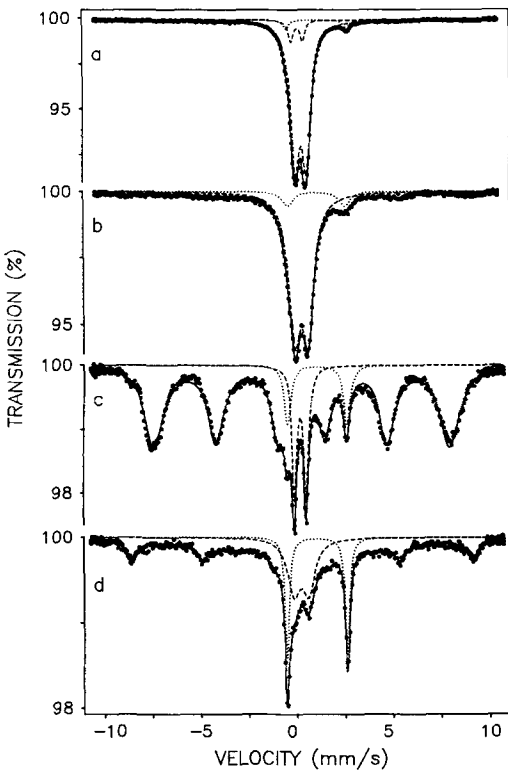


FIG. 4. Mössbauer spectra of the (a) Muloorina, (b) Eldorado, (c) NP 548 and (d) RM5 illites taken at 4.2 K. Non-relaxing paramagnetic Fe^{3+} components are indicated with broken lines and Fe^{2+} components with dotted lines.

For purposes of comparison, room-temperature spectra of two microcrystalline (<20 μm) $2M_1$ muscovites ('sericites') of hydrothermal origin from Japan were also taken. The Shirashi (Kodama, 1965) and Nasu samples (Kodama & Brydon, 1968) had Kubler indices of 0.42 and 0.28, respectively, and were thus more highly crystalline than any of the illites described here. The rather low Fe contents of 1.07% and 0.82 wt% Fe resulted in spectra that were only of moderate quality. The spectra showed a predominance of Fe^{3+} (relative areas 80 and 92%, respectively). The average Fe^{3+} and Fe^{2+} quadrupole splittings of 0.63 and 2.82 mm/s did not differ substantially from those of the illites.

DISCUSSION

The validity of fits interpreted in terms of di- and trivalent Fe in *cis* and *trans* octahedral sites and, where applicable, trivalent Fe in tetrahedral sites, depends on the possibility of resolving these contributions. The subspectra resulting from multidoublet fits, however, often have high line-widths and, for the same Fe valence, show considerable overlap. In the published work on illite, neither the Fe^{3+} nor the Fe^{2+} doublets were visibly resolved. In their fits of illite spectra, Ericsson *et al.* (1977) constrained the line-widths of all but one doublet, and line-widths were as high as 0.52 mm/s in the spectrum of the illite described by Johnston & Cardile (1987). This is not surprising, as the poor crystallinity would cause possibly distinct parameters for the *cis* and *trans* sites of many clay minerals to be smeared out. Dollase (1975) has given criteria for the distinction of discrete crystallographic sites on the grounds of Mössbauer spectra, and pointed out that, as the separation of neighbouring peaks decreases below ~0.6 times the peak half-width, the probable errors in determining the various peak parameters increase spectacularly.

The establishment of definitive *cis* and *trans* assignments are also in conflict with calculations on biotites by Mineeva (1978) who showed that the quadrupole splittings of Fe^{3+} at the *cis* and *trans* OH sites fall closely together, and that structural defects produce variations of the quadrupole splitting in biotite that exceed the difference between the ideal parameters. This problem was also addressed in a recent paper on phlogopite for which Hargraves *et al.* (1990) showed that

meaningful *cis/trans* spectral-area ratios cannot be obtained by attempting to resolve the relevant overlapping spectral components by a fitting procedure.

Rancourt *et al.* (1992) recently showed that tetrahedral Fe³⁺ cannot be positively identified in biotites if the presence of this is not shown up by a distinct shoulder on the low-velocity peak (although biotites are generally of much better crystallinity than most clay minerals). We believe that the same holds for the possible presence of Fe in *cis* and *trans* OH sites. Because clay minerals tend to have non-ideal structures, even spectra of an excellent quality will hardly allow a reliable discrimination of *cis* and *trans* OH sites to be made. It follows that the assignment of specific crystallographic sites to overlapping doublets with which Mössbauer spectra of illites have been fitted must be considered an overinterpretation of results. Such doublets would in fact only give a qualitative indication of the spread of parameters, and fitting the spectra with distributions of Fe³⁺ and/or Fe²⁺ doublets could be a more appropriate approach.

The question arises as to what conclusions can be drawn from fits that imply distributions of parameters. If properly performed, all fitting techniques should allow reasonably accurate determinations of Fe²⁺/Fe³⁺ ratios to be made. For Fe³⁺, the quadrupole splitting of maximum probability allows an assessment of the average site distortion to be made, and the distribution half-width gives an indication of the variability of Fe sites. Reliable assessments of the quadrupole splitting of maximum probability can be made for examples where the resonant absorption is high enough to reduce adequately data scatter at the absorption maxima. Our studies have, however, shown that this may be problematic for samples that are low in Fe (<1 wt% Fe). For the sake of internal consistency, we have, therefore, resorted to using fits that imply one doublet for Fe²⁺ and Fe³⁺ each throughout.

CONCLUSIONS

The studied illites may be classified according to their Fe content in an Fe-rich (>5 wt% Fe) and an Fe-poor (<1 to ~3 wt% Fe) group. With the exception of the Muloorina illite, which has some tetrahedral Fe³⁺, acceptably good fits of the Mössbauer spectra of all the studied illites could

be obtained by consistently using one Lorentzian doublet each for Fe²⁺ and Fe³⁺. For the Fe-poor illites, up to 8% of the spectral areas at room temperature and up to 55% at 4.2 K could, in addition, be accounted for by slow paramagnetic relaxation. The fits implying only one doublet each for paramagnetic Fe²⁺ and Fe³⁺ have the advantage that they can be performed for the spectra of all samples, and the parameters they yield are adequately informative. Although more intricate fitting models (multidoublet or quadrupole-splitting distribution fits) result in lower χ^2 values, they yield no additional unequivocal information (e.g. on *cis*- and *trans*-OH site occupancies) and render comparison with results published elsewhere unnecessarily complicated.

The illites of the Fe-rich group had noticeably lower Fe²⁺/(Fe²⁺ + Fe³⁺) ratios (<0.1) than those of the Fe-poor group (0.2–0.44), possibly reflecting a stronger octahedral character of the Fe-rich illites. For illites containing Fe mainly in the trivalent state, we observed a quadrupole splitting Δ of 0.59 mm/s that is independent of the absorber temperature and an isomer shift δ /Fe of 0.37 mm/s. Both the Fe³⁺ and Fe²⁺ spectral components indicate Fe to be in distorted octahedral coordination. Higher quadrupole splittings averaging 0.73 mm/s were observed for those illites that had higher proportions of Fe²⁺, indicating that the incorporation of Fe²⁺ in the structure causes the octahedral site distortion to increase. This may be due to the fact that the ionic radius of Fe²⁺ (78 pm) differs more from that of Al³⁺ (53.5 pm) than that of Fe³⁺ (64.5 pm; Shannon, 1976). A similar behaviour has been described for Fe-containing kaolinites by Murad & Wagner (1991).

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