MÖSSBAUER SPECTRA OF DIOCTAHEDRAL SMECTITES

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Abstract—Mössbauer spectra of 15 smectites were investigated. In these samples, ferric iron occupies both M(1) and M(2) octahedral sites, the distribution being partly determined by the relative covalency of the bonds formed.

The quadrupole splittings are linearly related to b^{-3}. They show that Fe^{3+} octahedra are much more distorted in montmorillonite and beidellite than in nontronite and volkonskoite and that M(1) sites are more prone to change than M(2). Ferrous iron occurs in relatively undistorted octahedra in some otherwise distorted octahedral sheets and vice versa.

INTRODUCTION

In recent years, Mössbauer spectroscopy has become a tool of increasing importance in mineralogy. The spectra of clay minerals have been described in various publications (Weaver *et al.*, 1967; Taylor *et al.*, 1968; Cousins and Dharmawardena, 1969; Malathi and Puri, 1969; Kohyama *et al.*, 1972; Brunot, 1973; Coey, 1975; Tennakoon *et al.*, 1974; Goodman *et al.*, 1976). Many of the descriptions are qualitative, centering on the determination of the Fe^{2+}/Fe^{3+} ratio. Goodman *et al.* used Mössbauer spectroscopy to ascertain the amount of tetrahedrally coordinated iron. In the present study, an attempt is made to establish relationships between some parameters of the Mössbauer spectra of dioctahedral smectites and their structures.

METHODS OF INVESTIGATION

X-ray diffractometer traces of unoriented samples containing quartz as internal standard were used to determine d_{060} and of oriented specimens for mineralogical identification.

Mössbauer spectra were obtained using a ^{57}Co in Pd source with a 255 channel analyser. Between 2×10^6 to 4×10^6 counts per channel were accumu-

lated for each spectrum. Samples containing about 5 mg of iron per cm^2 were ground with glucose to prevent preferred orientation. Both sample and source were at room temperature. Center shifts are quoted relative to Pd.

The spectra were fitted to two or three doublets, corresponding to Fe^{3+} in two sites or Fe^{3+} in two sites and Fe^{2+} in one site, respectively. Resolution of the Fe^{2+} or addition of a further Fe^{3+} doublet did not reduce the values of χ^2. In the final fit the only constraints imposed were equal Fe^{3+} line widths, but these were allowed to differ from the Fe^{2+} line width.

MINERALOGICAL COMPOSITION

The samples studied are composed predominantly of smectites associated with minor amounts of impurities (Table 1). A sample of metabentonite was also investigated.

Experiments showed that even mild chemical treatment, such as cation exchange, affects the oxidation state of iron in smectites (paper in preparation). No attempt was made, therefore, to separate size fractions in aqueous suspension or to purify the samples. From the point of view of Mössbauer spectroscopy the impurities may be divided into two categories: those which contain appreciable amounts of iron and those

Table 1. Mineralogical composition of samples from various localities

No.	Smectite	Locality	Impurities
1	M	Wyoming, U.S.A. (S.C.M.)	Quartz, K-Felspar
2	M	Wyoming, U.S.A. (S.C.M.)	Quartz, K-Felspar
3	M	Ramon, Israel (Frenkel, 1975)	Illite, quartz, iron oxides
4	M	Mississippi, U.S.A. (Ward's)	Quartz
5	M	Camp Bertaux, Morocco	—
6	M	Texas, U.S.A.	Quartz, iron oxides
7	M	Texas, U.S.A. (S.C.M.)	—
8	M	Cameron, Arizona, U.S.A. (Ward's)	Quartz, kaolinite
9	M	Belle Fourche, U.S.A. (Ward's)	—
10	M	Almaria, Spain	Quartz, plagioclase
11	B.S.	Scan Raft, Sweden	—
12	B.S.	Scan Raft, Sweden	—
13	N	Washington, U.S.A. (S.C.M.)	Quartz, iron oxides
14	V	Bahia, Brazil (Besnus *et al.*, 1975)	Chlorite
15	M.B.	High Bridge, Kentucky, U.S.A. (Ward's)	Quartz

Abbreviations: M = montmorillonite, B.S. = beidellitic smectite, N = nontronite, V = volkonskoite, M.B. = metabentonite, S.C.M. = Source Clay Minerals Project.

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Table 2. Mössbauer parameters of the samples studied

No.	Smectite	Fe³⁺ in M(1) (trans configuration)			Fe³⁺ in M(2) (cis configuration)			Fe²⁺					
		(1) I.S.	(2) Q.S	(3) Γ	(4) I.S.	(5) Q.S.	(6) Γ	(7) I.S.	(8) Q.S.	(9) Γ	(10) $\frac{Fe^{2+}}{Fe^{3+}}$	(11) $\frac{AM(1)}{AM(2)}$	(12) χ^2
1	M	0.12 ± 0.02	1.32 ± 0.03	0.48 ± 0.03	0.09 ± 0.00	0.57 ± 0.02	0.48 ± 0.03	0.89 ± 0.01	3.00 ± 0.03	0.46 ± 0.02	0.45	0.30	310
2	M	0.12 ± 0.01	1.29 ± 0.03	0.49 ± 0.02	0.09 ± 0.01	0.61 ± 0.03	0.49 ± 0.02	0.88 ± 0.01	2.95 ± 0.03	0.46 ± 0.02	0.39	0.26	290
3	M	0.20 ± 0.09	1.22 ± 0.02	0.41 ± 0.03	0.18 ± 0.01	0.45 ± 0.02	0.41 ± 0.03	—	—	—	—	0.80	360
4	M	0.16 ± 0.01	1.07 ± 0.02	0.44 ± 0.02	0.11 ± 0.01	0.57 ± 0.02	0.44 ± 0.02	—	—	—	—	0.18	280
5	M	0.14 ± 0.01	0.99 ± 0.02	0.49 ± 0.04	0.10 ± 0.01	0.53 ± 0.03	0.49 ± 0.04	—	—	—	—	0.36	273
6	M	0.23 ± 0.01	1.16 ± 0.02	0.48 ± 0.03	0.11 ± 0.00	0.54 ± 0.02	0.48 ± 0.03	—	—	—	—	0.16	280
7	M	0.12 ± 0.01	1.03 ± 0.03	0.44 ± 0.03	0.18 ± 0.01	0.53 ± 0.03	0.44 ± 0.03	—	—	—	—	0.80	290
8	M	0.13 ± 0.01	0.85 ± 0.01	0.51 ± 0.03	0.11 ± 0.02	0.49 ± 0.03	0.51 ± 0.03	—	—	—	—	0.38	260
9	M	0.24 ± 0.02	1.09 ± 0.02	0.50 ± 0.03	0.12 ± 0.01	0.56 ± 0.02	0.50 ± 0.03	0.89 ± 0.01	2.80 ± 0.03	0.39 ± 0.02	0.44	0.43	265
10	M	0.15 ± 0.01	1.26 ± 0.02	0.47 ± 0.03	0.11 ± 0.01	0.43 ± 0.03	0.47 ± 0.03	0.90 ± 0.01	2.76 ± 0.02	0.33 ± 0.02	0.07	0.20	270
11	B.S.	0.30 ± 0.01	1.35 ± 0.02	0.56 ± 0.04	0.12 ± 0.01	0.59 ± 0.03	0.56 ± 0.04	0.92 ± 0.01	2.74 ± 0.03	0.34 ± 0.02	0.21	0.07	268
12	B.S.	0.19 ± 0.01	1.28 ± 0.02	0.56 ± 0.03	0.10 ± 0.01	0.56 ± 0.02	0.56 ± 0.03	0.89 ± 0.01	2.56 ± 0.03	0.46 ± 0.01	0.14	0.19	280
13	N	0.09 ± 0.00	0.70 ± 0.02	0.39 ± 0.01	0.08 ± 0.00	0.28 ± 0.02	0.39 ± 0.01	—	—	—	—	0.50	260
14	V	0.14 ± 0.00	0.72 ± 0.02	0.35 ± 0.03	0.15 ± 0.01	0.31 ± 0.03	0.35 ± 0.03	—	—	—	—	0.90	273
15	M.B.	—	—	—	0.14 ± 0.00	0.62 ± 0.02	0.45 ± 0.01	—	—	—	—	—	270

Abbreviations: M, B.S., V and M.B. as in Table 1. I.S. = isomer shift relative to Pd; Q.S. = quadrupole splitting; Γ = peak width, all in mm/sec, AM(1)/AM(2) = ratio of amount of Fe^{3+} in sites M(1) to that in sites M(2).

which do not. Quartz, calcite and felspar, though relatively abundant, do not affect the Mössbauer spectra, whereas iron oxides coating the clay particles or admixed micaceous impurities may do so.

Iron oxides are difficult to detect by X-ray methods, due to their fine particle size. In Mössbauer spectra they may give rise to a magnetic six-line pattern at low temperatures, but may show a paramagnetic pattern at room temperature. If the particles are sufficiently large, the six-line pattern will also appear at room temperature. Of the samples examined only No. 8 shows a magnetic spectrum at room temperature. This practically disappears on treatment of the sample with dilute HCl. Chemical analysis using the method of Mitchell and Mackenzie (1954) demonstrated that the amount of iron in the coating did not exceed 5% of the total. In the other samples examined, it ranged from 0 to 3%.

Micaceous impurities, if present, are below the limits of detection of X-ray and i.r. methods. Only iron-rich micas, therefore, could affect the Mössbauer spectra significantly. Since most of the iron in smectites is trivalent, the greater error would be expected in the Fe^{2+} parameters. It is shown below (Table 2) that only five of the samples contain appreciable amounts of Fe^{2+}. Of these, montmorillonite from Wyoming (samples 1 and 2) and the beidellitic smectites (samples 11 and 12) have been investigated in detail in previous studies (Rozenson and Heller-Kallai, 1976; Bystrom-Brusewitz, 1975) without any indication of the presence of iron-containing impurities. Only in sample No. 9 can the presence of Fe^{2+} containing impurities not be entirely excluded, though no evidence for their presence was found either in this or in a previous study (API Project 49).

THE MÖSSBAUER SPECTRA

A typical spectrum is shown in Figure 1 and the calculated parameters are given in Table 2. Most of the spectra recorded show only one broad doublet,

with parameters characteristic of Fe^{3+}. Some samples give rise to an additional, smaller doublet corresponding to Fe^{2+}. The strong doublet generally could be resolved into two, with isomer shifts and quadrupole splittings typical of octahedrally coordinated Fe^{3+} (Bancroft, 1974). There is no evidence for the presence of tetrahedrally coordinated iron in any of the samples we investigated. Goodman et al. (1976) found tetrahedral iron in all the nontronites they examined, including a specimen of sample 13, for which they report 6% tetrahedrally coordinated Fe^{3+}. Our data for a two-doublet fit resemble those of Goodman et al., but no improvement in χ^2 was achieved by addition of a further doublet. We therefore concluded that no tetrahedral iron was present, in agreement with the results of our wet chemical analysis and the microprobe analysis of Goodman et al. The original sample is inhomogeneous and our specimen may differ slightly from that studied by Goodman et al. Moreover, as pointed out by these authors, there is considerable uncertainty in the interpretation of all the data, and the presence of less than about 5% tetrahedrally coordinated iron in any of the samples we studied cannot be ruled out.

Each unit cell of smectites contains three possible octahedral sites: M(1), with hydroxyl groups arranged in *trans* positions and two sites M(2) with hydroxyl groups arranged in *cis* positions. In the ideal structure, the two M(2) sites are equivalent. In fact, the symmetry of these sites may differ, as, for example, in 3T muscovite (Güven and Burnham, 1967). The question therefore arises whether the two Fe^{3+} doublets should be assigned to M(1) and M(2) sites or to two non-equivalent M(2) sites. Simple calculations show that for a square bipyramidal arrangement of groups like $Fe^{3+}A_2B_4$ the absolute value of the ratio of the quadrupole splitting for the *trans* to that of the *cis* configuration is 2. The ratio observed for the two Fe^{3+} doublets in the smectite spectra is close to 2 (see below). This suggests that the first alternative is the more probable. It was also adopted for non-
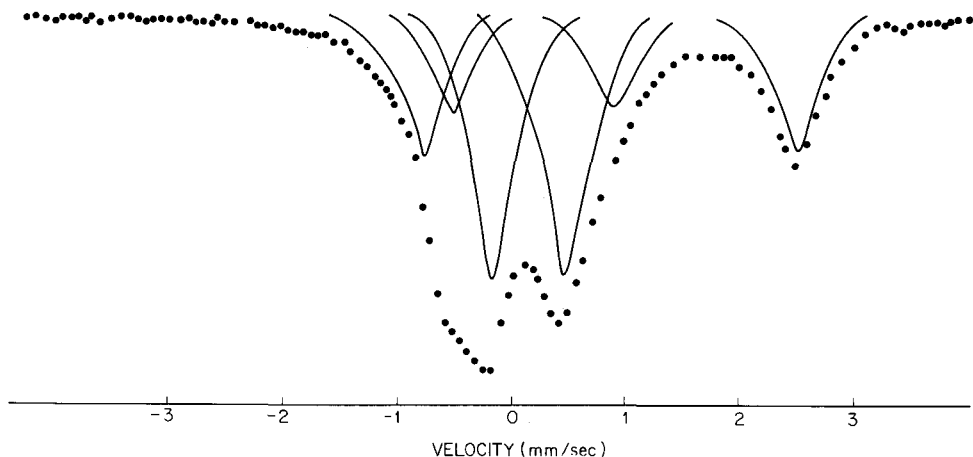

Figure 1. Mössbauer spectrum of montmorillonite (sample No. 1) fitted to three octahedral doublets— two Fe^{3+} and one Fe^{2+}.

tronites by Goodman *et al.* (1976). The possibility remains, however, that there are three independent octahedral sites, although attempts to resolve the spectra accordingly did not give meaningful results.

The line widths of both Fe^{3+} doublets (Table 2) are generally greater than 0.38 mm/sec, the width reported for Fe^{3+} in most other silicates (Bancroft, 1974). It seems that each doublet corresponds to several sites of slightly different symmetry with similar but not identical Mössbauer parameters (Rozenson and Heller-Kallai, 1976). These sites may occur within the same octahedral sheet or in different layers of the same mineral.

The Fe^{2+} doublets are symmetrical. The doublet for samples 10 and 11 is relatively narrow. In contrast, it is broad for samples 1, 2 and 12, but χ^2 could not be decreased by resolution into two doublets. This suggests that Fe^{2+} in samples 1, 2 and 12 occupies several similar sites, M(1) *or* M(2), but that the range of electric field gradients is more limited in sample 9 and even more so in samples 10 and 11.

A small error in the Mössbauer parameters may be introduced by the presence of minor amounts of iron oxides in some of the samples, as discussed, but since the amount of iron in this phase never exceeded 5% of the total, this error is probably negligible.

QUADRUPOLE SPLITTING (Q.S.)

The quadrupole splitting in a Mössbauer spectrum of ^{57}Fe is given by the equation

$$Q.S. = \tfrac{1}{2}e^2qQ\left(1 + \frac{\eta^2}{3}\right)^{1/2},$$

where Q.S. is the quadrupole splitting, Q is the quadrupole moment of the nucleus, e^2q (or V_{zz}) is the z component of the electric field gradient (EFG) tensor and $\eta[= (V_{xx} - V_{yy})/V_{zz}]$ is the asymmetry parameter.

V_{xx}, V_{yy} and V_{zz} are the components of the EFG tensor in three mutually perpendicular directions.

Two factors determine the magnitude of q: the contribution of the surrounding ligand ($q_{lattice}$) and the distribution of the valence electrons ($q_{valence}$), i.e.

$$q = (1 - \gamma\infty)q_{lattice} + (1 - R)q_{valence}$$

where $\gamma\infty$ and R are empirical constants.

Fe^{3+} in silicates occurs in the high spin, spherically symmetrical electronic configuration $(t_{2g})^3(e_g)^2$. $q_{valence}$ is therefore equal to zero. $q_{lattice}$ is proportional to r^{-3}, where r is the ligand–cation distance, and to a trigonometric function which depends upon the ligand–cation configuration. For a square bi-pyramidal arrangement, MA_2B_4, the absolute ratio K between the quadrupole splittings of atoms in *trans* to those in *cis* sites is 2:1. The derivation is based on three assumptions: (1) η, the asymmetry factor, is zero; (2) the charges involved are point charges or the bonding is of the σ type; (3) the contribution to the quadrupole splitting from parts of the structure other than nearest neighbours can be neglected (Bancroft, 1974).

Figure 2 is a plot of the quadrupole splitting of Fe^{3+} in one of the trivalent sites of the smectile relative to that in the other. It is evident that, for the smectites studied, the value of K is either equal to or close to two. This indicates that for some of the samples, at least, the above assumptions are valid. In samples for which K differs from 2, the octahedra are probably distorted. This may involve some π bonding analogous to that postulated for pyroxenes (O'Nions and Smith, 1973) and a more significant effect of the next nearest neighbours. It is difficult to judge which of these factors are the cause and which the effect of the configuration adopted by the mineral.

The magnitude of the Q.S. of the M(1) doublets is large for the montmorillonites and beidellitic smectites, indicating that the octahedra are very distorted. Moreover, the range of magnitudes of the Q.S. of
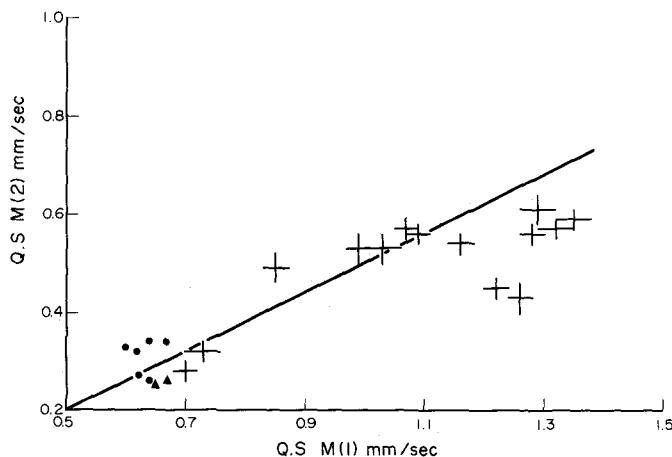

Figure 2. Relationship between quadrupole splitting of Fe^{3+} in M(1) and M(2) sites. + data obtained in this study (the magnitude of the line represents the error), ▲—Brunot (1973), ●—Goodman *et al.* (1976).
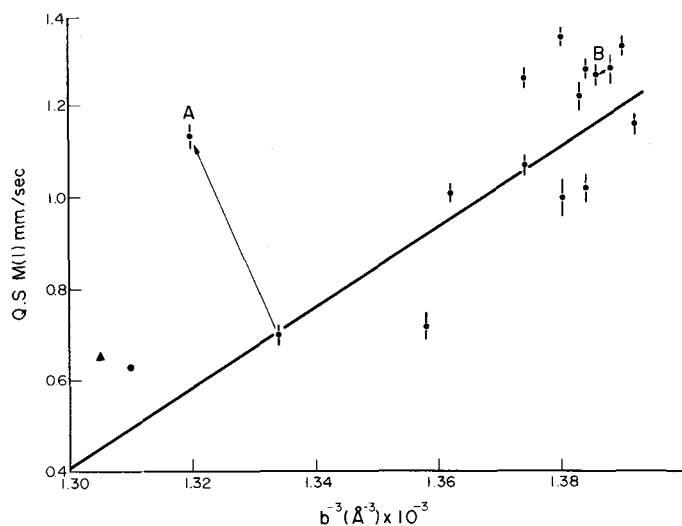
Figure 3. Dependence of quadruple splitting of Fe^{3+} in M(1) sites on b^{-3}. Legend as for Figure 2. For explanation of points A and B see text.

Fe^{3+} in the M(2) and, in particular, in the M(1) series (Table 2) is greater than in other mineral groups, e.g. amphiboles (Ernst and Wai, 1970). In the nontronite series studied by Goodman et al. (1976) these differences are relatively small. It appears that in montmorillonites and beidellites, both M(1) and M(2) sites are sensitive to structural changes of the minerals. The larger differences in Q.S. suggest that the M(1) sites are the more easily deformed. This is plausible in view of the fact that in dioctahedral phyllosilicates M(1) sites are generally larger than M(2), rendering them more prone to distortion. It appears that octahedral layers occupied by the larger cations Fe^{3+} and/or Cr^{3+} (sample 14) are less distorted.

Figures 3 and 4 show the relationship between the b repeat distance and the Q.S. of Fe^{3+} in sites M(1) and M(2), respectively. The plots of Q.S. against b^{-3} are approximately linear, with correlation coefficients of 0.910 and 0.898, respectively. Simple calculations show that the values of Q.S. are more sensitive to

changes in bond angles than bond lengths. To account for a difference of about 50% in Q.S., as observed between some montmorillonites and beidellites on the one hand and nontronites on the other, an increase in Fe^{3+}—O bond length of at least 27% would be required. Since this is not reasonable, it must be inferred that differences in Q.S. are largely due to distortions of the octahedra, which govern the values of η, in agreement with the postulates of Radoslovich and Norrish (1962), that changes in bond angles occur in preference to changes in bond lengths. Since b is determined by the chemical composition, so also is the Q.S. The Mössbauer spectra clearly demonstrate that the octahedral sheets of montmorillonite and beidellite are very distorted, but those of nontronite and volkonskoite much less. This conclusion is not unexpected, but Mössbauer spectra provide the possibility of interpreting the phenomena quantitatively. This will be attempted in a separate study.
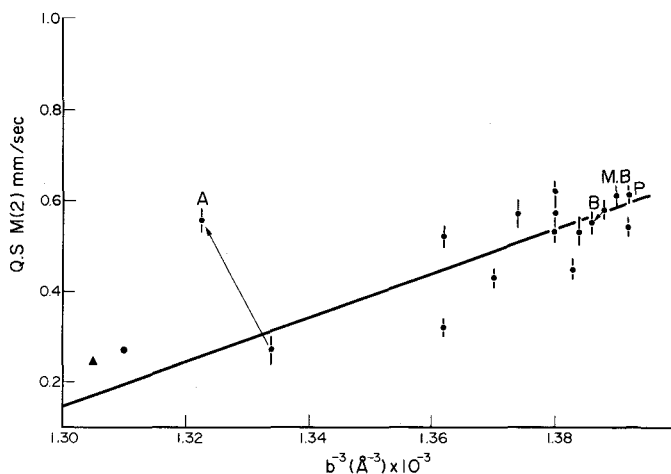

Figure 4. Dependence of quadrupole splitting of Fe^{3+} in M(2) sites on b^{-3}. Legend as for Figure 2. For explanation of points A, B, MB and P see text.

Exchange of interlayer cations has a small but significant effect on the Mössbauer parameters. The points corresponding to sample 1 saturated with various cations fall on the straight lines, but, for clarity, are not included in the figures. Points corresponding to metabentonite (MB, sample 15) and to pyrophyllite (P), for which the parameters were taken from the literature (Wardle and Brindley, 1970; Hogg and Meads, 1970) and which contain Fe^{3+} in M(2) sites only, fall on the straight line of Figure 4, as shown.

Two further points, A and B, are plotted on the graphs, corresponding, respectively, to nontronite (sample 13) and montmorillonite (sample 1) reduced with $Na_2S_2O_4$ and reoxidized. Point A does not fall on the straight lines, whereas point B does. An additional point C, corresponding to montmorillonite heated at 700°C lies completely outside the range of the diagrams, with Q.S. = 1.40 mm/sec, $b^{-3} = 1.13.10^{-3}A^{-3}$. It was previously shown that reduction with $Na_2S_2O_4$ decreases the coordination number of some of the ions in the octahedral sheet of nontronite to five irreversibly, but in montmorillonite no such change occurs (Rozenson and Heller-Kallai, 1976). Heating at 700°C causes dehydroxylation of smectites, which involves a change to five-coordination of all the octahedral cations. Points corresponding to reduced or reduced and reoxidized montmorillonites, like point B, therefore fall near the straight lines of Figures 3 and 4, while the drastic structural changes involved in reduction of nontronite and, even more, on dehydroxylation of the smectites, account for the deviation of points A and C from the straight lines.

Fe^{2+} is not a spherically symmetrical ion and the $q_{valence}$ term cannot be neglected. It is therefore more difficult to interpret the quadrupole splittings obtained for Fe^{2+} quantitatively. In general, the smaller the value of the Q.S., the greater the distortion of the Fe^{2+} octahedra.

The Q.S. for Fe^{2+} in the smectites examined ranges from 3.00 mm/sec in sample 1 to 2.56 mm/sec in sample 12, indicating that the Fe^{2+} octahedra are more distorted in sample 12 than in sample 1. There is no apparent correlation between the symmetry of the sites occupied by Fe^{3+} and Fe^{2+} ions. The high values of the Q.S. of Fe^{3+} in samples 1, 2, 10, 11 and 12 indicate that these sites are very distorted. The sites occupied by Fe^{2+} in samples 10, 11 and 12 are also distorted, but those in samples 1 and 2 are considerably more regular. Moreover, when additional Fe^{2+} ions were produced by reduction of samples 1 and 2 with hydrazine, this also occupied relatively undistorted sites (Rozenson and Heller-Kallai, 1976). In contrast, on reduction of nontronite (sample 13) with hydrazine, Fe^{2+} is formed which gives rise to a Q.S. of 2.64–2.67 mm/sec, indicating that the octahedra are appreciably distorted. It is noteworthy that Fe^{2+} occupies relatively undistorted sites in the otherwise distorted octahedral sheets of samples 1 and 2, but not of 10, 11 and 12, and occu-

pies irregular octahedra in the otherwise relatively symmetrical sheets of nontronite.

ISOMER SHIFT (I.S.)

The isomer shifts for Fe^{3+} in the various smectites differ, though they all fall in the region commonly assigned to six-coordinated Fe^{3+} in silicates. The values for Fe^{3+} in M(2) range from 0.08–0.18 mm/sec, clustering around 0.10–0.12 mm/sec, while those for Fe^{3+} in M(1) sites cover a wider range, from 0.09 to 0.25 mm/sec. For montmorillonites and beidellitic smectites the I.S. in position M(1) exceeds that in M(2), whereas for nontronites and volkonskoite all the isomer shifts are similar (Table 1 and Goodman et al., 1976).

The I.S. arises from the interaction between the nucleus and the overlapping electron orbitals. The lower the I.S. for Fe^{3+}, the greater the covalent contribution to the Fe^{3+}–ligand bond. In montmorillonites and beidellites Fe^{3+} occupying M(2) sites is thus more covalently bonded than Fe^{3+} in M(1) sites. This is reasonable in view of the fact that the M(2) sites in dioctahedral minerals are usually smaller, thus permitting stronger overlap between metal and ligand orbitals. It appears that when the octahedral sheets are predominantly occupied by the relatively large cations Fe^{3+} and Cr^{3+}, sites M(1) and M(2) become very similar, as was also indicated by the quadrupole splittings.

The differences between the various smectites may be due to the effect of next nearest neighbours, though no direct correlation could be established between the chemical composition and the observed isomer shifts. The wider range of values for Fe^{3+} in M(1), like that of the Q.S., suggests that this site is the more susceptible to structural changes. In the absence of accurate structure determinations of smectites, it is futile to attempt a more quantitative treatment at this stage.

The isomer shifts of all the Fe^{2+} doublets are similar.

DISTRIBUTION OF Fe^{3+} BETWEEN M(1) AND M(2) SITES

The ratio of the amount of Fe^{3+} occupying M(1) to that occupying M(2) sites ($A_{M(1)}/A_{M(2)}$) is shown in column 11 of Table 2. Since there are twice as many M(2) sites as there are M(1), the ratio of 0.5 indicates completely random distribution of Fe^{3+} between M(1) and M(2). The values range from zero, corresponding to a structure in which Fe^{3+} occupies M(2) exclusively, to 0.9, indicating strong preference for M(1) sites. The errors in these values are relatively large, because the areas of the doublets, which are taken to be proportional to the amount of Fe^{3+}, are very sensitive to small changes in the Mössbauer parameters.

Figure 5 shows the relationship between the ratio $A_{M(1)}/A_{M(2)}$ and the difference in I.S. for Fe^{3+} in M(1) and M(2) sites for 14 of the 15 samples examined.
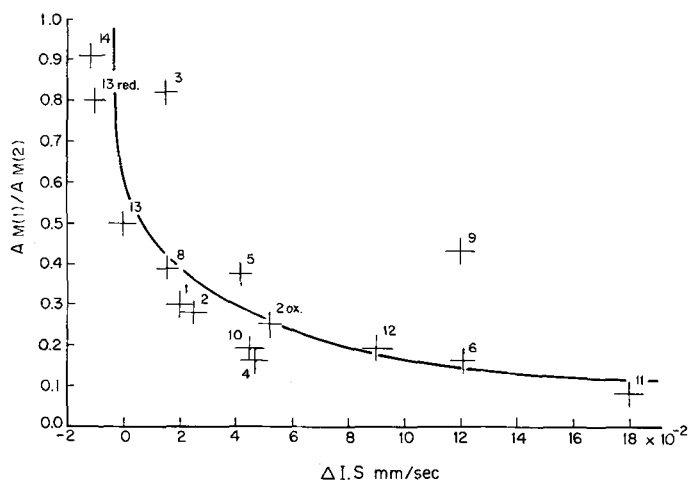
Figure 5. Distribution of Fe^{3+} in octahedral sheets. Legend as for Figure 2. The numbers correspond to those in Table 1. ox = oxidized, r = reduced.

In general, the smaller the difference, the greater the tendency for Fe^{3+} to occupy M(1) sites, i.e. the more nearly the covalency of Fe^{3+} in site M(1) resembles that in M(2), the greater the tendency for this site to be populated. It appears that in the absence of crystal field stabilization, which is precluded by the electronic structure of Fe^{3+}, the tendency to form more covalent Fe–O bonds is a decisive factor in determining the distribution of Fe^{3+} among the available sites. Sample No. 7 does not conform to the relationship. It contains very little iron and requires further examination.

Data presented in Table 2 of the paper by Goodman et al. (1976) show that for nontronites the difference in I.S. between sites M(1) and M(2) is close to zero and $A_{M(1)}/A_{M(2)}$ ranges from 0.33 to 0.68. It thus appears that with nontronites other factors, e.g. tetrahedral site occupancy, must also be taken into account.

Cation ordering in layer silicates has been extensively studied and was recently reviewed by Bailey (1975) who claimed that all dioctahedral silicates have ordered vacant octahedral sites. Selected area diffraction patterns have shown that the elementary layers of montmorillonite are non-centrosymmetric, while those of nontronite and beidellite are centro-symmetric (Mering and Oberlin, 1971; Güven and Pease, 1975). It was concluded that the octahedral cations in montmorillonite occupy equal numbers of M(1) and M(2) sites, while in nontronite and beidellite only M(2) sites are occupied. It should be stressed that the electron optical investigations relate to all the octahedral cations, whereas the present study is confined only to octahedral Fe^{3+}. Our data are thus compatible with the electron optical data for montmorillonite, but not for nontronite, as reported previously (Rozenson and Heller-Kallai, 1976). For the beidellitic smectites, the Mössbauer spectra indicate almost complete preference for M(2) sites, in agreement with the electron-optical data. The presence of minor amounts of Fe^{3+} in M(1) positions in our

samples may be due to the fact that they were not true beidellites. Unfortunately, no true beidellites were available. In the various montmorillonites Fe^{3+} ions occupy different proportions of M(1) and M(2) sites, but since these constitute only a small fraction of the octahedral cations, the results are compatible with electron optical data, though they do not necessarily confirm them. In nontronite, however, Fe^{3+} is the dominant octahedral cation and its random distribution between the two sites is incompatible with the centro-symmetric configuration inferred from the electron optical data. As previously suggested (Goodman et al., 1976; Rozenson and Heller-Kallai, 1976) it seems probable that nontronite is built of domains, in some of which Fe^{3+} occupies M(1) and M(2) sites equally and in others M(1) sites only. These may occur within the same sheet, as suggested by Goodman et al., or in the octahedral sheets of different layers.

In metabentonite, which is composed of illite and a mixed-layer illite–smectite, Fe^{3+} occupies M(2) sites exclusively. This does not, however, necessarily apply to all the other octahedral cations. Metabentonite shows the same relationship between Q.S. and b^{-3} as the smectites and may thus be regarded as the end-member of the series of smectites studied.

CONCLUSIONS

The absolute ratio of the quadrupole splittings of Fe^{3+} in cis and trans sites of dioctahedral smectites is approximately 1:2, as predicted by theory. The actual values, which vary widely throughout the series, show that the octahedra are very distorted in montmorillonites and beidellites and considerably less in nontronites and volkonskoite, in agreement with the concepts of Radoslovich and Norrish (1962). The larger Fe^{2+} ions, however, occupy relatively symmetrical sites in some montmorillonites and more distorted sites in hydrazine reduced nontronites, in which the environment of the remaining Fe^{3+} ions

is not changed appreciably. For Fe^{3+}, plots of Q.S. against b^{-3} (Figures 3 and 4) are approximately linear. Structural changes involving very large distortions of the octahedra, leading to a change in coordination number, such as are brought about by dithionite reduction of Fe^{3+} in nontronites or dehydroxylation of smectites, destroy the linear relationship. The plots can be used to detect such deviations and may thus provide some information about the history of the samples.

Differences between the isomer shifts show that Fe^{3+} ions in M(2) sites of montmorillonites and beidellites are more covalently bonded than in M(1). The smaller the difference in covalency between Fe^{3+} in the two sites, the more Fe^{3+} ions occupy M(1) sites. It appears that the tendency to form covalent bonds is one of the factors governing the distribution of Fe^{3+} in the octahedral sheets of these minerals. The relative importance of other factors, e.g. entropy or structural inheritance, is not known at present. In nontronites, for which all the isomer shifts are similar, both M(1) and M(2) sites are populated, but the distribution of Fe^{3+} is determined by factors other than the tendency to form covalent bonds.

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