# THE ORIENTATION OF THE PRINCIPAL AXES SYSTEM OF THE ELECTRIC FIELD GRADIENT IN Fe (III) VERMICULITE DETERMINED BY MÖSSBAUER SPECTROSCOPY

INTRODUCTION

During previous work on Fe(III)–montmorillonite and vermiculite we noted the dichroic character of the quadrupole doublet of Fe(III) (Helsen *et al.*, 1970; Helsen *et al.*, 1972). From that dichroic character we determined now the inclination of the z-axis of the principal axis system (PAS) of the electric field gradient (EFG) with respect to the axis c^* of Fe(III)–vermiculite (Fig. 1).

The work has been performed on a vermiculite obtained near Llano (Texas). It is suitable for preparing oriented films and contains only traces of structural iron. The full characterization has been published by Hougardy *et al.* (1970). The unit cell formula according to these authors is:

$$[Si_{5.28}Al_{2.72}][Al_{1.32}Mg_{4.58}Fe_{traces}]O_{20}(OH)_4 - M_{1.6}^+$$
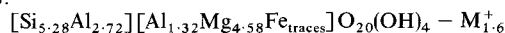
EXPERIMENTAL: PREPARATION OF Fe(III) SATURATED ORIENTED FILMS OF VERMICULITE

The pure mineral was subsequently saturated with Na^+, transformed into the propylammonium complex and filtered off on a millipore filter according to a technique used by Hougardy* resulting in a film with (001) parallel to film surface. The propylammonium ions of the oriented film are exchanged for Na^+, partially protonated with HCl and treated with Fe(III) ions. The exchanges go on without loosing the orientation.

After exchange, the film was washed with distilled water and conditioned in order to obtain a sample of mean (001) spacing of 14·2 Å (double layer of H_2O), comparable to the value found by Clementz *et al.* (1973) for Cu(II)–vermiculite. Finally, the film was made ready for the Mössbauer apparatus by encapsulating in thin Al foil. It was attached
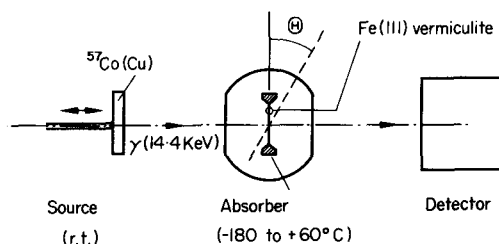
Fig. 2.

to a sample holder which allowed the sample to be oriented with respect to the gamma beam and to be kept at constant temperature (−185 to 50°C) (Fig. 2).

A mean (001) spacing of 14·2 Å was calculated from an X-ray diffractogram containing up to 9 rational orders; no other reflections could be detected. However, a photograph taken with a Laue set-up using monochromatic radiation with the vermiculite film perpendicular to the X-ray beam and a photographic plate at 6 or 9 cm from the film showed the orientation not to be perfect because (001) reflections appeared on the Laue photograph.

Together with a certain degree of disorder, another possible source of error in the final result may be the presence of a small amount of exchangeable Na^+ ions (3·8% of total CEC). However, the vermiculite on one hand and the properties of Fe(III) on the other, do not allow very much freedom without either destroying the vermiculite or precipitating ferric hydroxide. Thus, a compromise has to be accepted as long as no other suitable Mössbauer isotopes are available.

MÖSSBAUER SPECTROSCOPY AND COMMON SPECTRAL PARAMETERS

The Mössbauer spectrometer was a conventional electromechanical velocity scanning device, activated by a triangular oscillator signal with a frequency of about 20 counts/sec. The single line source was a ^{57}Co diffused into a copper matrix. The spectra were analysed by a non linear least square fit computer program, assuming Lorentz form for the peaks.

The common parameters derived from the spectra are collected in Table 1: isomer shift (I.S.), quadrupole splitting (Q.S.), recoilless fraction (f') and Debye temperature. The recoilless fraction is estimated according to the formulae given by Hafemeister (1966) and the Debye temperature by the simplified formula for $T \geqslant 1/2\,\theta_D$ according to Greenwood (1971, p. 11).
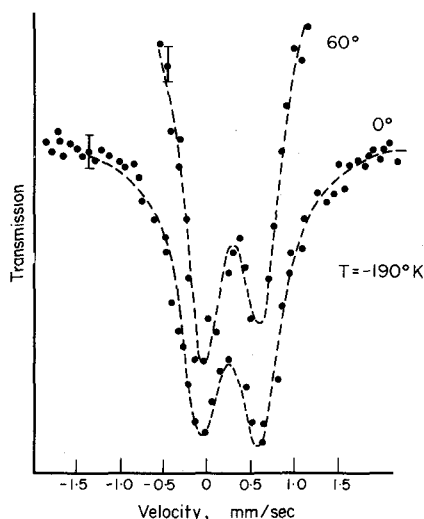

Fig. 1. Two spectra recorded at the same temperature but with different orientations to gamma beam.

* Hougardy J., Laboratoire des Sciences de la Terre, Université de Louvain, Heverlee (Belgium). Private communication.

Table 1. Mössbauer parameters for Fe (III)–vermiculite

Temp. (°K)	+ 50	+ 20	− 40	− 190
I.S. (mm.sec⁻¹)* Temp. coeff. of	0·123 (24)	0·137 (20)	0·173 (27)	0·252 (21)
I.S. (mm.sec⁻¹. °C⁻¹)		$(5.3 \pm 0.2)\,10^{-4}$		
Q.S. (mm.sec⁻¹)*	0·647 (24)	0·669 (20)	0·675 (27)	0·681 (21)
f' (approx.)	0·23	0·18	0·47	0·59
Debye temp. (°K)		190 ± 50		

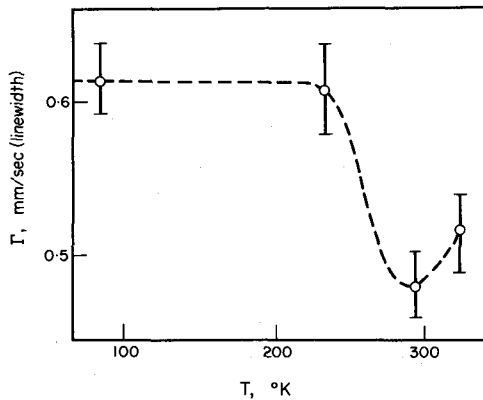* Values between brackets: S.D. (only two last figures).

Fig. 3.

The evolution of line widths with temperature is represented in Fig. 3. The broadening in the lower temperature region is considered as a non homogeneous broadening (existence of different exchange sites; see e.g. Wey and Le Dred, 1972) and above room temperature to diffusional motion (Singwi and Sjölander, 1960).

DISCUSSION: ORIENTATION OF EFG

The quadrupole doublet peaks have an intensity ratio which was experimentally found to be a function of the angle θ between the gamma ray and the axis c^* of vermiculite (Fig. 1) but independent of the angle ϕ (for the significance of the angles, see Fig. 4). This means that order of vermiculite crystallites occurs only along c^* but that the ab-axes are randomly distributed. It was experimentally deduced from spectra recorded with $\theta = 0$ and ϕ varying from 0 to 2π.

The theoretical treatment of the intensity ratio is basically derived from Zory (1965) by the following formula:

$$I' = \frac{p_2}{p_1} = \frac{4\sqrt{(3+\eta^2)/3} + (3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi)}{4\sqrt{(3+\eta^2)/3} - (3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi)} \quad (1)$$

in which p_2 and p_1 are the transitions indicated in Fig. 5 and designated on Fig. 1; η is the 'asymmetry parameter' of the electric field gradient tensor.

Equation (1) can be transformed to a function of the macroscopic angles θ and ϕ, and the Euler angles α, β and γ relating the principal axes of the EFG- tensor to crystal coordinates (Goldstein, 1966).

As shown, I' is independent of Φ which means that our system is axially symmetric, with respect to c^* and the obtained function may be integrated over angles $\Phi = 0$–
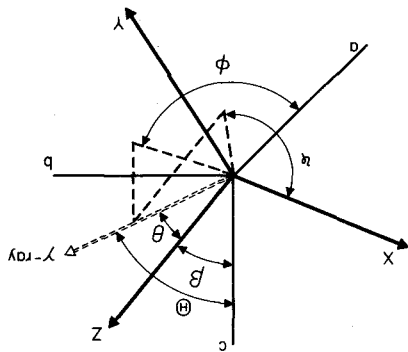

Fig. 4. Polar and azimuthal angle of the gamma ray propagation vector with respect to PAS of EFG (X, Y, Z) and the crystal axes (a, b, c) (Zory, 1965).
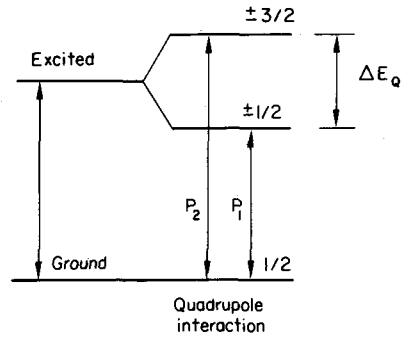

Fig. 5. Nuclear energy level diagram of ^{57}Fe.

2π; the final result is:

$$\int_0^{2\pi} I' d\Phi = I = \frac{A + \cos^2\theta}{A + 2/3 - \cos^2\theta} \quad (2)$$

with

$$A = \frac{8\sqrt{(3+\eta^2)/3} - 2 + (3 + \eta\cos 2\gamma)\sin^2\beta}{6 - 9\sin^2\beta - 3\eta\sin^2\beta\cos 2\gamma}. \quad (3)$$

In this equation are η, λ and β unknown but are limited to $0 \leqslant \eta \leqslant 1$, $0 \leqslant \gamma \leqslant \pi/2$ and $0 \leqslant \beta \leqslant \pi/2$. Because we do not have a single crystal, none of the unknowns can be determined and eliminated from (2) and (3). To get an approximate solution, we calculated a numerical value for A by fitting the experimental points $I = f(\theta)$ to equation (2) by the least square method. The result is represented on Fig. 6. The best value for A was found to be -14. Tabulating now a series of possible values for η, γ and β, we find that, for $A = -14$, we may conclude β to be: $50 < \beta < 70°$. β is the angle between the z-axis of the PAS of EFG and c^* of vermiculite, γ remaining undetermined.

Without identification of each peak, the quadrupole interaction (e^2qQ), can be either positive or negative. However, attributing the negative sign to e^2qQ, more consistent parameters are found to fit the results according to equations (2) and (3). This result is supported by the results summarized by Goldanskii and Suzdalev (1971) for atoms on a surface. No similar determinations on clay minerals have been done up to now. A 'fragile' exchangeable cation such as Fe (III) does not allow any freedom in experimental conditions. Therefore this single result does not permit the elucidation of either the origin or the consequences of the determined orientation. We may just refer to the inclination with similar angles of absorbed organic molecules observed by Brindley (1970) and to the inclination of the axially elongated tetragonal $Cu(H_2O)_6^{2+}$ ion reported by Clementz et al. (1973). Another possibility is that the observed orientation is related to the internal crystallographic structure of the mineral. The striking differ-
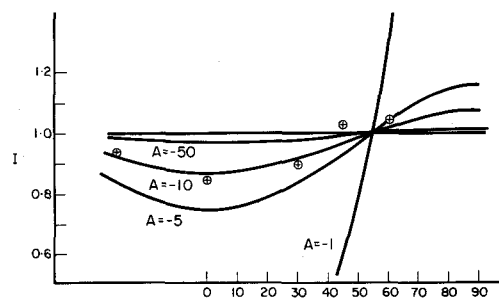

Fig. 6. Intensity ratios calculated as a function of θ for different values of A.

ence between the Mössbauer behaviour of Fe(III) on vermiculite and on montmorillonite (Helsen et al., 1970) may suggest a new approach to the distinction between surfaces of di- or trioctahedral phyllosilicates.

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POSITION OF EXCHANGEABLE CATIONS IN MONTMORILLONITES

IT IS WELL known that the surface of montmorillonites with two or less layers of adsorbed water molecules exhibits strong Brønsted acidity. In our work on the determination of the acid strength of montmorillonites from Camp Bertau, Morocco, a remarkable difference in acidity was observed depending on the cation occupying the exchange site (Helsen, 1971). The acid strength was calculated from the degree of transformation of triphenylmethanol (Ph_3COH) into its carbonium ion (Ph_3C^+) on the clay surface. The amount of Ph_3C^+ that could be formed by the montmorillonites with different cations is tabulated in Table 1. This acidity is due to the enhanced dissociation of residual water molecules.

The origin of the enhanced dissociation is commonly attributed to the polarizing power of the cations occupying the exchange sites. If this is so, the total amounts of carbonium ions formed should strongly depend on the cation. A glance at Table 1, shows this to be the case for alkali ions but not in the way we would have expected. Indeed, there is no smooth decrease as a function of atomic number, ionic radius, charge density etc. This suggests that several effects are operative simultaneously.

Since the first publication of the results, more data has become available which confirm our results and allow the following hypothesis to be formulated. The polarizing action on the water molecules depends on the charge density of the cation and more generally on the electric field

conditions in the interlamellar space (Mamy, 1968; p. 197). Considering, however, the geometry of the surface to which they are attached, the position of the cation with respect to both the surface with the hexagonal cavities and the water molecules of the hydration sphere apparently can modify the influence of the charge density. When a cation of the right radius ($\neq$ as small as possible) is more or

Table 1

Mont-morillonite	Radius in Å (*)	Ph_3C^+ max. am. μmol/g	H_2O %	001-spac. Å
Li	0·68	24·7	7·0	12·20
Na	0·97	6·5	4·2	11·65
K	1·33	4·2	1·4	11·55
Rb	1·47	23·6		—
Cs	1·67	22·6		—
Be	0·35	35·7		—
Mg	0·66	39·8	13·5	14·15
Ca	0·99	28·1	11·0	14·15
Sr	1·12	22·7		—
Ba	1·34	18·7		—

* *Handbook of Chemistry and Physics,* Chemical Rubber Cy., 46th Edition, p.F. 117.