

A MÖSSBAUER AND I.R. SPECTROSCOPIC STUDY OF THE STRUCTURE OF NONTRONITE

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Abstract—Mössbauer and i.r. spectra of a series of nontronites show that Fe^{3+} and Al^{3+} are distributed between tetrahedral and octahedral sites. The Mössbauer results have reaffirmed the occupation by Fe^{3+} of octahedral sites at which these ions are coordinated to pairs of OH groups in both *cis* and *trans* configurations. The distribution of Fe^{3+} between these two sites varies considerably but in all of the nontronites some Fe^{3+} occurs in the *trans* site in contrast to the all *cis* occupancy of the centro-symmetric structure proposed by Mering and Oberlin (1967). In one of the nontronites the distribution of Fe^{3+} between these two sites approaches that in the ideal non-centrosymmetric structure proposed for montmorillonite.

INTRODUCTION

Ferruginous smectites are of widespread occurrence in rocks and soils, but have been investigated much less closely than their aluminum analogues. Nontronite, an end-member of the dioctahedral iron smectites is defined as an iron-rich analogue of beidellite, deriving its layer charge almost exclusively from Al-for-Si substitution (Brown, 1961). The ideal formula, $\text{M}_{0.67}^{+}(\text{Si}_{7.33}\text{Al}_{0.67})\text{Fe}_4\text{O}_{20}(\text{OH})_4$ shows only this type of substitution, in agreement with the limitations placed by Ross and Hendricks (1945) on the compositional range of high-iron montmorillonites. In the beidellite–nontronite series, however, complete isomorphous replacement of Al^{3+} by Fe^{3+} should be possible, giving rise to Fe^{3+} in tetrahedral sites. Therefore there should be three possible sites for iron in nontronite, one tetrahedral and two octahedral, the two octahedral sites corresponding to *cis* and *trans* arrangements of the hydroxyl groups, respectively.

Although indirect evidence of tetrahedral occupancy has come from chemical analysis (e.g. Osthaus, 1954), Mössbauer spectroscopy has the potential for directly probing the coordination of iron in minerals, as for example in the investigations of many iron-containing minerals by Bancroft *et al.* (1967). Mössbauer spectra of nontronites have been reported by several workers (Weaver *et al.*, 1967; Taylor *et al.*, 1968; Bischoff, 1972; Brunot, 1973) but only Brunot has attempted to analyze well-defined spectra in terms of both octahedrally- and tetrahedrally-coordinated iron.

I.r. spectroscopy is also sensitive to the structure and composition of layer silicates, although the field of nontronites has not yet been well explored (Serra-

tosa, 1960, 1962; Stubican and Roy, 1961; Farmer and Russell, 1964). Here, both i.r. and Mössbauer techniques are applied in studying a variety of nontronite samples covering a wide range of composition.

EXPERIMENTAL

Materials

The nontronites were purified by saturation with Na^+ (Li^+ for the Californian specimen), dispersion in water, then separation of $< 1.4 \mu\text{m}$ and $< 0.2 \mu\text{m}$ fractions by centrifuging. These fractions were re-saturated with Na^+ using conventional centrifuge procedures, then freeze dried. Si, Fe, Al, Mg, Ca, Na and K were determined using electron microprobe analysis, and cation exchange capacities were measured on NH_4^+ -saturated specimens using the colorimetric method of Fraser and Russell (1969). Sources, approximate chemical compositions and cation exchange capacities (C.E.C.) are shown in Table 1. The high C.E.C. of the Californian specimen is consistent with the need to use a Li-saturated sample to achieve efficient dispersion in water, in agreement with observations made on the dispersion of vermiculite of comparable C.E.C. (Walker and Garrett, 1967).

Instrumental techniques

Mössbauer. Spectra were recorded in 512 channels of a spectrometer (Harwell Scientific Services, Didcot, Berks.), incorporating an Ortec Model 6200 analyzer. A ^{57}Co in Pd source of nominal strength 25 mCi was used with an argon-methane proportional counter as γ -ray detector. Velocity calibration was carried out with a high purity metallic iron foil using

Table 1. Composition and cation exchange capacities (m-equiv./100 g air-dry clay) of nontronites from various sources

Source		C.E.C.	Composition per O ₂₀ (OH) ₄
Washington, U.S.A. (Source clay minerals repository)†	(WAS)	103	(Si _{7.30} Al _{0.70})(Al _{1.06} Fe _{2.73} Mg _{0.26})
Garfield, Washington, U.S.A. (A.P. 1. H33b)	(GAR)	117	(Si _{6.84} Al _{1.05} Fe _{0.11})(Fe _{3.96} Mg _{0.04})
Clausthal, Zellerfeld, Germany	(CLA)	115	(Si _{6.81} Al _{0.13} Fe _{1.06})(Fe _{4.01} Mg _{0.07})
A crocidolite deposit, Koegas, Cape Province, South Africa	(CRO)	137	(Si _{6.75} Al _{0.06} Fe _{1.19})(Fe _{3.90} Mg _{0.24})
Koegas, Cape Province, S.A.	(KOE)	134	(Si _{6.61} Al _{0.08} Fe _{1.31})(Fe _{4.06} Mg _{0.10})
An amosite deposit, Penge, Cape Province, S.A.	(AMO)	115	(Si _{6.84} Al _{0.04} Fe _{1.12})(Fe _{4.04} Mg _{0.15})
Panamint Valley, California, U.S.A.	(CAL)	155	(Si _{6.21} Al _{0.14} Fe _{1.65})(Fe _{4.04} Mg _{0.21})

All nontronites contain traces of Ca, K and Ti.

† Selected, purified sample, Source Clay Minerals Project (*Clays & Clay Minerals* (1973) **21**, 71).

the data of Preston *et al.* (1962). To minimize thickness effects the absorbers contained 3 mg iron/cm² freeze-dried nontronites. They were prepared, either by direct weighing of the sample into a perspex holder and sealing with the minimum of pressure, or by grinding the sample thoroughly with five times its weight of alumina, then sealing in a perspex holder. Identical spectra were obtained from absorbers prepared by both methods and in most of the later experiments they were prepared by the former method.

The spectra were fitted to a sum of doublets having Lorentzian peak shapes using a least squares computer program. The peaks of each doublet were constrained to have equal areas and widths. A parabolic baseline was assumed and χ^2 was used as a goodness-of-fit parameter. For statistically acceptable fits χ^2 is required to lie between the 1% and 99% limits of the χ^2 distribution i.e. between about 416 and 561 for 486 *d.f.*, where the number of degrees of freedom is equal to the number of channels fitted minus the number of variables in the fit.

I.r. spectroscopy. Spectra were recorded from 4000–400 cm⁻¹ on a Grubb Parsons Spectromaster and from 500–40 cm⁻¹ on a Beckmann-RIIC FS 720 interferometer. The nontronites were in the form of either self-supporting films (2 mg/cm²), prepared by evaporating aqueous suspensions on to polyethylene sheet from which they were peeled when air-dry, or thinner, supported films (0.3 mg/cm²) prepared by evaporation on to 1 mm AgCl or polyethylene plates.

RESULTS AND INTERPRETATION

Mössbauer spectroscopy

The isomer shift, δ , is sensitive not only to the oxidation state of high spin ions, but also to the coordination number of these ions. For Fe³⁺, δ decreases with a decrease in coordination number as a result of an increase in the covalent character of the bonding. As an example ferriphlogopite, which contains tetrahedrally-coordinated Fe³⁺, has $\delta = 0.17$ mm/sec relative to iron metal (Annersten *et al.*, 1971), whereas in montmorillonite, which contains octahedrally-coordinated Fe³⁺, $\delta = 0.35$ mm/sec (Tennakoon *et*

al., 1974), both values being obtained with absorbers at room temperature. The quadrupole splitting, Δ , is a measure of the electric field gradient at the ⁵⁷Fe nucleus and in the case of high spin Fe³⁺ is predominantly determined by the distortion from cubic symmetry of the lattice surrounding the iron atom. Thus a simple point charge model predicts that the *trans* arrangement of the OH groups in the octahedral complex Fe³⁺(OH)₂O₄ will produce an electric field gradient of twice the magnitude of, but opposite sign to, the corresponding *cis* grouping.

The Mössbauer spectrum of the nontronite *ex crocidolite* (CRO) at 77°K which is typical of all the nontronite spectra, (Fig. 1) appears to consist of two peaks of unequal intensity. Identical spectra were obtained when the absorber was rotated through 30° and 45°, thus demonstrating the absence of texture effects (Gonser and Pfannes, 1974). Very similar spectra were also obtained at room temperature, thus eliminating the possibility of any significant anisotropy of the recoil-free fraction (Goldan'skii *et al.*, 1963). It would appear, therefore, that the asymmetry in the spectra must arise from the presence of more than one component.

The results of fitting the spectrum to one, two and three doublets are shown in Fig. 1. From the isomer shifts it is clear that all of the iron is in the ferric form (Bancroft *et al.*, 1967). The fits illustrated in Fig. 1(ii) and (iii) correspond to different models assumed when making initial estimates of the parameters for the least squares program. Figure 1(ii) illustrates the results of assuming two octahedral environments with similar isomer shifts for Fe³⁺, while Fig. 1(iii) shows the results of assuming one octahedral and one tetrahedral site, the isomer shift for the tetrahedral site being markedly lower than that of the octahedral site. In both cases the χ^2 values were too high to be acceptable. The use of three doublets, Fig. 1(iv), with initial values based on a combination of those shown in Fig. 1(ii) and (iii), produced a fit having a significantly lower χ^2 value. Similar results were also obtained with the other nontronites studied, with the exceptions of those from Garfield and Washington, which produced fairly good fits with Fe³⁺ in two

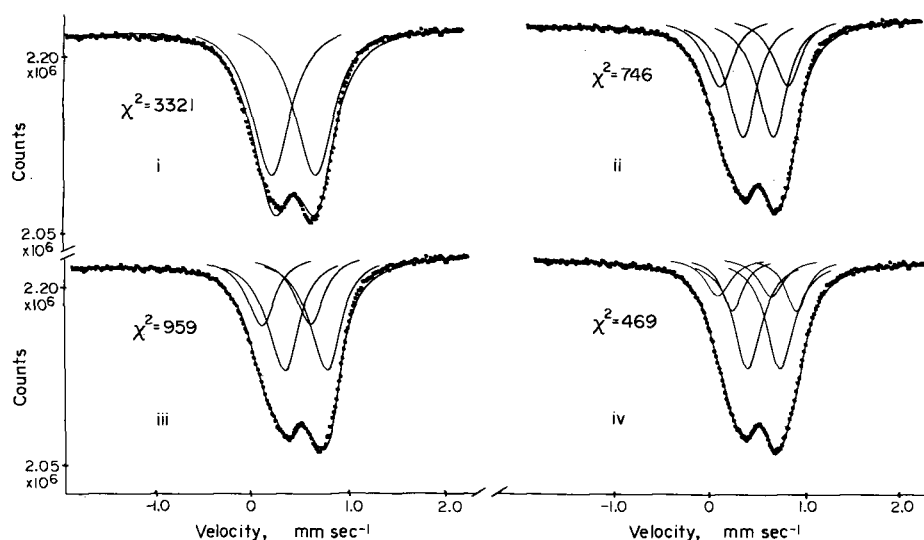


Fig. 1. Mössbauer spectrum at 77°K of nontronite *ex* crocidolite (CRO) fitted to (i) one octahedral doublet, (ii) two octahedral doublets, (iii) one octahedral and one tetrahedral doublet, (iv) two octahedral and one tetrahedral doublets.

octahedral sites only. The three-doublet fits to the spectra of these nontronites showed a small amount of the tetrahedral doublet and these results are shown in Table 2 together with those for the other nontronites. If a constant recoil-free fraction can be assumed for iron in the three types of structural site then the % columns in Table 2 are a measure of the percentage of the total iron in each site. The computed standard deviations quoted in Table 2 are minimum errors because the effects of finite sample thickness, non-linearity of the waveform and calibration errors have been ignored, although these are all likely to be small. However, in this work six peaks with a total of fourteen variables have been fitted to two slightly asymmetric peaks. The necessity of using such

a large number of variables has been adequately demonstrated and the model adopted is justified by the fact that there are only three possible sites for Fe^{3+} in nontronite and the Mössbauer parameters are similar to those expected for Fe^{3+} in such sites.

A somewhat different interpretation of a nontronite Mössbauer spectrum has been presented by Brunot (1973) who studied a hydrothermal and a sedimentary nontronite at room temperature. The spectrum of the hydrothermal nontronite was analyzed in terms of two doublets with parameters similar to those obtained from the two-doublet fit to the sample from Garfield (Table 2) when account is taken of the effects of the different temperature used on the isomer shifts, δ . For this sample Brunot's assignment of the com-

Table 2. Computed results from the Mössbauer spectra of nontronites

Nontronite	$\text{Fe}_{\text{oct}}^{3+}$				$\text{Fe}_{\text{tet}}^{3+}$				χ^2				
	Δ	<i>cis</i> OH		%	Δ	<i>trans</i> OH		%					
		δ	Γ			δ	Γ						
WAS	0.29	0.48	0.37	70	0.62	0.48	0.35	24	0.60	0.29	0.26	6	485
	(0.02)	(0.01)	(0.02)	(11)	(0.02)	(0.01)	(0.02)	(8)	(0.02)	(0.01)	(0.02)	(3)	
WAS (2 doublets)	0.27	0.47	0.35	52	0.62	0.45	0.41	48					675
	(0.01)	(0.01)	(0.01)	(4)	(0.01)	(0.01)	(0.01)	(4)					
GAR	0.27	0.50	0.32	54	0.62	0.50	0.29	37	0.47	0.30	0.22	9	437
	(0.01)	(0.01)	(0.01)	(4)	(0.01)	(0.01)	(0.01)	(3)	(0.01)	(0.01)	(0.01)	(2)	
GAR (2 doublets)	0.25	0.48	0.34	59	0.65	0.47	0.31	41					567
	(0.01)	(0.01)	(0.01)	(3)	(0.01)	(0.01)	(0.01)	(3)					
CLA	0.33	0.50	0.38	64	0.67	0.50	0.27	21	0.61	0.30	0.31	15	636
	(0.01)	(0.01)	(0.01)	(5)	(0.01)	(0.01)	(0.02)	(4)	(0.01)	(0.01)	(0.01)	(2)	
CRO	0.34	0.49	0.36	59	0.67	0.49	0.28	22	0.56	0.29	0.32	19	469
	(0.01)	(0.01)	(0.01)	(4)	(0.01)	(0.01)	(0.01)	(3)	(0.01)	(0.01)	(0.01)	(2)	
KOE	0.32	0.50	0.36	54	0.62	0.51	0.25	19	0.53	0.31	0.29	27	541
	(0.01)	(0.01)	(0.01)	(5)	(0.01)	(0.01)	(0.02)	(3)	(0.01)	(0.01)	(0.01)	(2)	
AMO	0.34	0.49	0.34	51	0.64	0.50	0.27	21	0.54	0.31	0.35	28	556
	(0.01)	(0.01)	(0.01)	(4)	(0.01)	(0.01)	(0.01)	(3)	(0.01)	(0.01)	(0.01)	(3)	
CAL	0.33	0.50	0.33	44	0.60	0.50	0.28	24	0.48	0.31	0.31	32	475
	(0.01)	(0.01)	(0.01)	(4)	(0.01)	(0.01)	(0.01)	(4)	(0.01)	(0.01)	(0.01)	(3)	

Quadrupole splittings, Δ , isomer shifts, δ , and peak widths, Γ , all in mm/sec with δ relative to iron metal. Figures in brackets indicate one S.D.

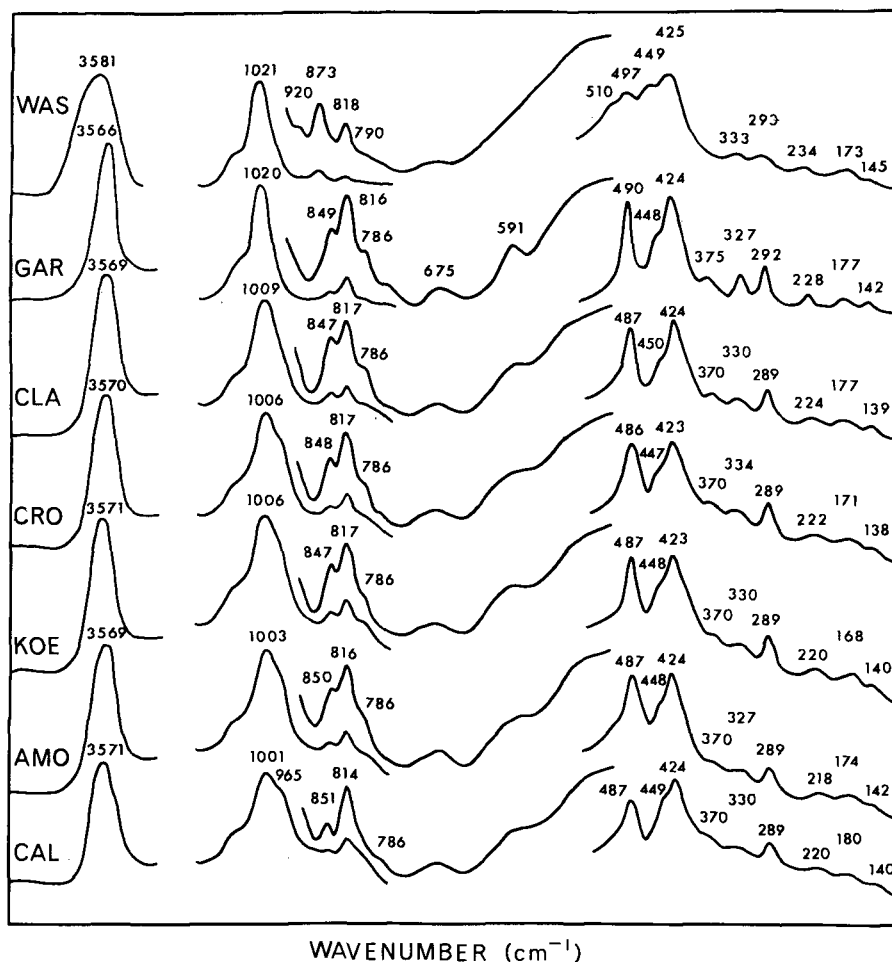


Fig. 2. I.r. absorption spectra of nontronites from various sources (See Table 1).

ponents to octahedral sites with *cis* and *trans* hydroxyl groups was analogous to the assignments in the present work. The nontronite of sedimentary origin however had an additional doublet with $\Delta = 1.22$ mm/sec and $\delta = 0.40$ mm/sec (relative to iron metal) and this was assigned to Fe^{3+} in tetrahedral sites. For reasons mentioned earlier this value of δ is higher than expected for tetrahedral iron which would be expected to have parameters similar to the iron in ferriphlogopite ($\Delta = 0.50$ mm/sec, $\delta = 0.17$ mm/sec, relative to iron metal, Annersten *et al.*, 1971) and it is similar to that observed for Fe^{3+} in octahedral coordination. Although the value of Δ for Brunot's additional doublet is higher than is usually expected for octahedral Fe^{3+} , such values have been observed in microcrystals of iron oxide minerals (e.g. Schroer, 1968). In another investigation the spectrum of a natural ferric gel from a fresh water lake was analyzed in terms of a range of quadrupole splittings, a value of $\Delta = 1.05$ being obtained at the half height of the distribution function (Coey and Readman, 1973). It is therefore possible that the additional doublet is caused by the presence of a microcrystalline ferric oxide or gel ferric hydroxide impurity, a conclusion

that is supported by Brunot's observation that this doublet is lost preferentially by treatment with sodium dithionite solution, an established method for the removal of poorly crystalline iron oxides from mineralogical specimens (Mitchell and Mackenzie, 1954; Mehra and Jackson, 1960).

I.r. spectroscopy

The i.r. spectra of six of the seven nontronites (Fig. 2) are generally similar with only small spectral variations, but that of the Washington sample is obviously different over the entire spectral range shown. This difference is reflected in its chemical composition (Table 1), having more Al^{3+} and less Fe^{3+} than the others. The variations in spectra occur in several well defined regions and these will be dealt with in turn, beginning with that centred on 850 cm^{-1} .

760–960 cm^{-1} region. Librational vibrations of OH groups in dioctahedral layer silicates occur in this frequency range in which the nontronites generally show three absorption bands. The strong band at $814\text{--}818\text{ cm}^{-1}$ arises from OH groups coordinated to two

Fe^{3+} ions, an assignment which is now well established (Serratos, 1960; Stubican and Roy, 1961). The weaker band at $847\text{--}851\text{ cm}^{-1}$ (873 cm^{-1} for the Washington sample) has a less certain assignment, but it is thought to be the libration of the $\text{AlFe}^{3+}\text{OH}$ group in agreement with the proposal of Serratos (1960) and Heller *et al.* (1962). This assignment, however, requires that the analytical compositions (Table 1) be altered. They are conventionally calculated on the assumption that the tetrahedral deficit of Si is made up by Al^{3+} as far as possible, then by Fe^{3+} as required. This results in most of the nontronites having no octahedral Al^{3+} . The alterations would be such that Al^{3+} and therefore Fe^{3+} are distributed between octahedral and tetrahedral sites. The Mössbauer results indicate the distribution of Fe^{3+} between these sites (Table 2), but no direct information is available on how Al^{3+} is distributed. Some idea of the abundance of Al in octahedral sites can be obtained from the intensity of the AlFeOH libration which varies considerably within the group of nontronites. Using a nontronite band near 675 cm^{-1} as an internal standard, the order of absorbances, and therefore of octahedral Al^{3+} , is $\text{WAS} > \text{CLA} > \text{KOE} > \text{CRO} > \text{GAR} > \text{AMO} > \text{CAL}$. The position of the absorption maximum of the AlFeOH libration varies within the group of nontronites. It shifts from $847\text{--}851\text{ cm}^{-1}$ in six of the nontronites containing relatively small amounts of Al to 873 cm^{-1} in the Washington sample, of highest total Al^{3+} , and therefore highest octahedral Al content. This upward shift in frequency of the AlFeOH libration continues in the more aluminous smectites, rising to 877 cm^{-1} for Woburn Fuller's Earth and 890 cm^{-1} for Wyoming montmorillonite (Farmer and Russell, 1964). From this it would appear that the AlFeOH librational vibration occurs at higher frequencies when the neighbouring cations are aluminium and at lower frequencies when they are iron.

The possibility of assigning the 816 cm^{-1} and 850 cm^{-1} absorption bands to librations of OH groups in *trans* and *cis* octahedral configurations was considered. This was rejected, however, because the relative intensities of the two bands did not agree with the octahedral site occupancies indicated by the Mössbauer results (Table 2), and also because of the unrealistically large frequency difference between vibrations of the two types of OH group. Apart from the slightly different stereochemistry round Fe^{3+} ions, these OH groups have identical relationships to the oxygen ions in the silicon-oxygen framework of the tetrahedral layers, and would be expected to exhibit essentially the same librational frequencies.

All of the nontronites contain octahedral Mg^{2+} (Table 1), which, because of the high content of Fe^{3+} , is almost certain to have three Fe^{3+} neighbours in the octahedral layer and therefore to be involved in a $\text{Fe}^{3+}\text{MgOH}$ grouping. By analogy with AlMgOH which in montmorillonites absorbs at 843 cm^{-1} compared with 915 cm^{-1} for AlAlOH (Farmer and Rus-

sell, 1964) $\text{Fe}^{3+}\text{MgOH}$ in nontronite should absorb at a lower frequency than the 817 cm^{-1} for Fe^{3+}OH . The inflection near 785 cm^{-1} in all of the nontronite spectra (Fig. 2) has been found to shift to 585 cm^{-1} on deuteration and is therefore tentatively assigned to the libration of $\text{Fe}^{3+}\text{MgOH}$. Its frequency is in fair agreement with the value of 800 cm^{-1} found for this vibration in a synthetic Fe^{3+}Mg celadonite (Farmer *et al.*, 1967), considering that the frequency will vary with the composition of the octahedral layer.

975–1200 cm^{-1} region. The position of the intense Si-O stretching absorption band shifts from 1021 cm^{-1} in the Washington and Garfield samples, to 1009 cm^{-1} in Clausthal, to 1006 cm^{-1} in Crocidolite and Koegas, to 1003 cm^{-1} in Amosite, to 1001 cm^{-1} in the California sample (Fig. 2). This progressive shift to lower frequencies correlates well with the increasing content of Fe^{3+} in tetrahedral sites calculated from chemical compositions and from Mössbauer results (Table 3) and must be due to increasing Fe-for-Si substitution. In an analogous manner, replacement of Si by Al causes the Si-O stretching band to shift from 1014 cm^{-1} in talc, to 1005 cm^{-1} in saponite, to 994 cm^{-1} in a synthetic phlogopite (Farmer, 1974), and from 1070 cm^{-1} in pyrophyllite, to 1041 cm^{-1} in beidellite, to 1022 cm^{-1} in muscovite (Farmer and Russell, 1964). A band near 965 cm^{-1} in the nontronite spectra also intensifies with increasing tetrahedral Fe^{3+} content. It is strongest in the spectrum of the California sample in which about 1 in 5 Si^{4+} ions is replaced by Fe^{3+} and may be analogous to the band at 958 cm^{-1} in the spectrum of ferriphlogopite in which the replacement of Si by Fe^{3+} is 1 in 4 (Farmer, 1974).

3550–3650 cm^{-1} region. The absorption bands due to the OH stretching vibration of six of the nontronites show little variation in position, occurring in the frequency range $3566\text{--}3571\text{ cm}^{-1}$. This is consistent with $\text{Fe}^{3+}\text{Fe}^{3+}\text{OH}$ being the predominant grouping in these nontronites. The corresponding band in the spectrum of the Washington sample is centred on 3581 cm^{-1} with broader absorption on the high-frequency side of the band. This is indicative of considerable replacement of octahedral Fe^{3+} by Al giving rise to $\text{AlFe}^{3+}\text{OH}$ and AlAlOH groups which absorb in the range $3600\text{--}3630\text{ cm}^{-1}$ (Farmer and Russell, 1964). These conclusions are substantiated by the presence in the spectrum of the Washington sample of the $\text{AlFe}^{3+}\text{OH}$ libration frequency at 873 cm^{-1} discussed above, and a weak band near 915 cm^{-1} due to hydroxyl libration of the AlAlOH group.

100–700 cm^{-1} region. Absorption patterns of the nontronites in this region are included mainly for completeness and to supplement the spectrum shown by Larson *et al.* (1972) covering the range $400\text{--}200\text{ cm}^{-1}$. The nontronites generally show the same pattern of absorption bands, but that of the Washington sample is more diffuse. Additional strong bands near

Table 3. Relationship between the Si-O stretching frequencies of various nontronites and their tetrahedral Fe³⁺ contents calculated from Mössbauer results and chemical compositions

Nontronite	Fe on tetrahedral sites (% of total Fe)		Si-O (cm ⁻¹)
	Mössbauer	Microprobe analysis	
CAL	32 ± 3	29	1001
AMO	28 ± 3	22	1003
KOE	27 ± 2	24	1006
CRO	19 ± 2	23	1006
CLA	15 ± 2	21	1009
GAR	9 ± 2	3	1020
WAS	6 ± 3	0	1021

450 cm⁻¹ and 510 cm⁻¹ in the spectrum of the latter testify to its more aluminous composition (compare for example 467 and 521 cm⁻¹ in montmorillonite and 479 and 537 cm⁻¹ in beidellite, Farmer and Russell, 1964). The spectrum of the Garfield sample is notable for the good definition and sharpness of its absorption bands. With increasing tetrahedral iron content in the series Garfield to California (Table 3) bands become progressively broader, weaker and less well defined but remain relatively constant in position. The diffuseness of the Washington spectrum in this region must be due to the presence of considerable octahedral Al.

DISCUSSION

The Mössbauer spectra, using the new interpretations described earlier, indicate the presence of tetrahedral iron in most if not all of the nontronites.

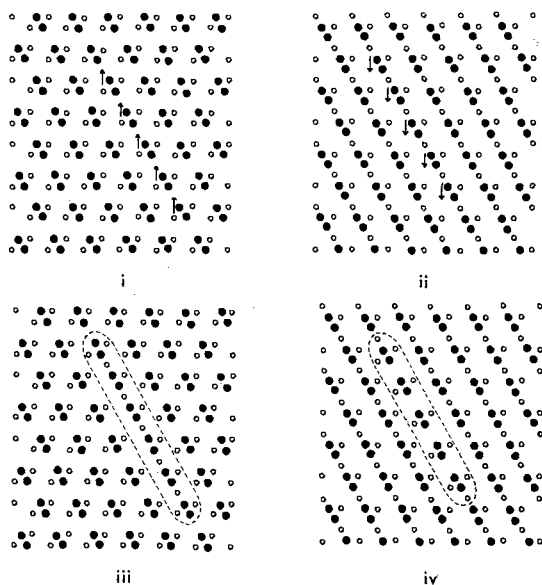


Fig. 3. Diocahedral arrangements of Fe³⁺ ions (●) and OH groups (○). (i) centrosymmetric (all *cis*) (ii) non-centrosymmetric (*cis/trans* = 1/1). Arrows indicate movement of Fe³⁺ ions generating (iii) a *cis/trans* region in an all *cis* array and (iv) an all *cis* region in a *cis/trans* array.

The order of tetrahedral iron content is WAS < GAR < CLA < CRO < KOE < AMO < CAL, which is similar to that deduced from the analytical results and Si-O frequencies (Table 3). The main discrepancies between the Mössbauer and analytical results occur with the Washington and Garfield samples where 0 and 3%, respectively, of the iron is required in tetrahedral sites to satisfy the analytical results, but appreciably higher amounts are indicated by the Mössbauer experiments. The i.r. spectra show the presence of a peak consistent with an AlFeOH libration indicating octahedral Al contents in the order WAS > CLA > KOE > CRO > GAR > AMO > CAL. The presence of such a peak in spectra of these samples provides further evidence that the distribution of iron and aluminium is more random than is usually assumed. Unfortunately the Mössbauer estimations are subject to appreciable errors because of the high degree of overlap of the peaks, so that accurate estimates of tetrahedral iron contents are unobtainable. A similar problem exists with quantitative estimation using the AlFeOH libration in the i.r. spectra, thus making a reliable recalculation of the structural formulae impossible at present.

The Mössbauer results have also indicated a distribution of octahedral cations over the two types of site, the one with *trans* hydroxyl accounting for between 25 and 41% of the octahedral cations. These conclusions contrast sharply with those of Mering and Oberlin (1967), from their work on selected area electron diffraction of a nontronite from Pfaffenreuth, that a centrosymmetric structure existed (i.e. one in which all the octahedral cations are bound with *cis* hydroxyl groups). Similar work by these authors indicated the presence of a non-centrosymmetric structure for Wyoming montmorillonite (i.e. equal numbers of octahedral cations with *cis* and *trans* hydroxyl groups). These two structures are illustrated in Fig. 3(i) and (ii) which for simplicity shows only the positions of the octahedral cations and the hydroxyl groups. The Garfield nontronite with 41% of its octahedral iron in sites with *trans* hydroxyl groups (calculated from Table 2) would appear to have a structure similar to that of Wyoming montmorillonite. The

remaining samples with between 25 and 35% of their octahedral iron in such sites have structures intermediate between the centro- and non-centrosymmetric types. None of the samples shows any tendency to approach the structure proposed for the Pfaffenreuth nontronite.

The Mössbauer results give only averages for the relative proportions of the two types of octahedral site throughout the structure. Figure 3(iii) and (iv) illustrates ways in which local defects in the ideal structures could produce mixtures of the two types of site within one sheet. At the intersection of two phases a hydroxyl group is produced which is bound either to three cations or less likely to one cation and two vacancies. Trioctahedral sites are almost certain to occur but while they were not detectable in infrared spectra, their presence was indicated by the overfilling of the octahedral layers in all but one of the nontronites.

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