

THE MÖSSBAUER SPECTRA OF NONTRONITES: CONSIDERATION OF AN ALTERNATIVE ASSIGNMENT

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In a recent publication (Goodman et al., 1976) the Mössbauer spectra of a series of nontronites were interpreted in terms of Fe^{3+} in two different types of octahedral site and one tetrahedral site on the basis of quadrupole splittings and isomer shifts. The amounts of Fe^{3+} in the tetrahedral sites calculated from the Mössbauer spectra showed reasonable agreement with those predicted from the analytical results. However, the existence of the two different types of octahedral site involved the postulate that each of the samples consisted of a mixture of phases corresponding to the centro- and noncentrosymmetric structures determined by Mering and Oberlin (1967) for a nontronite from Pfaffenreuth and a Wyoming montmorillonite, respectively.

The Mössbauer spectrum of a specimen of nontronite from Pfaffenreuth has now been obtained (Figure 1). The weak peaks AA' corre-

spond to Fe^{3+} in tetrahedral sites, consistent with the elemental composition $\text{Na}_{1.03}(\text{Si}_{6.83}\text{Al}_{0.93}\text{Fe}_{0.24})(\text{Fe}_{4.06}\text{Mg}_{0.06})(\text{O}_{20}(\text{OH})_4)$ (Russell and Clark, 1977). The presence of two different types of octahedral site (BB' and CC') is, however, inconsistent with the electron diffraction results of Mering and Oberlin (1967), which require that all of the octahedral ions should occupy sites with *cis* OH groups. This dichotomy could be resolved if the ferric ions in crystallographically distinct sites possess different quadrupole splittings, the magnitudes of which depend on the nature of the ions in neighboring cation sites. This effect has been demonstrated for neighboring octahedral cations in micas (Goodman, 1976), but the centrosymmetric structure of Mering and Oberlin has a regular octahedral cation structure and should, therefore, produce a unique contribution to the electric field gradient. In Pfaffen-

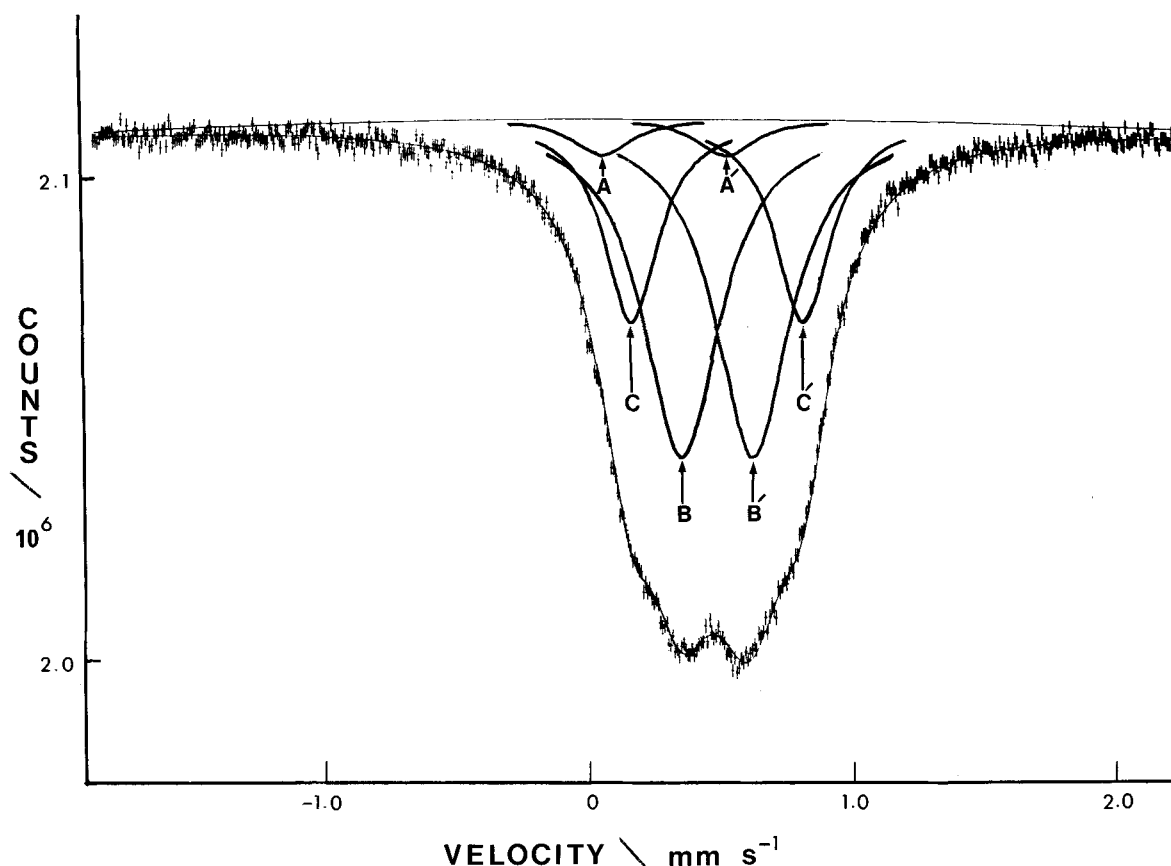


Fig. 1. The Mössbauer spectrum of Pfaffenreuth nontronite (sodium saturated) at 77°K. Computed parameters for the 3 doublets are: AA'— $\Delta = 0.47 \pm .02$ mm s⁻¹, $\delta = +0.28 \pm .01$ mm s⁻¹, $\Gamma = 0.25 \pm .01$ mm s⁻¹, 5 ± 2%; BB'— $\Delta = 0.27 \pm .01$ mm s⁻¹, $\delta = +0.48 \pm .01$ mm s⁻¹, $\Gamma = 0.35 \pm .01$ mm s⁻¹, 66 ± 4%; CC'— $\Delta = 0.65 \pm 0.1$ mm s⁻¹, $\delta = +0.48 \pm .01$ mm s⁻¹, $\Gamma = 0.25 \pm .01$ mm s⁻¹, 29 ± 3%; where Δ , δ , and Γ refer to the quadrupole splitting, the isomer shift, and the full width at half peak height, respectively.

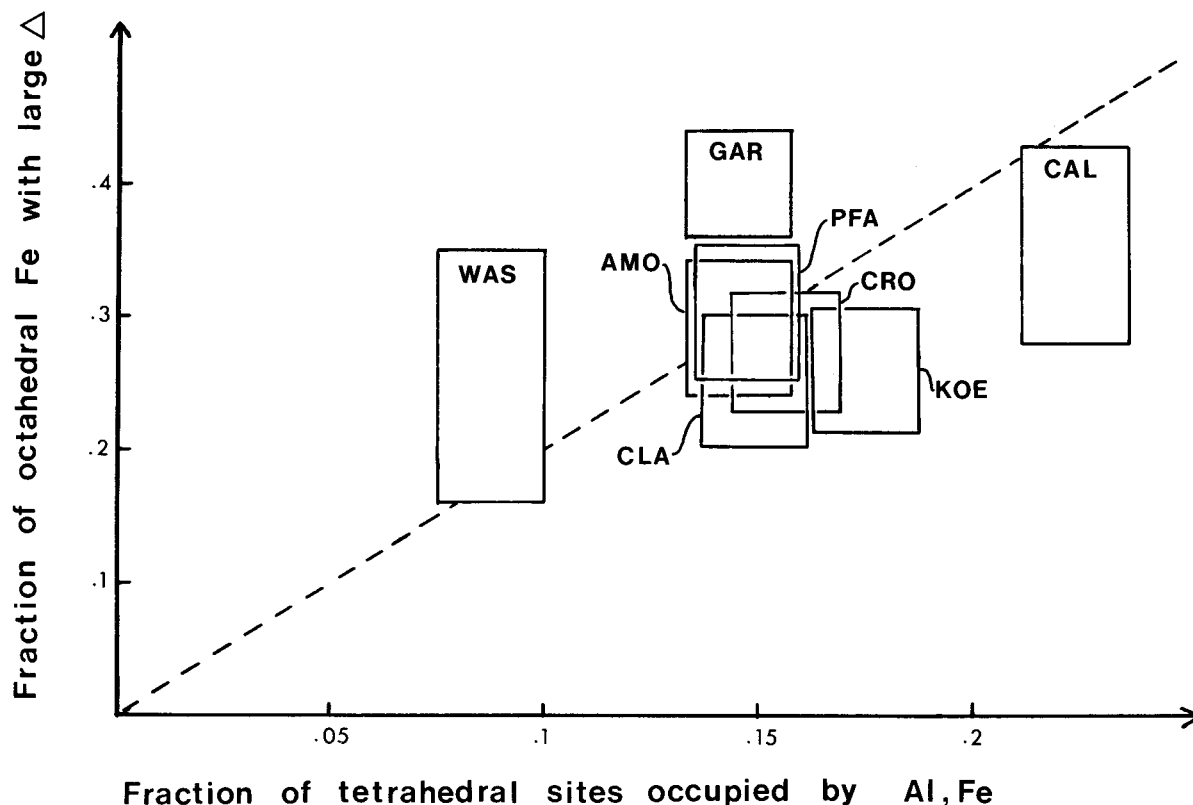


Fig. 2. The relationship between the fraction of the octahedral Fe^{3+} ions having the large value of Δ in the Mössbauer spectra and the fraction of the tetrahedral sites occupied by a trivalent ion for several nontronite specimens. The dashed line is obtained by assuming that the magnitude of the electric field gradient at 50% of the octahedral sites, with one oxygen bound to a trivalent tetrahedral cation, is greater than at the other octahedral sites. The boxes indicate the error limits on the parameters. PFA = Nontronite from Pfaffenreuth, Bavaria (Mering and Oberlin, 1967). Other samples are described by Goodman et al. (1976).

reuth nontronite, however, about 15% of the tetrahedral sites are occupied by trivalent ions. If these substitutions are randomly distributed throughout the structure in such a way that no two trivalent ions are in adjacent tetrahedral sites, approximately 60% of the octahedral sites should have one trivalent ion in a neighboring tetrahedral site, since there are four tetrahedral sites neighboring each octahedral site. These octahedral sites are not all equivalent since the trivalent ion may be coordinated to an oxygen atom which is adjacent to both the hydroxyl groups, or to an oxygen which is adjacent to one hydroxyl but opposite the other. On the basis of point charge considerations, the former case will tend to increase the electric field gradient at the octahedral site and the latter, although its effect is more difficult to envisage, would probably result in some decrease in the quadrupole splitting. Thus, one might expect that about 30% of the octahedral sites with *cis* OH groups will have a quadrupole splitting somewhat larger than the remainder, which will have their peaks broadened. This is precisely what is observed experimentally.

In view of this alternative assignment of the spectrum of the Pfaffenreuth nontronite, the earlier results of Goodman et al. (1976) merit closer examination, since in this series the degree of substitution of trivalent ions in the tetrahedral layers ranges from approximately 1 in 11 to 1 in 4.5. Figure 2 illustrates a plot of the fraction of the octahedral Fe^{3+} with the larger quadrupole splitting against the fraction of the tetrahedral sites occupied by a trivalent ion. It can be seen that most of the specimens have points within experimental error of the theoretical line drawn on the assumption that one half of the octahedral cations, which are bound to an oxygen, which in turn is bound to a trivalent tetrahedral cation, has the larger quadrupole splitting discussed above.

It is possible, therefore, to explain the existence of two different

types of octahedral site in the Mössbauer spectra of nontronites without postulating the existence of more than one phase. It should be remembered, however, that the errors on the points in Figure 2 are so large that the correlation may be fortuitous. Moreover, the amount of sample on which Mering and Oberlin's structural deductions were based is very much smaller than that used for a Mössbauer spectrum. Consequently, the presence of more than one phase in the samples of nontronite cannot be entirely discounted.

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