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NOTES

TETRAHEDRAL IRON IN SMECTITE: A CRITICAL COMMENT

Key Words—Iron, Mössbauer spectroscopy, Nontronite, Smectite, Tetrahedral coordination.

Traditionally, researchers have considered that only Al^{3+} substitutes in the SiO_4 tetrahedral layer of 2:1 phyllosilicates, particularly, in smectites. The traditional approach of assigning all Si present in a chemical analysis to the tetrahedral layer and then making up the atomic unit cell deficit with Al^{3+} was well established by Ross and Hendricks (1945). They were unable to distinguish tetrahedral Fe^{3+} ($^{IV}Fe^{3+}$), however, and therefore the possible tetrahedral substitution of Fe^{3+} was never taken into consideration. If a calculation of the chemical formula of a particular nontronite showed so much Fe as to suggest $^{IV}Fe^{3+}$, they appear to have assumed that the additional Fe was present as an impurity. Osthaus (1954) used acid dissolution rates to demonstrate that this simplistic approach was not warranted, and that Fe^{3+} was indeed present in Garfield nontronite in both the tetrahedral and octahedral sheets. Several nontronite analyses were presented by Goodman *et al.* (1976) and Cardile and Johnston (1985) which indicated on a chemical formulae basis such a low Al^{3+} content and such a high Fe^{3+} content that $^{IV}Fe^{3+}$ substitution must exist.

If $^{IV}Fe^{3+}$ is indeed present in a given smectite, its presence should be accounted for when presenting structural formulae. This is clearly not being done. Furthermore, disagreement still exists in the literature concerning the fitting of $^{IV}Fe^{3+}$ resonances to the Mössbauer spectra of nontronites. This is exemplified by Lear and Stucki (1987) who disputed the $^{IV}Fe^{3+}$ assignment of Goodman *et al.* (1976) for standard SWa-1 nontronite from Grant County, Washington, as supplied by the Source Clay Minerals Repository of The Clay Minerals Society. The intent of the present note is to draw attention to the necessity of adopting a standard procedure for determining the $^{IV}Fe^{3+}$ content of smectites using Mössbauer spectroscopy and to show that such an analysis should be carried out when presenting structural formulae of clay minerals.

MÖSSBAUER EVIDENCE FOR TETRAHEDRAL Fe^{3+}

The advent of Mössbauer spectroscopy gave mineralogists a tool by which Fe^{2+} and Fe^{3+} could be assigned to 4- and 6-fold coordination; however, even ^{57}Fe Mössbauer spectroscopy does not completely eliminate the difficulties associated with measuring $^{IV}Fe^{3+}$. Some early Mössbauer results (e.g., Taylor *et al.*, 1968; Brunot, 1973) were taken to indicate the presence of $^{IV}Fe^{3+}$, but these assignments seem unlikely for the following reasons. Taylor *et al.* (1968) assigned a component (δ = 0.41,0.46; Δ = 1.00,1.10 mm/s) to $^{IV}Fe^{3+}$ in vermiculites and chlorites, respectively, but Coey (1980) noted that these workers simply resolved the octahedral Fe^{3+} ($^{VI}Fe^{3+}$) resonance into two doublets, neither having $^{IV}Fe^{3+}$ parameters. Brunot (1973) resolved a nontronite spectrum into two $^{VI}Fe^{3+}$ doublets and an additional resonance (δ = 0.41, Δ = 1.22 mm/s) which he assigned to $^{IV}Fe^{3+}$. Here also, this δ value is too high for $^{IV}Fe^{3+}$ (cf. Table 1) and is more indicative of iron oxides/oxyhydroxides, as was confirmed by the reduction of the intensity of this component after dithionite treatment (Brunot, 1973).

Goodman *et al.* (1976) identified $^{IV}Fe^{3+}$ in a series of nontronite samples, including the Garfield, Washington, type material by Mössbauer spectroscopy. The $^{IV}Fe^{3+}$ content was estimated to range from ~6 to 32% of the total Fe present in the samples, and was consistent with the unit-cell formulae calculated from chemical analyses. The reported $^{IV}Fe^{3+}$ isomer shifts (δ) were considerably smaller than those of $^{VI}Fe^{3+}$, reflecting the more covalent bonding associated with tetrahedral coordination. Similar data were also presented by Cardile and Johnston (1985) and Johnston and Cardile (1985) for a series of nontronite samples, including some of the samples studied by Goodman *et al.* (1976). In addition, Besson *et al.* (1983) identified $^{IV}Fe^{3+}$ in Garfield nontronite using Mössbauer spectroscopy and electron diffraction. In contrast, Rozenson and Heller-Kallai (1977) reported that they could find no evidence of $^{IV}Fe^{3+}$ in Garfield nontronite by Mössbauer spectroscopy, and concluded that as the Garfield nontronite sample was inhomogeneous their sample may have differed from that used by Goodman *et al.* (1976). They indicated some uncertainty in their interpretation and that the presence of $<5\%$ $^{IV}Fe^{3+}$ could not be ruled out.

Another study of the Garfield nontronite by Bonnin

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et al. (1985) using various spectroscopic methods (Mössbauer, optical, X-ray absorption edge, extended X-ray absorption fine structure, and nuclear magnetic resonance) also failed to recognize significant $^{IV}Fe^{3+}$; however, these workers used a sedimentated sample consisting of 'thin particles'. Such a sample preparation may have had a significant effect upon the Mössbauer spectrum obtained. Sedimentation of the nontronite would have resulted in an oriented sample, which may have led to the $^{IV}Fe^{3+}$ resonance being reduced beyond detection. Such a preparation method has not been adequately investigated.

Furthermore, if the term 'thin particles' indicates a small particle size, then Cardile *et al.* (1987) showed that the intensity of the $^{IV}Fe^{3+}$ Mössbauer resonance was a function of the particle size of untreated, size-fractionated Garfield nontronite. For the clay-size fraction (<2 μm) 1(1)% $^{IV}Fe^{3+}$ was measured; 3(1)% $^{IV}Fe^{3+}$ was measured for the silt-sized fraction (2–20 μm), and 6(1)% was measured for the sand-sized fraction (>20 μm). For the whole nontronite sample 3(1)% $^{IV}Fe^{3+}$ was measured, which is the mean of values listed above for the three size fractions. Berry *et al.* (1986) noted no significant difference in the Mössbauer spectra of >2-, 1–2-, and <0.05-μm, particle-size fractions for montmorillonite samples containing very low Fe contents computer-fitted to a single doublet. No $^{IV}Fe^{3+}$ was identified in these spectra.

The type of interlayer cation may also have significantly affected the results of Bonnin *et al.* (1985); unfortunately, they did not state which cations were present. The nature of the interlayer cation was shown by Johnston and Cardile (1985) to exert a significant influence on the Mössbauer detection of $^{IV}Fe^{3+}$ in Garfield nontronite. The $^{IV}Fe^{3+}$ intensity varied from 9(1)% for Ca^{2+} as the interlayer cations, 6(1)% for the "as received" sample, to 1(1)% for K^+ as the interlayer cation. $^{IV}Fe^{3+}$ intensities as high as 12(1)% were obtained if Fe^{3+} was the interlayer cation (Cardile, 1985). Besson *et al.* (1983), however, reported a $^{IV}Fe^{3+}$ intensity of 5% for K-saturated Garfield nontronite.

Apparently, both the nature of the interlayer cations and particle size may significantly affect the $^{IV}Fe^{3+}$ resonances in the Mössbauer spectra of smectites. Such effects may account for some of the discrepancies between results reported in the literature by different workers. Luca and Cardile (1988) demonstrated for montmorillonite that different interlayer cations significantly affected ^{VI}Fe Mössbauer resonances. Li^+ interlayer cations produced a three-fold increase in intensity for $^{VI}Fe^{2+}$ with respect to Na^+ interlayer cations. They suggested that high-charge-density interlayer cations, such as Li^+, effectively reduced the phonon energy (and, thus, increased the recoilless fraction) of $^{VI}Fe^{2+}$.

Russell and Clark (1978), using the nontronite samples of Goodman *et al.* (1976), showed a linear relationship between the *b*-cell dimension and the number of $^{IV}Fe^{3+}$ atoms as determined by Mössbauer spectroscopy. Cardile and Johnston (1985) were unable to confirm this result for several nontronite samples nor for several montmorillonite samples (Cardile and Johnston, 1986; Cardile, 1987; Johnston and Cardile, 1987), although Cardile (1988) demonstrated for this series of nontronite and montmorillonite samples and for glauconite samples (Cardile and Brown, 1988; Johnston and Cardile, 1987) that the *b*-cell dimension varies linearly with wt. % total Fe.

A summary of the Mössbauer spectral parameters for a variety of 2:1 phyllosilicates is presented in Table 1. No correlations are apparent for any of the parameters, suggesting that $^{IV}Fe^{3+}$ substitution is a random process. This is not a surprising result, however, considering the difficulties of producing quantitative results (*vide supra*). The data of Goodman *et al.* (1976) and Goodman (1978) for a series of nontronites show a correlation between $^{IV}Fe^{3+}$ and content of structural Fe. Moreover, their spectral parameters demonstrate an extent of consistency not apparent in the results of others (e.g., Cardile and Johnston, 1985). A notable disparity between these studies was that Goodman recorded the Mössbauer spectra at 77 K, which may have contributed to the consistency of the Mössbauer measurements, particularly with respect to the recoilless fractions for the various sites.

THEORETICAL CONSIDERATIONS

The traditional assignment of Si and Al to the tetrahedral layers for smectites assumes fundamentally that Al has a greater preference for tetrahedral coordination than Fe^{3+}, Fe^{2+}, and Mg^{2+}. For other systems, however, such as spinels, where both tetrahedral and octahedral sites are available, thermodynamic considerations (Navrotsky and Kleppa, 1967) suggest that whereas Fe^{3+}, Fe^{2+}, and Mg^{2+} have a small preference for tetrahedral sites, Al^{3+} has a large octahedral-site preference. A recent Mössbauer study of $MgAl_2O_4$ spinel having Fe substitutions of as much as 15 mole % of the Al present showed that all of the Fe^{3+} and Fe^{2+} substitutes into the tetrahedral sites (Brown and Cardile, 1988).

The mean metal-to-oxygen bond length for the octahedral site and for the two tetrahedral sites in $MgAl_2O_4$ is 1.93 and 1.91 and 1.94 Å respectively (Grimes *et al.*, 1983). The dioctahedral smectite models of Tsipursky and Drits (1984) indicate a mean Si–O bond length of ~1.62 Å. The tetrahedral site in a smectite is therefore smaller than a tetrahedral site in a spinel, suggesting a steric reason why Mg^{2+} and Fe^{2+} do not substitute into the tetrahedral layers of smectites, if indeed they do not. If ionic size is the limiting factor in tetrahedral layer substitution, Al^{3+} (r = 0.51 Å) may show some preference over Fe^{3+} (r = 0.64 Å).

Gibbs energies of formation data by Tardy and Garrels (1974) for phyllosilicates are not sensitive enough

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Table 1. Summary of reported Mössbauer spectral parameters of tetrahedral Fe^{3+} for 2:1 phyllosilicates.

Mineral	No. of samples	δ[1] (mm/s)	Δ (mm/s)	Γ (mm/s)	A (%)	References
Mica	18	0.09–0.22	0.11–0.70	0.21–0.63	2–62	Heller-Kallai and Rozenson (1981); Dyar and Burns (1986); MacKenzie *et al.* (1987).
Vermiculite	8	0.07–0.29	0.61–0.95	0.31–0.58	14–70	Cardile and Slade (1987, 1988)
Glauconite	8	−0.02–0.25	0.11–0.96	0.22–0.40	4–16	Johnston and Cardile (1987); Cardile and Brown (1988).
Montmorillonite	9	−0.10–0.15	0.10–0.36	0.13–0.45	1–6	Cardile and Johnston (1986); Cardile (1987); Johnston and Cardile (1987).
Nontronite	8	0.15–0.21	0.42–0.59	0.21–0.32	4–21	Besson *et al.* (1983); Cardile and Johnston (1985); Johnston and Cardile (1985).
Nontronite[2]	7	0.28–0.31	0.47–0.61	0.22–0.35	5–32	Goodman *et al.* (1976); Goodman (1978).

[1] Relative to iron metal foil.
[2] 77 K spectra.
(Isomer shift, δ; quadrupole splitting, Δ; linewidth, Γ; relative peak area, A.)

to determine differences between cation substitution into tetrahedral or octahedral sites, due to a lack of sufficiently accurate ΔG°_f values. The quantum-chemical model of smectites of Aronowitz *et al.* (1982) did not consider tetrahedral layer substitution for Si, but did calculate that the favored cations for the octahedral sites were $Al^{3+} > Fe^{3+} > Mg^{2+} > Fe^{2+} > Na^+ > K^+$.

Zeolites are AlO_4 and SiO_4 framework structures in which Al and Si are both in tetrahedral coordination and in which the mean T–O bond lengths are notably similar (~1.64 Å) (Baur, 1964) to those present in smectites. Calculations using quantum-chemical methods have indicated that structural Fe^{3+} and Al^{3+}, if substituted for Si in faujasite, gave very similar properties (Beran *et al.*, 1982). These workers calculated that Fe–O bonds should be stronger than Al–O bonds, suggesting a preference for Fe^{3+} over Al^{3+} in these tetrahedral sites. Mössbauer studies of ZSM-5 zeolite (Meagher *et al.*, 1988) have shown $^{IV}Fe^{3+}$ to have similar spectral parameters ($\delta \approx 0.24$, $\Delta = 0.4$–0.6 mm/s) to those found in smectite (Table 1), indicating similar sites for the two silicate structures.

CONCLUSIONS

The theoretical considerations discussed above suggest that Fe^{3+} should substitute into the tetrahedral sites of smectite materials. For many structures, Fe^{3+} apparently has a preference over Al^{3+} for tetrahedral sites, whereas Al^{3+} has a preference over Fe^{3+} for octahedral sites. Some $^{IV}Fe^{3+}$ substitution in smectites should therefore exist. This assertion is supported by Mössbauer spectroscopic evidence.

Although no easy way exists for determining the $^{IV}Fe^{3+}$ content of clay minerals, to present chemical formulae without consideration of $^{IV}Fe^{3+}$ is unacceptable. Mössbauer spectroscopy has the potential for determining the presence of $^{IV}Fe^{3+}$, but not necessarily quantitatively, particularly if samples have different interlayer cations and particle size. Mössbauer spectroscopy is also advantageous in that Fe^{2+}/Fe^{3+} ratios may be simultaneously determined without recourse to a separate wet chemical analysis. If Mössbauer spectroscopy is used to estimate $^{IV}Fe^{3+}$ contents, some standard procedure must be adopted to allow comparisons to be carried out. Such a standard procedure may include the recording of spectra at 77 K for samples containing a specified interlayer cation and a specified particle size range.

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