Origin of the two quadrupole doublets in NAu-1 nontronite

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Abstract. Mössbauer spectra of octahedral Fe³⁺ in NAu-1 nontronite, saturated with Na⁺, K⁺, NH₄⁺, Ca²⁺ and La³⁺ have been analysed as two quadrupole doublets. The interlayer cations were found to affect the mean isomer shift, the quadrupole splitting and the spectral area. By considering the statistically significant nearest cation neighbour coordination environments, the inner doublet has been assigned to an octahedral Fe³⁺ surrounded by three Fe³⁺ in the octahedral sheet and eight Si⁴⁺ in the tetrahedral sheets. The outer doublet is due to the same octahedral coordination, but combined with [7Si⁴⁺, 1Al³⁺] and [6Si⁴⁺, 2Al³⁺].

1. Introduction
The true end-member nontronite contains ferric iron [1] in the octahedral sheet, although Fe³⁺ is partly replaced by Al³⁺ (and to a lesser extent Mg²⁺) in most nontronites. They also typically have Al³⁺ and/or Fe³⁺ substitutions (~1 in 8 atom) in the tetrahedral sheet [2]. Substituted Al³⁺ often occupies preferentially tetrahedral sites so that some well-characterised nontronites (e.g. Garfield) contain Fe almost entirely in the octahedral layers [3, 4, 5]. However, since both Fe³⁺ and Al³⁺ can be in both tetrahedral and octahedral sites, variations in nontronite chemistry can produce distributions in Fe³⁺ occupancy within sites of both the octahedral and tetrahedral sheets [6].

Considerable disagreement exists in the literature regarding fitting Mössbauer spectra of nontronite and other smectites and in the interpretation of the origin of doublets. Pitfalls associated with fitting nontronite spectra are well covered previously [7]. Analysis of the spectra is complicated by overlapping lines and because a distribution of quadrupole splittings is often used, but the fitted parameters depend markedly on the quality of the data and ambiguous fits are frequent. For example, the two most common doublets (quadrupole splitting, QS, of ~0.25 and ~0.65 mm/s, and with similar isomer shift, (IS)) have been assigned to cis and trans sites [8, 9], but, perhaps more correctly, also to ferric iron in octahedral layers occupying cis sites [3, 10, 11]. The existence of a tetrahedral site in many nontronites has been controversial, and fitted parameters are inconsistent; IS = 0.16 mm/s and QS = 0.50 mm/s being most common. Gates et al. [6] observed that the results of some fittings were incompatible with the actual chemistries of the nontronites under study.

We have developed [11] a systematic means of identifying potential nearest neighbour cation arrangements within the octahedral sheet, based on combining chemistry and infrared data [12]. Each Fe atom has three nearest octahedral cation neighbours, Fe, Al or Mg, and an array can be produced which details the distribution of octahedral neighbours to Fe, namely Fe(xyz), where x, y and z are integers (which must sum to 3) representing, respectively, octahedral Fe, Al and Mg atoms. Thus, Fe(210)
represents a central Fe atom surrounded by 2 Fe and 1 Al atoms in the trigonal array of the octahedral sheet. An important advance was to find real examples in which a doublet can be identified by other means, such as spectra of several closely related clay minerals. In the case of cis-vacant ferruginous smectites, we identified [11] that the doublet with the largest splitting was due to a cis-Fe$^{3+}$ ion which contained at least one Mg$^{2+}$ ion as an octahedral neighbour. For nontronites, however, substitutions of Mg in the octahedral sheet are negligible. Thus, another explanation for the occurrence of two doublets in nontronites is needed.

The array[11] can be expanded to incorporate the tetrahedral sheet. In the trans-vacant nontronites [13], tetrahedral Si$^{4+}$ is substituted by either Fe$^{3+}$ or Al$^{3+}$, so a given octahedral Fe centre could have as nearest neighbour environments eight Si, Fe or Al in the tetrahedral sheets, in addition to Fe, Al and Mg in the octahedral sheet. Thus the predominant sites of a central octahedral Fe in a representative nontronite would be: Fe(300)[Si8], Fe(300)[Si-Fe], and Fe(300)[Si-Al] where the [Si], [Fe] and [Al] represent tetrahedral substitutions. With increasing aluminium content the above sites could be mixed with Fe(210)[Si8], Fe(210)[Si-Al] and possibly Fe(210)[Si-Fe]. For the highly Al-enriched nontronites, Fe(210)[Si8], or Fe(210)[Si-Al] sites will also become common.

We contrast the present approach to the crystallographically intensive approach of Ballet and Amthauer [14] and other work reviewed there. We believe that the concepts of point group symmetry of the cation sites are not useful in these mixed substitution systems and our approach is very similar to that of Dainyak, Drits and co-workers [e.g. 3, 15, 16] who have done detailed Mössbauer effect, IR and EXAFS studies of various layer silicates. We are concentrating on selecting simple systems in order to avoid ambiguities involved even in careful fitting of “sites”, as emphasized by Dyar et al. [17].

2. Experimental

2.1. Sample preparation

The nontronites used here were the same as studied by Gates et al. [6]. As detailed in that study, all samples were carefully purified by saturating initially with either Na$^+$ or Li$^+$ and washing by centrifugation to obtain dispersed fine fractions, generally of <0.2, 0.15 or 0.1 µm. Random and orientated powder X-ray diffraction and infrared spectroscopy were used to check the purity. To prepare samples with different counter cations, a portion of each sample was reacted and washed three times with 0.1M chloride salts of the following cations NH$_4^+$, Na$^+$, K$^+$, Ca$^{2+}$ and La$^{3+}$. Pure fine fractions were then dialyzed to remove excess salts. All materials were finally oven dried at 105 °C. The mean structural formula [6] of NAu-1 is M$^{+1.05}$[Si$_{7.00}$Al$_{1.00}$](Al$_{0.29}$Fe$_{3.68}$Mg$_{0.04}$). Thus, the octahedral layer is strongly ferric, with Fe$_{3+}$ : Al$_{3+}$ : Mg$_{2+}$ as 1 : 0.08 : 0.01. However, on average, one Al$_{3+}$ in the eight tetrahedral positions is coordinated to octahedral Fe$_{3+}$.

2.2. Mössbauer spectroscopy

Mössbauer spectra were taken at room temperature of the samples described above. The spectra were collected using a $^{57}$Co in Rh source mounted on a conventional, symmetrical waveform, constant acceleration drive. The spectra were fitted with Voigtian profiles using the program Recoil. All IS are quoted relative to α-Fe at room temperature.

3. Results and fitting

The spectra obtained are shown in figure 1. It can be seen that the top four spectra all have the same basic shape of two nested quadrupole doublets, while the La$^{3+}$ spectrum has some additional structure. The first simple analysis that we can do is to determine the centre of the spectral intensity by simply treating the spectra as histograms, which is completely independent of any fitting models. This gave the centres as: NH$_4^+$: 0.380 mm/s, K$^+$: 0.378 mm/s, Ca$^{2+}$: 0.370 mm/s, Na$^+$: 0.369 mm/s and La$^{3+}$: 0.349 mm/s. The second model-independent parameter which we can obtain is the spectral area normalized to equal sample masses, which is the effectively the relative recoilless fraction. These gave a variation of nearly 40%, with the order NH$_4^+$ > Na$^+$ > Ca$^{2+}$ > K$^+$ > La$^{3+}$.
The spectra, except for La$^{3+}$, were all fitted with two nested Voigtians. No attempt was made to include a possible tetrahedral site as its existence amounts to only $\sim$2% [6] and such a small contribution would not affect the larger-picture conclusions which we were trying to draw about the octahedral sites. The fitted spectrum of the Ca$^{2+}$ sample is shown in figure 2. The mean parameters for the inner doublet of the four spectra (excluding the La$^{3+}$ spectrum for which we do not yet have a definite fit) were IS = 0.38(1) mm/s, QS = 0.18(2) mm/s, area = 34(4)% and for the outer doublet, IS = 0.38(1) mm/s, QS = 0.56(3) mm/s, area = 66(5)%.

4. Discussion
The hydrated radii of the cations used are, in increasing order, \(\text{NH}_4^+ \sim \text{K}^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{La}^{3+}\); which correlates well with the model-independent mean isomer shift, \(\text{NH}_4^+, \text{K}^+ < \text{Na}^+, \text{Ca}^{2+} < \text{La}^{3+}\). The electron density at octahedral Fe therefore appears to be influenced by the hydrated interlayer cations according to the relative localization of tetrahedral layer charge neutralization.

From the atom concentrations, it is clear that the dominant octahedral coordination is Fe(300). Assuming that tetrahedral substitution is random we can use the binomial theorem to estimate the proportions for the tetrahedral coordinations as Fe(300)[Si$_8$] : 34%, Fe(300)[Si$_7$Al$_1$] : 39%, Fe(300)[Si$_6$Al$_2$] : 20%. Since we would expect the symmetrical [Si$_8$] to produce the smallest quadrupole splitting, we see that its expected area agrees perfectly with the experimental area of the inner doublet. The outer doublet is then due to the sum of, principally, the other two configurations. This interpretation is supported by comparison with the spectrum of NAu-2 which has the composition \(\text{M}^+\text{.83[Si}_x\text{Al}_{1-x}\text{Fe}_{2.5}]\text{(Al}_{2.5}\text{Fe}_{3.43}\text{Mg}_{0.04})\). Note that the silicon content of the tetrahedral layer for NAu-2 is 94% compared to 87.5% for NAu-1, so one would expect the contribution of the narrow central doublet due to [Si$_8$] to increase accordingly. This is the case as can be seen from the spectrum of Jaisi et al. [18] (inset in their figure 2A), which agrees with our spectrum (not shown). They have fitted it to a single doublet with IS = 0.38 mm/s, QS = 0.44 mm/s. Our detailed interpretation of the spectra of NAu-2, including in applied magnetic field, will be published separately.

There have been two previous very detailed papers on the Mössbauer spectra of nontronites. NAu-1 has a very similar composition to Garfield nontronite [6] and the spectra obtained by Johnston and
Cardile [8] are very similar to ours. They strongly favoured a two octahedral site model, distinguished electrostatically as suggested by Goodman [10], but no definitive configurations were suggested. Their fitted quadrupole splittings are larger by about 0.8 mm/s than ours and the relative intensity of their inner doublet is slightly larger than their outer doublet. We believe that these changes are due mainly to their use of Lorentzians, whereas we have used Voigtians for which the quoted QS is <QS> of the Gaussian distribution, and they also included a tetrahedral site. We note that they observed the outer doublet to be broader than the inner one, compatible with our conclusion that it is due to two different configurations.

Luca [9] studied the effect of different exchangeable cations and of dehydration in SWa-1 nontronite. However, the octahedral layer of SWa-1 [6] has Fe$^{3+}$ : Al$^{3+}$ : Mg$^{2+}$ as 1 : 0.42 : 0.10, making the major configuration Fe(210)[Si$_8$], followed by Fe(210)[Si$_7$Al] and Fe(300)[Si$_8$], with other configurations, including Mg$^{2+}$ contributions, unable to be neglected. Such a combination resulted in a smooth envelope with no definite bumps to aid the analysis. We note that the large QS of ~ 0.7-1.0 mm/s in the ferruginous smectites assigned by Cashion et al. [11] to cis-Fe$^{3+}$ having at least one Mg$^{2+}$ octahedral neighbour, is not observed here, helping to confirm the correctness of the assignment.

5. Conclusions
By considering the most likely nearest cation neighbour configurations for octahedral Fe$^{3+}$ in NAu-1 nontronite, we have identified the two major quadrupole split doublets as being due to Fe(300)[Si$_8$] for the narrower doublet, and to Fe(300)[Si$_7$Al] and Fe(300)[Si$_6$Al$_2$] for the broader doublet. These assignments are also compatible with the spectra taken by other workers on Garfield, SWa-1 and NAu-2 nontronites, and therefore we expect them to be universal.

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