

Identification of Fe³⁺ Site Coordinations in NAu-2 Nontronite

J.D. Cashion^a, W.P. Gates^b, T.L. Greaves^{a1} and O. Dorjkhaidav^{a2}

^a School of Physics, Monash University, Victoria 3800, Australia.

^b Department of Civil Engineering, Monash University, Victoria 3800, Australia.

⁵⁷Fe Mössbauer spectra of NAu-2 nontronite show a quadrupole split spectrum with no trace of magnetic ordering down to 5 K. Two quadrupole doublets are due to octahedral *cis* Fe³⁺ and one to tetrahedral Fe³⁺. However, the fourth doublet, with a splitting of 1.28 mm/s is attributed to a new Fe³⁺ species, possibly in a ditrigonal cavity or a polyoxocation species in the interlayer.

1. Introduction

Nontronites are the iron-rich end-members of the smectite group of clay minerals. Structurally, they consist of a sheet of octahedrally coordinated cations (Fe³⁺, Al³⁺, Mg²⁺, Fe²⁺) which is sandwiched between two tetrahedrally coordinated sheets of cations (Si⁴⁺, Al³⁺, Fe³⁺). The charge imbalance introduced by the lower valency ions in each sheet is compensated by the incorporation of additional cations, usually alkali or alkaline earths, into the interlayer region between two opposing layers.

Iron in the octahedral sheet is coordinated to four oxygen ions and two hydroxyl ions which allows for three different sites, two *cis* and one *trans* with respect to the hydroxyl ions. The smectites are di-octahedral, so that only two of these sites are filled. At the nontronite end, it is accepted that both occupied sites are *cis*, while at the iron-poor montmorillonite end, iron is probably randomly distributed between one *cis* and the *trans* sites. Thus, iron can exist in three different arrangements with respect to its coordinating anions, convoluted with many more arrangements with respect to its nearest and next nearest neighbour cations. In the general case, there is insufficient resolution in ⁵⁷Fe Mössbauer spectra to distinguish these possibilities. It was pointed out some while ago that there were cases where the literature assignments were not consistent with the crystallography [1] and that the effect of cation neighbours could be important [2,3]. Recently, positive identifications of Mössbauer parameters with particular iron coordinations have been made [4,5], by selection of clay minerals with particularly simple or related chemistry.

In this paper, we consider the South Australian Uley nontronite, NAu-2, for which the literature structural formula is M⁺_{0.72}[Si_{7.55}Al_{1.16}Fe_{0.29}](Al_{0.34}Fe_{3.54}Mg_{0.05}) [6]. This is similar to the NAu-1 sample previously analysed [5] whose composition is M⁺_{1.05}[Si_{7.00}Al_{1.00}](Al_{0.29}Fe_{3.68}Mg_{0.04}). The major differences which will affect the Mössbauer spectra are the higher Si⁴⁺ concentration, the presence of some tetrahedral Fe³⁺ and the resulting, much smaller tetrahedral Al³⁺ concentration in NAu-2. The Mössbauer spectrum of NAu-2 has previously been published [7] and we will return to their assignment of the two principal features of the spectrum to *cis* and *trans* sites in the Discussion.

2. Experimental

The sample was carefully purified by saturating initially with Na⁺ and washing by centrifugation to obtain a dispersed fine fraction of < 0.15 μm [6]. Random and orientated powder X-ray diffraction and infrared spectroscopy were used to check the purity. The sample

¹ Present address: CSIRO Materials Science and Engineering, Clayton, Vic 3169, Australia.

² Present address: Dept. of Safeguards, I.A.E.A., Vienna, Austria

was then reacted and washed three times with 0.1M CaCl₂ to produce calcium saturated NAu-2 and then dialyzed to remove excess salts before being finally oven dried at 105 °C.

Mössbauer spectra were taken using a ⁵⁷Co in Rh source, mounted on a conventional, symmetrical waveform, constant acceleration drive. All isomer shifts (IS) are quoted relative to α -Fe at room temperature. The spectra were fitted with Lorentzian profiles.

3. Results

Spectra were taken at both low and high velocity but only the former will be shown since no evidence was seen for magnetically ordered species. A room temperature spectrum is shown in Fig. 1. It is an unusual spectrum for a clay mineral because of the pronounced outer structure, requiring it to be fitted with four doublets, the parameters for which are in Table 1. The spectra at 78 K and 5 K are almost identical, except for the thermal shift and the parameters for the 5 K spectrum are also given in Table 1. The only changes of note are the increase in the areas of doublets 3 and 4 at low temperatures which should be the more reliable estimates of their proportion. It is usual that the bonding in tetrahedral sites is weaker than that for octahedral sites in the same material. The increase in the outer doublet area also indicates weaker bonding and helps provide evidence for its origin as will be discussed later.

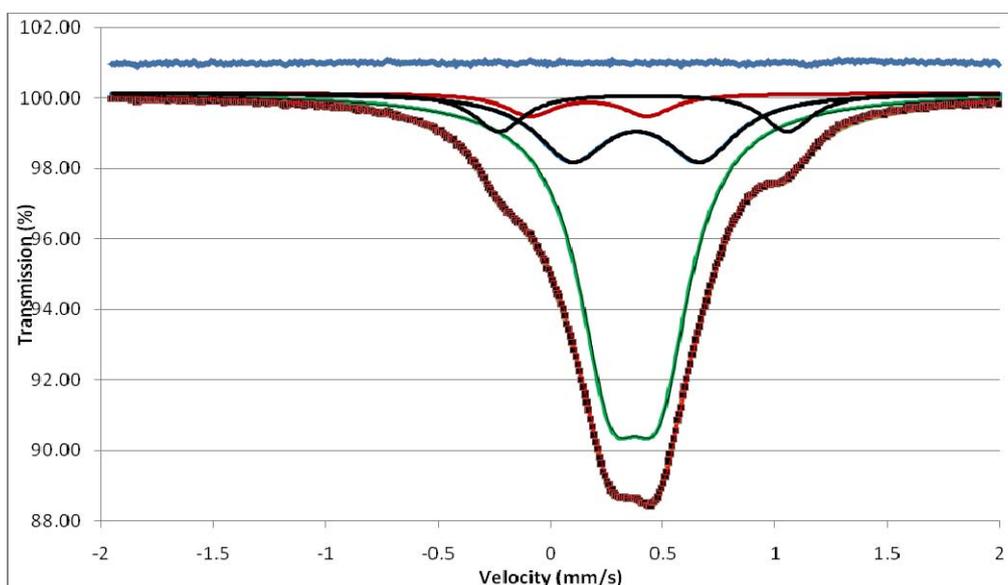


Fig. 1. ⁵⁷Fe spectrum of NAu-2 at room temperature

4. Discussion

The dominant doublet has parameters very close to those of the first NAu-1 doublet which was assigned [5] the coordination of three octahedral Fe³⁺ neighbours and then eight tetrahedral Si⁴⁺ neighbours, or Fe(300)[Si₈] in our terminology, where the number in parentheses refers to the number of octahedral Fe³⁺, Al³⁺ and Mg²⁺ neighbours respectively. This is the most symmetrical coordination and so should produce the smallest quadrupole splitting (QS). It is also the most probable, based on the chemical analysis and random site occupation. The second doublet also has parameters almost the same as those in NAu-1 and is ascribed [5] to the configurations Fe(300)[Si₇Al] and Fe(300)[Si₇Fe], the latter being absent in NAu-1. The higher Si⁴⁺ concentration in NAu-2 means that substitutions for two Si⁴⁺ ions have probabilities of <4%. The third doublet is due to tetrahedral Fe³⁺, with an intensity of 9%, consistent with estimates from a variety of other techniques [6].

The first three assignments agree very well with the conclusions of Besson *et al* [8] in their experiments on Garfield nontronite. We note that our values for the relative areas of the

two doublets for both NAu-1 and NAu-2 as a function of the R^{3+} tetrahedral substitution fit very well on their Fig. 8.

Table 1. Parameters from least squares fits to the spectra of nontronite NAu-2.

Temperature	Site	IS (mm/s)	QS (mm/s)	Γ (mm/s)	Area (%)
Room	Oct 1	0.37(1)	0.22(1)	0.35(1)	68(4)
	Oct 2	0.37(1)	0.58(1)	0.37(1)	20(5)
	Tet	0.16(1)	0.53(1)	0.27(1)	5(1)
	Doublet 4	0.41(1)	1.28(1)	0.26(1)	8(1)
5 K	Oct 1	0.49(1)	0.22(1)	0.31(1)	57(2)
	Oct 2	0.51(1)	0.55(1)	0.30(1)	21(2)
	Tet	0.29(1)	0.47(1)	0.26(1)	9(1)
	Doublet 4	0.52(1)	1.25(1)	0.25(1)	13(1)

Assigning the outer doublet is not so straightforward. Jaisi *et al* [7] tentatively ascribed it to *trans*- Fe^{3+} , even though it is recognised that nontronites are normally *trans* vacant [9]. It is noteworthy that, along with the tetrahedral Fe^{3+} , it was the most easily reduced of the Fe^{3+} sites in their experiments and there seems little reason for the *trans* site to be so much more susceptible to reduction than the *cis* sites. The QS of 1.28 mm/s is very large for Fe^{3+} in clay minerals. Examination of the spectra of related clay minerals such as montmorillonites, which are known to have *trans* occupancy and a large Mg^{2+} concentration, which widens the splitting [4], shows that the QS of the outer doublets can reach 1.2 mm/s (e.g. [10]) but are usually broadened and featureless, as was Garfield nontronite [8]. Consequently, we would argue that this feature is not due to a *trans* configuration but a definite and new configuration.

We have noted two experiments which produced similar parameters as a well-defined doublet. Bakas *et al* [11] observed a doublet in successive oxidation-reduction experiments on a montmorillonite with parameters IS = 0.34(1) mm/s, QS = 1.27(5) mm/s which became magnetically ordered at low temperatures and which they attributed to superparamagnetic maghemite. We are confident, with the benefit of 17 years of hindsight, that their species was not superparamagnetic maghemite, but its true origin is unknown. The concentration of our species is much smaller and this could account for the lack of magnetic ordering. Lego *et al* [12] observed similar parameters in three Czech bentonites, with the Hroznětín outer doublet being well defined and ascribed generically as being octahedrally coordinated.

We can define the following requirements to help in identification of the configuration: (1) the species is not ion-exchangeable [6]; (2) it must be in a very distorted site and have relatively weak bonding; (3) there is no low temperature splitting of the spectrum, so it is not due to any of the usual ferric (oxyhydr)oxides; (4) it must be able to contribute to the structural collapse on reduction, during which it will suffer significant dissolution.

One possibility is that the ions responsible for this signature are in the interlayer. They cannot be isolated Fe^{3+} ions because the resulting interlayer charge would be much too large [6]. There are various structures which can be in the interlayer, of which the best known is pillaring through the incorporation of the Al^{3+} or Fe^{3+} based Keggin molecule, $[FeO_4 Fe_{12}(OH)_{24}(OH_2)_{12}]^{7+}$. This only has 7+ rather than the 39+ of the metal ions which brings the effective charge contribution of the Fe^{3+} to an acceptable level. There is little Mössbauer data on pillared clays, but Gangas *et al* [13] showed that pillaring in the SWa-1 nontronite and an unnamed montmorillonite can produce magnetic ordering by providing magnetic bridges to overcome the magnetic frustration of the honeycomb octahedral sheet. However, only low temperature spectra were shown, without fits, so it is not possible to discern the QS of the

unordered component. Whether magnetic ordering occurs will depend on the concentration of pillars. Aouad *et al* [14] observed pillaring in a saponite and a montmorillonite which they attributed to akaganéite and whose parameters do not match ours. It has been shown ([15] and refs. within) that Fe^{3+} in Fe and Fe/Al pillared montmorillonite can be reduced by various liquid and vapour treatments, sometimes resulting in the collapse of the interlayer structure. Of course, it is not essential that the Keggin molecule is the cause, any polyoxocation incorporating several Fe^{3+} ions, with some anions to reduce the total charge, and satisfying the previous criteria, would also be acceptable.

Another possibility is that the Fe^{3+} ions are in the ditrigonal cavity. There have been many observations of Li^+ and Ca^{2+} there, but the only 3d elements observed have been Cu^{2+} [16] and Cr^{3+} [17]. However, there seems no reason why Fe^{3+} could not also be accommodated. Thus, with the lack of prior observations, there are no known Mössbauer parameters for this site, but it would be very distorted, the ions would be isolated and, importantly, it does seem to satisfy all the requirements listed above. A final possibility of Fe^{3+} being on clay particle edges seems unlikely as one would expect observations of such a site in many other clay minerals.

5. Conclusions

We have shown that three of the components of the Mössbauer spectrum of N Au-2 are the same as those identified in other nontronites. However, the final component is due to a new species which we assign to probably Fe^{3+} in a ditrigonal cavity or possibly a naturally occurring polyoxocation pillaring molecule. We note that, although we disagree with Jaisi *et al* [7] over the origin of the outer doublet, this does not affect their overall results, nor the interpretations of the results of their bioreduction experiments.

Acknowledgements

We are grateful for the support of the Australian Research Council, Monash University and SmecTech Research Consulting and to T W Turney for helpful discussions.

References

- [1] Johnston J H and Cardile C M 1985 *Clays Clay Miner.* **33** 21
- [2] Rancourt D G and Ping J Y 1991 *Nucl. Instr. Meth. Phys. Res.* **B 58** 85
- [3] Rancourt D G 1994 *Phys. Chem. Min.* **21** 250
- [4] Cashion J D, Gates W P and Thomson A 2008 *Clay Miner.*, **43** 83
- [5] Cashion J D, Gates W P and Riley G M 2010 *J. Phys.: Conf. Series* **217** 012065
- [6] Gates W P, Slade P G, Manceau A and Lanson B 2002 *Clays Clay Miner.* **50** 223
- [7] Jaisi D P, Kukkadapu R K, Eberl D D and Dong H 2005 *Geochim. Cosmochim. Acta.* **69** 5429
- [8] Besson G *et al* 1983 *J. Appl. Cryst.* **16** 374
- [9] Manceau A *et al* 2000 *Amer. Miner.* **85** 153
- [10] Cardile C M and Johnston J H 1986 *Clays Clay Miner.* **34** 307
- [11] Bakas T, Moukarika A, Papaefthymiou V and Ladavos A 1994 *Clays Clay Miner.* **42** 634
- [12] Lego S, Morháčová E and Komadel P 1995 *Clay Miner.* **30** 157
- [13] Gangas N H J, van Wonerghem J, Mørup S and Koch C J W 1985 *J. Phys. C: Solid State Phys.* **18** L1011
- [14] Aouad A *et al* 2010 *Clays Clay Miner.* **58** 164
- [15] Komadel P, Doff D H and Stucki J W 1994 *J. Chem. Soc., Chem. Commun.* 1243
- [16] Madejová J, Arvaiová B and Komadel P 1999 *Spectrochim. Acta A* **55** 2467
- [17] Drljaca A, Anderson J R, Spiccia L and Turney T W 1992 *Inorg. Chem.* **31** 4894