



## Mössbauer Analysis of Iron Sites in Four Na- and Ca-Saturated Ferruginous Smectites

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<sup>57</sup>Fe Mössbauer spectra of the Na- and Ca-saturated forms of four ferruginous smectites, having a range in composition, have been fitted with Voigtian profiles to represent, principally two, correlated distributions of isomer shifts and quadrupole splittings. Correlation between the areas and hyperfine parameters of the distributions determined from Mössbauer spectroscopy and those from chemical analyses and infrared spectroscopy enable interpretations in terms of near neighbour cations in the octahedral sheet.

### 1. Introduction

Many techniques have been used to determine the distribution of cations in smectites [1-5], but the results are debatable because different techniques sample clay chemistry differently. Smectites are 2:1 layer (tetrahedral:octahedral) clay minerals: within the octahedral sheet, some Al<sup>3+</sup> is substituted by Fe<sup>3+</sup> and Mg<sup>2+</sup>. Two of three octahedral sites within the AlO<sub>4</sub>(OH)<sub>2</sub> (gibbsite-like) sheet are occupied. The metal ions within these sites form a trigonal array so each atom has three neighbours. The distribution may be statistical, but there is a tendency for Mg<sup>2+</sup> ions to avoid being neighbours and thus some clustering of other ions may occur [2, 3, 5]. The tetrahedral sheets are predominantly SiO<sub>2</sub>, but some Al<sup>3+</sup> for Si<sup>4+</sup> substitution can occur there as well.

Mössbauer spectroscopy has in the past been used to identify different iron sites in minerals, but this has often been subject to heated discussion [6]. For several decades, Lorentzian fitting of two quadrupole split doublets have been commonly attributed to *cis*- and *trans*-coordinated Fe<sup>3+</sup> [7-8]. However, it has recently been pointed out [9] that the effect of the different neighbours on the quadrupole splitting is probably larger than that caused by *cis*- or *trans*-coordination. Rancourt [6, 9] has strongly advocated that Mössbauer spectra of inhomogeneous materials should be fitted with Voigtian lineshapes. Since the Voigtian is essentially a Gaussian distribution of Lorentzians, the Gaussian component allows the incorporation of the broadening caused by variation in the identity of neighbours.

### 2. Sample preparation

We have applied a Voigtian curve fitting procedure to the room temperature Mössbauer spectra of four ferruginous smectites (Table 1), prepared in their Na<sup>+</sup>- and Ca<sup>2+</sup>-forms, in order to study the octahedral occupancy. The Ca<sup>2+</sup>-form of the same samples have been studied by infrared and chemical analysis [4].

**Table 1. Useful site data of the smectites studied.**

Clay	Oct Fe	Oct Al	Oct Mg	Oct charge
	per unit cell			%
Stebno	1.79	1.87	0.50	3
Drayton	1.02	2.18	1.06	27
Nibost	0.90	2.26	1.03	37
Redhill	0.77	2.50	0.74	87

### 3. Results

A representative fit of the Mössbauer spectrum for Na-Nibost smectite is shown in Fig. 1 and full tabulation of the major parameters from the quadrupole splitting distribution fits for all smectites is shown in Table 2. Note that two main quadrupole splitting groups were



observed, one with a narrow splitting distribution (ND) and one with a broad splitting distribution (BD). Perusal of Table 2 shows that the results of fitting are not systematic as a function of iron content.

**Table 2. Hyperfine parameters obtained from the Voigtian fitting of the Mössbauer spectra.**

Clay	Ca form									
	Narrow distribution					Broad distribution				
	IS	QS	SD	Skew	Area	IS	QS	SD	Skew	Area
	mm/s	mm/s	mm/s		%	mm/s	mm/s	mm/s		%
Stebno	0.35	0.45	0.18	0.08	81	0.33	0.72	0.39	0.29	19
Drayton	0.36	0.48	0.04	~0	55 (57)	0.34	0.86	0.32	0.04	42 (43)
Nibost	0.35	0.50	0.13	~0	57 (63)	0.36	0.94	0.38	0.08	33 (37)
Redhill	0.34	0.45	0.06	~0	61 (62)	0.34	0.90	0.47	0.28	37 (38)

Clay	Na form									
	Narrow distribution					Broad distribution				
	IS	QS	SD	Skew	Area	IS	QS	SD	Skew	Area
	mm/s	mm/s	mm/s		%	mm/s	mm/s	mm/s		%
Stebno	0.35	0.45	0.19	0.11	77	0.34	0.78	0.46	0.42	23
Drayton	0.35	0.51	0.04	~0	74 (77)	0.37	1.06	0.17	~0	22 (23)
Nibost	0.35	0.51	0.06	~0	62 (65)	0.35	0.98	0.38	~0	34 (35)
Redhill	0.35	0.45	0.15	0.02	38 (47)	0.32	0.80	0.47	0.40	43 (53)

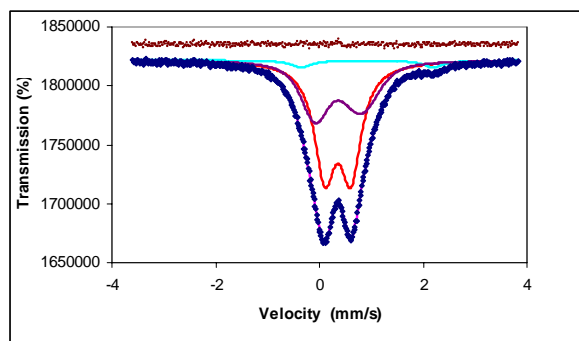
Area values in parentheses are corrected to show the proportions of the Fe<sup>3+</sup> components only.  
 Skew = (mean – mode) / standard deviation

### 3.1. Mössbauer-based Interpretations.

The quadrupole splitting (QS) is principally determined by the charge distribution of the nearest neighbours which produces an electric field gradient (EFG) at the Fe<sup>3+</sup> site. A comparison of the three ions shows that Al<sup>3+</sup> has the same charge as Fe<sup>3+</sup> but a smaller diameter (0.051 nm c.f. 0.064 nm) while Mg<sup>2+</sup> has almost the same radius (0.066 nm) but a different charge. The larger intensity of the ND distribution in the Stebno samples strongly suggests that it is associated with an absence of Mg<sup>2+</sup> neighbours. Including Mg<sup>2+</sup> as nearest neighbours may correspond to the BD distribution and increases in its standard deviation (SD) correspond to an increased number of Mg<sup>2+</sup> neighbours. The smaller charge of Mg<sup>2+</sup> causes an increase in the EFG and hence the QS. However, it is unclear how lattice relaxation due to the smaller Al<sup>3+</sup> would affect the EFG. Also unexplained are the changes in peak areas invoked by changing exchange cations.

### 3.2. A Combined Mössbauer – Infrared Interpretation

The distribution of the OH-sharing octahedral cation pairs, based on infrared absorption spectra [2, 4, 5], enables us to simulate an octahedral layer for each smectite. The distribution of the three neighbours about an Fe<sup>3+</sup> centre, as shown in Fig. 2 for Redhill, can be estimated and compared with the number expected from simple Poisson statistics. The main reason for the observed difference is the avoidance of OH-sharing Mg–Mg neighbours, as MgMg-OH absorption bands are not observed in the IR. The net effect then is to increase the population



**Figure 1. Best fit of the Mössbauer spectrum of Na-Nibost smectite using Voigtian profiles.**



in the 111 centre of the plot, corresponding to a central Fe having 1Fe<sup>3+</sup>, 1Al<sup>3+</sup>, 1Mg<sup>2+</sup> as neighbouring cations.

The ND feature is therefore probably attributable to Fe<sup>3+</sup> centres having no Mg<sup>2+</sup> neighbours. These are principally of 210 and 120 coordination for the four smectites studied here. The larger SD for Stebno may be due to an appreciable number of 300 coordination, which the other smectites lack. It is expected that in the Ca<sup>2+</sup>-form, Ca<sup>2+</sup> ions are located in the interlayer as close as possible to sites of substitution (Mg for Al in the octahedral sheet and Al for Si in the tetrahedral sheet) to achieve charge neutrality over a smaller distance.

Changing from Ca<sup>2+</sup>- to Na<sup>+</sup>-form creates twice as many ions in the interlayer space in preserving charge neutrality. For Stebno, Drayton and Nibost, there is a decrease in BD QS in the Na<sup>+</sup>-form compared to the Ca<sup>2+</sup>-form. A large proportion of Na<sup>+</sup> ions are neutralising layer charge not associated with Mg<sup>2+</sup>, but rather with tetrahedral Al<sup>3+</sup>. For Redhill nearly 90% of exchangeable Na<sup>+</sup> neutralises charge associated with octahedral Mg<sup>2+</sup>. In the Ca<sup>2+</sup>-forms of Nibost, Drayton and Stebno, the Ca<sup>2+</sup> is potentially “close” to all the Mg, and acts to reduce the EFG effect caused by Mg<sup>2+</sup>. However, Ca<sup>2+</sup> can only be “close” to about half the Mg in Ca<sup>2+</sup>-Redhill. Exchanging with Na<sup>+</sup> improves the charge neutralisation effect on the EFG for Redhill, but introduces more disorder for the other three Na<sup>+</sup>-form smectites.

The main mystery remaining is why the QS of Redhill is markedly less than Drayton and Nibost. This could be due to the larger number of symmetrical 030 coordination or lower Mg<sup>2+</sup> concentration. It may also be possible that Fe<sup>3+</sup> is even more clustered within the octahedral sheet of this smectite than can be discerned by IR, as has been shown recently for other montmorillonites [5, 6, 7].

In conclusion, our results provide strong evidence that aspects of Mössbauer spectra for 2:1 layer silicates can be largely explained by the identity of neighbouring cations. We emphasise here that Mössbauer spectroscopy should be used in combination with other spectroscopic tools such as infrared and X-ray absorption spectroscopy.

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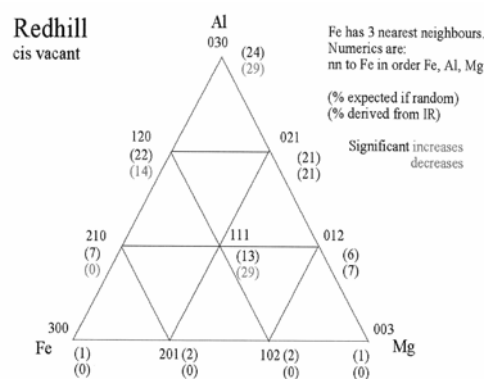


Figure 2. Distribution of Al, Mg and Fe about an Fe centre in the octahedral sheet of Redhill smectite.