Nearest neighbour distributions of site occupancies in nontronites

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Abstract
The actual site occupancies of smectites continue to defy unambiguous assignment. Presented here are calculations of the most probable distributions of nearest neighbour octahedral and tetrahedral occupancies around octahedral iron in nontronite. Calculations are in good agreement with recent interpretations of Mössbauer spectra.

Key words: multinomial distribution, random, isomorphic substitution,

Introduction
Fitting of Mössbauer spectra of clay minerals has many pitfalls (Murad 1987). Spectral analysis is complicated by overlapping lines from different components and also by the fact that a particular configuration, e.g. octahedral Fe(III), can have more than one set of quadrupole splitting parameters because of different nearest neighbour arrangement in the octahedral sheet (Besson et al., 1983, 1987; Johnston and Cardile, 1985; Luca and Cardile, 1989). In the case of *cis*-vacant ferruginous smectites, Cashion et al. (2008) identified that the doublet with the largest splitting was due to a *cis*-Fe(III) ion that had at least one Mg ion as an octahedral neighbour. For *trans*-vacant nontronites, however, substitutions of Mg in the octahedral sheet are negligible. Thus, another explanation for the occurrence of two doublets in nontronites is needed.

Cashion et al. (2008, 2009, 2011) developed a systematic means of identifying potential nearest neighbour cation arrangements within the octahedral sheet, based on combining chemistry and infrared data (Gates, 2008). The Mössbauer effect 'sees' the influence of the surrounding chemical environment of ^{57}Fe, and therefore, within the dioctahedral sheet of a smectite structure, each octahedral Fe atom has three nearest octahedral cation neighbours (generally a mixture of Fe, Al or Mg) and also eight nearest tetrahedral cation neighbours (mainly Si, but with small amounts of Al or Fe as well). The octahedral array can be expressed as a coordinate detailing the distribution of octahedral neighbours to Fe, namely Fe(xyz), where x, y and z are whole number integers summing to three, and representing, respectively, octahedral Fe, Al and Mg. For example Fe(210) represents a central Fe atom surrounded by 2 Fe and 1 Al atoms in the trigonal array of the dioctahedral sheet. The coordinate array for the tetrahedral sheet depends on the degree of substitution for tetrahedral Si^{4+} by either Fe^{3+} or Al^{3+}, so a given octahedral Fe centre could have as nearest tetrahedral neighbour environments any combination of Si, Fe or Al that sums to eight. The predominant sites of a central octahedral Fe in nontronite may be therefore $Fe(300)Si_8$, $Fe(300)Si_7Fe$ or $Fe(300)Si_7Al$. In this paper, tetrahedral substitutions by either Al or Fe are combined as for example, $Si_7(AlFe)_1$, for simplicity.

Results and discussion
Calculations for nearest neighbour occupancies for several nontronites, based on the structural formula detailed in Gates et al. (2002), are given in Table 1. Note that the distributions (presented in percentages) sum to >99.6% in all samples, thus essentially all nearest neighbour site occupancies are represented. Most of the samples are relatively rich in $Fe(300)Si_8$, $Fe(300)Si_7(AlFe)_1$, $Fe(300)Si_6(AlFe)_2$, $Fe(210)Si_8$ and $Fe(210)Si_7(AlFe)_1$. Likewise, most samples show relatively low contributions by Fe(012), Fe(021), Fe(030), Fe(111), Fe(120), Fe(102), Fe(210) and Fe(201) nearest neighbours in the octahedral sheet and also $Si_5(AlFe)_3$ and $Si_4(AlFe)_4$ nearest neighbours in the tetrahedral sheet.

The Spokane Mössbauer spectrum (data not shown) is narrower than most other samples. Based on its minimal Al and Mg substitution (Table 1), the Spokane sample has $Fe(300)Si_8$ as the main component (Table 2), which together with the strong contributions from only two other nearest neighbour occupancies, $Fe(300)Si_7(AlFe)_1$ and $Fe(300)Si_6(AlFe)_2$, accounts for >92% of the chemistry. For this sample, essentially all the tetrahedral substitution is by Fe(III), thus these are correctly assigned as $Fe(300)Si_7Fe_1$ and $Fe(300)Si_6Fe_2$.

These three sites satisfy >70% of the chemistry for two other samples C.Z. (Clausthal Zellerfeld) and NAu-2, both of which also have several contributions from Fe(210) sites. Sample C.Z. also contains Si_7Fe_1 and Si_6Fe_2 sites due to greater tetrahedral substitutions than either Spokane or NAu-2.

Table 1. Structural formulae of the samples under study. After Gates et al. (2002).

Sheet	Occupancy	Samples						
		SWa-1	NAu-1	Garfield	NG-1	NAu-2	Spokane	C.Z.
Tetrahedral	Si	7.40	7.07	7.10	7.12	7.55	7.26	7.04
	Al	0.60	0.81	0.88	0.26	0.16	0.04	0.04
	Fe	--	0.12	0.10	0.62	0.29	0.70	0.92
Octahedral	Fe	2.62	3.47	3.63	3.22	3.54	3.89	3.73
	Al	1.10	0.42	0.33	0.34	0.34	0.03	0.23
	Mg	0.25	0.12	0.03	0.05	0.05	0.04	0.04
Charge	Tetrahedral	0.60	0.93	0.98	0.88	0.45	0.74	0.96
	Octahedral	0.35	0.09	0.09	0.08	0.27	0.18	0.03
	Total	0.95	1.02	1.07	0.96	0.72	0.92	1.00

Table 2. Probability distribution of nearest neighbour site occupancies about octahedral Fe for ferruginous smectite (SWa-1) and several nontronites studied in Gates et al. (2002).

(Fe,Al,Mg)	SWa-1	NAu-1	Garfield	NG-1	NAu-2	Spokane	C.Z.
Fe(3,0,0) Si_8	15.4	25.5	26.5	20.7	46.0	43.6	29.2
Fe(3,0,0) $Si_7(AlFe)_1$	10.0	28.6	29.6	20.5	21.9	35.6	31.8
Fe(3,0,0) $Si_6(AlFe)_2$	2.8	14.1	14.4	8.8	4.6	12.7	15.2
Fe(3,0,0) $Si_5(AlFe)_3$		4.0	4.0	2.2	0.5	2.6	4.1
Fe(3,0,0) $Si_4(AlFe)_4$		0.7	0.7	0.3		0.3	0.7
Fe(2,1,0) Si_8	19.4	7.6	7.2	13.9	13.3	1.0	5.4
Fe(2,1,0) $Si_7(AlFe)_1$	12.6	8.6	8.1	13.7	6.3	0.8	5.9
Fe(2,1,0) $Si_6(AlFe)_2$	3.6	4.2	3.9	5.9	1.3	0.3	2.8
Fe(2,1,0) $Si_5(AlFe)_3$	0.6	1.2	1.1	1.5			0.8
Fe(2,1,0) $Si_4(AlFe)_4$	0.1	0.2	0.2	0.2			0.1
Fe(2,0,1) Si_8	4.4	0.8	0.7	1.0	1.9	1.3	0.9
Fe(2,0,1) $Si_7(AlFe)_1$	2.9	1.0	0.7	1.0	0.9	1.1	1.0
Fe(2,0,1) $Si_6(AlFe)_2$	0.8	0.5					0.5
Fe(2,0,1) $Si_5(AlFe)_3$	0.1	0.1	0.1	0.1		0.1	0.1
Fe(1,2,0) Si_8	8.1	0.8	0.7	3.1	1.3		
Fe(1,2,0) $Si_7(AlFe)_1$	5.3	0.9	0.7	3.1	0.6		
Fe(1,2,0) $Si_6(AlFe)_2$	1.5			1.3			
Fe(1,2,0) $Si_5(AlFe)_3$	0.2	0.1	0.1	0.3			
Fe(1,1,1) Si_8	3.7	0.2	0.1	0.4	0.4		0.1
Fe(1,1,1) $Si_7(AlFe)_1$	2.4	0.2	0.1	0.4	0.2		0.1
Fe(1,1,1) $Si_6(AlFe)_2$	0.7	0.1	0.1	0.2			0.1
Fe (1,1,1) $Si_5(AlFe)_3$	0.1						
Fe(1,0,2) Si_8	0.4						
Fe(0,2,1) Si_8	0.8			0.1			
Fe(0,2,1) $Si_7(AlFe)_1$	0.5			0.1			
Fe (0,2,1) $Si_6(AlFe)_2$	0.1						
Fe(0,3,0) Si_8	1.1			0.2			
Fe(0,3,0) $Si_7(AlFe)_1$	0.7			0.2			
Fe(0,3,0) $Si_6(AlFe)_2$	0.2			0.1			
SUM	99.7	99.7	99.7	99.6	99.6	99.8	99.7

The Mössbauer spectrum of Garfield nontronite is probably the most studied, and is considered typical for a nontronite. The Garfield and NAu-1 have very similar chemistry (Table 1), and this is reflected in the nearest neighbour site distributions determined (Table 2). The NAu-1 contains more Fe(201), Fe(210) and Fe(111) sites compared to Garfield.

Despite co-locality in origin of NAu-1 and NAu-2 (Keeling et al., 2000) their site occupancy distributions represent better the observed differences in their properties (Gates et al., 2002; Cashion et al., 2009; Cashion et al., 2011). The $Fe(300)Si_7(AlFe)_1$ site is predominantly Si_7Al_1 in NAu-1, but likely Si_7Fe_1 in NAu-2 (or at least a mixture of the two chemistries). Also, NAu-2 has a larger contribution of $Fe(xyz)Si_8$ sites, indicating the lack of tetrahedral substitution in this nontronite compared to NAu-1.

Sample SWa-1, due to its high rate of substitution by Al and Mg for Fe in the octahedral sheet, as well as Al for Si substitution in the tetrahedral, shows the most complex nearest neighbour cation distributions of all the samples studied here. This complexity is reflected in the broadness of its Mössbauer spectrum (e.g. Luca and Cardile, 1989) compared to NAu-1 or NAu-2 (Cashion et al., 2009, 2011). Despite having greater Fe content (Table 1) than Garfield, sample NG-1 is intermediate in its nearest neighbour site distributions (Table 2) compared to the Garfield/NAu-1 and the SWa-1 sample. Both NG-1 and SWa-1 have higher percentages of $Fe(210)Si_7(AlFe)_1$ as well as all sites associated with Fe(120) compared to the other samples. Since SWa-1 has no tetrahedral Fe (Gates et al., 2002), the substituted tetrahedral sites are correctly assigned to Si_7Al_1 and Si_6Al_2 for this sample.

Conclusions

Multinomial distribution calculations have been made based on our best representation of the smectite structure and nontronite chemistry. The calculations, in general, reveal that random distributions of site occupancies provide an accurate approach to interpreting Mössbauer spectra. The calculations indicate that increased substitution of Al and Mg in the octahedral sheets increases the total number of site occupancies possible, which appears to be partly responsible for the broadness of the Mössbauer spectra of ferruginous smectites. It is noteworthy that this increase in site occupancies also is represented in the infrared spectra of the same samples (e.g. Gates, 2008).

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