

Intercalation and dynamics of hydrated Fe^{2+} in the vermiculites from Santa Olalla and Ojén

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Received: 26 July 2010 / Revised: 5 August 2010 / Accepted: 5 August 2010 / Published online: 29 August 2010
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Abstract Although the intercalation of Fe^{3+} into layered phyllosilicates—especially into smectites—attracted much attention in the past two decades, the information about Fe^{2+} loaded phyllosilicates is sparse. Here we present an investigation of the Fe^{2+} exchanged vermiculites from Santa Olalla and Ojén (Andalusia, Spain) by means of Mössbauer spectroscopy. The room temperature Mössbauer spectra are very similar to those of the starting compounds (Na forms) except for a decrease of the contribution of structural Fe^{3+} and a concomitant increase of the contribution of Fe^{2+} sites, indicating an internal redox process. The extent of this redox reaction is different for the two vermiculites. Thus, the intercalated Fe^{2+} acts as an electron mediator from the external medium to the structural Fe^{3+} ions. A new component attributable to intercalated Fe^{2+} is practically invisible in the room temperature Mössbauer spectra, but increases strongly and continuously during cooling to 4.2 K, where it is the dominant feature of the Mössbauer patterns. At 4.2 K, its quadruple splitting

amounts to 3.31 mm/s, which is in excellent agreement with the quadrupole splitting of Fe^{2+} coordinated to six water molecules in a highly symmetric octahedral arrangement. The strong decrease of the Mössbauer–Lamb factor of this component with increasing temperature indicates a weak bonding of the Fe^{2+} in the interlayer space.

Keywords Vermiculite · Intercalation · Ferrous iron · Mössbauer spectroscopy · Mössbauer–Lamb factor · Redox reaction

Introduction

Vermiculites and smectites loaded with Fe^{3+} —especially with Fe^{3+} isopolyoxo cations—have attracted attention because of their potential application as catalysts [1–4], although the uptake of Fe^{3+} into the interlayer space of phyllosilicates is a delicate process because the Fe^{3+} ions can be maintained in the monomeric hydrated form that is best for ion exchange only at the pH values of the aqueous solution below 1.5, which can lead to a deterioration of the phyllosilicates. At higher pH values, polymerization will set in and eventually result in the formation of iron oxo-hydroxides, which will be deposited preferentially on the external surfaces of the clay minerals because of their positive surface charge [5–9].

The insertion of Fe^{2+} should be much easier because, owing to its lower charge, the hexaaquo complex of Fe^{2+} is less acidic. Thus, the tendency toward dimerization and polymerization is strongly reduced, and the limit of precipitation shifted toward higher pH values. The lower cation charge also reduces the strength of electrostatic interactions with the negatively charged phyllosilicate layers. For this reason, the mobility of the hydrated Fe^{2+}

Dedicated to Prof. Dr. Robert Schöllhorn at the occasion of his 75th birthday

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ions in the interlayer space and concomitantly the rate of ion exchange should be higher than for Fe^{3+} .

However, except for two early studies [7, 8], the uptake of Fe^{2+} into the interlayer space of phyllosilicates has been investigated only recently [10–13] and interestingly enough in the context of bentonites used as contamination barriers for nuclear waste. This is surprising since clays are of importance in the iron chemistry of soils, e.g., in connection with the bacterially mediated reduction of iron in phyllosilicates [14–17] and the concomitant release of Fe^{2+} [16, 18] and the importance of Fe^{2+} for the formation of chlorites [19–22].

In the work presented here, we have studied the alteration of vermiculites from Santa Olalla and Ojén (Andalusia, Spain) by exposure to hydrous solutions of Fe^{2+} mainly by means of Mössbauer spectroscopy. This method allows one to distinguish the different Fe sites present in the solid and the oxidation state of iron on the different lattice sites. It will be shown that the insertion of Fe^{2+} into the interlayer space can be carried out easily and to the full ion exchange capacity without simultaneous deposition of ferric oxides and that the products obtained are fairly stable toward oxidation. At liquid helium temperature, the interlayer Fe^{2+} is the dominant component in the Mössbauer spectra, but it is virtually invisible at ambient temperature because of exceptionally strong temperature dependence of the Mössbauer–Lamb factor. In addition, the amount of structural Fe^{3+} is also strongly reduced by the intercalation of Fe^{2+} ions in the interlayer space. These internal redox processes have strong implications for clay-modified electrodes in electrocatalysis.

Experimental

The vermiculites were used as powder samples with a particle size $<80 \mu\text{m}$ obtained by grinding in a knife-mill (Netzsch ZSM-1, Germany). The structural formulas of the magnesium vermiculites are as follows: $\text{Mg}_{0.385}[(\text{Si}_{2.69}\text{Al}_{1.31}) (\text{Mg}_{2.48}\text{Al}_{0.15}\text{Fe}^{3+}_{0.33}\text{Fe}^{2+}_{0.03}\text{Ti}_{0.01})\text{O}_{10}(\text{OH})_2]$ (Santa Olalla, SO) and $\text{Mg}_{0.265}[(\text{Si}_{2.83}\text{Al}_{1.17})(\text{Mg}_{2.01}\text{Al}_{0.2}\text{Fe}^{3+}_{0.4}\text{Fe}^{2+}_{0.16}\text{Ti}_{0.14})\text{O}_{10}(\text{OH})_2]$ (Ojén) [23]. The sodium forms of the vermiculites used for the intercalation experiments were obtained by repeated soaking of the Mg-vermiculites in 1 M solutions of NaCl and stirring at room temperature (RT). For the replacement of sodium ions by Fe^{2+} , 0.1 M solutions of Fe(II)-gluconate hydrate (Fluka) in deaerated water were used. The clay minerals were added to these solutions immediately after preparation. The iron content of the solution was twice as high as the cation exchange capacity of the vermiculites used. The suspensions were stirred for 1 h in closed centrifugation tubes. Then the solution was exchanged for a freshly prepared solution, and the stirring

was continued for another hour. After centrifugation, the solid was then washed with deionized water at least five times. After the final centrifugation, the solid was dried in a stream of argon at RT.

X-ray diffraction (XRD) measurements were carried out with a Philips X'Pert (or alternatively with an AXS-Bruker D8 Advance) diffractometer using Ni-filtered Cu $K\alpha$ radiation.

Mössbauer spectra were recorded in transmission geometry using a sinusoidal velocity waveform and a source of about 2 GBq of ^{57}Co in Rh. Measurements below ambient temperature were performed in a liquid He bath cryostat in which the source and the absorber were kept at the same temperature. Temperatures above 4.2 K were obtained during the slow warming phase of the cryostat. A krypton proportional counter with single-channel windows set on the 14.4-keV photo peak and the K escape peak at about 2 keV was used for the detection of the gamma rays. The measurements of the temperature dependence of the Mössbauer patterns were performed within a few days with the same single-channel settings in order to make the absolute intensities of the Mössbauer spectra comparable.

Least squares fits of the spectra were performed either with Lorentzian or with Voigt profile line shapes grouped into quadrupole doublets. Details of this will be discussed below together with the results. All center shifts are given as measured, i.e., with respect to the source of ^{57}Co in Rh having the same temperature as the absorber. With source and absorber being at the same temperature, the second-order Doppler shift is expected to be absent to a good approximation. To obtain the isomer shifts with respect to α -iron at the temperature of the absorber, 0.11 mm/s must be added to the measured isomer shifts.

At low temperatures, broad magnetically split components appear in the spectra. These were fitted by Gaussian distributions of static hyperfine fields as described in more detail when these spectra are discussed.

Results and discussion

The layer distances of both Fe^{2+} exchanged vermiculites in the air-dried state was found to be 14.3 Å, practically the same as the values for the original Mg^{2+} forms [24], and somewhat larger than the values of 12.5 Å found for both Na^+ -exchanged vermiculites. This is a strong indication that Fe^{2+} enters into the interlayer space in a similar configuration as the Mg^{2+} in the original vermiculites [24].

The Mössbauer spectra of the Fe^{2+} exchanged Santa Olalla and Ojén vermiculites at room temperature (RT) and 4.2 K are shown in Figs. 1 and 2. For comparison, the corresponding spectra of the Na^+ forms of the two vermiculites [9, 23, 25, 26] are shown in Figs. 3 and 4.

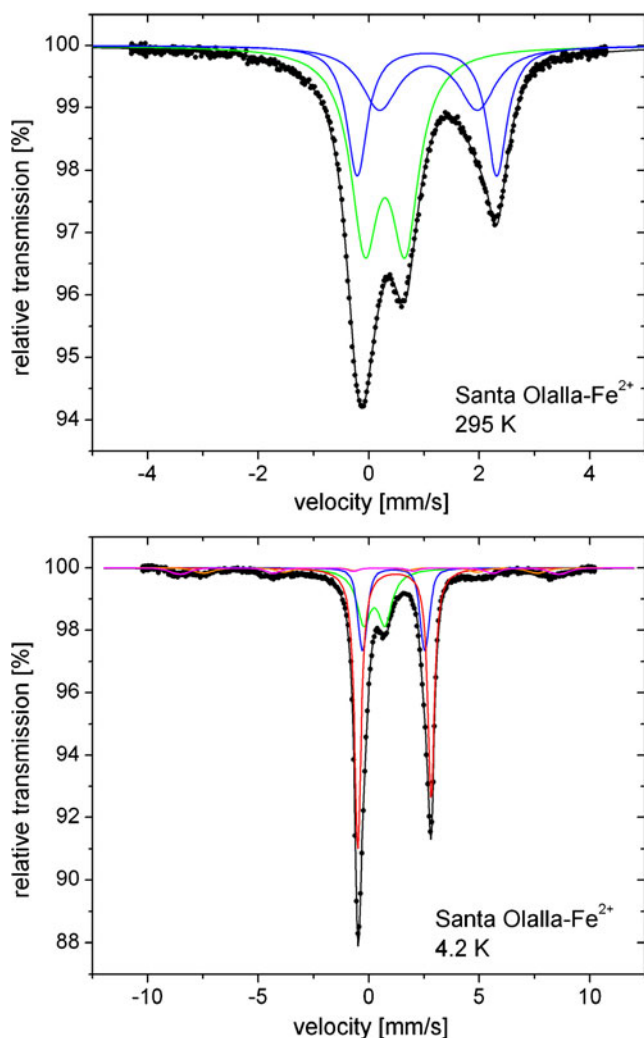


Fig. 1 Mössbauer spectra of the Fe^{2+} -intercalated Santa Olalla vermiculite at RT (*top*) and at 4 K (*bottom*). In addition to the data points and the fitted curve, the individual components discussed in the text are shown

At a first glance, the RT spectra of the Fe^{2+} exchanged vermiculites and the Na^+ forms are quite similar. They all consist of a prominent, rather broad component attributable to structural Fe^{3+} and a weaker component attributable to structural Fe^{2+} .

In contrast, the 4.2-K spectra of the Fe^{2+} exchanged vermiculites differ substantially from those of the starting materials (Figs. 1, 2, 3, 4, bottom). In the spectra of both Fe^{2+} forms, one observes strong additional Fe^{2+} component with a quadrupole splitting that is substantially larger than that of the structural Fe^{2+} , and an intensity of about 50% of the spectral area in the Santa Olalla vermiculite and of about 40% in that from Ojén. This component is attributed to intercalated Fe^{2+} . Its absence in the RT spectra can be explained by a strong decrease of the Lamb–Mössbauer f -factor (f -factor) of this component with increasing temperature, as has been observed previously in smectites [7, 8]. It

is worth mentioning that after storage of the intercalated Ojén specimen for about 6 months in ambient air, the intercalated Fe^{2+} component was still observed, although with only about a third of the intensity observed immediately after the preparation of the sample. Oxidation of the intercalated Fe^{2+} thus is taking place, but only very slowly.

All 4.2-K spectra also exhibit a broad magnetically split component, which for the Na^+ forms of the vermiculites was attributed to slow paramagnetic relaxation of part of the structural Fe^{3+} [9]. The magnetic patterns of the Fe^{2+} loaded vermiculites are similar to those of the unloaded ones and can be explained in the same way. There is no evidence for the typical magnetic hyperfine patterns of ferric oxyhydroxides that have been observed after the treatment of the Santa Olalla and Ojén vermiculites with Fe^{3+} [9].

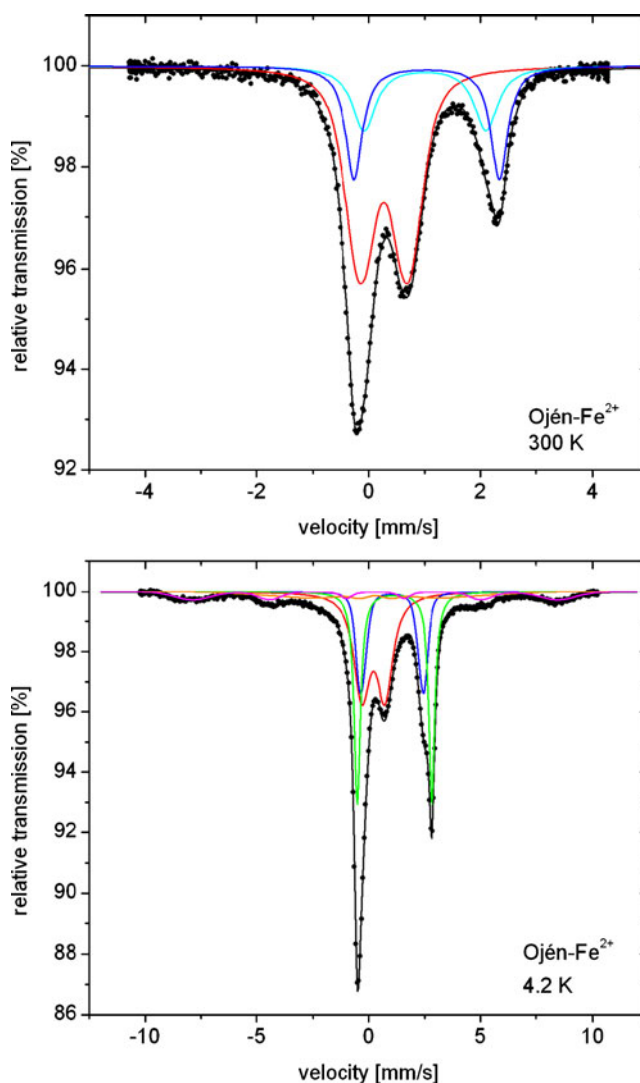


Fig. 2 Mössbauer spectra of the Fe^{2+} -intercalated Ojén vermiculite at RT (*top*) and at 4 K (*bottom*). In addition to the data points and the fitted curve, the individual components discussed in the text are shown

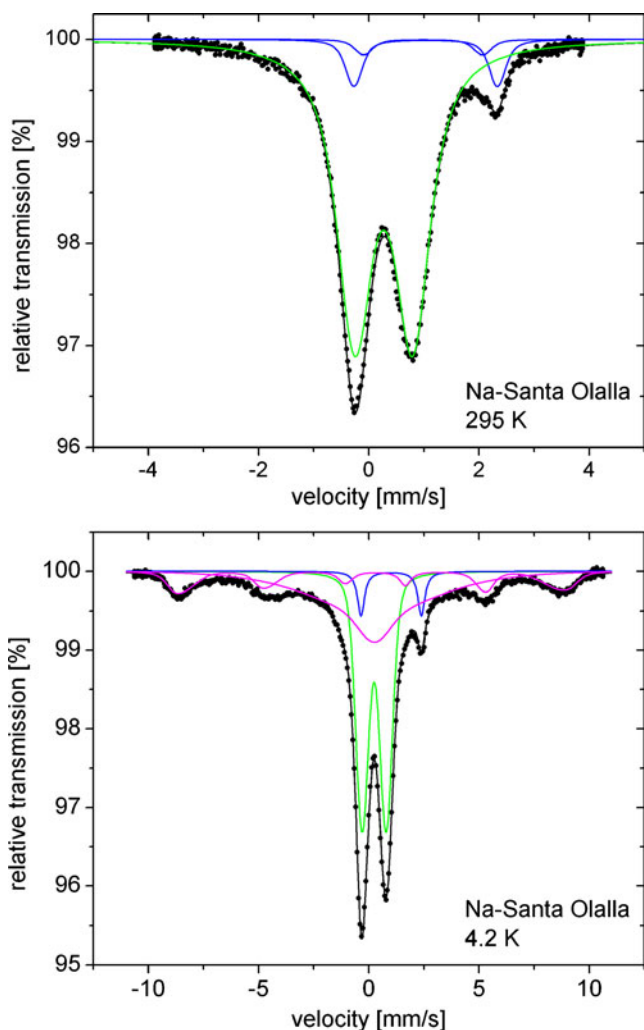


Fig. 3 Mössbauer spectra of Na form of the Santa Olalla vermiculite at RT (*top*) and at 4 K (*bottom*). In addition to the data points and the fitted curve, the individual components discussed in the text are shown

The RT spectra were fitted essentially as described previously [9, 23, 25, 26]: The rather large linewidth of the Fe^{3+} doublet was assumed to arise at least in part from a Gaussian distribution of quadrupole splittings. The corresponding Voigt profiles were calculated by superimposing many Lorentzian doublets with a Gaussian intensity distribution. However, the Lorentzian width of the Voigt profiles had to be allowed to be quite large [about 0.5 mm/s full-width half maximum (FWHM)] in order to reproduce the wide wings of the Fe^{3+} pattern, which are attributed to effects of slow paramagnetic relaxations [9, 23]. The high velocity peak of the Fe^{2+} component at about +2.5 mm/s is slightly asymmetrical and was fitted by two hardly resolved Lorentzian doublets. The results of these fits are summarized in Table 1.

In the 4.2-K spectra of the Na^+ forms of the vermiculites, the two components of the structural Fe^{2+} can no longer be

separated even approximately (Figs. 3 and 4). Here, a single Voigt profile doublet with the Lorentzian width fixed to 0.25 mm/s yielded a good fit. The broad Fe^{3+} doublet observed at 4.2 K was again fitted by a Voigt profile. In addition to these components, one observes a broad magnetic hyperfine pattern that is attributed to slow paramagnetic relaxation of part of the structural Fe^{3+} with a distribution of relaxation times. It was approximated in the least squares fits by two static Gaussian distributions of magnetic hyperfine fields, of which one is very broad to approximate the structureless background, while the other is narrower and centered around a mean hyperfine field of about 53 T, with a variance of the Gaussian distribution of hyperfine fields of about 3 T. The component of intercalated Fe^{2+} that is dominant in the 4.2-K spectra of the iron-exchanged samples was fitted by a Lorentzian quadrupole doublet, which had to be allowed to have asymmetrical intensities, with the right line being weaker than the left one

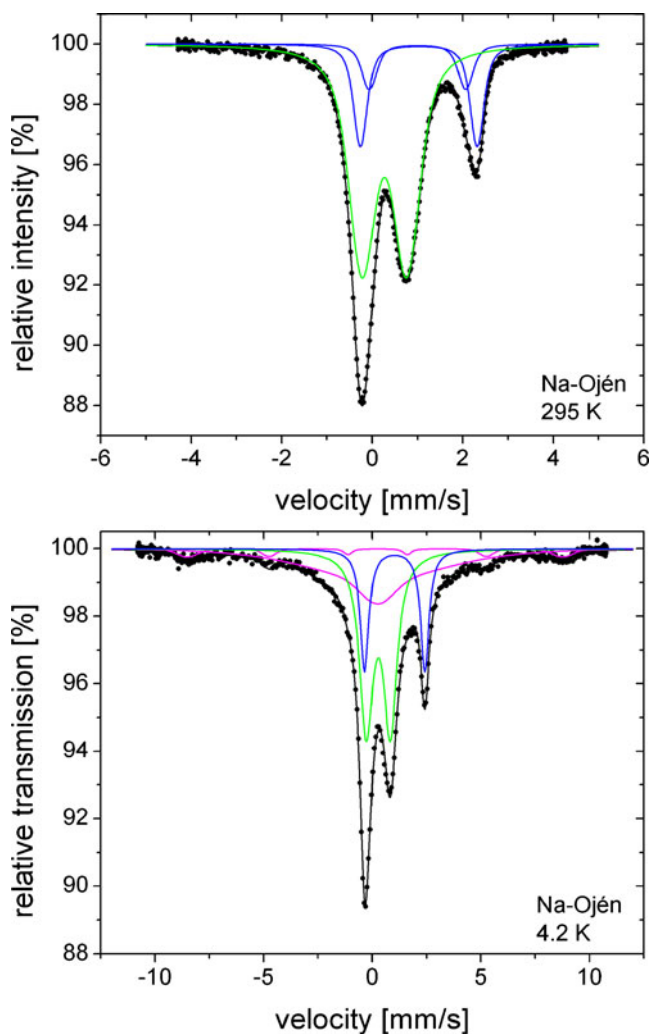


Fig. 4 Mössbauer spectra of Na form of the Ojén vermiculite at RT (*top*) and at 4 K (*bottom*). In addition to the data points and the fitted curve, the individual components discussed in the text are shown

Table 1 RT values of the quadrupole splittings QS (mm/s) isomer shifts IS (mm/s), FWHM Lorentzian line widths *W* (mm/s), and relative areas *A* of the structural octahedral iron sites (o-Fe³⁺, o-Fe²⁺(1), o-Fe²⁺(2)) for

the Na⁺ forms, and the Fe²⁺ intercalated forms of the vermiculites from Santa Olalla and Ojén

Sample	o-Fe ³⁺				o-Fe ²⁺ (1)				o-Fe ²⁺ (2)			
	QS (mm/s)	IS (mm/s)	<i>W</i> (mm/s)	<i>A</i> (%)	QS (mm/s)	IS (mm/s)	<i>W</i> (mm/s)	<i>A</i> (%)	QS (mm/s)	IS (mm/s)	<i>W</i> (mm/s)	<i>A</i> (%)
Na ⁺ —Santa Olalla	1.06	0.27	0.69	90.4	2.60	1.03	0.34	7.1	2.15	1.00	0.35	2.5
Fe ²⁺ —Santa Olalla	0.74	0.28	0.53	49.0	2.54	1.05	0.48	28.7	1.77	1.06	0.84	22.3
Na ⁺ —Ojén	1.00	0.27	0.45	71.1	2.62	1.03	0.30	13.5	2.23	1.02	0.41	15.4
Fe ²⁺ —Ojén	0.81	0.28	0.51	60.9	2.62	1.04	0.35	19.6	2.22	0.99	0.55	19.5

The intercalated Fe²⁺ is invisible in the RT Mössbauer spectra because of its low Lamb–Mössbauer *f*-factor. Typical errors of QS, IS, and *W* are in the order of 0.01 mm/s; the typical error of the *A* is in the order of 0.5 percentage points

(Figs. 1 and 2). This asymmetry could be due to texture effects, but since none of the other components exhibit similar asymmetries, it is most probably due to the anisotropy of the *f*-factor indicating that the vibrational motion of the intercalated Fe²⁺ is strongly anisotropic. With the plausible assumption that the vibrational amplitudes are larger in the basal plane of the phyllosilicates than perpendicular to it, the observed asymmetry can be explained if the sign of the electric field gradient and hence the electric quadrupole interaction is negative. In Table 2, which summarizes the results obtained at 4.2 K, only the magnitude of the quadrupole splitting is given.

In order to obtain a more detailed picture of the temperature dependence of the Mössbauer patterns, spectra were also taken between 4.2 K and about 280 K. For both iron-exchanged vermiculites, the Fe²⁺ component was

found to decrease monotonically in this temperature range to become virtually invisible at 300 K (Figs. 1 and 2). For the Santa Olalla vermiculite, the results for the intensities of the individual components in the spectra are shown in Fig. 5. The intensities given in Fig. 5 are proportional to the product of the Lorentzian widths and the relative depths of the individual components in the Mössbauer patterns. In case of Gaussian distributions, they represent the sums over the areas of all constituent Lorentzian components.

Figure 5 shows that the intensity of the intercalated Fe²⁺ component decreases by a factor of 15 between 4.2 and 284 K, where it is just barely discernible in the Mössbauer pattern. The intensity of the spectrum of a thin (2.3 mg/cm²) Fe₂O₃ absorber measured under the same circumstances as the Fe²⁺ vermiculites decreases only by a factor of 1.3 between 4.2 and 250 K (Fig. 5), which includes the decrease

Table 2 Values (4.2 K) for the quadrupole splitting QS (mm/s), isomer shifts IS (mm/s), FWHM Lorentzian line widths *W* (mm/s), and relative areas *A* (%) of the structural and intercalated iron sites

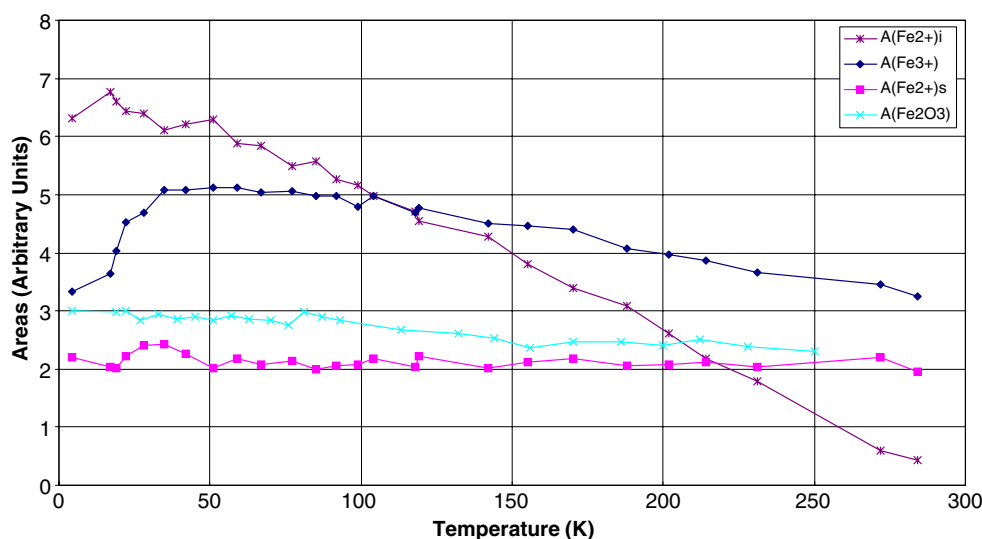
o-Fe³⁺, o-Fe²⁺, and i-Fe²⁺ for the Na forms and the Fe²⁺-intercalated vermiculites from Santa Olalla and Ojén

	o-Fe ³⁺				m-Fe ³⁺		o-Fe ²⁺				i-Fe ²⁺			
	QS (mm/s)	IS (mm/s)	<i>W</i> (mm/s)	<i>A</i> (%)	<i>A</i> (%)	QS (mm/s)	IS (mm/s)	<i>W</i> (mm/s)	<i>A</i> (%)	QS (mm/s)	IS (mm/s)	<i>W</i> (mm/s)	<i>A</i> (%)	
Na ⁺ —Santa Olalla	1.09	0.24	0.43	46.9	48.9	2.76	1.01	0.25	4.4	—	—	—	—	
Fe ²⁺ —Santa Olalla	0.96	0.24	0.77	21.2	10.3	2.82	1.12	0.25	18.6	3.31 ^a	1.15	0.37	49.9	
Calc. Santa Olalla				44.5				4.5				49.5		
Na ⁺ —Ojén	1.11	0.28	0.73	42.0	42.8	2.76	1.03	0.25	15.2	—	—	—	—	
Fe ²⁺ —Ojén	0.99	0.24	0.79	32.0	8.1	2.74	1.06	0.25	19.0	3.36 ^a	1.16	0.34	40.9	
Calc. Ojén				48				19				33		

For the magnetically split Fe³⁺ components (m-Fe³⁺), only the total area *A* is given. The calculated contents of the individual components were obtained as described in the text. Typical errors of QS, IS, and *W* are in the order of 0.01 mm/s; the typical error of the *A* is in the order of 0.5 percentage points

^a As discussed in the text, the asymmetry of the quadrupole doublet indicates that the sign of the electric quadrupole interaction is negative; here only the magnitude is given

Fig. 5 Temperature dependence of the areas of the various iron sites ($o\text{-Fe}^{3+}$, $o\text{-Fe}^{2+}$ and $i\text{-Fe}^{2+}$) in the Mössbauer spectrum of the Fe^{2+} exchanged Santa Olalla vermiculite. For comparison the area of a $2.3 \text{ mg/cm}^2 \text{ Fe}_2\text{O}_3$ absorber is also shown



of the f -factor of the source. The intensity of the structural Fe^{2+} component decreases hardly at all, which may be an artefact of the fitting procedure arising from the incomplete separation of the structural and the intercalated Fe^{2+} in the Mössbauer patterns, which causes some uncertainty in the relative intensities. The electric quadrupole splitting of the intercalated Fe^{2+} decreases from 3.36 mm/s at 4.2 K to 3.00 mm/s at 284 K , while to isomer, shift increases slightly from 1.15 to 1.20 mm/s , presumably because of a slightly different temperature dependence of the second-order Doppler shifts of the source and the absorber.

The intensity of the Fe^{3+} component increases by a factor of 1.56 when the temperature is lowered from 284 to 40 K , more strongly than that of the structural Fe^{2+} and of Fe_2O_3 . Below 40 K , the intensity of the Fe^{3+} component drops again by about 35% (Fig. 5). The reason for this is that part of the ferric iron splits magnetically at temperatures below 40 K , presumably because of slow paramagnetic relaxation, although one cannot exclude that there are iron-rich domains that order magnetically at low temperatures. Since the temperature dependence of the Mössbauer patterns was measured within a velocity range of about 4 mm/s only, the magnetically split component largely escapes detection in these measurements, which leads to a decrease of the intensity of the remaining Fe^{3+} quadrupole pattern.

The observed quadrupole splitting for the intercalated Fe^{2+} site is in good agreement with the values given by Helson and Goodman [7] and Goodman et al. [8] and Charlet and Tournassat [12] and assigned to the Fe^{2+} hexaaquo complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$. Such a Fe^{2+} site in the interlayer space has also been observed at 4.2 K but not at ambient temperature in the Fe^{3+} intercalated Ojén vermiculite and the Wyoming smectite after reduction with pyrrole [9].

The intensities of the individual components in the spectra of the Fe^{2+} exchanged vermiculites can be compared with those expected from composition as given the

formulas in the experimental part of this article, assuming that the interlayer Mg^{2+} present in the original vermiculites was replaced completely by Fe^{2+} . The relative intensities calculated in this way are given in Table 2. A comparison with the intensities observed in the Mössbauer patterns can be made assuming that the f -factors of all components are equal. For the structural iron, this assumption seems justified, even though the Fe^{2+} tends to have slightly smaller f -factors than the Fe^{3+} [27, 28]. The strong temperature dependence of the f -factor of the intercalated iron suggests that it has also a smaller f -factor at 4.2 K , but we will neglect this in the following discussion.

At a first glance, the expected and observed amount of intercalated Fe^{2+} agrees very well for Fe^{2+} Santa Olalla vermiculite, indicating a complete ion exchange, whereas for the Fe^{2+} Ojén vermiculite, the experimental value for $i\text{-Fe}^{2+}$ is substantially higher than the expected one.

The most striking effect is a change in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio within the octahedral sheet in both vermiculites, i.e., a substantial increase of the amount of structural Fe^{2+} and a concomitant decrease of the amount of structural Fe^{3+} . The reduction of structural Fe^{3+} to Fe^{2+} is connected with an increase of the layer charge and would lead, consequently, to a change of the cation exchange capacity. An increase of the layer charge in the Ojén vermiculite has been observed recently after ultrasound-induced reduction in water [23], but in the case of the Fe^{2+} loading, the susceptibility for reduction seems to be stronger for the Santa Olalla vermiculite.

In the present case, only the intercalated Fe^{2+} or the Fe^{2+} in the aqueous solution can act as the reducing agent. If the intercalated Fe^{2+} is the reducing agent, one would expect Fe^{3+} to form in the interlayer space. This could indeed be the case since the temperature dependence of the Fe^{3+} component in the Mössbauer spectra (Fig. 5) indicates the presence of an intercalated Fe^{3+} species that is more weakly bound than the structural Fe^{3+} . With some Fe^{3+} present in

the interlayer space, the relative amount of intercalated Fe^{2+} becomes higher than expected from the composition for both of the vermiculites.

An explanation for the unexpectedly high amount of intercalated Fe^{2+} could be that some iron left the octahedral sheet. This is not uncommon, since it is known that structural iron can be lost after reduction (e.g. [16, 18]).

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