

MÖSSBAUER AND INFRARED STUDY OF HEAT-TREATED NONTRONITE

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Abstract—The Mössbauer and infrared spectra of Li- and Rb-saturated nontronites from Washington, USA (SWa-1), heat treated at different temperatures, were measured. The Mössbauer results show that diffusion of Li⁺ into the 2:1 layer by heat treatment at 250–300°C does not affect the magnetic hyperfine interactions of the octahedral iron centers. In contrast, significant changes were observed by calcination at temperatures >300°C for Li-saturated nontronites. The main features of the Mössbauer spectra recorded at different temperatures reveal superparamagnetic behavior with a blocking temperature of ~5 K. The superparamagnetic behavior is related to small magnetic domains created by partially broken Fe-O-Fe bonds upon heat treatment. The infrared spectra of Li-rich nontronite, heat treated at 300°C, show changes attributed to Li migration into the hexagonal cavities. Heating to higher temperatures, produced changes in the spectra of the Li- and Rb-saturated nontronites owing to the dehydroxylation of the layer structure. The dehydroxylation process begins with the loss of OH groups in the FeOHFe bridges and is completed with the disruption of the Al-O bonds at >600°C.

Key Words—CMS Clay SWa-1, Dehydroxylation, Infrared Spectra, Lithium Migration, Mössbauer Spectra, Nontronite, Superparamagnetic Behavior.

INTRODUCTION

Nontronite, The Clay Minerals Society Source Clay, SWa-1, from Grant County Washington, USA, with the structural formula: $\text{Si}_{7.30}\text{Al}_{0.70}(\text{Al}_{1.06}\text{Fe}_{2.73}\text{Mg}_{0.26})\text{O}_{20}(\text{OH})_4$ (Goodman *et al.*, 1976; Goodman, 1978), differs from other nontronite samples in that it does not contain iron in the tetrahedral sheet. The lack of tetrahedral iron makes for an ideal system for magnetic studies of iron in a two-dimensional environment where iron is present in the octahedral sheet only.

SWa-1 orders antiferromagnetically only below 2 K, although its paramagnetic Curie temperature is ~20 K (Ballet and Coey, 1982). Coey *et al.* (1984) attributed this very low ordering temperature to a high degree of frustration in the antiferromagnetic interactions resulting from the random distribution of trivalent iron among the *cis* and *trans* positions of hydroxyl groups in the octahedral sites. Such a distribution produces the formation of the magnetic moments in triangles (or other odd-numbered rings) which, in the case of antiferromagnetic interactions, “frustrates” the magnetic moments because a magnetic moment can not be simultaneously antiferromagnetically coupled to two moments which are also antiferromagnetically coupled (Ballet and Coey, 1982; Coey *et al.*, 1984). This explanation seems to be in contradiction with evidence from selected-area electron diffraction, Mössbauer spectroscopy, and X-ray diffraction studies suggesting that nontronites from different sources are centrosymmetric, which implies that the *trans* octahedral sites are vacant and therefore all octahedral iron atoms occupy the *cis* sites (Mering and Oberlin, 1967; Besson *et al.*, 1982; Tsipursky and Drits, 1984; Drits 1987; Sakharov *et al.*, 1990; Goodman, 1978). In a centrosymmetric environment, the undesired triads of three

opposing superexchange interactions are not possible and therefore, long-range magnetic ordering can be achieved rather easily, as is the case for ferripyrophyllite with a Néel temperature (T_N) of ~18 K (Coey *et al.*, 1984). However, as noted by Guggenheim *et al.* (1983), the determination for a centric or acentric structure is better based on piezoelectric or second harmonic generation (SHG) data.

Lear and Stucki (1990) in a thorough analysis of the magnetic properties and site occupancy of iron in several nontronite samples showed, by computer simulation, that occupancy of the *trans* site at as low as 13% can prevent long-range magnetic order. They suggested that trivalent iron may be accommodated in *trans* sites either instead of the *cis* site or in addition to the *cis* site to produce a trioctahedral domain. Lear and Stucki also discussed the effect of magnetic dilution caused by the presence of diamagnetic Al³⁺ or Mg²⁺ in the octahedral sheet which would prevent large magnetic domains. Computer simulations revealed that random replacement of octahedrally coordinated Fe³⁺ cations with diamagnetic ions can produce sufficient dilution that magnetic domains are reduced to insignificant sizes. For a structure of type A_xB_{1-x} , where A is a paramagnetic ion and B is diamagnetic, long range magnetic ordering requires that $x \geq 0.67$. Because $x = 0.67$ in SWa-1, the lack of magnetic ordering even at 4.2 K is possibly caused by the effect of magnetic dilution. Attempts to modify the local environment of iron in the octahedral sheet, and therefore the magnetic ordering of the mineral, were made by pillaring with iron or aluminum polyoxo cations (Gangas *et al.*, 1985, 1988).

Another way to modify the electronic environment at the iron site is by diffusion of small interlayer cat-

ions, such as lithium or magnesium, to positions near the layer charges. Such diffusion may be possible by heating the mineral at 200–300°C for a few hours (Hofmann and Klemen, 1950). Possible compensation of the local electron density can, in turn, affect magnetic interactions. Also, the environment at the octahedral sites can be modified by thermal treatment above 300°C where dehydroxylation reactions may occur. These reactions may induce modifications in the immediate environment about the iron centers, such as a change from octahedral coordination to five-coordination (Heller-Kallai and Rozenson, 1980) or the creation of iron-rich clusters. Migration of Fe^{3+} into vacant octahedral sites upon heating was demonstrated also by Tspursky and Drits (1984). In the present work, we study the effect of Li and Rb diffusion (after dehydration of the mineral) on the magnetic properties of the octahedral iron nontronite. We also examine if these magnetic properties are affected by thermal treatment at temperatures above 300°C. We present detailed Mössbauer spectra of Li-exchanged and heat-treated SWa-1 nontronite. To follow the thermally induced dehydroxylation of the Li-rich nontronite, we supplement the Mössbauer results with detailed Fourier transform infrared (FT-IR) measurements.

MATERIALS AND METHODS

The <2- μm fraction of nontronite SWa-1 was used. The clay was Na^+ saturated, centrifuged to remove excess alkali salt, diluted with water, and then the upper half portion of the resulting suspension was collected. This is denoted as the “untreated clay”. For the removal of the iron oxides, the material was treated according to Mehra and Jackson (1960). Li^+ - and Rb^+ -exchanged samples were prepared by immersing the nontronite in 1 M solutions of lithium and rubidium chlorides, respectively. Cation exchange was completed by washing and centrifuging four times with the appropriate solutions. The samples were washed with deionized water, transferred into dialysis tubes to obtain Cl^- -free nontronites and then dried at room temperature. Thin films for infrared-absorption measurements were prepared, using appropriate suspensions of Li- and Rb-rich nontronites, which were deposited on aluminum foil and then dried in air. Resulting films and powders were heated at various temperatures for 24 h.

Infrared spectra were measured with a Nicolet 550 infrared spectrometer in the region 400–4000 cm^{-1} equipped with a DTGS detector. Each spectrum was the average of 100 scans collected at 2- cm^{-1} resolution. The nontronite films were analyzed without any substrate. Mössbauer spectra were recorded with a conventional constant-acceleration spectrometer and a $^{57}\text{Co}(\text{Rh})$ source. The parameters were obtained by a *least-squares* program assuming Lorentzian line shapes. Relative errors were less than $\pm 0.01 \text{ mm s}^{-1}$. Temperatures below 4.2 K were determined by vapor-

pressure thermometry. The system was calibrated with an iron-foil absorber. All isomer-shift values reported here are with respect to iron at room temperature.

RESULTS AND DISCUSSION

Mössbauer spectra

SWa-1 nontronite contains iron oxides and iron-oxyhydroxide impurities on very fine particles at concentrations below detection by conventional mineral analysis. These impurities must be removed to avoid misinterpretations in the Mössbauer spectra. Mössbauer spectroscopy may detect their presence, but because of the nanosize dimensions of the grains (Dickson and Cardile, 1986), the oxides are usually supermagnetic at 80 K whereas their presence as magnetic sextets in the spectra is obvious at 4.2 K. Treatment of nontronite according to Mehra and Jackson (1960) removes all partially crystalline iron-oxide species. Sodium dithionite used in this treatment causes partial reduction of structural Fe^{3+} to Fe^{2+} . However, reoxidation by air is easily obtained by air-drying and thus the process is reversible (Russell *et al.*, 1979; Komadel *et al.*, 1990). All spectra discussed are free of iron oxides based on 4.2-K Mössbauer spectra.

The Mössbauer spectrum at 4.2 K for Li^+ -saturated nontronite is shown in Figure 1a. The intense, unresolved doublet with isomer shift $\delta = 0.448 \text{ mm s}^{-1}$ is attributed to Fe^{3+} in octahedral coordination. The linewidth of the unresolved doublet is very broad, 0.69 mm s^{-1} , with respect to the instrumental linewidth (0.24 mm s^{-1}) suggesting that the iron sites have slightly different local environments, which cause this broadening. Charge defects near the iron sites may cause this inequality of the iron sites. Such defects may be related to empty octahedral sites, divalent octahedral neighbors, and/or trivalent cation substitution in the tetrahedral sheets. These substitutions produce an excess negative charge, which affects the surrounding anions and which causes different electric-field gradients at the iron sites (Coey *et al.*, 1984). The distribution of these cations in dioctahedral smectites has been modeled previously based on the number and relative intensities of the observed Mössbauer doublets (*e.g.*, Drits *et al.*, 1995).

Figure 1b shows the 4.2-K Mössbauer spectrum of Li-rich nontronite calcined at 300°C for 24 h. No indication of magnetic hyperfine splitting among the iron centers is observed, and thus there is no observable effect on the magnetic properties by possible diffusion of Li cations into the structure. In contrast, significant changes in the Mössbauer spectra were observed for samples heated at $>300^\circ\text{C}$; see Figure 1c for Li-rich nontronite heated at 500°C and Figure 2 for a Li-rich nontronite calcined at different temperatures. The spectrum in Figure 1c was recorded at 80 K and it was fitted with two quadrupole doublets.

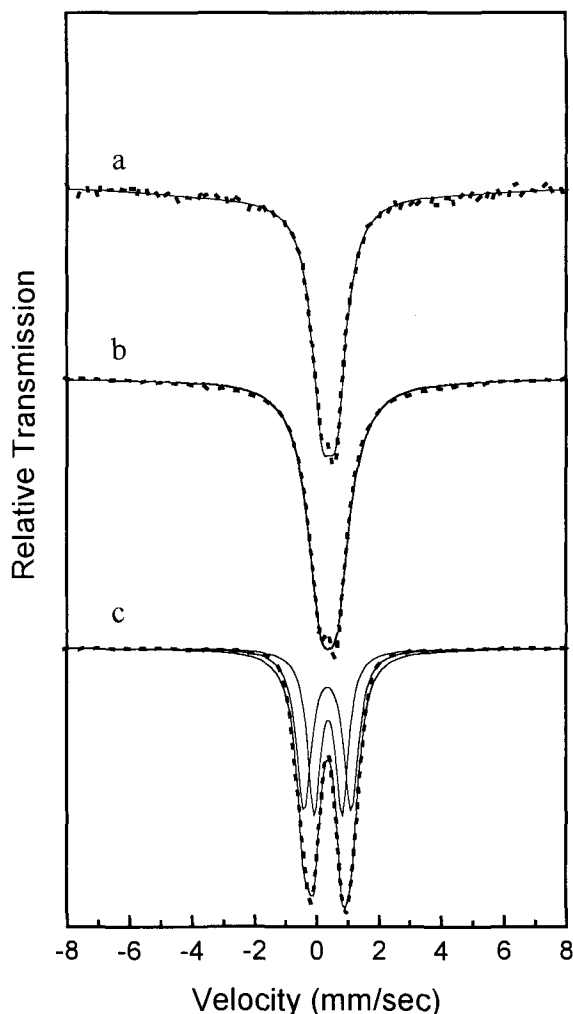


Figure 1. Mössbauer spectra at 4.2 K of Li-rich nontronite: (a) air-dried, (b) heat treated at 300°C for 24 h, and (c) Mössbauer spectra of Li-rich nontronite heat treated at 500°C for 24 h recorded at 80 K.

The isomer shifts and quadrupole splittings $\delta_1 = 0.47$ mm s⁻¹, $QS_1 = 1.52$ mm s⁻¹ and $\delta_2 = 0.49$ mm s⁻¹, $QS_2 = 0.90$ mm s⁻¹ agree well with those reported by Heller-Kallai and Rozenon (1980) for Ca²⁺ and Mg²⁺-exchanged heat-treated SWa-1. These authors suggested that the two doublets are related to Fe³⁺ occupancy of *trans* and *cis* positions in the untreated mineral, which upon dehydroxylation produces iron in five-fold and six-fold coordination sites with different quadrupole splittings. However, as noted above, the centrosymmetric nature of nontronites is incompatible with Fe³⁺ occupancy of the *trans* sites. Tshipursky and Drits (1984), based on electron-diffraction patterns, suggested that some Fe³⁺ ions migrate to *trans* sites during dehydroxylation of nontronites. Therefore, the spectra of heat-treated nontronites may show two Fe³⁺ doublets, one relating to

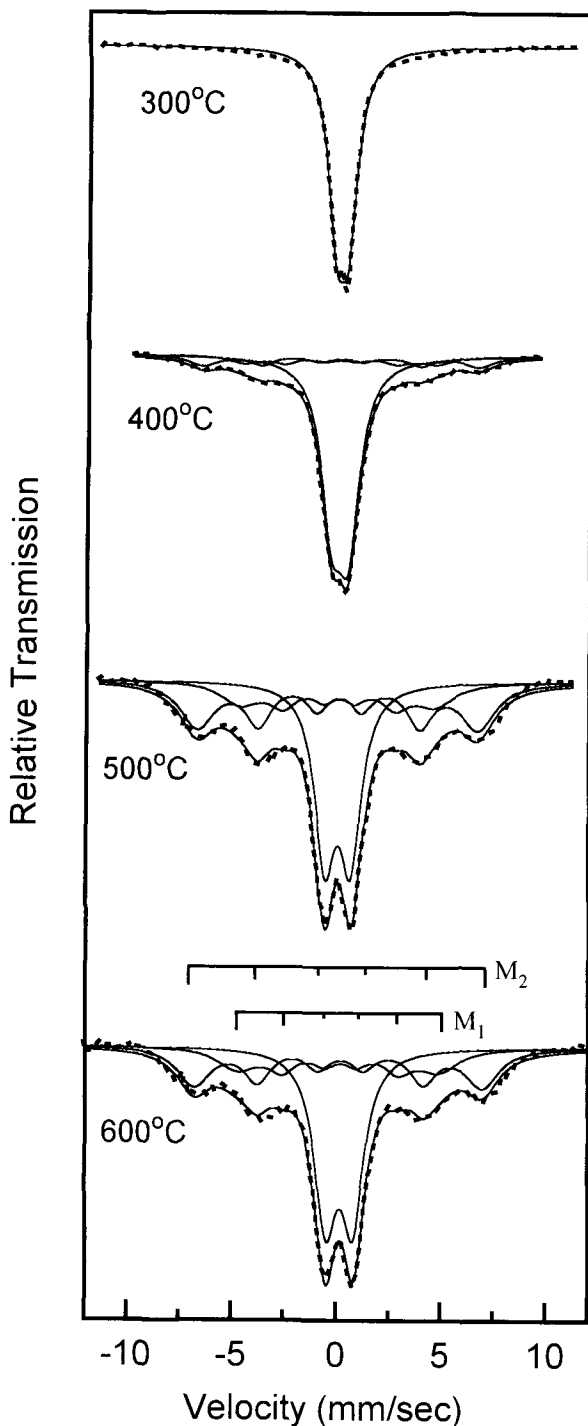


Figure 2. Mössbauer spectra of Li-rich nontronite at 4.2 K for 24 h heat treated at the temperatures indicated.

Fe³⁺ in five-fold coordination from the dehydroxylation of the *cis* sites and the other from *trans* sites of Fe³⁺. The dehydroxylate structure affects significantly the exchange interactions among the iron centers,

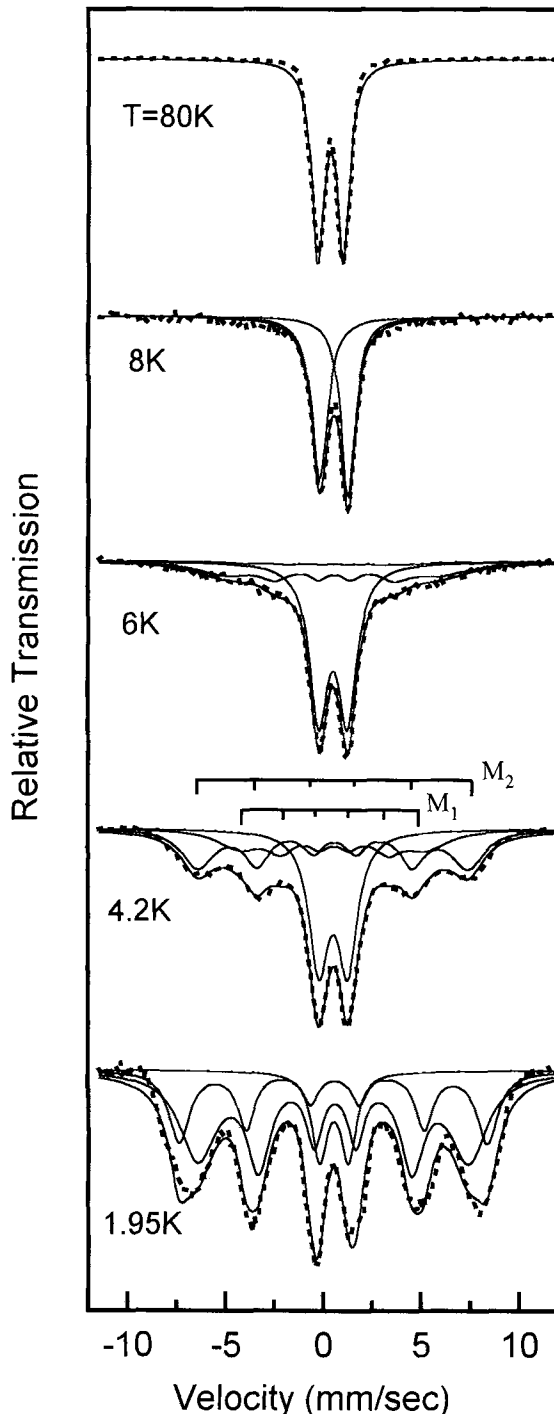


Figure 3. Mössbauer spectra for a Li-rich nontronite sample heat-treated at 500°C for 24 h and recorded at the temperatures indicated.

as is clearly shown by the well-developed magnetic hyperfine sextets in a series of spectra recorded at 4.2 K for Li-rich nontronite calcined at different temperatures (Figure 2). The spectra in Figure 2 show that

the contribution of magnetic hyperfine interactions increases with increasing calcination temperature.

Mössbauer spectra of the Li-rich nontronite heated at 500°C were measured at different temperatures (Figure 3). The salient features of these spectra are: 1) At <10 K, an asymmetric broadening develops in the doublet. At ~6 K, magnetic hyperfine structure appears together with a paramagnetic doublet. The hyperfine pattern is clearly developed at 4.2 K. 2) As the temperature of measurement is lowered, the magnetic component increases at the expense of the paramagnetic quadrupole doublet. 3) Considerable changes occur in the spectra between 4.2–1.92 K. The quadrupole doublet represents 13% of the area of the 1.95-K spectrum. However, even at 1.95 K, the magnetic moments of the magnetic phase are not entirely blocked (see discussion below), and therefore a spectrum with fully developed hyperfine splitting is not observed.

These characteristic features of the Mössbauer spectra indicate superparamagnetic behavior for the heat-treated Li-rich nontronites (Gangas *et al.*, 1973; Mørup *et al.*, 1980). In general terms, in superparamagnetism, all spin vectors of iron atoms within a particle point in the same direction, but thermal fluctuations cause this direction to vary with a frequency depending upon the particle size, anisotropy energy, and temperature. If this frequency is greater than the Larmor precession frequency of the ^{57}Fe nucleus (10^8 s^{-1}), the magnetic hyperfine splitting collapses to give a single line or a doublet if a quadrupole interaction is present. In the opposite case of slow relaxation of the iron spins, a complete magnetic hyperfine splitting is observed. However, because of particle-size distribution in a sample, the spectra typically consist of a doublet owing to small particles with a short relaxation time and a sextet owing to larger particles with longer relaxation times. As the temperature increases, the spin-relaxation frequency increases owing to thermal fluctuation, resulting in an increase of the area of the “paramagnetic” doublet as the area of the “magnetic” sextet decreases, because larger particles occur in the fast-relaxation limit. In summary, particles below a certain diameter, typically 10 nm for Fe, become a single domain and above a certain temperature these particles exhibit paramagnetic behavior, but with a magnetic moment which may be as large as that of 10^5 atoms coupled ferromagnetically. The temperature at which the two components become equal is called the blocking temperature, T_B . With the exception of very small synthetic-Fe particles (Bødker *et al.*, 1998), all systems studied thus far have characteristic blocking temperatures in the range of ~50–150 K.

The present results suggest that the system has a T_B of ~5 K. If this system consists of small particles, then the average particle size is near 1–2 nm (assuming a typical anisotropy constant for the iron oxides) which

Table 1. Spin-relaxation rate f (in 10^8 s^{-1}) and magnetic-order parameter n for the two magnetic components M_1 and M_2 . The relative abundance of the magnetic components and the paramagnetic component P is given by A.

T(K)	M_1			M_2			P
	f	n	A(%)	f	n	A(%)	A(%)
6.0	2.2	0.61	31	5.8	0.47	5	64
4.2	2.0	0.81	37	4.6	0.56	24	39
1.95	0.7	0.93	28	1.3	0.79	29	13

is not physically reasonable. Instead, we suggest that the superparamagnetic effects are related to iron-rich layers of the nontronite structure. Each layer may be a network of Fe-O-Fe exchange interactions which are interrupted by vacant octahedral sites or non-magnetic ions, *e.g.*, Mg, in the octahedral sheet. Heat treatment, dehydroxylation, and subsequent iron migration to empty *trans* positions (Tsipursky and Drits, 1984) results in the formation of small (<3–5 nm) magnetic-iron clusters, which behave superparamagnetically at low temperatures.

The spectra were analyzed using a spin-relaxation program based on a model developed by van der Woude and Dekker (1965) for ordered spin systems. In this program, the hyperfine magnetic field occurs at random between the values, $+H$ and $-H$ along the z axis, the major axis of the electric-field gradient tensor. The Hamiltonian for the nucleus under these conditions is:

$$H = H_0 + \epsilon(3I_z^2 - I^2)/3 + g\mu_B H_z f(t) \quad (1)$$

where H_0 is the static Hamiltonian, ϵ is the electric-field gradient at the nucleus, I and I_z are the nuclear spin and its projection along the z axis, respectively, g is the gyromagnetic ratio of the nucleus and μ_B is the nuclear Bohr magneton, H is the hyperfine field and $f(t)$ is a random function of time which takes on the values ± 1 . This Hamiltonian describes the nucleus in the presence of relaxing-cluster magnetization. We approximated the size distribution of the clusters with two magnetic components, M_1 and M_2 and one paramagnetic component P. The former simulate clusters relaxing with long but different relaxation times and the latter simulates small clusters relaxing with short relaxation time (fast limit) giving rise to a paramagnetic doublet with splitting of 1.40 mm s^{-1} . In the fitting procedure, the hyperfine field H was kept constant at a (typical) value for an Fe^{3+} of $S = 5/2$ ion (500 kOe) and the value of the isomer shift, δ , as determined from the spectrum at 78 K for both components was $\delta = 0.45 \text{ mm s}^{-1}$, with respect to Fe. A broad linewidth was assumed ($\sim 0.8 \text{ mm s}^{-1}$) for the different iron environments. The results are given in Table 1. Note that fits of similar quality can be achieved by employing a static model with many components. Since the present system is two dimensional and there is no estimate of the magnetic-anisotropy constant and

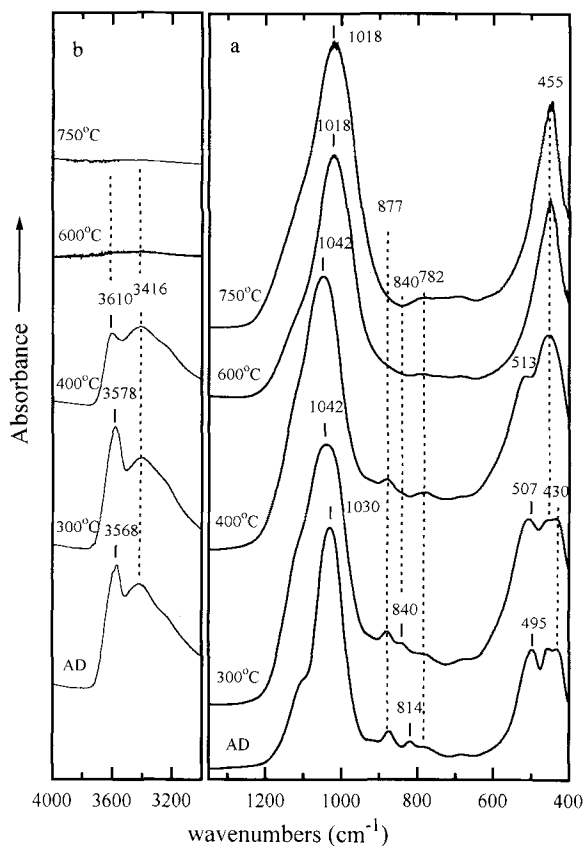


Figure 4. Infrared spectra of Li-rich nontronite air-dried (AD) and heat treated for 24 h at the temperatures indicated: (a) low frequencies (b) high frequencies.

the pre-exponential factor, τ_0 , the size of the magnetic islands cannot be evaluated. However, we suggest intuitively that these iron-loaded regions are of ultrafine size with an average diameter not exceeding 2 nm. Na- and Rb-exchanged SWa-1 nontronites showed similar behavior, with low-temperature Mössbauer spectra after calcination at 500°C comparable to Li-rich nontronite.

Infrared spectroscopy

The infrared spectra of air-dried and heat-treated Li-rich nontronite films are shown in Figure 4. The spectrum of air-dried nontronite exhibits absorption maxima in three regions: (1) the $950\text{--}1200\text{-cm}^{-1}$ region features the stretching vibrations of Si-O-Si and Si-O-M ($M = \text{Fe}^{3+}, \text{Al}^{3+}, \text{Mg}^{2+}$), (2) the $750\text{--}950\text{-cm}^{-1}$ region, in which the librations of the OH groups in the octahedral sheet occur, and (3) the region $<600 \text{ cm}^{-1}$, where the bending vibrations of Si-O-Si and Si-O-M appear. In region (2), the band at 877 cm^{-1} was assigned to the libration of the AlFeOH group (Serratosa, 1960; Goodman *et al.*, 1976), the band at 814 cm^{-1} to the libration of FeFeOH , and the third band

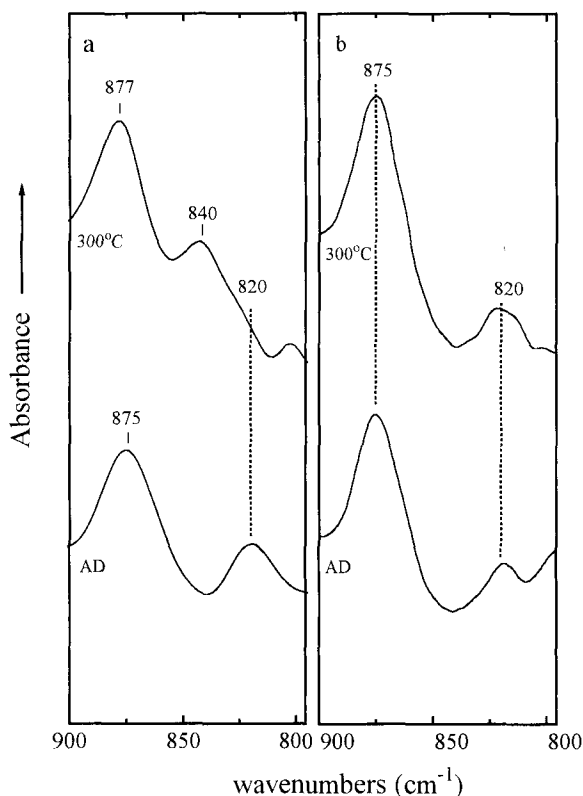


Figure 5. Infrared spectra of (a) Li-rich nontronite and (b) Rb-rich nontronite films, air-dried (AD) and heat treated for 24 h at 300°C.

at 782 cm^{-1} to the libration of FeMgOH groups (Seratossa, 1960; Stubican and Roy, 1961). In the absorption of the 782- cm^{-1} band, a contribution from the Si-O vibrations is also possible (Russell *et al.*, 1979). Three peaks occur also in region (3); the peaks at 495 and 430 cm^{-1} were attributed to the vibrations of Si-O-Fe, and the third at 455 cm^{-1} to the Si-O-Si bending vibrations (Goodman *et al.*, 1976).

As shown in Figure 4a, heat treatment of the Li-rich nontronite sample caused significant spectral changes. Heating the sample at 300°C caused a shift in frequency of Si-O stretching from 1030 to 1042 cm^{-1} and increased the bandwidth. In region (2) the peak frequency of the FeFeOH libration was shifted from 814 to 840 cm^{-1} . Region (3) seems to be unaffected by heat treatment. Because nontronite has a charge deficiency mainly in the tetrahedral sheets, most interlayer lithium ions are expected to move towards the negatively charged, hexagonal rings. Lithium, therefore, will enter the hexagonal cavities and perturb the vibrations of Si-O bonds and OH groups. The migration of interlayer lithium cations in montmorillonites has been correlated with changes in the Si-O vibrational spectrum after heat treatment (Madejová *et al.*, 1996; Karakassides *et al.*, 1997). On the other hand, the in-

teraction of Li^+ ions with the OH groups is expected to be weaker than where Li^+ migrates into octahedral vacancies as in the case for montmorillonites. This may explain the smaller effect of the lithium ions on the AlFeOH librations in heat-treated Li-rich nontronite, where the frequency of the AlFeOH libration remained unchanged after heating (Figure 4a). In contrast, the possible presence of lithium cations in the hexagonal cavities affects the librations of FeFeOH because of the weaker Fe-O bond and the higher degree of deformation of the (Fe-O) electron cloud. The effect of Li^+ diffusion on OH vibrations in the air-dried and heat-treated Li- and Rb-exchanged nontronites is shown more clearly in Figure 5. Li-rich nontronite exhibits significant changes after heating, whereas Rb-rich nontronite remains similar to that before calcination. Because Rb^+ ions are too large to penetrate into the hexagonal cavities, we conclude that Li^+ migration is responsible for the observed changes in the OH vibrations. Another explanation for the diminution of the FeFeOH band at 814 cm^{-1} after heating natural nontronites (with Mg^{2+} and Ca^{2+} as interlayer cations) is based on proton migration from the FeFeOH bridges (Heller-Kallai and Rozenson, 1980).

The infrared spectra of air-dried and heat-treated nontronites in the frequency region between 2500–4000 cm^{-1} are presented in Figure 4b. The spectrum of air-dried nontronite is characterized by a broad absorption at 3416 cm^{-1} attributed to adsorbed water, and a relatively narrow band at 3568 cm^{-1} attributed to stretching vibrations of structural OH groups (Farmer and Russell, 1964). The intensity of the broad band at 3416 cm^{-1} decreases upon heating of nontronite at 300°C, owing to the removal of interlayer H_2O , whereas the band at 3568 cm^{-1} , although at higher frequencies, retains the same intensity. This result implies that the number of structural OH groups does not alter significantly, and therefore dehydroxylation of nontronite begins at higher temperatures.

Heat treatment (Figure 4) of the sample at 400°C reduces significantly the intensity of the band at 840 cm^{-1} , which is assigned to FeFeOH librations, whereas a smaller decrease in the intensity of the band at 877 cm^{-1} resulting from AlFeOH librations is observed. The stretching band resulting from structural OH at 3578 cm^{-1} shifts to 3610 cm^{-1} and decreases in intensity at higher temperatures. According to Madejová *et al.* (1996), this shift is attributed to the removal of FeFeOH or FeMgOH groups, which produce bands at lower frequencies. These groups contribute to the composite M-OH vibrational envelope. These spectral changes indicate that the dehydroxylation reaction occurs by 400°C. Small effects of heating on the AlFeOH libration band (Figure 5) suggest that dehydroxylation starts mostly with the hydroxyl-groups FeFeOH clusters.

At lower frequencies of the spectrum, the intensities of the bands at 515 and 430 cm^{-1} decrease owing to the bending vibrations of Si-O-Fe. This behavior may occur from the destruction of Si-O-Fe connections upon dehydroxylation. As discussed above, dehydroxylation transforms the octahedral iron to a five-fold coordinated geometry, which minimizes the number of Si-O-Fe bridges.

With increasing temperatures from 400 to 750°C, the intensities of all bands decreased, with weak features at 877, 840 (Figure 4a), and 3610 cm^{-1} (Figure 4b). The intensity loss indicates a small number of remaining structural OH groups. These weak bands vanished at 750°C, suggesting the destruction of the nontronite structure.

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