

NUCLEAR MAGNETIC RESONANCE AND X-RAY PHOTOELECTRON SPECTROSCOPIC INVESTIGATION OF LITHIUM MIGRATION IN MONTMORILLONITE

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Abstract—When Li-saturated montmorillonite is heated to 200–300 °C, the Li ions migrate from interlayer positions to sites in the layer structure. However, the identity of these sites has not been clearly established. Here we have investigated the migration of Li ions in montmorillonite, after heat treatment at 250 °C, using chemical and instrumental analyses. The latter include X-ray diffractometry (XRD), ⁷Li-nuclear magnetic resonance (NMR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Heating causes a large reduction in cation exchange capacity (CEC) and an almost complete loss of interlayer expansion with glycerol as shown by XRD. Static and magic angle spinning (MAS) ⁷Li-NMR spectroscopy shows that the quadrupole coupling constant of Li increases markedly over the corresponding value for unheated Li-montmorillonite (where Li occupies exchange sites in the interlayer space) and for hectorite (where Li is located in the octahedral sheet). This would indicate that, in heated montmorillonite, Li occupies structural sites of low symmetry which, however, cannot be identified with octahedral vacancies in the layer structure as is commonly assumed. XPS shows that the binding energy (BE) for Li in unheated montmorillonite is comparable to that for other exchangeable cations. Heating broadens the Li 1s band and decreases the BE. The BE for Li in heated montmorillonite is significantly higher than that in either spodumene or lepidolite, where Li is known to occupy octahedral sites. The combined data suggest that heating induces Li to migrate from interlayer sites to ditrigonal cavities in the tetrahedral sheet, rather than into vacancies in the octahedral sheet, of montmorillonite.

Key Words—Lithium, Migration, Montmorillonite, NMR Spectroscopy, X-ray Photoelectron Spectroscopy.

INTRODUCTION

Hofmann and Klemen (1950) were the first to report that Li-saturated montmorillonite lost most of its exchange capacity after mild heating (<200 °C). As a result, the ability of the mineral to show interlayer expansion (swelling) in glycerol and water is greatly reduced (Greene–Kelly 1953a; Quirk and Theng 1960). The commonly accepted explanation for the Hofmann–Klemen effect is that heating induces the small Li ions to migrate from interlayer exchange positions to vacant octahedral sites within the layer structure. By this means the negative layer charge of montmorillonite, arising from isomorphous replacement of Al³⁺ by Mg²⁺ in the octahedral sheet, is largely neutralized (Jaynes and Bigham 1987). This hypothesis, however, has been called into question by Tettenhorst (1962) on infrared (IR) spectroscopic evidence. He suggested that heating caused Li to move only as far as the hexagonal—in reality, ditrigonal—cavities in the tetrahedral sheet. In following up this work, Calvet and Prost (1971) proposed that a fraction of the Li

might still be able to penetrate into the octahedral sheet. However, the observation by Greene–Kelly (1957) and Farmer and Russell (1967) that the loss of exchange capacity and interlayer expansion can, under certain conditions, be partially or wholly restored tends to support Tettenhorst's (1962) suggestion. More recently, Alvero et al. (1994) used a variety of solid-state analytical techniques to follow Li migration in montmorillonites. They found evidence to indicate that, in heated samples, the Li ions were indeed located in the ditrigonal holes of the tetrahedral sheet from where they could move back to interlayer (exchange) positions by hydrothermal treatment.

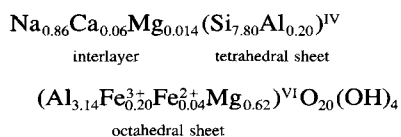
Nuclear magnetic resonance spectroscopy has been useful in assessing the coordination state and chemical environment of elements, notably Al and Si, in clay mineral structures (Lippmaa et al. 1980; Sanz and Seratosa 1984a, 1984b; Goodman and Chudek 1994). Similarly, XPS has provided valuable information on the bonding state of cations in, and the surface composition of, layer silicates and related structures (Seyama and Soma 1984, 1985; Soma et al. 1992; Paterson and Swaffield 1994). Gonzalez–Elipe et al. (1988), for example, were able to correlate the XPS binding energy shifts with the NMR chemical shifts for Al and

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Si in a range of layer silicates. Here we have used a combination of chemical and spectroscopic methods, including ^7Li -NMR spectroscopy and XPS, to investigate the migration of Li ions in heated montmorillonite, and to probe their location by comparing the data with those of other Li-bearing silicate minerals.

MATERIALS AND METHODS

The montmorillonite used was a sodium-rich specimen supplied by Kunimine Industries Co., Japan. The material is known and marketed as "Kunipia-F" or "KpF", and has the following structural formula (Iwasaki and Onodera 1995):



Li saturation was achieved by washing the clay 3 times with 1 M LiCl, centrifuging and removing excess electrolyte by dialysis against distilled water. The dialyzed material was freeze-dried and portions were heated in air at 250 °C (and in 1 instance at 450 °C) for 16 h using a muffle furnace. Synthetic hectorite was obtained from Topy Industries and purified by sedimentation–separation. The samples of spodumene (from Nuristan, Afghanistan) and lepidolite (from Governador Valadares, Minas Gerais, Brazil) were used as received.

The CEC of the Li-saturated montmorillonite, before and after heating, was determined by leaching with 1 M ammonium acetate at pH 7, washing with 90% ethanol, displacing the NH_4^+ with 1 M NaCl and measuring the amount displaced with an autoanalyzer (Blakemore et al. 1987). XRD was carried out by air-drying an aqueous suspension on a glass slide, spraying with an aerosol of 10% v/v glycerol, and scanning at a rate of 2 °2 θ min⁻¹ using a Philips PW1010 diffractometer and $\text{CoK}\alpha$ radiation (Whitton and Churchman 1987).

To obtain X-ray photoelectron spectra, the powdered clay was fixed by double-sided adhesive tape to a stainless steel sample holder, fitted to a manipulator through which liquid nitrogen was circulated in order to keep the sample cool and inhibit any subsequent movement of Li during analysis. The sample was subjected to $\text{AlK}\alpha$ radiation at 10 kV and 5 mA using a Vacuum Generators ESCALAB 5 instrument, accumulating the signals with a Laboratory Equipment Company data acquisition system. Binding energies were measured relative to the $4f_{7/2}$ line of Au at 84.0 eV (Seyama and Soma 1984). For Li 1s, the uncertainty in BE values is ± 0.1 eV.

Solid-state ^7Li -NMR spectra of the samples, packed in zirconia rotors, were obtained at room temperature using a Bruker MSL400 and a Bruker ASX200 spec-

trometer. The respective magnetic fields were 9.4 and 4.7 T and the Larmor frequencies were 155.51 and 77.78 MHz. Static spectra were measured using a single-pulse (SP) sequence with a pulse width of 1.5 and 1.0 μs , corresponding to $\pi/8$ pulse for solution, and a repetition time of 5 and 2 s, respectively. Magic angle spinning spectra were also recorded from samples spun at 4.0 and 6.0 kHz using the Bruker ASX200 equipment. Chemical shifts are expressed with respect to 1.0 M aqueous solution of LiCl, the higher-frequency side being positive.

RESULTS AND DISCUSSION

Cation Exchange Capacity and X-ray Diffractometry

The CEC of unheated Li-saturated montmorillonite was 94 cmol(+) kg⁻¹, appreciably less than the value of 115 cmol(+) kg⁻¹ given by the manufacturer for the original KpF clay. Iwasaki and Onodera (1995) reported a value of 110 cmol(+) kg⁻¹ for the Na form of KpF but did not provide experimental details. It would appear that mere freeze-drying of the Li form has induced some 20% of the Li ions to move from exchange sites to the layer structure. After heating to 250 °C, the CEC decreases to 22 cmol(+) kg⁻¹. This value is larger than might reasonably be accounted for by exchange from external crystal surfaces (Quirk and Theng 1960). That is, some Li ions from interlayer surfaces appear to have contributed to the CEC of the heated sample. These ions are presumably associated with interlayers that do not completely collapse on heating. The XRD pattern of heated Li-montmorillonite, described below, lends further support for this hypothesis.

Nevertheless, the bulk of the interlayer Li ions can no longer be displaced by NH_4^+ in solution. Thus, heating has caused Li to migrate from the interlayers into the structural framework of the mineral. Its location within the structure, however, cannot be ascertained from CEC measurements alone, since movement to either octahedral vacancies or ditrigonal cavities would render the Li nonexchangeable. In either case, irreversible layer collapse would occur as a result. In keeping with this hypothesis, the XRD pattern of heated Li-montmorillonite showed a strong basal reflection at 0.96 nm after glycerol treatment. A shoulder at 1.78 nm indicates that this collapse is not uniform, presumably because the layers within a crystal are irregularly superposed (Brown et al. 1978). By contrast, the XRD pattern of the unheated sample, after treatment with glycerol, showed an intense peak at about 1.78 nm with a sharp second-order reflection at 0.89 nm.

^7Li -NMR Spectroscopy

Figure 1 shows the static ^7Li -NMR spectra at 155.51 MHz of Li-montmorillonite, before and after heating at 250 °C, and of synthetic hectorite. The MAS and

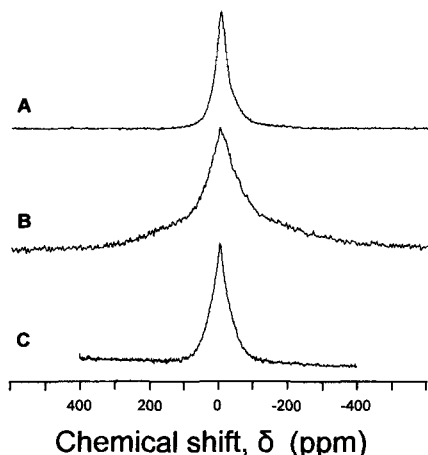


Figure 1. Static ${}^7\text{Li}$ NMR spectra measured at 155.51 MHz and ambient temperature for (A) unheated Li-montmorillonite; (B) Li-montmorillonite heated at 250 °C; (C) synthetic hectorite.

static ${}^7\text{Li}$ -NMR spectra of unheated and heated Li-montmorillonite, recorded at 77.78 MHz, are shown in Figure 2.

Under static conditions, the shape of the ${}^7\text{Li}$ line is influenced by chemical shift and dipole–dipole interactions, bulk magnetization from paramagnetic species (Fe) and quadrupole interaction. In the case of ${}^7\text{Li}$, the chemical shift interaction is small (Hayashi and Hayamizu 1990) while the effects of dipole–dipole interaction (involving such nuclear spins as ${}^1\text{H}$ and ${}^{27}\text{Al}$) and of paramagnetic species are averaged out under MAS. The quadrupole interaction can be divided into first- and second-order effects. Under MAS, first-order effects are averaged but the second-order interaction is only partially averaged, and can shift the position of the ${}^7\text{Li}$ line. The magnitude of this shift, ν_{QS} (in Hz), is given by Behrens and Schnabel (1982):

$$\nu_{\text{QS}} = -\frac{2}{5}a_{\text{Q}}\left(1 + \frac{\eta_{\text{Q}}^2}{3}\right) \quad [1]$$

$$a_{\text{Q}} = \frac{1}{12}\left[I(I+1) - \frac{3}{4}\right]\frac{\nu_{\text{Q}}^2}{\nu_{\text{L}}} \quad [2]$$

$$\nu_{\text{Q}} = \frac{3}{2I(2I-1)} \cdot \text{QCC} \quad [3]$$

where I is the nuclear spin quantum number (for ${}^7\text{Li}$ = 3/2), η_{Q} the asymmetry factor, ν_{L} the Larmor frequency and QCC the quadrupole coupling constant.

The narrow line width under MAS for both unheated (Figure 2B) and heated (Figure 2D) Li-montmorillonite indicates that the second-order quadrupole interaction is small. We were able to simulate the spectra obtained at the 2 magnetic fields, using the same parameters for the quadrupole interaction, and assuming that line shape was determined by the first-order quad-

Table 1. Isotropic chemical shift (δ), quadrupole coupling constant (QCC), asymmetry factor in the quadrupole interaction (η_{Q}) and line width of ${}^7\text{Li}$ MAS NMR spectra.

Sample	δ † (ppm)	QCC (kHz)	η_{Q}	Line width‡ (ppm)
Li-montmorillonite				
Unheated	0.1 ± 0.5	<10	—	10
Heated at 250 °C	-0.6 ± 0.5	70	0.7	10
Synthetic hectorite	-0.8 ± 0.1	20	0	2

† Relative to 1.0 M LiCl solution, determined by MAS NMR.

‡ Full width at half maximum.

rupole interaction. Results of the simulations together with the isotropic chemical shift values derived from the MAS spectra are summarized in Table 1.

Unheated Li-montmorillonite shows a featureless line shape (Figure 1A) because of line broadening by dipole–dipole interaction and bulk magnetization from paramagnetic species. The former effect is independent of the magnetic field (compare Figure 2A) whereas the latter is proportional to it. Thus, only the maximum possible value of the quadrupole interaction can be obtained, giving a QCC of 10 kHz at most (Table 1). Being surrounded by water molecules, interlayer Li ions in (air-dry) unheated montmorillonite apparently exist in a relatively high-symmetry environment. By contrast, heated Li-montmorillonite (Figure 1B) has a QCC of 70 kHz and the asymmetry factor in the

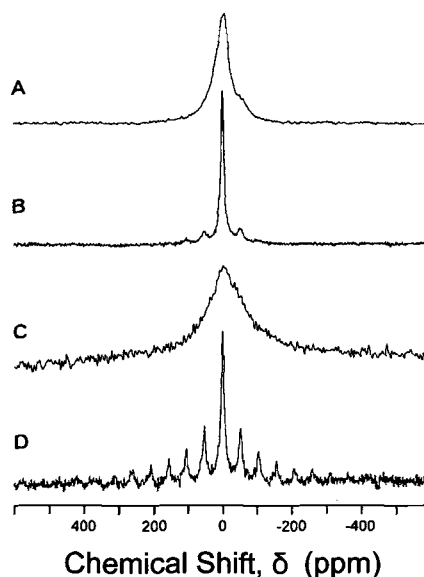


Figure 2. ${}^7\text{Li}$ NMR spectra measured at 77.78 MHz and ambient temperature for (A) unheated Li-montmorillonite, static sample; (B) unheated Li-montmorillonite, spun at the magic angle at 4.0 kHz; (C) Li-montmorillonite heated at 250 °C, static sample; (D) Li-montmorillonite heated at 250 °C, spun at the magic angle at 4.0 kHz.

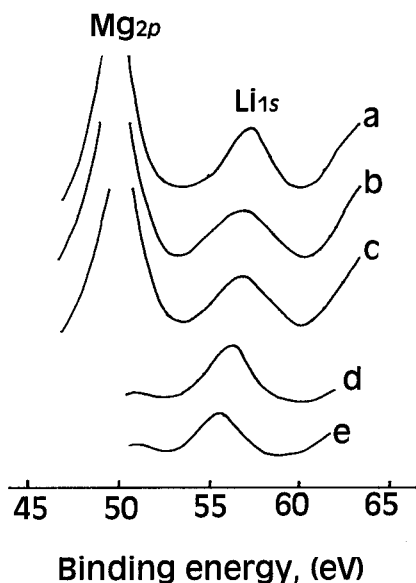


Figure 3. X-ray photoelectron spectra showing smoothed out Li 1s band shape for (a) unheated Li-montmorillonite; (b) Li-montmorillonite heated at 250 °C; (c) Li-montmorillonite heated at 450 °C; (d) spodumene; (e) lepidolite.

quadrupole interaction, η_Q , is 0.7 (Table 1). The contribution to line broadening of dipole–dipole interaction and bulk magnetization is estimated to be 3.9 kHz and 45 ppm, respectively. For hectorite (Figure 1C) the QCC is 20 kHz and η_Q is zero (Table 1), indicating that Li ions in the octahedral sheet of hectorite occupy sites of higher symmetry than those in heated montmorillonite. The contribution of dipole–dipole interaction, however, is the same as for heated Li-montmorillonite (3.9 kHz), but the effect of bulk magnetization is negligible since the synthetic hectorite used is almost free of structural Fe.

The large increase in QCC for heated Li-montmorillonite over both the unheated sample and hectorite indicates that, in heated montmorillonite, Li ions occupy sites of low symmetry which, however, cannot be identified with octahedral vacancies. It therefore seems reasonable to deduce that heating has induced the Li ions to migrate from interlayer positions to the ditrigonal cavities in the tetrahedral sheet. As a result, cation–cation repulsion in this sheet increases, leading to further distortion of the 6-membered oxygen rings (Bailey 1966). The suggested migration mechanism is supported by Alvero et al. (1994), who found that the Al^{IV} signal in the ²⁷Al MAS-NMR spectrum of Li-montmorillonite disappeared after heating the sample at 300 °C. These workers proposed that the Al tetrahedra were distorted by near-neighbor Li ions occupying ditrigonal cavities. This effect strongly increased the QCC, producing so broad a line as to become invisible.

Table 2. Li 1s BE and corresponding line shape, as measured by the FWHM parameter, for unheated and heated Li-montmorillonite, spodumene and lepidolite.

Sample	BE† (eV)	FWHM (eV)
Li-montmorillonite		
Unheated	57.0	2.9
Heated at 250 °C	56.7	3.7
Heated at 450 °C	56.7	3.6
Spodumene	56.1	2.7
Lepidolite	55.4	2.8

† The uncertainty is ± 0.1 eV.

As already mentioned, the second-order quadrupole interaction is not averaged under MAS, giving rise to line broadening of the order of $a_Q/2$. In the MAS spectrum of heated Li-montmorillonite at 77.78 MHz (Figure 2D), the contribution from this source is about 0.03 ppm, and hence can be neglected. The line widths in the MAS spectra of 10 ppm (Table 1) are considered to arise from the anisotropic part of the bulk magnetization. Since the content in paramagnetic (Fe) species is the same for unheated and heated Li-montmorillonite, the 2 samples have identical line widths.

X-ray Photoelectron Spectroscopy

Figure 3 shows the X-ray photoelectron spectrum of the Li 1s band for Li-montmorillonite, before and after heating at 250 and 450 °C, together with that for spodumene and lepidolite. The corresponding BE and full-width-at-half-maximum (FWHM) values are listed in Table 2. The data for hectorite are not included because the Li 1s line here is subject to interference from the adjacent Mg 2p line (Figure 3). This is due to the high Mg content and the larger Mg 2p binding energy of hectorite relative to montmorillonite. Thus, the Li 1s line for hectorite appears as a small shoulder (from 53.8 to 56.8 eV) on the Mg 2p line, making the determination of peak binding energy and line shape somewhat problematical. However, the estimated Li 1s binding energy of 55.3 eV for hectorite is close to that for lepidolite.

As might be expected, the binding energy for Li in unheated montmorillonite is comparable with that of other exchangeable cations in this mineral (Seyama and Soma 1984, 1985). Heating leads to a slight decrease in binding energy, and a marked broadening of the Li 1s band, consistent with Li ions moving from exchange sites into the structure. The (Li 1s)/(Si 2s) ratio by XPS, however, does not change appreciably on heating, varying by only $\pm 6\%$. The migration of Li from interlayer to structural sites has apparently little effect on the (Li/Si)_{XPS} ratio, and none would be expected.

What is significant is that the Li 1s binding energy for both spodumene and lepidolite, where Li occupies octahedral sites, is lower than that for heated Li-mont-

morillonite (Table 2). Equally noteworthy is that the Li 1s binding energy for spodumene is higher than that for lepidolite, presumably because the octahedral M_2 sites occupied by Li in spodumene are relatively distorted (Deer et al. 1992; Klein and Hurlbut 1993). In support of the NMR data, XPS indicates that the Li ions in heated montmorillonite are likely to be located in ditrigonal cavities of the tetrahedral sheet, rather than in vacant sites of the octahedral sheet.

CONCLUSIONS

Both CEC and XRD measurements confirm that Li-montmorillonite loses most of its exchange capacity, and fails to expand with glycerol, after being heated to 250 °C. These observations are consistent with the migration of Li ions from interlayer positions to structural sites, leading to an overall reduction in layer charge. However, the question of whether Li has moved to vacant octahedral sites, or become entrapped in the ditrigonal cavities of the tetrahedral sheet, cannot be ascertained from these measurements alone.

⁷Li-NMR spectroscopy and XPS are complementary in indicating that the chemical environment of Li in heated montmorillonite is very different from that of Li occupying octahedral sites as in hectorite and lepidolite. Our data also indicate that the positions occupied by Li ions in heated montmorillonite are sites of low symmetry. These sites may be identified with distorted ditrigonal cavities in the tetrahedral sheet, as suggested previously by Tettenhorst (1962) and Alvero et al. (1994).

The question arises why Li-beidellite retains its swelling capacity and CEC after heating (Greene-Kelly 1953a, 1953b), whereas Li entrapped in ditrigonal cavities of the (external) basal plane in heated muscovite is not exchangeable (Nishimura et al. 1995). Unlike montmorillonite, the layer charge in both minerals arises from substitution of Al for Si in the tetrahedral sheet (see structural formula), but the extent of isomorphous replacement in beidellite is only about half that in muscovite (Brown et al. 1978). It seems probable that Li migration in beidellite leads to little distortion of the ditrigonal cavities because there is less cation-cation repulsion as compared with montmorillonite. If so (and this point needs to be checked experimentally), the Li ions that move to these cavities by heating can rehydrate with relative ease. However, for muscovite with a tetrahedral layer charge deficit of 2 units per $O_{20}(OH)_4$ anionic group, the electrostatic attraction between Li and structural anion is presumably so large as to preclude rehydration of the entrapped Li.

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