

The thermal reactions of synthetic hectorite studied by ^{29}Si , ^{25}Mg and ^7Li magic angle spinning nuclear magnetic resonance

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Abstract

The thermal decomposition sequence of synthetic hectorite (Laponite CP) is shown by a combination of thermal analysis, X-ray powder diffraction and solid-state MAS-NMR to be very similar to that of the structurally related mineral talc, in transforming smoothly into the high-temperature product without the intervention of any crystallographically distinguishable intermediates. Loss of interlayer water at about 200°C causes little change in the hectorite basal spacing or in the ^{29}Si , ^{25}Mg or ^7Li MAS-NMR spectra; small but significant changes in the latter after heating to 600–650°C may however be related to the movement of interlayer Na^+ closer to the tetrahedral sheets, influencing the octahedral Li (but not the octahedral Mg). Dehydroxylation above 650°C disrupts the phyllosilicate structure into pyroxene units (MgSiO_3) and amorphous silica with distortion of the octahedral Mg sites, as evidenced by the broadening and loss of intensity of the ^{25}Mg resonance. The ^7Li MAS-NMR spectra suggest that the Li becomes mobile just prior to dehydroxylation, and may eventually be incorporated, together with the interlayer Na, in the siliceous phase.

INTRODUCTION

Hectorite is a trioctahedral 2:1 layer lattice silicate structurally related to talc, $\text{Mg}_6\text{Si}_8\text{O}_{20}(\text{OH})_4$, by substitution of some octahedral Mg by Li, with charge balance provided by the presence of interlayer cations (Na or Ca). These substitutions, which give the mineral its useful cation exchange properties, also influence its thermal behaviour, a study of which may thus provide interesting information on the factors controlling the thermal reaction mechanism in this and related smectite minerals.

The thermal decomposition sequence of synthetic hectorite is broadly

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similar to that of talc, except that the interlayer water (not present in talc) is lost progressively between about 200–700°C, and the dehydroxylation temperature is lowered by about 200°C to 750°C by the presence of the Li and interlayer alkalis [1]. The reaction products (enstatite, MgSiO_3 , and cristobalite, SiO_2) are as for talc; the Li is assumed to enter the silica phase, since the presence of additional Li in the exchangeable interlayer sites results in the eventual formation of crystalline lithium silicates [1].

Solid state nuclear magnetic resonance with magic angle spinning (MAS-NMR) has proved to be a very useful technique for examining the thermal transformations of related minerals, including talc, which has recently been studied by both ^{29}Si and ^{25}Mg MAS-NMR [8]. A ^{29}Si NMR study of hectorite thermal decomposition, with particular reference to the dehydration of interlayer cations, has been reported [2] but ^{25}Mg MAS-NMR studies have not previously been made. Some ^7Li NMR work on synthetic hectorite has been previously reported [3], for the purpose of comparison with ^6Li studies, which have the advantage of narrower resonance linewidths but the disadvantage of poorer sensitivity [3]. The aim of the present work was to apply NMR studies of all three nuclei, in conjunction with the more usual thermal analysis and X-ray powder diffraction, to the decomposition of synthetic hectorite, with particular reference to the role played by substituent lattice ions such as Li in modifying the reaction.

EXPERIMENTAL

The synthetic hectorite (Laponite CP) was the material described by Green et al. [1] as having the composition $[\text{Mg}_{5.26}\text{Li}_{0.59}]\text{Si}_8\text{O}_{20}(\text{OH})_4\text{Na}_{0.87} \cdot n\text{H}_2\text{O}$. The X-ray diffraction pattern indicates a fairly poorly crystalline material which however contains all the expected hectorite spacing (JCPDS card no. 9–31). Thermal analysis was carried out in air at a heating rate of $10^\circ\text{C min}^{-1}$, using a Perkin-Elmer DTA 1700 differential thermal analyser and a Stanton-Redcroft TG770 thermobalance. Powdered samples for NMR studies were heated to various temperatures for 15 min in platinum foil-lined ceramic boats in a pre-heated electric muffle furnace. After cooling in a closed vessel, the samples were examined by X-ray powder diffraction (Philips PW1700 computer-controlled diffractometer with graphite monochromator and $\text{Co K}\alpha$ radiation).

The ^{29}Si MAS-NMR spectra were acquired at 4.7 T using a Varian XL-200 spectrometer with a Doty probe spun at 4–5 kHz and a 90° pulse of $6 \mu\text{s}$ with a delay of 0.5 s. The ^{29}Si MAS-NMR spectra were referenced to tetramethylsilane (TMS).

The ^{25}Mg MAS-NMR spectra were acquired at 11.7 T (Varian Unity 500 spectrometer operating at 30.584 MHz) using a 3.5 mm Doty MAS probe at spinning speeds of 19.5–20 kHz and a 90° (solids) pulse of $3 \mu\text{s}$ with a

recycle delay of 0.1 s. Gaussian line broadening of 300 Hz was applied after acquisition of 20 000–40 000 transients, and the ^{25}Mg spectra were processed using a linear prediction method available in the Unity 500 software, to remove the baseline distortions introduced by probe ringdown. The ^{25}Mg chemical shifts are quoted with respect to a saturated solution of MgSO_4 .

The ^7Li MAS-NMR spectra were also obtained at 11.7 T using a 5 mm Doty probe at spinning speeds of about 8 kHz. Acquisition was at 194.246 MHz with $3\ \mu\text{s}$ pulses corresponding to about $\pi/12$ solution pulses, with a delay of 1 s. The spectra were processed with a gaussian line broadening of 50 Hz and are referenced to a 0.1 M LiCl solution. A limited number of ^6Li MAS-NMR spectra were also obtained, to investigate the improvement in spectral linewidth which should be possible with this nucleus [3].

RESULTS AND DISCUSSION

The thermal analysis curves for synthetic hectorite are shown in Fig. 1. These curves indicate the endothermic loss of interlayer water (21.9% mass loss) starting at 60°C , the corresponding DTA peak being at 145°C (curve C). Endothermic loss of hydroxyl water occurs at 730°C , with a 2.8% mass loss. The DTA record of this event (Fig. 1, curve C) indicates a double endotherm, the second endotherm possibly preceded by an exotherm. This DTA feature is not identical with the DTA trace previously published for this sample by Green et al. [1], which contained a single endotherm at 680°C , immediately followed at 710°C by a sharp exotherm associated with rapid recrystallization of the products. These differences are most probably due to differences in sample particle size, the present material containing a wider particle size range of generally larger particles.

X-Ray diffraction shows that removal of interlayer water at 200°C makes very little difference to the basal spacing, although further heating to 600 – 650°C collapses the interlayer distance by about $5.5\ \text{\AA}$ and produces a generally more diffuse hectorite pattern, suggesting that the interlayer cations have migrated from their original positions at these temperatures. Heating to 700°C destroys the basal spacing, and produces an X-ray pattern of poorly crystalline enstatite superimposed on a broad background hump of amorphous material, but with remnants of the broad higher-angle hectorite reflections still present. Heating to 800°C improves the crystallinity of the enstatite reflections slightly, and by 1100°C the product shows the X-ray trace of well crystallized enstatite (JCPDS card no. 11–273), but with no trace of cristobalite as previously found by Green et al. [1].

The ^{29}Si MAS-NMR spectra of synthetic hectorite, unheated and heated to various temperatures, are shown in Fig. 2. The ^{29}Si spectrum of unheated synthetic hectorite (Fig. 2, curve A) is identical to that reported by Mandair et al. [2] for Laponite CP. The principal resonance is 3.5 ppm downfield

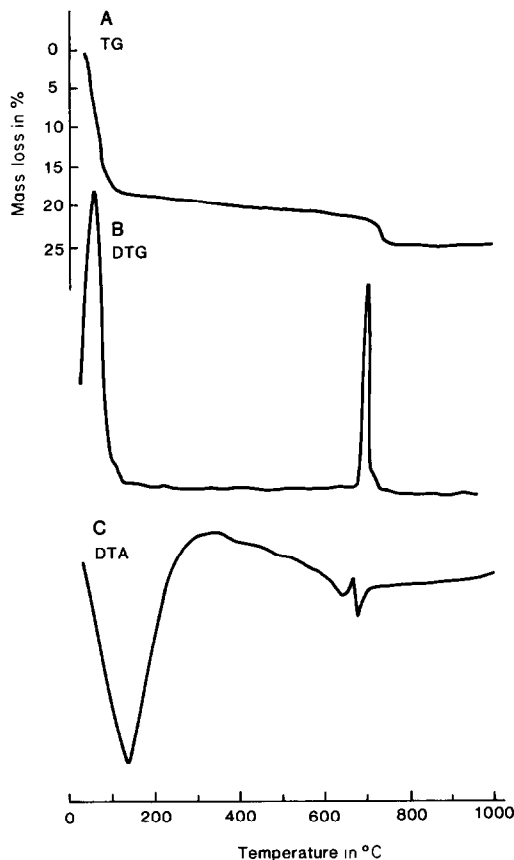


Fig. 1. Thermal analysis traces of synthetic hectorite; heating rate $10^{\circ}\text{C min}^{-1}$ in air.

from that of talc, attributed [2] to deshielding of the tetrahedral layer by the substitution of Li for Mg in the octahedral layer. The minor resonance at about -86 ppm is attributed [2] to the Q^2 sites at the edges of the silicate sheets.

Heating to 650°C produces an upfield shift in the major resonance to -97.5 ppm and a pronounced shoulder at about -84 ppm, indicating the incipient appearance of enstatite (Fig. 2, curve B). Although they did not publish their spectrum, Mandair et al. [2] describe a similar development in their Laponite RD sample heated to 600°C , in which they ascribe the upfield shift to the removal of Li from the octahedral sites to edge sites, resulting in a phyllosilicate structure similar to talc. It is worth noting that the formation of layer-lattice dehydroxylate phases in pyrophyllite [4], kaolinite [5] and chrysotile [9] is accompanied by upfield shifts of a few ppm in the ^{29}Si spectra, which correspond to a flattening of the tetrahedral layer as a consequence of dehydroxylation. Caution should however be exercised in interpreting this result as evidence for the formation of an independent

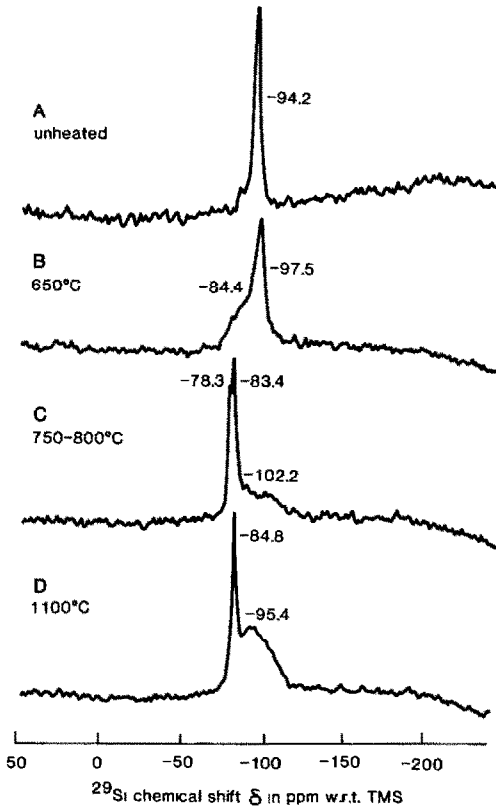
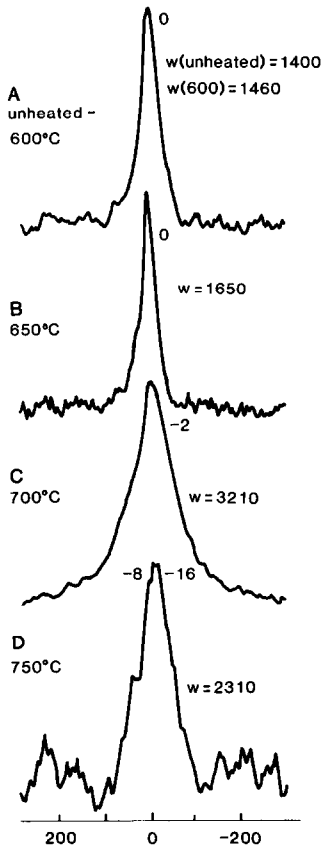


Fig. 2. ^{29}Si MAS-NMR spectra of synthetic hectorite, unheated and heated to the indicated temperatures.

hectorite dehydroxylate phase, since an analogous shift is not observed in talc [8].

Heating at $750\text{--}800^\circ\text{C}$ produces a sharp double resonance characteristic of clinoenstatite [6], with a broad shoulder at about -102 ppm indicative of an amorphous siliceous phase containing the interlayer alkali ions (Fig. 2, curve C). On heating at 1100°C , the double enstatite resonance becomes a single sharp resonance at -84.8 ppm (Fig. 2, curve D), indicating a change from clinoenstatite to orthoenstatite [7]. At the same time, the broad shoulder arising from the glassy component shifts to -95.4 ppm, suggesting the inclusion of further alkalis, and especially Li, in the siliceous phase, which however, remains X-ray amorphous.

The ^{25}Mg MAS-NMR spectra of unheated and heated synthetic hectorite samples are shown in Fig. 3. The spectrum of unheated hectorite (Fig. 3, curve A) is similar to that of talc, in having a symmetric peak of width 1400 Hz as compared to 1800 Hz for talc (these linewidths include the 300 Hz of line broadening introduced during processing). The featureless resonance of synthetic hectorite militates against an unambiguous choice of



^{25}Mg chemical shift δ in ppm w.r.t. MgSO_4 soln.

Fig. 3. ^{25}Mg MAS-NMR spectra of synthetic hectorite, unheated and heated to the indicated temperatures; peak positions in ppm, widths in Hz.

parameters for a spectral simulation. Reasonable approximations to the hectorite spectrum can be obtained using values for the nuclear quadrupole coupling constant χ from 0 (corresponding to a non-EFG-broadened gaussian peak) up to about 2.2 MHz, together with gaussian line broadenings varying from 1400 Hz to a minimum of about 750 Hz, respectively. The electric field gradient (EFG) tensor asymmetry parameter η can take the full range of values from 0 to 1. With these combinations of χ and line broadening, the resulting values of δ_0 , the chemical shift corrected for EFG effects, range from 0 (for the non-EFG-broadened gaussian simulation) to a maximum value of 43 ppm. To the extent that any conclusion can be drawn from these results, it appears that the presence of lithium in the octahedral layer does not influence the environment of the octahedral Mg to any great degree.

The ^{25}Mg spectrum is unchanged by the removal of interlayer water up

to 600°C (Fig. 3, curve B), is broadened slightly at 650°C, and considerably broadened by the onset of dehydroxylation at 700°C (Fig. 3, curve C). The broadened, non-gaussian peakshape of the 700°C spectrum suggests an increase in the EFG compared with the starting material. The spectrum can be approximated with $\chi = 3.5$ MHz, $\eta = 0.7$, with gaussian linebroadening of 1070 Hz, giving a value for δ_0 of 94 ppm. This chemical shift seems very high; however, the spectrum can be approximated using lower values of χ and larger gaussian linebroadenings (up to 3000 Hz), giving lower values of δ_0 ranging down to zero in the absence of EFG effects. The reason for the large gaussian (non-EFG) linewidths required in these simulations is not clear.

Complete dehydroxylation at 750°C (Fig. 3, curve D) results in the narrowing and slight upfield shift of the peak, with a reduction in the amount of NMR-visible Mg to about 33% of its initial intensity. A loss of signal also occurs in the ^{25}Mg spectral intensity of chrysotile during dehydroxylation [9], and has been attributed to broadening of the Mg resonance due to distortions of the octahedral sites. By contrast, this effect is not observed in talc, in which the intensity of the unheated ^{25}Mg NMR signal survives dehydroxylation and subsequent recrystallization of product phases [8]. Heating to 750°C produced a ^{25}Mg spectrum slightly broader (2310 Hz) than that of the enstatite formed in the thermal decomposition of talc at 1300°C (width 1780 Hz). The increased width of the hectorite resonance could be due to a contribution from another peak downfield of enstatite.

The ^7Li MAS NMR spectra of unheated and heated synthetic hectorite samples are shown in Fig. 4. The changes in the ^7Li MAS-NMR spectra on heating are slight but significant, with the sideband pattern extending out further with increasing firing temperature. This probably reflects the width of the satellite transitions where first-order quadrupolar effects will cause a rapid broadening as the EFG increases. Thus the trend is of increasing EFG with temperature in the order 20°C \approx 200°C < 600°C < 650°C < 700°C \approx 750°C \approx 800°C < 1100°C \approx 1300°C. The linewidth of the central transition also increases in a similar order (Fig. 5, curve A), with a linear increase between 200 and 800°C. This increase could also be ascribed to the effect of increasing EFG, possibly also with a greater dispersion of chemical shifts. An increase in EFG should cause an upfield shift of -0.849 times the EFG-induced width. However, Fig. 5, curve B shows that in general the peak position shifts downfield with increasing temperature, a trend which is even greater if the correction for the maximum EFG width is applied. It should be noted that a downfield shift with increasing temperature has also been reported for ^6Li spectra of heated synthetic hectorite [3], where the EFG effect is expected to be much less; this shift was ascribed by Bond et al. [3] to movement of Li from trioctahedral sites to edge sites. The ^7Li peak position does not shift smoothly downfield with increasing temperature

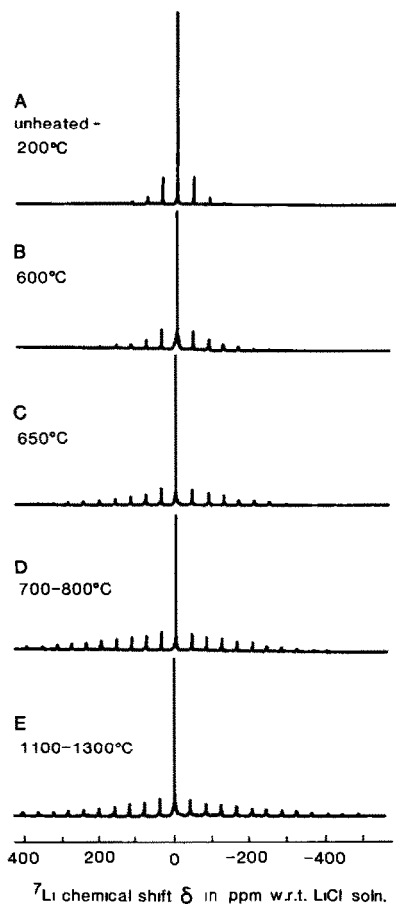


Fig. 4. ${}^7\text{Li}$ MAS-NMR spectra of synthetic hectorite, unheated and heated to the indicated temperatures.

(Fig. 5, curve B) but shows discontinuities between 600 and 700°C (corresponding to the onset of dehydroxylation). This is not an artifact, but may be reflecting the movement of Li to different sites in several stages, or be a consequence of the movement of the interlayer Na^+ during dehydration.

Of the limited number of ${}^6\text{Li}$ MAS spectra run, that of the 800°C sample has a linewidth of 86 Hz (1.168 ppm) compared to the ${}^7\text{Li}$ linewidth of 302 Hz (1.554 ppm), possibly reflecting a distribution of chemical shifts (dominant in the ${}^6\text{Li}$ spectrum) with a small EFG effect.

In another experiment, a static ${}^7\text{Li}$ spectrum of the 650°C sample was run, which had a linewidth of 2500 Hz compared to the MAS width of 280 Hz. MAS should cause a reduction in EFG-induced linewidth by a factor of 3.625, thus the much greater width of the static spectrum is probably due to dipolar couplings (removed by MAS).

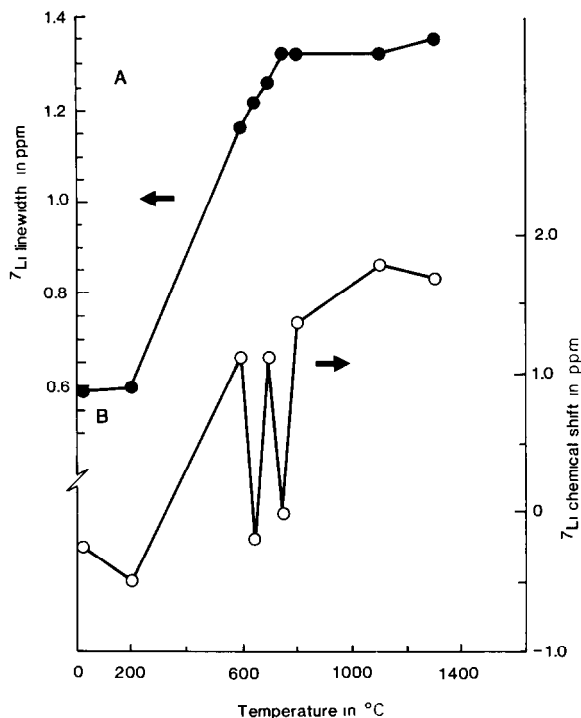


Fig. 5. ${}^7\text{Li}$ spectral parameters of synthetic hectorite as a function of temperature: curve A, linewidth of the central resonance; curve B, chemical shift of the central resonance, with respect to 0.1 M LiCl solution.

CONCLUSIONS

The combination of MAS NMR, thermal analysis and X-ray diffraction indicates that synthetic hectorite undergoes the following thermal decomposition sequence:

(i) The loss of interlayer water at 200°C causes minimal change to the mineral structure as reflected in its basal spacing or the environment of the octahedral or tetrahedral atoms.

(ii) Although the hectorite structure is maintained on heating to 600–650°C, a small decrease in the basal spacing may signify the movement of the interlayer Na^+ into closer proximity to the tetrahedral silicon layer, with a consequent effect on the EFG broadening of the octahedral Li atoms (but apparently little effect on the octahedral Mg, which retains its spectral intensity and peak width). By 650°C, the onset of dehydroxylation has produced small changes in the Si configuration, with a shift of about -3 ppm in the Q^3 hectorite resonance, and the appearance of a broad shoulder corresponding to incipient enstatite.

(iii) By 700°C, poorly crystalline enstatite and amorphous material are detectable by XRD as well as by ${}^{29}\text{Si}$ MAS NMR. Dehydroxylation has

caused a degree of distortion of the octahedral Mg sites, as evidenced by a broadening of the ^{25}Mg resonance from 1746 Hz at 650°C to 2472 Hz at 700°C, and the loss of about 60% of the octahedral Mg intensity. These changes in the Mg environment appear to be preceded by changes in the octahedral environment of the more mobile Li, as reflected by fluctuations in the ^7Li chemical shift between 600 and 700°C. Although the present results give no direct information about the eventual destination of the Li, they are not inconsistent with its incorporation (together with the interlayer Na) in the siliceous phase, which by 1100°C has assumed a ^{29}Si chemical shift (–95.4 ppm) considerably different from that of pure silica (about –110 ppm).

These results reveal considerable similarities between the thermal reaction sequences of synthetic hectorite and talc. The latter undergoes a smooth transformation, uncomplicated by the intervention of identifiable intermediate phases [8]; this situation is not greatly changed in synthetic hectorite by the presence of octahedral Li and interlayer Na^+ .

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