

Thermal reactions of chrysotile revisited: A ^{29}Si and ^{25}Mg MAS NMR study

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ABSTRACT

The thermal decomposition sequence of chrysotile samples from New Zealand and Canada has been found by ^{29}Si and ^{25}Mg MAS NMR to be more complex than previously indicated by X-ray diffraction and electron optical studies. The greater part of the mineral dehydroxylates, producing a Mg-rich X-ray amorphous phase containing essentially Mg in octahedral coordination and characterized by a broad ^{29}Si resonance centered at about -73 ppm with respect to tetramethylsilane. This transforms to forsterite, Mg_2SiO_4 , at $670\text{--}700$ °C, at which temperature the unreacted chrysotile (possibly the deepest layers of the fibrils) forms a different, Si-rich X-ray amorphous dehydroxylate. This phase, called dehydroxylate II, has a ^{29}Si chemical shift (-97 ppm) not unlike that of talc, but with Mg sites that may be distorted beyond NMR detection, because most of the ^{25}Mg spectral intensity is lost over this temperature range. Dehydroxylate II forms enstatite (MgSiO_3) and free silica at $770\text{--}800$ °C, further enstatite being formed by reaction of the silica with forsterite at 1150 °C. The stoichiometry of these reactions is consistent with NMR measurements of the partitioning of Si between the various phases.

INTRODUCTION

Chrysotile (white asbestos) is a predominantly fibrous form of serpentine, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, the trioctahedral magnesian analogue of the 1:1 layer-structure aluminosilicate kaolinite. Because of its historical importance as an insulating material with refractory applications, the properties and thermal reactions of chrysotile have been extensively investigated. Although the industrial importance of asbestiform minerals has progressively declined as their health hazards have become increasingly recognized, their thermal decomposition reactions continue to be of practical interest as a means of converting the material to less hazardous products (MacKenzie and Meinhold, 1994a). Furthermore, there remain some interesting questions concerning the mechanism of this thermal decomposition reaction that also bear on the thermal behavior of related layer-structure silicates.

When chrysotile is heated in air, it undergoes an endothermic weight loss of about 14% between about 600 and 720 °C (Khorami et al., 1984), representing the removal of structural H_2O . The resulting phase, chrysotile dehydroxylate, is amorphous to X-rays, but in some samples contains a broad, low-angle diffraction band centered at about $10\text{--}15$ Å (Brindley and Zussman, 1957). There has been much speculation concerning the possible degree of residual structure in the dehydroxylated phase and the origin of the low-angle reflection, which may merely represent diffraction from long cavities observed by electron microscopy to open up in the fiber walls at these temperatures (Martin, 1977).

By comparison with kaolinite dehydroxylate, the amorphous phase from chrysotile exists over a very short

temperature range, with the first small crystallites of forsterite (Mg_2SiO_4) appearing at about 620 °C and in some samples overlapping with the remnants of the chrysotile X-ray pattern (Brindley and Zussman, 1957; Martin, 1977). The dehydroxylated product has been variously described as largely disordered (Ball and Taylor, 1963), partly disordered (Brindley and Hayami, 1965), and semiamorphous but preserving some of the original lattice order (Martin, 1977). Its composition is also debated; Ball and Taylor (1963) considered that it contains the same atomic ratios as the parent phase, with the observed topotaxy between the reactant and product suggesting inherited Mg-O order, rather than an inherited Si-O structure, as implicit in a scheme subsequently suggested by Brindley and Hayami (1965). The thermal reaction schemes so far advanced are summarized in Figure 1.

Support for the structural continuity of the silicate units rather than the Mg-O structure has recently been provided by radial distribution function measurements, which indicate that the Si-O bond lengths remain constant throughout the reaction (Datta et al., 1987). The heterogeneous reaction mechanism of Ball and Taylor (1963) demands a subsequent separation into a Mg-rich phase that becomes forsterite and a Si-rich phase that subsequently becomes enstatite (MgSiO_3) (Fig. 1A). Brindley and Hayami (1965) accepted the Ball and Taylor concept of the dehydroxylate, but, on the basis of quantitative X-ray determination of the amount of forsterite subsequently formed, considered that all the available Mg is accounted for by that phase, leaving a residual material of almost pure amorphous silica, which further reacts with the forsterite at higher temperatures to form enstatite (Fig. 1B). On the basis of electron microscopy, Martin (1977)

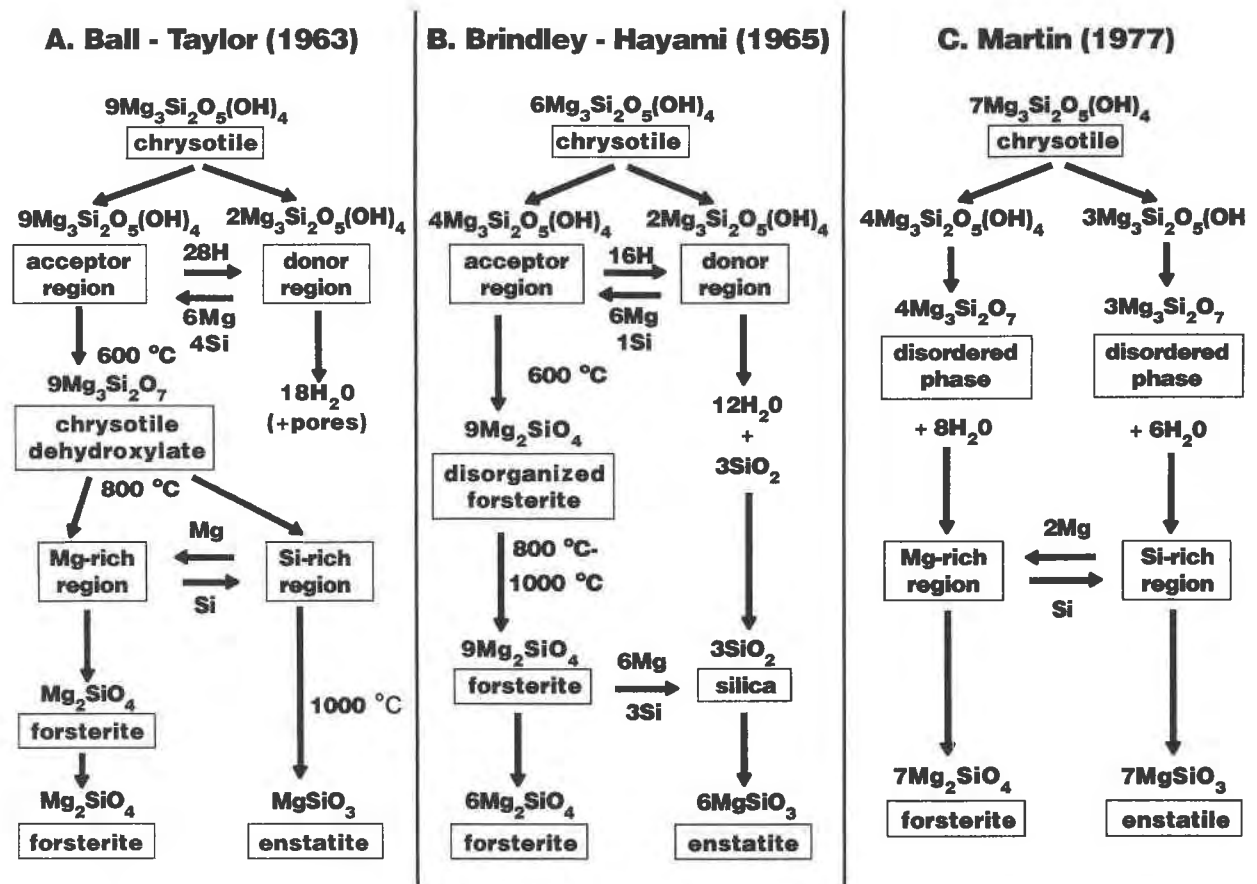


Fig. 1. Schematic representation of previously proposed chrysotile reaction sequences. (A) According to Ball and Taylor (1963), (B) according to Brindley and Hayami (1965), (C) according to Martin (1977).

has modified this scheme, suggesting that little separation of Mg and Si occurs below 800 °C; below this temperature, forsterite forms in regions of the disordered dehydroxylate by consuming whatever Mg is locally available (Fig. 1C). Martin suggested that the main countermigration of Mg and Si occurs rapidly at about 800 °C, the resulting spontaneous crystallization of forsterite and enstatite giving rise to the exotherm observed in the DTA trace at 810 °C (Martin, 1977). This is not consistent with the temperature at which enstatite is usually reported to appear (1000 °C: Santos and Yada, 1979), although Martin (1977) reported the presence of enstatite crystallites in samples heated at 800 °C for 24 h.

The origin of this exotherm at 810 °C has long been a source of debate because, like the exotherm at 980 °C in kaolinite, it is not accompanied by the sudden appearance of any new phase. Ball and Taylor (1963) attributed the exotherm to the change in O packing that results in the formation of forsterite, but that is not consistent with the appearance of forsterite at least 100 °C lower. The reaction scheme of Brindley and Hayami (1965) implied that the exotherm represents the recrystallization of disordered forsterite, although this is not supported by X-ray

diffraction observations, which show no sudden change in forsterite crystallinity at this temperature. Datta et al. (1986) attributed the exotherm to the partial conversion of chrysotile to forsterite and enstatite, the previously formed forsterite being the transformation product of a different type of chrysotile particle (type I), which is more reactive. Other workers are more vague, suggesting that the exotherm is due to "conversion of the chrysotile anhydride" within the fibrils (Santos and Yada, 1979).

The outstanding problems in the chrysotile reaction sequence can thus be summarized as (1) the nature and structure (if any) of the dehydroxylate, and their influence on the further course of the reaction sequence, and (2) the cause of the exotherm at 810 °C and its relation to the higher temperature products.

As with the thermal reaction sequence of kaolinite, progress in both these areas has been hampered by the lack of crystallinity of the intermediate phases. Solid-state nuclear magnetic resonance with magic angle spinning (MAS NMR) has provided new information on the behavior of Si and Al during the kaolinite reaction sequence (MacKenzie et al., 1985), but the application of ²⁵Mg MAS NMR to magnesian silicate problems has only recently be-

come possible, with the increasing availability of high-field spectrometers and high-speed MAS probes. Building on preliminary work by Dupree and Smith (1988), which demonstrated the feasibility of ^{25}Mg MAS NMR in some inorganic systems, the technique has been applied to studies of the thermal behavior of several Mg minerals, including magnesite (MacKenzie and Meinhold, 1993), dolomite (MacKenzie and Meinhold, 1994c), brucite (MacKenzie and Meinhold, 1994d), and hectorite (MacKenzie and Meinhold, 1994e). Working at high magnetic fields and very high spinning speeds decreases some of the problems associated with the spin $\frac{1}{2}$ ^{25}Mg nucleus (e.g., 10% natural abundance, low γ , and considerable second-order quadrupolar broadening of the central transition). Using high fields and high spinning speeds, the ^{25}Mg MAS NMR spectra of a number of representative mineral types have been collected, and the effect of the interaction with the quadrupolar ^{25}Mg nucleus of electric field gradients produced by deviations from octahedral symmetry has been investigated (MacKenzie and Meinhold, 1994b).

In the present study, MAS NMR is used to probe the behavior of the Si and Mg in the chrysotile reaction sequence, with particular attention to the nature of the dehydroxylate and the reactions related to the exotherm at 810 °C.

EXPERIMENTAL

Two chrysotile samples were used in this work. One was from the Upper Takaka Valley asbestos deposit, northwest Nelson, New Zealand (N.Z. Geological Survey sample no. 4519), the other from the Cassiar mine, British Columbia, Canada (sample AK 262C91). The X-ray diffraction patterns of both samples indicated monophase clinochrysotile. The major impurity (Fe) was present in the New Zealand and Canadian samples at levels of 1.16 and 1.12%, respectively. Thermal analysis was carried out in air at a heating rate of 10 °C/min, using a Stanton Redcroft TG770 thermobalance and a Perkin-Elmer DTA 1700 differential thermal analyzer. Samples for NMR studies were prepared by heating for 15 min in Pt foil-lined ceramic boats in a laboratory furnace at temperatures dictated by the thermal analysis results. After withdrawal from the furnace, the samples were examined by X-ray powder diffraction using a Philips PW1700 computer-controlled diffractometer with $\text{CoK}\alpha$ radiation and a graphite monochromator.

The room-temperature ^{29}Si NMR spectra were recorded both at 4.7 T (Varian XL-200 spectrometer with a Doty MAS probe, spinning speed 4 kHz) and at 11.7 T (Varian Unity 500 spectrometer 5-mm Doty MAS probe, spinning speed 8 kHz). The 11.7-T spectra were acquired using a 90° pulse of 6 μs with a delay of 0.5 s, all the ^{29}Si spectra being referenced to tetramethylsilane (TMS). After acquisition of several thousand transients, the spectra were processed with a Gaussian line broadening of 50 Hz. The room-temperature ^{25}Mg spectra were acquired at 11.7 T using a Doty 3.5-mm high-speed MAS probe,

spinning speed 19.5–20 kHz, with a 90° (solids) pulse of 3 μs with a recycle delay of 0.1 s. A spectral width of 100 000 Hz was used with an acquisition time of 0.02 s, giving 4096 points in the free induction decay. After the acquisition of, typically, 400 000 transients, the spectra were processed using a linear prediction method available in the Unity software to remove the base-line distortions introduced by probe ringdown. For the linear prediction, data acquired after 20 μs with the receiver off then had a further ten points (100 μs) dropped, and the resulting free induction decay used to calculate the linear prediction coefficients and the missing first 12 points after excitation. The resulting spectrum was then checked with those produced by starting the back linear prediction at different points and by applying a polynomial base-line correction to the spectrum produced with data acquired immediately after the receiver-off period or after left-shifting the free induction decay by a variable number of points before the Fourier transformation. Gaussian line broadening of 200 Hz was applied to all the processed spectra, which were referenced to a saturated solution of MgSO_4 .

RESULTS AND DISCUSSION

The thermal analysis traces of both chrysotile samples are shown in Figure 2. Both chrysotile samples show similar thermal behavior, the low-temperature endotherm being due to the loss of H_2O adsorbed on the fiber surfaces. The endothermic weight loss at about 700 °C due to dehydroxylation appears from the DTG curve to consist of two overlapping processes, most clearly seen in the Cassiar sample (Fig. 2E). Similar multistage dehydroxylation has also been reported by Datta et al. (1986), who attributed it to the presence of type I and type II chrysotile particles of different reactivity. X-ray diffraction sheds no light on the possible nature of these processes; samples heated below 700 °C show only chrysotile reflections, which gradually become less intense as heating progresses, whereas at 700 °C, forsterite suddenly appears, in addition to very weak residual chrysotile reflections. Both the Nelson and Cassiar samples heated at 700 °C show the broad, low-angle reflection commented on by Brindley and Zussman (1957) and Martin (1977). The only change in the X-ray pattern accompanying the exotherm at 810 °C is the loss of the broad, low-angle reflection. Heating to progressively higher temperatures results in the eventual appearance of some enstatite, at 1000 °C in Cassiar chrysotile, and slightly higher temperatures in the Nelson sample.

NMR spectroscopy

Typical room-temperature ^{29}Si spectra at 11.7 T of unheated and heated chrysotile samples are shown in Figure 3 (Nelson chrysotile) and Figure 4 (Cassiar chrysotile).

The chemical shift of the single Si resonance in the unheated minerals (−93 ppm) is in reasonable agreement with the one reported value of −94 ppm for serpentine of unspecified morphology (Magi et al., 1984). The spec-

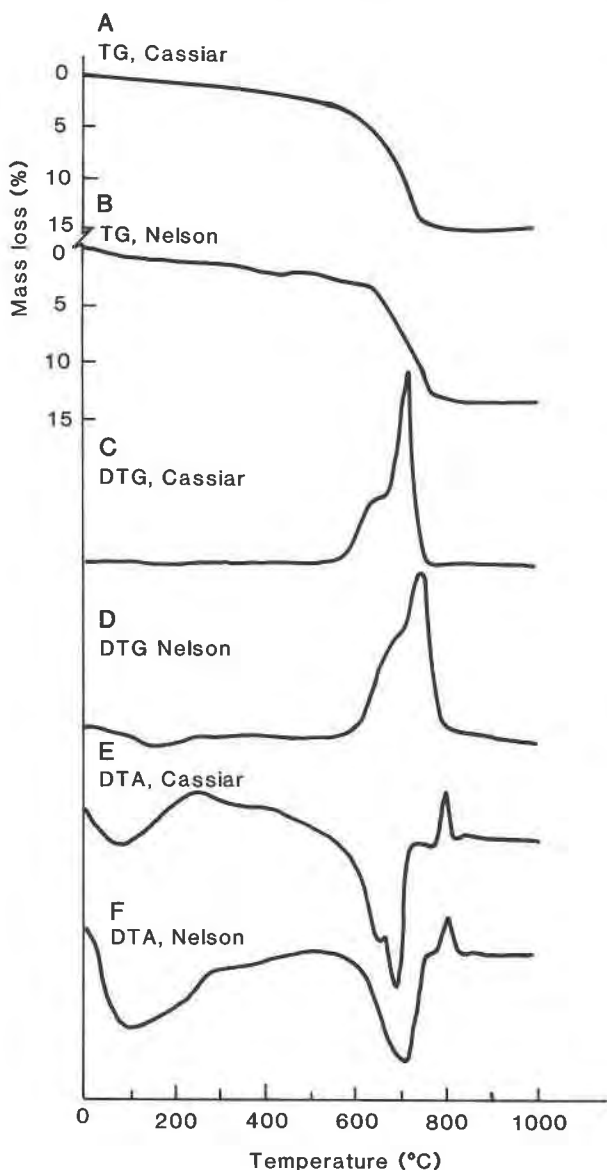


Fig. 2. Thermal analysis traces of Nelson (New Zealand) and Cassiar (Canadian) chrysotile samples. Heating rate 10 °C/min in air. A and B are thermogravimetric curves; C and D are differential thermogravimetric curves. E and F are differential thermal analysis curves.

tra are unchanged by heating below 600 °C, but at about this temperature, a slight asymmetry begins to develop in the low-field side of the main peak (Fig. 4A). By 650 °C, this feature has developed into a broad hump at about -72 to -74 ppm (Figs. 3B, 4C). Since the only crystalline phase detectable in these samples is chrysotile, which is also evident from the resonance at -93 ppm in these samples, the new broad peak is apparently associated with the amorphous anhydrous phase formed in the first of the two weight-loss processes. Similar broad peaks at about -73 and -80 ppm have been reported in the spectra of

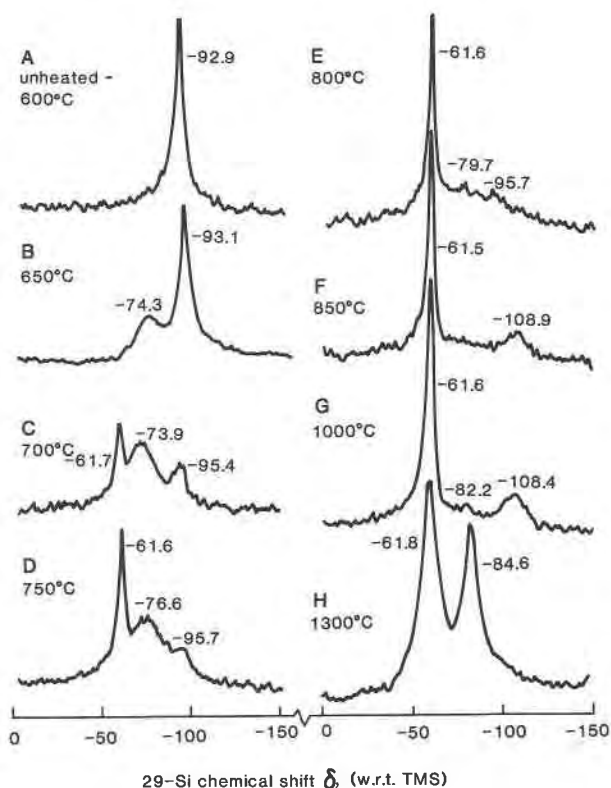


Fig. 3. Room-temperature ^{29}Si MAS NMR spectra of Nelson chrysotile at 11.7 T heated to various temperatures. A = unheated and heated to 600, B = 650, C = 700, D = 750, E = 800, F = 850, G = 1000, H = 1300 °C. Units in parts per million.

protosilicate gels formed from MgCl_2 and Na_4SiO_4 in which the ratio of Mg to Si is 1:1 (Hartman and Millard, 1990). The material giving rise to these resonances is described as amorphous, with a low degree of Si polymerization (Hartman and Millard, 1990). A similar broad peak near -80 ppm observed in a sample of MgSiO_3 with perovskite structure was attributed to ^{41}Si in an amorphous phase with an average of two bridging O atoms per tetrahedron, suggesting a composition close to MgSiO_3 (Kirkpatrick et al., 1991). Since the chemical shift of the amorphous dehydroxylate peak in the present samples spans the orthosilicate Q^0 region up to the inosilicate Q^2 region, it cannot distinguish between the composition of incipient forsterite (Q^0 , $\delta = -62$ ppm) and incipient enstatite (Q^2 , $\delta = -83$ ppm); the broadness of the peak suggests the presence of a range of tetrahedral configurations in this phase, which we designate dehydroxylate I.

Heating to 700 °C produces a decrease in the chrysotile resonance and the appearance of a sharp new resonance at -61.5 ppm, consistent with the chemical shift reported for forsterite (-61.9 ppm: Magi et al., 1984; -61.6 ppm: Hartman and Millard, 1990). The 11.7-T spectrum of Cassiar chrysotile heated at 700 °C (Fig. 4D) reveals that the broadness of the residual chrysotile resonance at -93 ppm is due to the appearance of an extra peak at -96.9

ppm, which survives to at least 800 °C (long after chrysotile has disappeared from the X-ray diffraction pattern of the sample), and is more thermally stable than the broad resonance of the amorphous phase. The chemical shift of this new peak is typical of the Q^3 Si atoms occurring in layer-structure phyllosilicates such as chrysotile itself, or the related 2:1 layer-structure silicate talc, $Mg_6Si_8O_{20}(OH)_4$, for which the reported ^{29}Si chemical shift is -97.2 ppm (Sherriff et al., 1991) to -98.1 ppm (Magi et al., 1984). Although talc is one of the decomposition products of chrysotile under hydrothermal conditions, where it forms in addition to forsterite (Ball and Taylor, 1963), its presence in the present samples could not be confirmed by the observation of its characteristic basal spacing in X-ray diffraction patterns. A more likely possibility is that the resonance at -97 ppm is related to the 1:1 layer-structure of chrysotile, rendered X-ray amorphous by dehydroxylation but still containing elements of the original silicate structure, i.e., a Si-rich dehydroxylate phase, which will be called dehydroxylate II.

On further heating above 800 °C, the resonances at -75 and -97 ppm are reduced, and a broad peak appears at about -108 ppm, corresponding to amorphous silica (Figs. 3F, 4H). The forsterite resonance at -61.5 ppm, which grows at the expense of the dehydroxylate I peak at -75 ppm, initially shows a shoulder or tail at about -58 ppm; this disappears with further heating as the crystallinity of the forsterite improves. The first appearance of enstatite in the X-ray pattern coincides with the appearance of a ^{29}Si resonance at about -82 ppm (Fig. 3G), which grows and broadens with further heating (Fig. 3H). The characteristics of this peak correspond better with those reported for orthoenstatite (single, broad peak centered at -82 ppm; Magi et al., 1984) than with those for clinoenstatite (two peaks at about -81.6 and -83.8 ppm; Hartman and Millard, 1990; Janes and Oldfield, 1985). The initial appearance of both amorphous silica and enstatite seems to be at the expense of the phyllosilicate-like dehydroxylate II, although the greatest degree of enstatite formation occurs at 1130 – 1150 °C by reaction of the excess silica with forsterite, as suggested by Brindley and Hayami (1965).

The ^{25}Mg MAS NMR spectra of unheated Nelson and Cassiar chrysotile samples, together with Cassiar chrysotile heated to various temperatures, are shown in Figure 5. In order to process the ^{25}Mg spectra to eliminate the base-line distortions caused by probe ringdown, the free induction decay acquired after a receiver-off period of 20 μs needs to be left-shifted by eight points (at 10 - μs intervals); this is equivalent to sampling the free induction decay 100 μs after excitation. Although this technique of left-shifting the free induction decay to eliminate probe ringdown effects appears to be quite satisfactory for some other Mg minerals (MacKenzie and Meinhold, 1994b), the effect in both Nelson and Cassiar chrysotile is to change the relative areas of the contributing resonances so that the spectrum processed with no left-shift has an upfield component that is much more intense. This be-

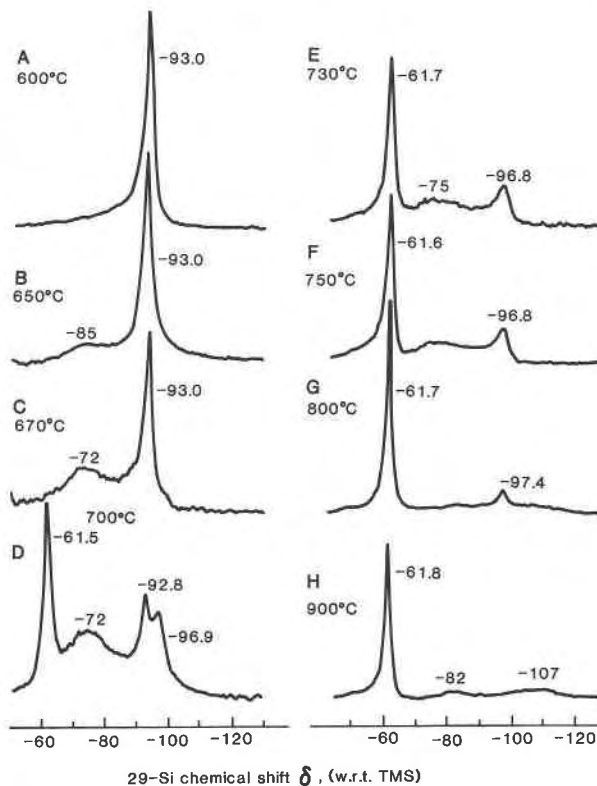


Fig. 4. Room-temperature ^{29}Si MAS NMR spectra of Cassiar chrysotile at 11.7 T heated to various temperatures. A = 600, B = 650, C = 670, D = 700, E = 730, F = 750, G = 800, H = 900 °C. Units in parts per million.

havior suggests that in chrysotile there are at least two component lines with very different T_2^* time constants, which have substantially different signal decay characteristics during ringdown. Processing the spectra using a range of left-shifts and fitting the two component heights to a Lorentzian decay gives values for T_2^* of 58 and 315 μs , corresponding to a Lorentzian line width of about 5520 and 1010 Hz for the components at about -90 and 8 ppm, respectively. Although it may be possible that a single quadrupolar pattern could have broad and narrow components, we have not hitherto observed the pronounced effects seen here and propose an alternative explanation.

The ratio (about 9:1 to 16:1) of these two types of site with very different electric field gradient (EFG) characteristics suggests that they are not the M1 and M2 octahedral sites, which, if distinguishable, should be much more nearly equally populated. Rather, their origin may lie in the fibrous morphology of the sample; it seems reasonable that the octahedral sites in the more tightly coiled layers located at greatest depth inside the fibrils might experience a different EFG from that of the sites in the surface layers. The Nelson chrysotile spectrum is slightly different from that of Cassiar, showing a third, broad component, near -22 ppm. Further evidence that the

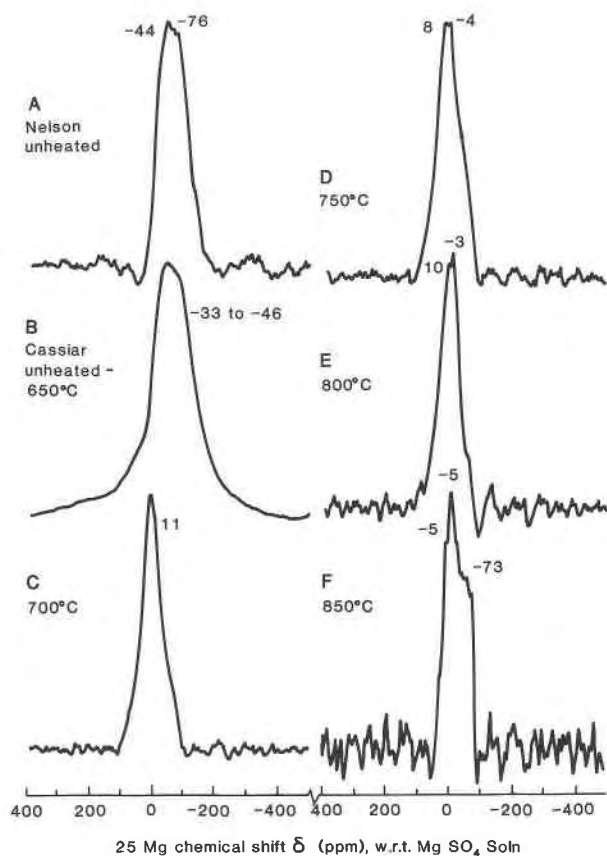


Fig. 5. Room-temperature ^{25}Mg MAS NMR spectra at 11.7 T of (A) unheated Nelson chrysotile, and (B–F) Cassiar chrysotile, unheated and heated to various temperatures. B = unheated and heated to 650, C = 700, D = 750, E = 800, F = 850 °C.

EFG splittings are morphology-related is provided by the ^{25}Mg spectrum of the nonfibrous serpentine antigorite, which contains only the site of longer T_2^* (lower EFG) (MacKenzie and Meinhold, 1994b). The apparent presence of two and three Mg sites in the Cassiar and Nelson chrysotile samples, respectively, may also be the origin of the differences in the thermal behavior of the two materials, as reflected in the less clearly resolved dehydroxylation endotherm of the Nelson sample (Fig. 2F). To try to compensate for the effects of T_2^* decay, all the ^{25}Mg spectra were processed using a linear prediction method.

The spectra of samples heated to the onset of dehydroxylation at 650 °C suggest only minor changes have occurred in the octahedral environment of the NMR-visible Mg (Fig. 5B), but possibly with a slightly diminished higher EFG component. Upon the formation of dehydroxylate I at 700 °C, the ^{25}Mg spectrum narrows, perhaps because of the disappearance of the higher EFG component (Fig. 5C). Heating to 800 °C, in which temperature range further forsterite is formed and dehydroxylate II appears and disappears, produces little further

change in the shape of the ^{25}Mg spectra (Fig. 5D, 5E); but at 850 °C the spectrum could be that of a single EFG-split site (Fig. 5F). However, not all the Mg is accounted for in these spectra; integrated intensity measurements indicate that by 650 °C, only about 36% of the original Mg intensity is observed, and this figure falls to a minimum value of 3% by 800 °C, rising slightly to 4% by 850 °C. A similar decrease in the ^{27}Al intensity observed during the dehydroxylation of kaolinite (MacKenzie et al., 1985) was interpreted in terms of the distortion of sites, broadening their NMR resonance beyond detection. A similar explanation may apply here, with the result that only the Mg in comparatively well-ordered octahedral sites in chrysotile or its dehydroxylates are represented in Figure 5. Using the data from the single-crystal study of forsterite by Derighetti et al. (1978), we have calculated the MAS spectra for the M1 and M2 sites (MacKenzie and Meinhold, 1994b). These calculations show that the maximum peak height is only a few percent of the intensity expected for a line of 3 ppm in width, because most of the intensity is present as a broad base to the peak (the calculated peak widths at half height and one-tenth height are 72 and 446 ppm for M1 and 119 and 288 ppm for M2, respectively). Thus, the large EFG values in forsterite cause the NMR peaks to be broadened and the maximum signal height decreased to such an extent that the signal is largely lost in the background noise. It is this EFG broadening effect that is responsible for the observed loss of the Mg signal.

The NMR results suggest that the thermal behavior of chrysotile is more complex than postulated in previous reaction sequences based on X-ray diffraction or electron microscopy, in that two different dehydroxylates are formed. Dehydroxylate I, formed first, contains Si environments with chemical shifts spanning the range of orthosilicates and inosilicates, but with interatomic distances and Mg coordination numbers not very different from the parent chrysotile (Datta et al., 1987).

As dehydroxylation proceeds further, forsterite crystallizes from this amorphous phase and dehydroxylate II appears, which, although X-ray amorphous, has well-defined Si sites with a fairly narrow chemical-shift range, but shifted upfield by about 5 ppm from the resonance of the parent chrysotile. Dehydroxylate II also has greater thermal stability than the amorphous dehydroxylated phase originally formed (it is still present above 800 °C). Its formation therefore involves minimal disruption of the parent Si structure, but because it is virtually anhydrous, considerable changes must have occurred in the coordination sphere of the Mg. This is also consistent with the loss of octahedral ^{25}Mg NMR intensity and with radial distribution function results that indicate a reduction in the coordination number of the Mg, which sets in at 700–750 °C (Datta et al., 1987).

Above 800 °C, there is an exothermic reaction that coincides with the complete loss of OH, the appearance of further forsterite, and the first indication of free silica, the last two at the expense of dehydroxylate II. This suggests

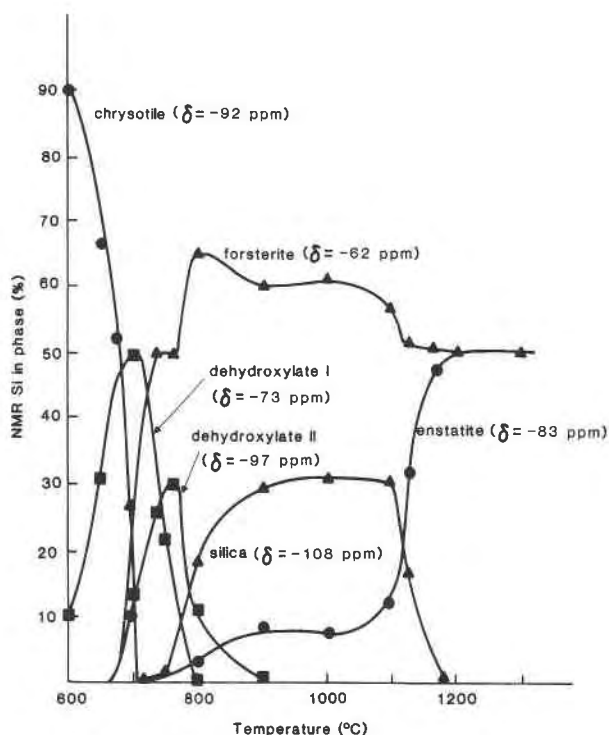


Fig. 6. Distribution of Si among the various phases in heated Nelson chrysotile, estimated from the ^{29}Si NMR spectra by fitting peaks to the indicated resonances. The ^{29}Si chemical shifts of the various phases are shown in parentheses.

that the exotherm may be related to the collapse of the O layers, with the separation of free silica, as is also the case with the exotherm of kaolinite at 980 °C (Brown et al., 1985). Further heating produces a slow but steady increase in the amount of enstatite, which accelerates at about 1150 °C because of the reaction of the amorphous silica with some of the forsterite, as suggested by Brindley and Hayami (1965).

Partitioning of the Si among the various phases

To make a semiquantitative estimate of the relative proportion of Si in each phase at each temperature, the ^{29}Si spectra were synthesized by superposition of a number of Gaussian peak shapes and the relative areas under each fitted peak calculated. A similar approach was adopted by Brindley and Hayami (1965), who used quantitative X-ray diffraction to estimate the amount of Si in each phase, but the NMR results provide a more complete Si balance, since they take into account the Si in the amorphous phases that is inaccessible to XRD. The relative Si contents in the various phases formed in Nelson chrysotile as a function of heating temperature are shown in Figure 6.

If comparable (or fast) relaxation times are assumed for all the phases present, Figure 7 indicates that at 700 °C, 10% of the Si is present in unreacted chrysotile, 27% in forsterite, 50% in dehydroxylate I, and 14% in dehy-

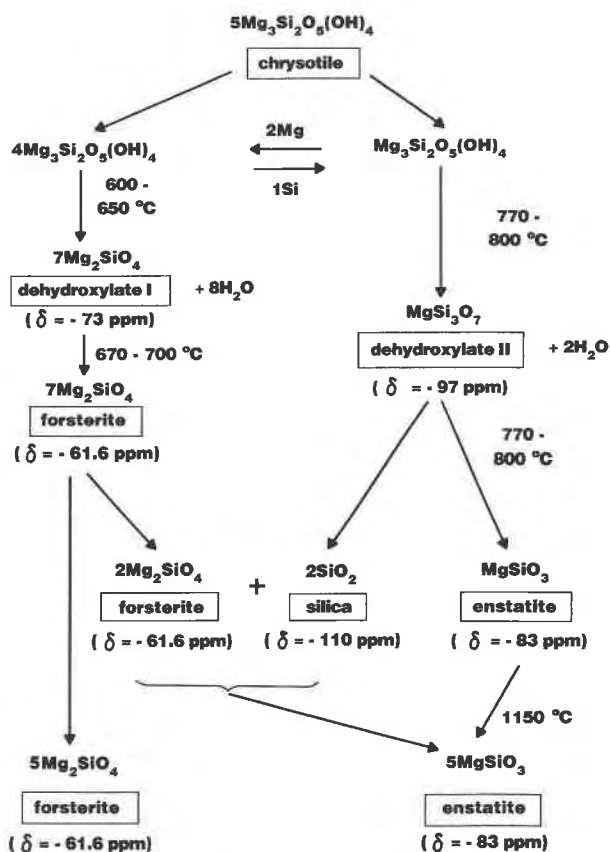


Fig. 7. Schematic representation of the proposed thermal decomposition sequence of chrysotile. The ^{29}Si chemical shifts of the various phases are shown in parentheses.

droxylate II, which is just appearing. If, as seems probable, the forsterite already present by this stage has also formed at the expense of dehydroxylate I, then this phase must account for 65–75% of the total Si in the system. When this is compared with the two alternative heterogeneous reaction schemes previously proposed, it can be seen that the Ball and Taylor scheme (1963) (Fig. 1A) implies the initial transformation of 1 mol of chrysotile into 1 mol of forsterite + 1 mol of an amorphous phase with an enstatite-like composition, i.e., the initially formed forsterite would contain 50% of the available Si. The scheme of Brindley and Hayami (1965) (Fig. 1B) proposes the initial conversion of all the available Mg into forsterite (1.5 mol of forsterite, containing 75% of the available Si) with the excess silica separating as the amorphous phase. Thus the present results for the initial stages of the reaction are more in accord with the scheme of Brindley and Hayami (1965), in that about 65% of the available Si forms forsterite, but at the expense of dehydroxylate I, which is Mg-rich, and retains nothing of the original Si configuration. The remaining Si (about 30%) is associated with dehydroxylate II, which, although Si-rich, also contains Mg and crystallizes at about 800 °C to enstatite, with the separation of the excess Si as SiO_2 . Thus, the overall

reaction sequence, as suggested by the NMR results, contains similarities to that of Brindley and Hayami (1965) but is more complex. The suggested reaction sequence, based on the NMR results, is shown schematically in Figure 7.

One outstanding question raised by the reaction sequence of Figure 7 is why chrysotile dehydroxylates yielding two different dehydroxylate phases. A clue to the answer may lie in the different ways in which the chrysotile lattice decomposes under dry and hydrothermal conditions (Ball and Taylor, 1963). Dry decomposition (such as would be expected in the outer layers of the fibril bundles, where the H₂O formed can readily escape) leads to decomposition of the silicate structure, with the Mg coordination remaining largely intact. By contrast, under hydrothermal conditions, the Si-O structure remains largely intact, with the major changes occurring in the Mg layer (Ball and Taylor, 1963). Although conditions in the innermost layers of the fibril bundles would not necessarily correspond to the most severe hydrothermal conditions that can be imposed experimentally and that lead to the formation of the 2:1 layer silicate talc (Ball and Taylor, 1963), nevertheless, the formation of a dehydroxylate retaining phyllosilicate characteristics may reflect the quasi-hydrothermal conditions in the deepest layers of the fibril structure.

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