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Solid state ^{29}Si NMR examination of the 2:1 ribbon magnesium silicates, sepiolite and palygorskite

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Abstract

The results of a ^{29}Si NMR study of the 2:1 magnesium ribbon silicates, sepiolite and palygorskite are presented. Separate resonances between −92 and −98 ppm for the three and two types, respectively, of silica units across the ribbons are observed. This provides information on factors other than tetrahedral aluminium substitution which can affect the Q^3 chemical shift. Also observed is a Q^2 SiOH resonance from crystal defects or edges. The structural changes which occur at the various stages of dehydration have been studied. Finally, some interesting observations on ^{29}Si relaxation and cross-polarization dynamics are presented.

Introduction

In numerous recent papers the utility of solid state ^{29}Si NMR to provide structural information has been demonstrated for a wide range of insoluble materials. While a large proportion of these studies have been concerned with problems in zeolite structures, presumably as a result of their commercial value, a smaller number of studies have appeared dealing with clay minerals. As part of our work in this latter area, we have recently examined samples from the palygorskite and sepiolite group of clay minerals.

Both minerals can be considered as 2:1 type phyllosilicates since they contain two dimensional tetrahedral sheets in which individual tetrahedra are linked with three neighboring tetrahedra by sharing three corners. Talc and pyrophyllite are the respective Mg and Al zero interlayer charge end members of this group. The sepiolite and palygorskite structures differ however in that, instead of 2:1 sheets, they are based on alternating 2:1 ribbon structures (Fig. 1). In the former the ribbons are eight octahedral positions across while in the latter, ribbons are five octahedral positions wide, and may be considered as consisting of three and two pyroxenic chains respectively. Although the tetrahedral sheets are continuous, the apices in adjacent bands point in opposite directions. Hence both structures contain open channels of fixed dimensions running parallel to the chains. These channels contain water and cations with two water molecules adjacent to the octahedral strip in order to satisfy coordination requirements of the octahedral sheet. The remaining water molecules occupy definite positions in the channels. Hence these clay minerals are in this way similar to zeolites. Ideal structural formulae are $(OH_2)_4(OH)_2Mg_2Al_2Si_8O_{20}4H_2O$ for palygorskite and $(OH_2)_4(OH)_4Mg_8Si_{12}O_{30}8H_2O$ for sepiolite (Bradley, 1940; Brauner et al., 1956; Preisnger, 1957). Whereas palygorskite can contain up to 50% aluminium in the octahedral sheet, in sepiolite the octahedral aluminium is much lower (<10%). Tetrahedral layer substitution is however relatively unimportant in both minerals.

The unusual structure of the 2:1 ribbon silicates presents a number of features which should prove interesting for a ^{29}Si NMR study. For example, while all silicons can be expected to be in a Q^3(0Al) environment (Lippmaa et al., 1980), the presence of the open channels, zeolitic and structural water, and inverted Si–O–Si linkages to adjacent ribbons might all be expected to result in variations of the Q^3(0Al) chemical shift as observed in normal 2:1 layer silicates. Hence further information on the range and variation of the Q^3(0Al) shift should be available. The last factor, the edge linkage, should prove a particularly interesting factor. Although, precise crystal structure data is not available, it is likely that these edge Q units must experience some strain and exhibit unusual bond lengths and angles compared to those within the ribbons and in normal 2:1 layer silicates. Variations in these parameters have resulted in some unexpected shift variations in framework silicates. For example, in zeolite A a high field shift of the Q^4 (4Al) silicon resonance was initially mistaken for a Q^4 (3Al) resonance (Thomas et al., 1981). This resulted in the conclusion that Loewenstein's aluminium avoidance

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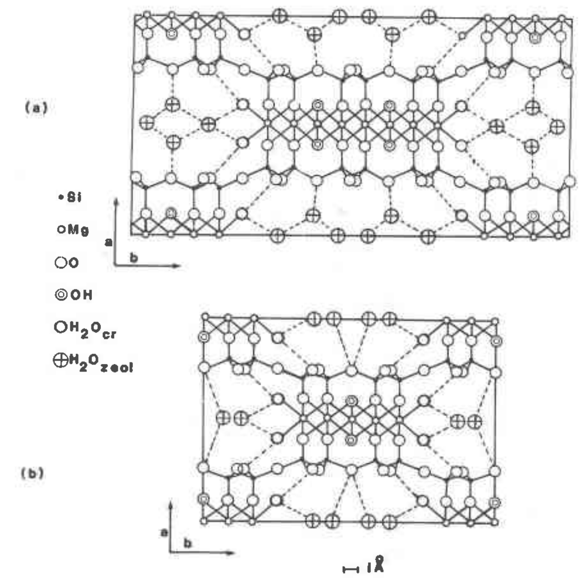

Fig. 1. (a) Schematic representation of the structure of sepiolite. (b) Schematic representation of the structure of palygorskite.

principle was violated. However, examination of similarly structured zeolites with lower Si/Al ratios showed that the resonance was in fact due to Q^4(4Al) silicons and the unusual shielding was tentatively attributed to unusual Si–O–Si angles in strained double four-membered rings (Thomas et al., 1982; Melchior et al., 1982). Subsequently Smith and Blackwell (1983) have demonstrated a good correlation for a range of silica polymorphs between ^{29}Si chemical shift and mean secant of Si–O–Si bond angles. Finally, these ribbon silicates undergo a series of well characterized structural changes with exposure to higher temperatures. The examination of these different stages by ^{29}Si NMR should provide further valuable information on the utility of the technique to probe the structure of silicates.

Experimental

^{29}Si NMR spectra were obtained at 59.61 MHz using a Bruker CXP-300 spectrometer. Both cross-polarization/magic angle spinning (CP/MAS) and single pulse ^{1}H dipolar decoupled (DD) spectra were obtained using H_1 fields of 10 and 50 G for ^{1}H and ^{29}Si respectively. Other relevant details are given in figure captions. ^{29}Si relaxation times were measured by the use of $\pi/2(y)$-τ-$(\pi/2)(y)$ sequence subsequent to cross-polarization being established on the x axis. ^{29}Si–^{1}H nuclear overhauser enhancement (NOE) measurements were carried out by preceding a single ^{29}Si pulse by a series of ^{1}H π pulses.

The palygorskite sample studied was from Attapulgus, Georgia and the sepiolite sample from Vallecas, Spain. Chemical analyses have been published (Caillere et al., 1961) and samples used were examined by X-ray diffraction for mineralogical purity. The former sample gave relatively poor spectra using cross-polarization with superior spectra generally obtained using single ^{29}Si pulses. Hence, except where noted, all spectra were obtained by the latter technique. In contrast, the sepiolite sample cross-polarized extremely well and spectra obtained by both methods are presented. Samples of both materials were heated at various temperatures for 20 hours unless stated otherwise.

Results and discussion

Assignments

^{29}Si spectra for sepiolite and palygorskite obtained both with and without cross-polarization are shown in Figure 2. The spectra of the former exhibit three major signals at -92, 95 and 98.5 ppm, while spectra of the latter exhibit two major signals at -92 and -98 ppm. For palygorskite the linewidths are much larger, single pulse spectra could be obtained with much shorter recycle times, and spinning sidebands were more evident at slow spinning speeds compared with the sepiolite. These observations are certainly consistent with a higher paramagnetic impurity content of the palygorskite (Barron et al., 1983). It is also possible that the larger linewidths to some extent result from the variable octahedral sheet occupancy i.e., aluminium and magnesium. ^{27}Al MAS spectra reveal only trace amounts of tetrahedral aluminium in both materials and a significant octahedral content for the palygorskite. The number of major ^{29}Si signals present for each material is consistent

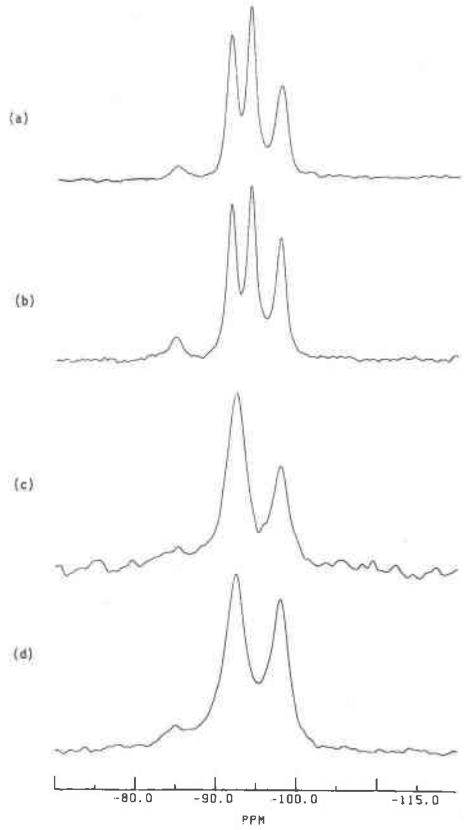

Fig. 2. ^{29}Si MAS spectra of (a) Sepiolite obtained using cross-polarization with a contact time of 5 ms. (b) Sepiolite obtained using a single $\pi/2$ pulse with 100 s recycle time. (c) Palygorskite obtained using cross-polarization with a 1 ms contact time. (d) Palygorskite obtained using a single $\pi/2$ pulse with a 2 s recycle time.

with the different ribbon widths of four and six silica units. Ideally the palygorskite would be expected to give two signals of equal intensity, corresponding to the edge and internal Q^3 silicons of the ribbons. Likewise, the sepiolite would be expected to give three resonances of equal intensity for the three types of silicons across the ribbons.

Clearly, substantial effects on the Q^3 chemical shift are present which cannot be due to tetrahedral substitution. The range of shifts observed for palygorskite and sepiolite of −92 to −98 ppm corresponds to that observed for normal layer 2:1 magnesium silicates. For example, talc, the zero interlayer charge endmember, yields a single resonance at −98 ppm (Lippmaa et al., 1980) while low charge examples, i.e., low tetrahedral aluminium substitution, such as saponite and hectorite (Fig. 3) exhibit a low field shift of the Q^3 (0Al) resonance to −95 ppm. This deshielding must be related to increased interlayer separation necessary to accommodate charge-balancing cations, or else to the associated introduction of interlayer water. Higher tetrahedral Al substitution results in even greater deshielding of the Q^3(0Al) resonance in 2:1 magnesium silicates as demonstrated by the spectrum of Llano vermiculite (Fig. 3) in which this resonance is observed at −92 ppm. This further deshielding presumably results from increased concentration of interlayer cations or a second nearest tetrahedral neighbor effect. Preliminary experiments have shown that Q^3(0Al) shift is independent of the type of interlayer cation.

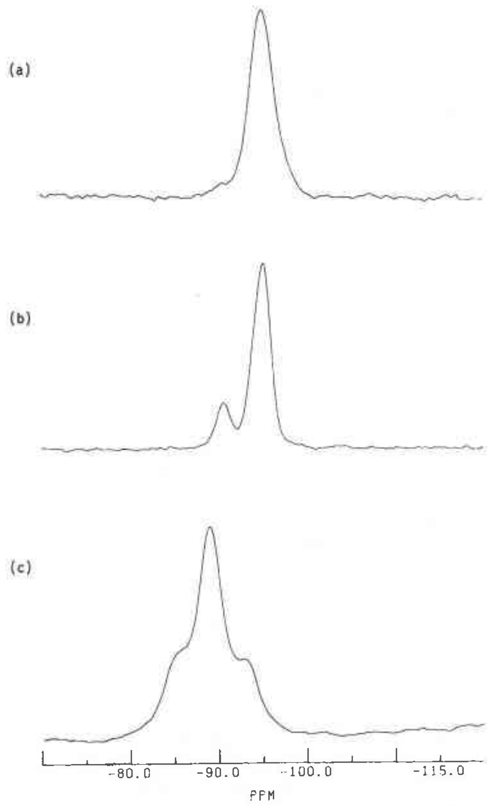

Fig. 3. ^{29}Si MAS spectra of (a) hectorite (Hector, California); (b) saponite (Milford, Utah) and (c) vermiculite (Llano, Texas).

The presence of zeolitic water in the channels of sepiolite and palygorskite and the absence of significant layer charge suggests that a chemical shift similar to that for saponite and hectorite, i.e. ~95 ppm would be observed. A resonance is observed in this region for sepiolite but not for palygorskite. This would be consistent with the silicon most remote from the ribbon edges in sepiolite. This central silicon is two Q units removed from the edge. The absence of a signal at −95 ppm in palygorskite is presumably due to the fact that the ribbon is only four Q units wide with the internal unit being only one removed from the edge. Hence the two remaining resonances in sepiolite and the resonances in palygorskite which occur at −92 and −98 are due to silicons on the edge of the ribbons and the silicons one removed from the edge. The assignment is clarified by the presence of weaker signals in the −80 to −90 ppm range in the spectra of both palygorskite and sepiolite, and the actual relative intensities of the major peaks in the single pulse spectra of Figure 2. The resonances at ~98 ppm in both cases have reduced intensity relative to the other major resonances. For the sepiolite, this loss of intensity of ~17% is accounted for by the signal at −86 ppm. Alrichs and coworkers (1975) have studied the OH stretches in the IR spectra of sepiolite and have assigned a peak at 3720 cm^{-1} to SiOH groups at crystal edges i.e., ribbons not bonded to other ribbons. The edge silicons are Q^2 units which would be expected to give ^{29}Si resonances in the vicinity of −86 ppm (Lippmaa et al., 1980). Hence the resonance of reduced intensity at −98 ppm is due to the silicon units at the edges of ribbons and bonded via a basal oxygen to an adjacent ribbon. It is worth noting that using infrared spectroscopy, although it was possible to detect edge SiOH groups, it was not possible to obtain reliable estimates from peak areas of the proportion of these groups present and hence the degree of crystallinity of the sepiolites studied. Clearly ^{29}Si spectra obtained using single ^{29}Si pulses and sufficiently long recycle times should be able to provide such accurate estimates. For the sepiolite used in this study, approximately 1 in 6.5 silicons on the edges of ribbons is also at a crystal edge of defect. Sepiolites from other locations also exhibit this extra resonance but in variable relative intensity. The palygorskite spectrum exhibits a similar but much broader shoulder in the vicinity of −85 ppm. The intensity indicates only slightly greater proportion of SiOH groups while the width suggests a greater chemical shift dispersion. Both factors indicate a slightly higher degree of disorder i.e. lower crystallinity of the palygorskite. Therefore, the much larger linewidths observed for the resonances in palygorskite are unlikely to be due to any large extent to significantly lower crystallinity.

Hence, the edge silica units resonating at −98 ppm are shielded relative to the internal silica units while those one unit removed from the edge, and which resonate at −92 ppm, are deshielded by a similar amount. The reasons for these shift variations are not easily explainable especially due to lack of precise crystal structure data. A dependence of the ^{29}Si chemical shift on mean secant Si–O–Si angle, as observed for framework silicates, may also be effective in layer silicates (Smith and Blackwell, 1983). For example, the Si–O–Si bond angle at the connection of adjacent ribbons must be significantly larger than those typical of continuous layer silicates (i.e., ~120°). The shielding of the edge silicon relative to those within the ribbon would be consistent with the shielding observed for larger Si–O–Si angles in framework silicates. On this basis, the resonance at 92 ppm would result from a decrease in Si–O–Si angles. Another possibility is a differing shielding effect of the water present in the channels. This consists of two types of molecules, those coordinated to magnesium at the edge of octahedral sheets and hydrogen bonded to basal oxygens of adjacent ribbons, and loosely held zeolitic water. The number of zeolitic water molecules per unit formula is eight for sepiolite and four for palygorskite. The locations of the zeolitic water molecules and the hydrogen bonding arrangement with the basal oxygen of silica ribbons can only be postulated. However, it appears that at least one of the three basal oxygens of each type of silicate unit must be involved in hydrogen bonding with water molecules located in the channels. Hence the hydrogen bonding from water molecules in the channels seems unlikely to be the cause of the large difference in shift between the two silicate units closest to the ribbon edge.

Gard and Follett (1968) proposed a structure for palygorskite which differed considerably from that proposed originally by Bradley (1940). Their model involved ribbons 6 silicate units wide, as in sepiolite, linked by single pyroxene chains and separated by channels. Our ^{29}Si NMR results clearly disprove this structure as it would require three ^{29}Si resonances for the ribbon as observed for sepiolite plus at least one additional signal from the pyroxene chains. The observation of only two major ^{29}Si resonances with shifts in close agreement with the analogous resonances in sepiolite confirms the original structure of Bradley (1940).

Thermal behavior

Samples of both sepiolite and palygorskite were heated for 20 hours at temperatures between 130 and 900°C. Spectra for sepiolite heated at 130, 400, 700 and 900°C are shown in Figure 4. DTA and thermogravimetric curves for sepiolite exhibit four endotherms at 90–120, 325–400, 450–580, and 750–810°C (Hayashi et al., 1969). The first endotherm corresponds to loss of zeolitic water and the second corresponds to loss of one of the two structural water molecules at the edge of the octahedral ribbon. Rehydration at both these stages occurs readily under normal humidity conditions. X-ray diffraction indicates that loss of zeolitic water does not result in any structural change (Nagata et al., 1974). However electron diffraction studies by Rautureau and Tchoubar (1976) carried out under vacuum suggest that some minor structural changes do occur. The second stage loss of one half of the edge water molecule results in a folding of the ribbon structure as indicated in Figure 7. The third endotherm results from the loss of the second edge water molecule. This state is irreversible. The final endotherm results from loss of structural hydroxyls with a transformation to clinoenstatite.

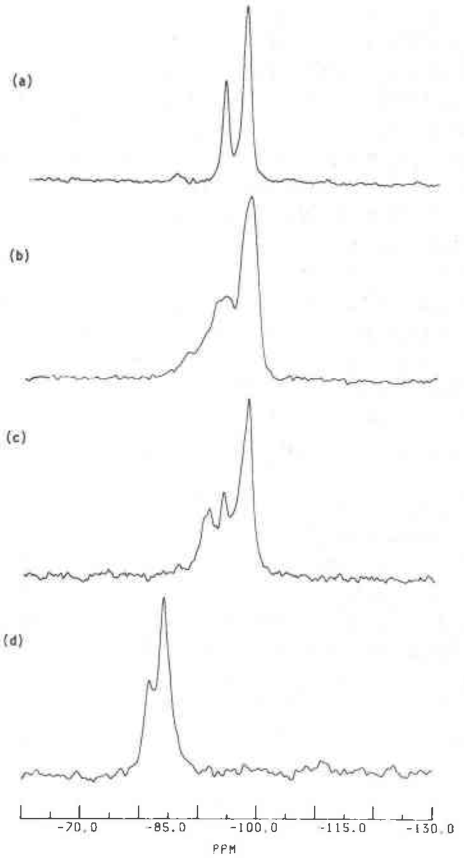

Fig. 4. ^{29}Si MAS spectra of sepiolite after heating at (a) 130°C; (b) 400°C; (c) 700°C and (d) 900°C. Spectra were obtained using cross-polarization except for (d).

The ^{29}Si spectrum obtained after heating at 130°C (Fig. 4a) is dramatically changed with only two major resonances being observed at −93 and −97 ppm. The latter resonance is approximately twice as intense as the lower field resonance. This could be taken to indicate that significant structural changes do occur on removal of the zeolitic water. However the changes appear to be consistent with the effects observed for interlayer water on ^{29}Si chemical shifts in layer 2:1 silicates. The presence of interlayer water induces a deshielding of ~3 ppm between talc and saponite. It appears that the resonances at −95 ppm has been shifted to ~−97 ppm due to loss of zeolitic water which is hydrogen bonded to the basal oxygens of this silicon. The other two resonances are only slightly shifted in contrast. This is consistent with the resonance at −95 ppm being the innermost silicon of the ribbon as the models proposed for the positions of the zeolitic water in the channels maintain that the basal oxygen of this silica unit are only hydrogen bonded to zeolitic water molecules. In contrast the basal oxygens connecting the edge silica units with that one removed from the edge, are hydrogen bonded to the water molecules coordinated to magnesium along the edge of the octahedral sheet of the ribbon. These latter water molecules are not removed by heating at 130°C and hence the deshielding effect of the loss of zeolitic water would be expected to be less pronounced than for the internal unit. The crystal edge Si–OH resonances are also not significantly affected by the loss of zeolitic water.

The ease with which rehydration occurs at this stage is demonstrated in Figure 5. A broadening of the resonance at -97 ppm is evident after the sample was sealed in a MAS rotor for 10 days. Reappearance of the signal at -95 ppm is clearly evident after 10 minutes exposure to air by removal of the rotor cap. The original resonances and linewidths are obtained after one hour exposure in this manner.

The folding which occurs on the loss of one half of the structural water molecules at 325–400°C could be expected to result in considerable changes in the ^{29}Si NMR spectrum. For instance the folding should result in the six silica units across the ribbon becoming non-equivalent due to the coordination of magnesium with the basal oxygens between the outer two silica tetrahedra at one end only of the adjacent ribbon. The remaining structural water molecules are supposedly located in such a position as to enable hydrogen bonding with the hydroxy group of the octahedral layer of the other adjacent ribbon (Serna et al., 1975). Furthermore the folding would be expected to involve a significant reduction in Si–O–Si angle between edge silicons of connected ribbons. Finally, no silicons will have basal oxygens involved in hydrogen bonding. The spectrum obtained at 400°C is not remarkably different however to that at 130°C. Both major resonances at ~ -93 and -97 ppm have broadened considerably. The former resonance in fact extends to below -90 ppm. Heating at 700°C and the loss of the remaining structural water results in a sharpening of the spectrum into three signals at -91, -94 and -98 ppm with intensities in the ratio of $\sim 1:1:4$. Samples after heating at both temperatures cross-polarized indicating that loss of structural hydroxyls had not occurred. Further, the edge Si–OH signal at -86 ppm is still present and is particularly evident in the 400°C spectrum due to the broadening of other signals.

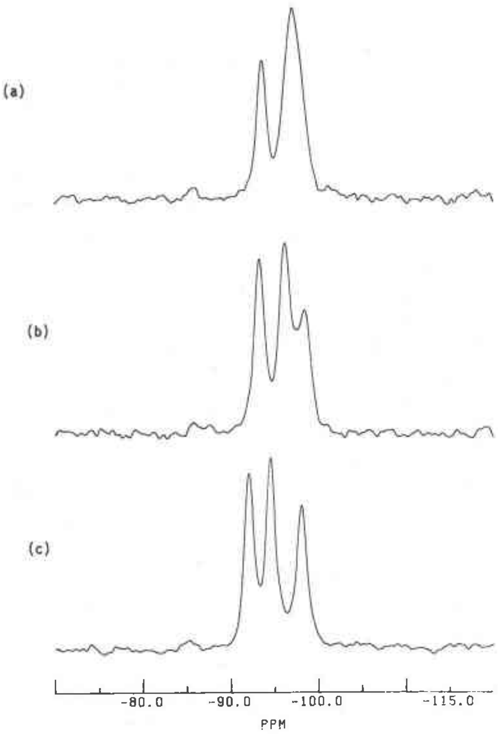

Fig. 5. ^{29}Si CP/MAS spectra of rehydration of sepiolite after heating at 130°C and exposure to atmosphere; (a) after ten days sealed; (b) after 10 minutes and (c) after 1 hour exposure.

It may have been expected that the folding would cause a shift of $\sim$1–3 ppm to higher field of the resonance at -98 ppm in the fully hydrated material due to the loss of the deshielding effect of the edge structural water. However, this must be offset by some other effect. The most likely reason is that the folding results in a significant reduction of the Si–O–Si angle of the edge silicons connecting ribbons and hence a deshielding of this resonance. In the folded structure, the edge magnesiums of the octahedral ribbons are coordinated to the basal oxygens at one edge of the ribbon which connect the edge silicon with the silicon one removed from the edge. This will result in two of the six silicons being deshielded by magnesium and these are presumably the peaks at -91 and -94 ppm. The remaining four silicons would thus appear to resonante at -98 ppm, close to the shift of talc.

At 750–800°C structural hydroxyl groups in the octahedral layer are lost resulting in a complete collapse of the sepiolite structure and the formation of clinoenstatite. Enstatite, $MgSiO_3$, is an orthopyroxene consisting of single pyroxene chains with each silicon sharing two basal oxygens with adjacent silicons. The chains are linked laterally by Mg ions. The spectrum of sepiolite after heating at 900°C for 20 hrs (Fig. 4d) consists of two peaks at -81.3 ppm and -83.7 ppm with relative intensities of $\sim 1:2$. These chemical shifts are consistent with the Q^2 structure of pyroxene chains. The appearance of two signals is interesting in that there are two major crystal forms of enstatite, ortho- and clinoenstatite and both have two distinct types of pyroxene chains of equal abundance (Morimoto et al., 1969; Stephenson et al., 1966). The presence of two signals in Figure 4d could indicate either that orthoenstatite is also formed as a minor product or else incomplete formation of one of the two types of chains present in clinoenstatite. X-ray diffraction of this sample indicates that both forms of enstatite are present.

Similar heating experiments were performed on the palygorskite and the results are shown in Figure 6. Like sepiolite, dehydration of palygorskite occurs in four stages. En-

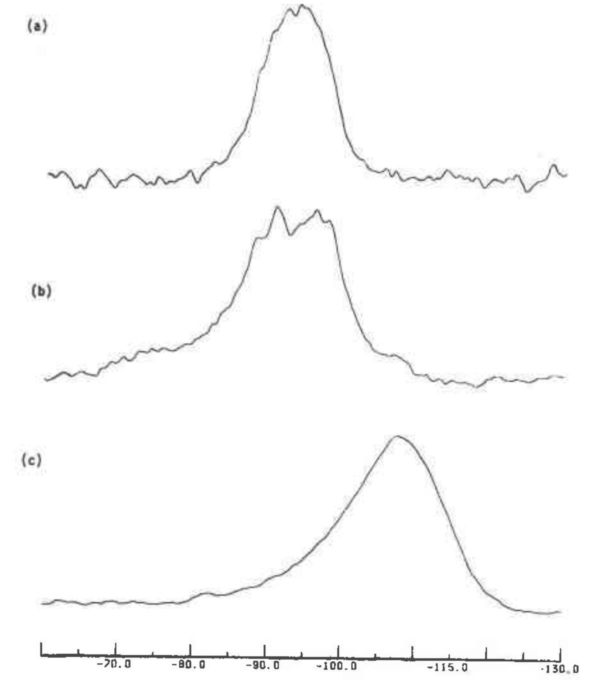

Fig. 6. ^{29}Si MAS spectra of palygorskite obtained after heating at (a) 400°C, (b) 700°C and (c) 900°C. Spectra were obtained using $\pi/2$ pulses and a recycle time of 2 s.

dotherms for these stages have been observed at 80–120, 210–325, 350–550, and 690–770°C (Hayashi et al., 1969). In contrast to sepiolite, no significant change is observed in the spectrum after heating at 130°C. However, this is consistent with the results for sepiolite as the resonance affected by the loss of zeolitic water in sepiolite is not present in palygorskite. This is the silicon two removed from the edge of the ribbon. Palygorskite has only two types of silicon units which share a basal oxygen and which is in turn hydrogen bonded to one of the structural water molecules. Hence neither resonance is significantly affected by the removal of zeolitic water.

As shown in Figure 6, substantial changes do occur in the ^{29}Si spectrum after heating at higher temperature. VanScoyoc et al. (1979) report that, unlike sepiolite, loss of 50% of the structural water does not result in uniform folding. An ordered folded state is apparently not reached until ~65% of this water is lost. After heating at 400°C, where a substantial portion of this water would be removed, virtually a single broad resonance at ~ −93 ppm is obtained. This resonance is significantly broader than the combined linewidths of the original pair of resonances and the center of gravity of the spectrum is shifted to low field by over 2 ppm. The increased linewidth, while it may be consistent with four non-equivalent silicons across the ribbon in the folded structure, is most likely due to non-uniformity of the structure. The shift to lower field is difficult to explain although it may be consistent with the changes in Si–O–Si angles of the edge silicons on folding. The spectra obtained after heating at 500 and 700°C, where folding and loss of structural water is completed, are similar and even broader. However, at least four partially resolved peaks are present between −89 and −98 ppm. The shift of intensity to both high and lower field, compared with the 400°C spectrum, would seem to be more than broadening due to increased disorder. The spectrum is in fact quite similar to that obtained for sepiolite after heating at 700°C when the presence of two internal silica units in the latter is considered. Broad shoulders are evident on either side of the main resonances, which extend to ~ −70 and ~ −110 ppm. The low field shoulder becomes much more pronounced after heating for 40 hours. Clearly, at this temperature considerable breakdown of the ribbon structure to chain or even monosilicate units is occuring.

Finally, at 900°C a broad resonance centered at −108 is obtained indicating the formation of an amorphous framework silicate phase. Preisinger (1957) reported that above 680°C, the hydroxyl groups within the octahedral strip were lost with the formation of enstatite as for sepiolite. Hayashi et al. (1969) however report that this dehydroxylation occurs above 800°C with the formation of an amorphous phase and that a transformation of this phase into enstatite and cristobalite occurs between 900 and 1000°C (Morimoto et al., 1969). The results appear to be consistent with the latter work, at least in the formation of an amorphous phase at 900°C.

Relaxation and cross polarization studies

Preliminary ^{29}Si relaxation and cross-polarization dynamics studies have been performed and some unusual features are present which are worthy of a brief discussion

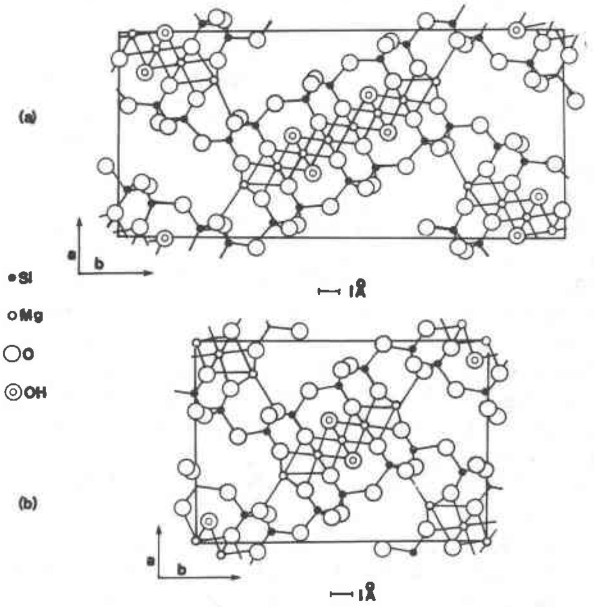

Fig. 7. Schematic structures of (a) dehydrated sepiolite and (b) dehydrated palygorskite.

here. In NMR experiments, the spin-lattice relaxation time, T_1, is the time constant for the recovery of magnetization after excitation. Hence, this determines the rate at which excitation can be repeated for the purpose of improving signal-to-noise via signal averaging. In rigid solids, the spin-lattice relaxation times of dilute spin-$\frac{1}{2}$ nuclei can generally be expected to be very long due to the inherent lack of molecular motion. In fact, the major advantage of the cross-polarization process, which is often used to obtain spectra of such nuclei, is that the ^1H spin-lattice relaxation time of the protons providing the polarization determines the recycle rate which can be used (Pines et al., 1973). This is generally much shorter than that of the low abundance nuclei being observed. The use of the time-saving cross-polarization process is of course dependent on the presence of protons within the structure being detected. Hence, many circumstances exist where cross-polarization is not feasible and spectra need to be obtained using single pulses and with the T_1 of the nucleus being observed determining the recycle rate. This is likely to be a common situation with ^{29}Si spectra of silicate minerals and an understanding of relaxation processes and rates expected is needed.

Fortunately, ^{29}Si relaxation times in rigid silicates have often been found to be shorter than expected. For example we have reported that ^{29}Si T_1's in the 1:1 layer aluminosilicates, kaolins, can vary by at least three orders of magnitude (Barron et al., 1983). Spin-lattice relaxation times of between 0.1 and 5×10^3 s were observed. The explanation of this variation lies in the effect of paragmagnetic centres, via very efficient spin diffusion, on ^{29}Si relaxation times. Small amounts of paramagnetic ions such as Fe^{3+} substituted in the octahedral layer for aluminium are clearly sufficient to result in this range of relaxation rates. For ^{29}Si, a T_1 of 10 s or less should enable spectra to be readily obtained without CP, whereas a T_1 of the order of 1000 s or more makes this a virtual impossibility. Relatively short ^{29}Si relaxation times have also been observed for zeolites which, given the frequent lack of structural protons for cross-polarization, has enabled this important group of silicates to be examined. Consequently we wish to report some preliminary relaxation measurements on sepiolite which provide further understanding of relaxation processes in layer silicates. The presence of mobile zeolitic water in the channels of sepiolite presents the possibility of a dipolar contribution to ^{29}Si relaxation through modulation of the dipolar interaction between ^{29}Si and the protons of the zeolitic water, as is observed in solution due to the random isotropic reorientation. Furthermore, as in solution, the contribution of dipolar relaxation to overall relaxation should result in a nuclear Overhauser enhancement (NOE) on irradiation of the coupled ^1H nuclei (Harris, 1983).

The measured spin-lattice relaxation times for the three major resonances of Vallecas sepiolite are all between 40 and 42 s. Figure 8 shows a single pulse spectrum obtained with a recycle time of 100 s and a spectrum obtained similarly except that during the recycle delay a ^1H π pulse was applied every 10 ms. The spectrum obtained with ^1H irradiation exhibits a reduction in intensity for all resonances including the SiOH resonance, by a factor of ~ -1.4. As the gyromagnetic ratio of ^{29}Si is negative, this reduction is consistent with a ^1H-^{29}Si NOE. The recycle time of 100 s is far less than $10 \times T_1$ normally used for NOE estimates. Hence the value of -1.4 cannot be considered an accurate estimate of the NOE and is undoubtedly an underestimation. Consequently a modulated dipolar interaction between ^{29}Si and protons exists in the sepiolite and a dipolar contribution to the ^{29}Si relaxation should be present. Replacement of the zeolitic water with D_2O should result in an increase in ^{29}Si relaxation and loss of the NOE if these protons are involved. This in fact did result in an increase of T_1's to 70–80 s for the three major resonances. Using the simple relationship

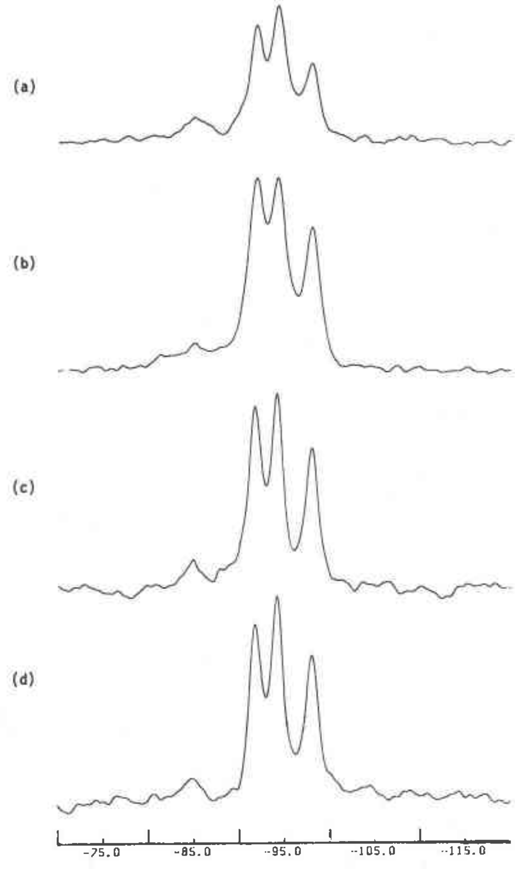

Fig. 8. ^{29}Si single pulse spectra of sepiolite obtained with (a) and without (b) ^1H irradiation during a recycle delay of 100 S. ^1H irradiation was via π pulses applied every 10 ms. Spectra obtained after D_2O exchange with (c) and without (d) ^1H irradiation are also shown.

$$R_1^{obs} = R_1^{dipolar} + R_1^{other}$$

where $R_1 = T_1^{-1}$, $R_1^{obs} = .025$ s and $R_1^{other} = .013\ s^{-1}$ yields a value for the dipolar contribution to relaxation of ~ 85 s. Furthermore no NOE was observable even for the edge SiOH groups suggesting that exchange of the hydroxy proton has occurred. After removal of the zeolitic water by heating at 130°C, no NOE is observable for the two major peaks. Thus the zeolitic H_2O is clearly responsible for the observed enhancement and the structural water and OH groups must be relatively rigid. The edge SiOH resonance however still exhibits a negative NOE derived from the hydroxy proton. Surprisingly the T_1's determined in this state are significantly reduced to ~ 10 s for the two major resonances. The explanation for this has not been investigated. However, it is highly likely that, in the absence of the zeolitic water within the channels, efficient relaxation via paramagnetic molecular oxygen is occuring. Cookson and Smith (1985) have observed efficient relaxation via this mechanism in silicalite which has a similar type of open cage/channel structure.

The cross-polarization process requires irradiation with matched ^1H and ^{29}Si rf fields to enable transfer of polarization (Pines et al., 1973). As shown in Figure 9, the peak at -95 ppm is extremely sensitive to this matching. The peak at -92 exhibits a slight sensitivity whilst that at -98 ppm is relatively insensitive to matching. Replacement of the zeolitic water with D_2O removes this sensitivity to Hartman–Hahn matching. Non-spinning spectra also do not exhibit any obvious sensitivity. This result is intriguing and obviously related to the cross-polarization dynamics. Mobile zeolitic water would be expected to have a reduced homonuclear dipolar coupling. For the ^{13}C spectrum of adamantane, Stejskal, Schaefer and Waugh (1977) have pointed out the extreme sensitivity to the matching of the Hartmann-Hahn condition. A semi-quantitative theoretical analysis indicated that such a sensitivity will arise when the spinning speed exceeds the dipolar interaction between protons. This would suggest that cross-polarization in sepiolite was derived from the different protons for the three resonances. However, contact time dependence studies do not reveal any other substantial variations in cross-polarization behaviour. One explanation is that the central silicon units are cross-polarized from relatively rigidly bound zeolitic water molecules hydrogen bonded to the basal oxygens joining these silicons to those one removed from the ribbon edge, and that these in turn experience only weak dipolar interaction with more mobile zeolitic water.

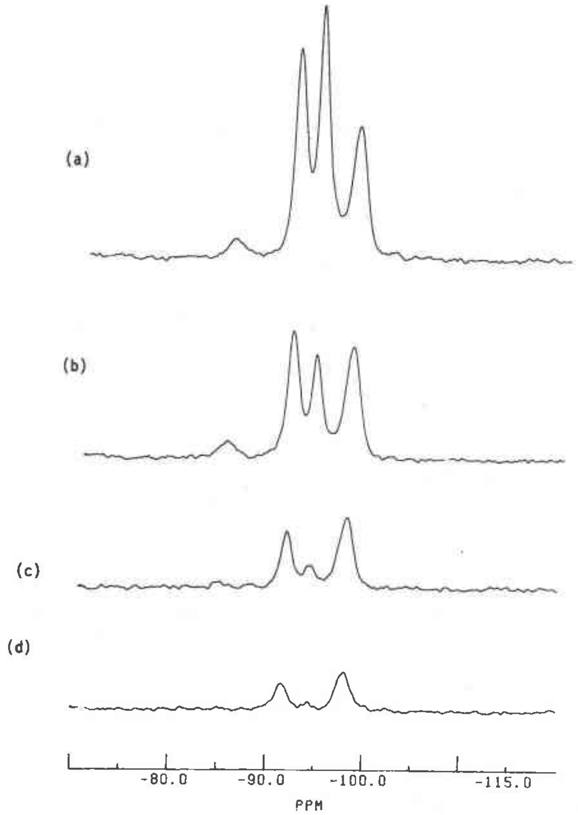

Fig. 9. ^{29}Si CP/MAS spectra of sepiolite as a function of Hartman–Hahn matching spectra were obtained with ^1H rf field of 10 G and ^{29}Si rf fields of (a) 50 G, (b) 43 G, (c) 40 G and (d) 37.5 G. 192 FID's were collected in each case and spectra are scaled relative to (a).

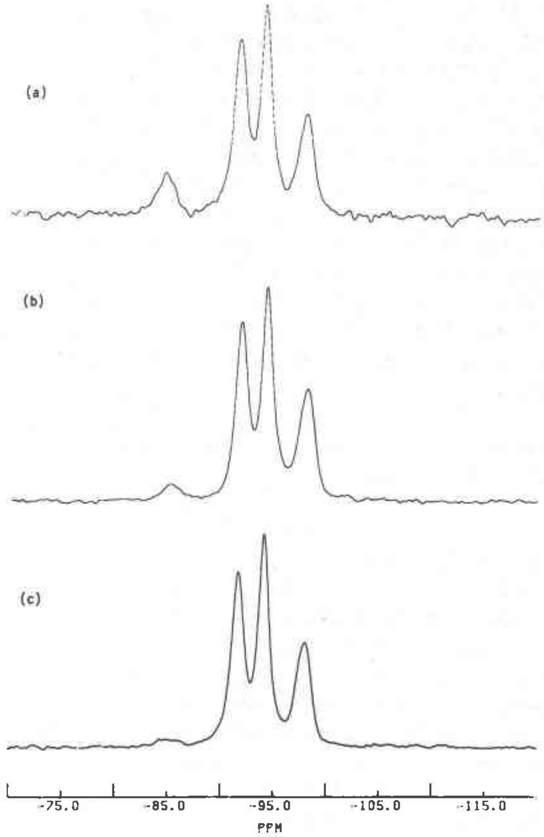

Fig. 10. ^{29}Si CP/MAS spectra of sepiolite with contact times of (a) 1 ms; (b) 5 ms and (c) 10 ms. 192 FID's were collected in each case and are scaled to the same height.

A further noteworthy point is the cross-polarization behavior of the edge SiOH resonance at -86 ppm. While this resonance is quite evident in spectra obtained with 5 ms contact, it is barely evident at contact times of 10 ms or greater (Fig. 10). The three major resonances still exhibit strong cross-polarization at greater than 20 ms. Hence, the edge Q^2 groups would appear to cross-polarize from the $-OH$ protons which apparently exhibit much shorter ^1H $T_{1\rho}$ values than do the internal protons. This suggests considerable motion of the OH group in the kHz range. These observations are consistent with earlier results for the mineral imogolite (Barron et al., 1982) which was observed to achieve maximum enhancement in the vicinity of 1–2 ms contact time. Imogolite consists of an isolated Q^1 orthosilicate group bonded to three octahedral aluminiums and an hydroxy group. After heating at 130°C and rehydration with D_2O, this resonance in sepiolite exhibits similar cross-polarization behavior to the major resonance and is still very evident at contact times of 10 ms or greater. This must be indicative of deuteration of the edge SiOH groups which are consequently cross-polarized from hydroxy protons within the octahedral layer and which are not exchanged under these conditions.

Conclusions

^{29}Si spectra of sepiolite and palygorskite show that factors other than tetrahedral aluminium substitution can significantly affect the chemical shift of the Q^3 resonance of layer silicates. The range observed for sepiolite and palygorskite is from -92 to -98 ppm. Coordination of basal oxygens of the silicate sheet with zeolite water certainly results in deshielding. The Q^2 Si–OH groups present at the edge of ribbons at crystal edges or defects give a resonance at ~ -86 ppm which provides a measure of crystallinity. Spectra obtained from heating at various temperatures are largely consistent with the well-known stages of dehydration and decomposition of these ribbon silicates. Relaxation studies show that ^1H–^{29}Si dipolar relaxation can contribute to ^{29}Si relaxation. In the case of sepiolite and palygorskite this dipolar contribution to relaxation arises from the presence of zeolitic water in the open channels. A similar contribution may also be expected for the normal expanded layer silicates such as vermiculites and smectites. The presence of zeolitic water also results in some minor effects on cross-polarization behaviour in sepiolite.

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