

SOLID-STATE NUCLEAR MAGNETIC RESONANCE STUDY OF SEPIOLITE AND PARTIALLY DEHYDRATED SEPIOLITE

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Abstract—The assignment of the ^{29}Si CP/MAS-NMR spectrum of naturally-occurring sepiolite clay was re-examined using ^{29}Si COSY and ^1H - ^{29}Si HETCOR pulse sequences. Each of the three main resonances at -92.1 , -94.6 and -98.4 ppm has been attributed to one of the three pairs of equivalent Si nuclei in the basal plane, and the resonance at -85 ppm to $\text{Q}^2(\text{Si-OH})$ Si nuclei. On the basis of the COSY experiment, the resonance at -92.1 ppm is unambiguously assigned to the intermediate, near-edge Si sites. The HETCOR experiment revealed that the resonance at -94.6 ppm cross-polarizes almost entirely from the Mg–OH protons, and therefore is assigned to the central Si position. The remaining resonance at -98.4 ppm correlates strongly to the protons of the structural water molecules and therefore is assigned to the edge Si sites. Nearly complete rehydration was achieved at room temperature by exposing sepiolite samples that had been partially dehydrated at 120°C to water vapor or to D_2O vapor. The rehydration results support the ^{29}Si NMR peak assignments that were made on the basis of the COSY and HETCOR experiments.

The ^{29}Si CP/MAS-NMR spectrum corresponding to the folded sepiolite structure in which approximately one half of the structural water has been removed by heating to 350°C is reported for the first time. The chemical shift values and relative intensities are significantly different compared to the resonances that are observed in the corresponding spectrum of the true sepiolite anhydride. These observations support the earlier claim that sepiolite heated to $\sim 350^\circ\text{C}$ exists as a distinct phase to be differentiated from that of the completely dehydrated state.

Key Words—Dehydrated Sepiolite, Magic Angle Spinning NMR, Sepiolite, ^{29}Si CP/MAS-NMR, ^{29}Si NMR Signals Assignment, 2-Dimensional Solid State NMR.

INTRODUCTION

Sepiolite is a naturally-occurring fibrous clay mineral with the theoretical half unit-cell formula $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$ (Preisinger, 1959). The structure of sepiolite is derived from talc-like T–O–T ribbons that expand infinitely along the z direction, with a width of three pyroxene chains (Figure 1a). Each ribbon is connected to the next through an inverted Si–O–Si bond, resulting in a staggered talc layer with a continuous tetrahedral sheet and a discontinuous octahedral sheet. The discontinuous nature of the octahedral sheet allows for the formation of rectangular, channel-like micropores, which run parallel to the fiber axis and which are filled completely by zeolitic water ($\text{H}_2\text{O}_{\text{zeol}}$) at room temperature. The channels measure $\sim 3.7 \times 10.6 \text{ \AA}$ in cross-section, and they account in large part for the large specific surface area and excellent sorptive properties of sepiolite, once the zeolitic water has been removed by thermal treatment that does not exceed 150°C . Finally, the terminal Mg^{2+} ions that are located at the edges of the octahedral sheets complete their coordination with two molecules of structural water ($\text{H}_2\text{O}_{\text{kr}}$), which are in turn hydrogen bonded to zeolitic water molecules located within the microporous channels.

Sepiolite crystals are progressively dehydrated as the thermal treatment temperature is increased, with four

stages of weight loss observed (Nagata *et al.*, 1974; Serna *et al.*, 1975; Jiménez-López *et al.*, 1978). Heating sepiolite in air at temperatures $<150^\circ\text{C}$ removes selectively the zeolitic water molecules from the nanoporous channels, while leaving the structural water molecules and the Mg–OH groups unaffected (Figure 1b). Coordinated structural water molecules are lost at higher temperatures in two steps; one $\text{H}_2\text{O}_{\text{kr}}$ per Mg^{2+} is removed, beginning at $\sim 300^\circ\text{C}$ in air (Figure 1c) and a second $\text{H}_2\text{O}_{\text{kr}}$ is released between 400 – 600°C , at which point the true sepiolite anhydride is obtained (Figure 1d). Folding of the sepiolite crystals occurs when approximately one half of the structural water has been removed, which allows the terminal Mg^{2+} to complete their coordination with the oxygen of the neighboring silica surface. Structural folding is nearly completely reversible provided that the treatment temperature does not exceed 250°C (Weir *et al.*, 2000), but becomes irreversible once the true anhydride is formed. Finally, the Mg–OH hydroxyl groups are released at ~ 780 – 850°C , and the anhydride is transformed into enstatite (d’Espinoze de la Caillerie and Fripiat, 1994; Pérez-Rodríguez and Galán, 1994).

Currently, a wide range of technological applications is based on the sorptive and catalytic properties of sepiolite (Galán, 1996). Sepiolite is being used increasingly as a decolorizing agent (Demirci *et al.*, 1995), as a catalyst or catalyst carrier (Corma and Martín-Aranda, 1991; d’Espinoze de la Caillerie and Fripiat, 1992;

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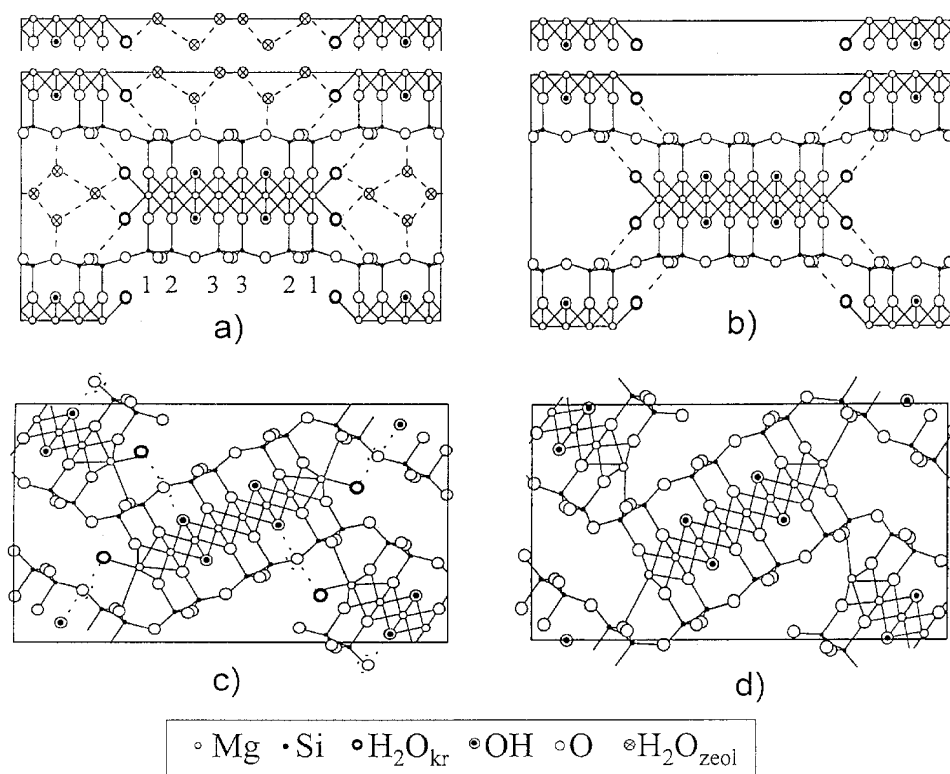


Figure 1. Schematic representation of the structure of sepiolite after (a) no thermal treatment, (b) heating in air to 120°C, (c) heating in air to 350°C, and (d) heating in air to 500°C (adapted from Preisinger, 1963).

Damyanova *et al.*, 1996), and as an odorant adsorbent in environmental applications (Sugiura, 1993; Sugiura *et al.*, 1990, 1991). Sepiolite has also been used recently as the major component for the fabrication of all-inorganic ultrafiltration membranes (Le Van Mao *et al.*, 1999; Wang *et al.*, 2001; Weir *et al.*, 2001). It is therefore of great interest to characterize fully and to understand the properties of sepiolite. In fact, several papers have discussed the structural, textural and sorptive properties of sepiolite (Rytwo *et al.*, 1988; Inagaki *et al.*, 1990; Shariatmadari *et al.*, 1999) and of sepiolite after acid or thermal treatment (Jiménez-López *et al.*, 1978; Pérez-Rodríguez and Galán, 1994; Vincente *et al.*, 1994; Myriam *et al.*, 1998). These studies utilized primarily powder X-ray diffraction (XRD), infrared spectroscopy (IR), TGA/DTA and a variety of adsorption/desorption techniques involving the adsorption of molecules or cations from either the vapor phase or from solution.

Magic-angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy can provide considerable additional information pertaining to the structure of solid-state microporous materials such as sepiolite. A number of studies have previously examined the ^{29}Si MAS-NMR spectrum of sepiolite and of the products that were obtained after thermal treatment at different temperatures. Barron and Frost (1985) and Komarneni *et*

al. (1986) relied on empirical comparison with the chemical shifts observed in other minerals and reported contradictory assignments. More recently, cross polarization techniques (^{29}Si CP/MAS-NMR) have been used to assign the main sepiolite resonances (d'Espinose de la Caillerie and Fripiat, 1992, 1994; Aramendía *et al.*, 1997; Shore *et al.*, 1998). Peak assignments were made based on the assumption that the transfer of magnetization to the Si nuclei is possible only from the immobile $\text{H}_2\text{O}_{\text{kr}}$ protons; hence the efficiency of the cross-polarization process was assumed to decrease as the distance between the Si nuclei and the $\text{H}_2\text{O}_{\text{kr}}$ protons increased.

In the current work we have re-examined the ^{29}Si MAS-NMR spectrum of sepiolite using the two-dimensional ^1H - ^{29}Si HETCOR and ^{29}Si -COSY pulse sequences, which can provide more detailed information about through-space and through-bond interactions, respectively, and about the Si atom connectivity in the sepiolite structure. In addition, using ^{29}Si CP/MAS-NMR, we have studied the rehydration of sepiolite samples that had been partially dehydrated at 120°C. Accurate information about the origin of the ^{29}Si MAS-NMR spectrum of sepiolite and of thermally-treated sepiolite will be of significant interest as the number of useful applications for sepiolite continues to grow.

MATERIALS AND METHODS

Materials

Sepiolite (SepSp-1) was obtained from the Source Clay Mineral Repository (University of Missouri) and was used without additional purification. Thermal treatment was carried out for 19–20 h under air in a baffle furnace, using sepiolite that had been gently ground in a mortar and then passed through a 100-mesh sieve. Rehydration of samples was performed immediately upon removing the partially-dehydrated clay from the furnace. Approximately 0.1 g of clay was transferred into a small open vial, which was placed inside a larger capped vial along with a small amount of water or D₂O.

Thermogravimetric analysis

Approximately 20 mg of sepiolite was placed in a crucible on the pan of a microbalance in a Polymer Laboratories TGA instrument. Analysis was performed under flowing air using an oven temperature ramp rate of 2°C/min.

Nuclear magnetic resonance studies

Solid state ¹H MAS-NMR and ²⁹Si CP/MAS-NMR spectra were recorded at 200.10 and 39.75 MHz, respectively, at room temperature on a Bruker ASX-200 spectrometer. Typical spinning rates of 5 kHz (¹H) or 4 kHz (²⁹Si) were used, respectively. The excitation pulse and recycle time for ¹H NMR were 3.5 μs ($\pi/2$ pulse) and 2 s (16 scans), respectively. A ramped CP pulse sequence was used for all ²⁹Si cross-polarization experiments with 10 ms contact time for the transfer of magnetization between protons and the ²⁹Si nuclei (2000 scans). The ²⁹Si COSY and ¹H-²⁹Si HETCOR experiments were performed using untreated sepiolite that had been gently ground to pass through a 100-mesh sieve. The ²⁹Si signals were externally referenced to tetrakis trimethylsilylsilane at -9.9 ppm, corresponding to tetramethylsilane (TMS) at 0 ppm.

RESULTS AND DISCUSSION

¹H MAS-NMR spectra of sepiolite and of thermally-treated sepiolite

The experimental conditions that were used to obtain the TGA data were also employed to prepare the partially dehydrated sepiolite samples for the NMR experiments. Four discrete weight loss steps are observed in the TGA plot (Figure 2) for sepiolite over the temperature range of room temperature to 900°C. Thermal pretreatment temperatures of 120, 350 and 500°C were selected after careful consideration of the TGA data in order to yield progressively dehydrated sepiolite samples of known composition for the NMR study. Specifically, heating sepiolite to 120°C under the current experimental conditions removes selectively the zeolitic and surface-bound water molecules. Additional heating to 350°C causes one molecule of structural water (H₂O_{kr}) per terminal Mg²⁺ ion to be lost, and finally the second molecule of structural water per terminal Mg²⁺ ion is removed by heating to 500°C, at which point the true 'sepiolite anhydride' is obtained. The series of ¹H MAS-NMR spectra that is presented in Figure 3a–d corresponds to untreated sepiolite and to sepiolite after heating to 120, 350 and 500°C, respectively. An unambiguous assignment of the ¹H NMR spectrum of the untreated sepiolite sample can be made by considering the spectral changes that occur as the sample is progressively dehydrated under controlled conditions. Correct peak assignments for the ¹H MAS-NMR spectrum of sepiolite are essential in order to be able to understand the ²⁹Si MAS-NMR results, and to make meaningful arguments concerning the ¹H-²⁹Si heteronuclear correlation (HETCOR) NMR experiments.

The ¹H MAS-NMR spectrum that was obtained using untreated sepiolite (Figure 3a) appears to consist of two overlapping resonances separated by ~4 ppm: a broad resonance that produces numerous spinning side-bands and a sharp resonance that produces only a few spinning

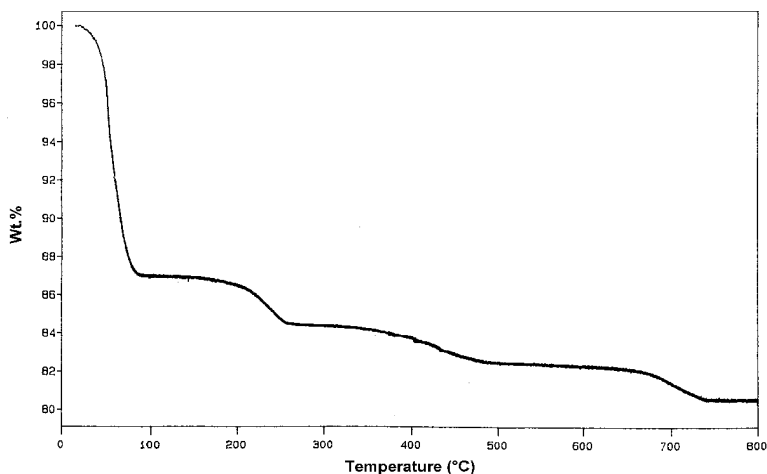


Figure 2. TGA of a sepiolite sample heated from room temperature to 900°C in air using an oven ramp rate of 2°C/min.

side-bands. The broad, lower-field resonance has previously been assigned to the protons of both the $\text{H}_2\text{O}_{\text{kr}}$ and of the zeolitic water molecules, whereas the resonance at higher field was attributed to Mg–OH groups (Aramendía *et al.*, 1997). Removal of the zeolitic water by heating to 120°C causes the broad, lower field resonance to disappear, revealing a third and previously unreported resonance that appears as a shoulder on the lower-field side of the sharp resonance in Figure 3b. This new resonance, which has almost the same chemical shift as the sharp resonance, gives rise to several broad spinning side-bands, and is assigned to the protons of the two molecules of $\text{H}_2\text{O}_{\text{kr}}$ coordinated to each terminal Mg^{2+} ion. The ^1H MAS-NMR spectrum that is shown in Figure 3c was obtained from a sepiolite sample that was heated to 350°C , at which point structural folding of the crystals has commenced concomitant with the removal of one half of the $\text{H}_2\text{O}_{\text{kr}}$ molecules. The lower field resonance in Figure 3c, which is due to the protons of the remaining $\text{H}_2\text{O}_{\text{kr}}$ molecules that are now situated in a more highly constrained environment and are therefore less mobile, is noticeably sharper than the corresponding resonance in Figure 3b. Removal of the second $\text{H}_2\text{O}_{\text{kr}}$ by heating the sepiolite to 500°C yielded a spectrum that contains only a single sharp resonance with two spinning side-bands on either side (Figure 3d), which was logically assigned to the protons of the Mg–OH groups (Aramendía *et al.*, 1997).

Assignment of the ^{29}Si MAS-NMR spectrum of sepiolite

The ^{29}Si CP/MAS-NMR spectra of untreated sepiolite and of sepiolite that was previously heated in air at 120 , 350 and 500°C are presented in traces a–d, respectively, of Figure 4. d’Espinoze de la Caillerie and Fripiat (1992, 1994) were the first to report the ^{29}Si CP/MAS-NMR

spectrum of sepiolite, which consists of three well-resolved resonances of approximately equal intensity at -92.7 , -94.3 and -98.2 ppm. A significantly less intense resonance around -85 ppm was also observed. It was plausibly attributed to terminal $\text{Q}^2(\text{Si}-\text{OH})$ in the micropores. The resonance at -94.3 ppm was found to be sensitive to the match of the Hartman-Hahn condition, namely $\gamma(^1\text{H})\text{H}_1(^1\text{H}) = \gamma(^{29}\text{Si})\text{H}_1(^{29}\text{Si})$, whereas the other two were not. We have also found that the intensity of the central line varied dramatically when the probe tuning drifted a small amount during overnight experiments. Thus, in all of the ^{29}Si CP/MAS-NMR and two-dimensional NMR studies a ramped cross-polarization pulse was utilized, which is far less sensitive to slight changes in the probe tuning. As a result, the spectrum shown in Figure 4a contains three well-resolved resonances of approximately equal intensity that we measure at -92.1 , -94.6 and -98.4 ppm. In previous ^{29}Si CP/MAS-NMR studies (d’Espinoze de la Caillerie and Fripiat, 1994; Aramendía *et al.*, 1997) it was assumed that polarization transfer is possible only from the non-mobile protons of the structural water molecules and not from Mg–OH protons. Under this assumption, the degree to which the signal intensity is enhanced in the ^{29}Si CP/MAS-NMR spectrum is related to the cube of the distance between the Si nuclei and protons of the $\text{H}_2\text{O}_{\text{kr}}$ molecules. Thus, the resonance at -94.6 ppm was assigned to Type 1 (edge site, see Figure 1a) Si atoms because it showed the greatest enhancement in the ^{29}Si CP/MAS-NMR spectrum. Similarly, the resonances at -92.1 and -98.4 ppm were assigned to Type 2 (near edge) and Type 3 (center) sites, respectively, on the basis that the intensity enhancement due to the transfer of polarization decreased in that order.

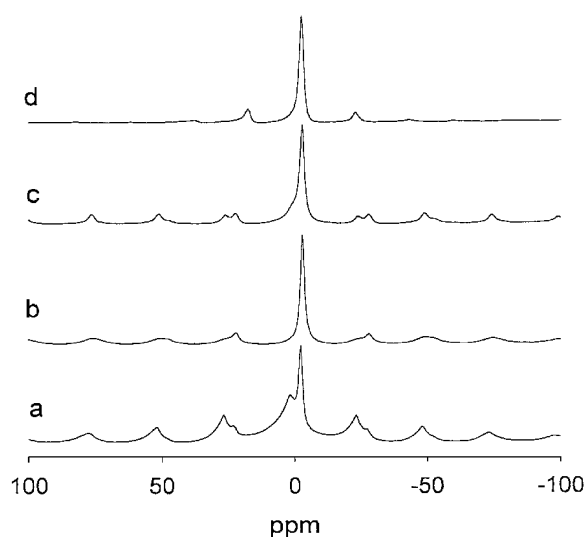


Figure 3. ^1H MAS-NMR spectra obtained at 25°C from (a) untreated sepiolite, (b) sepiolite heated to 120°C , (c) sepiolite heated to 350°C , and (d) sepiolite heated to 500°C .

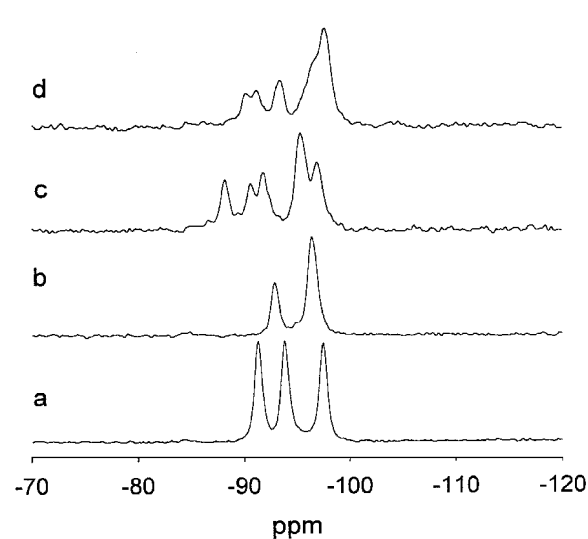


Figure 4. ^{29}Si CP/MAS-NMR spectra obtained at 25°C from (a) untreated sepiolite, (b) sepiolite heated to 120°C , (c) sepiolite heated to 350°C , and (d) sepiolite heated to 500°C .

In the current study we have re-examined the previously-proposed peak assignments with the aid of two-dimensional NMR pulse sequences. To the best of our knowledge, a ^{29}Si COSY spectrum is reported for sepiolite for the first time. The two-dimensional ^{29}Si COSY and ^1H - ^{29}Si HETCOR spectra appear in Figures 5 and 6, respectively. In each case untreated sepiolite was used, thus the COSY and HETCOR experiments were performed using samples that contained protons associated with zeolitic water, with $\text{H}_2\text{O}_{\text{kr}}$ and with Mg-OH groups. The ^{29}Si COSY spectrum shown in Figure 5 clearly indicates that the Si nuclei that give rise to the resonance at -92.1 ppm are connected by Si-O-Si bonding to the Si nuclei that give rise to the resonances at -94.6 and -98.4 ppm. This evidence positively identifies Type 2 (near edge) Si atoms as the origin of the resonance at -92.1 ppm, which is in agreement with previous assignments (see Table 1).

The two remaining resonances at -94.6 and -98.4 ppm can be assigned on the basis of the HETCOR spectrum that is shown in Figure 6, taking into account the discussion of the ^1H MAS-NMR spectrum that was presented in the previous section. Of interest in Figure 6 is the fact that the line at -94.6 ppm correlates to the sharp resonance in the proton spectrum, which is clearly the case due to the absence of any cross-peaks with the spinning side-bands. The resonance is therefore attributed to Type 3 (center) Si sites, which are located very close to the Mg-OH groups and would be expected to cross-polarize efficiently only with the hydroxyl group

proton. Conversely, the peak at -98.4 ppm correlates strongly to the broad resonance in the ^1H MAS-NMR spectrum, and gives rise to several cross-peaks with the spinning side bands that are associated with the broad resonance. It is proposed that the origin of the resonance at -98.4 ppm is the Type 1 (edge) Si atoms, which are situated very close to the structural water molecule protons that are located at the edges of the octahedral sheets. The resonance at -92.1 ppm is attributed to Type 2 (near edge) Si nuclei on the basis of the COSY spectrum. The HETCOR experiment reveals that this resonance is an intermediate case that shows correlation to both types of ^1H nuclei. This is consistent with the Type 2 Si sites occupying a position that is intermediate between the two types of protons.

A complete summary of the peak assignments is presented in Table 1, along with the assignments that have been proposed in earlier works. This attribution is also in agreement with the behavior of the intensity of the central peak when the Hartman-Hahn condition is not perfectly matched. Under these conditions, the central peak does not cross-polarize as efficiently as the other two peaks. A study of the variation of the peak intensities as a function of the ^{29}Si power showed that the central line signal could be completely lost while the other two resonances could still be observed. This is indicative of a weak dipolar coupling, with ^{29}Si nuclei behaving almost like structurally-isolated spins. This is in good agreement with the attribution of the central line to Type 3 (center) Si sites, located very close to the Mg-OH groups and expected to cross-polarize efficiently only with the hydroxyl group proton.

Sepiolite was heated to 120°C for 20 h, and subsequently exposed to D_2O for three days. The ^1H - ^{29}Si

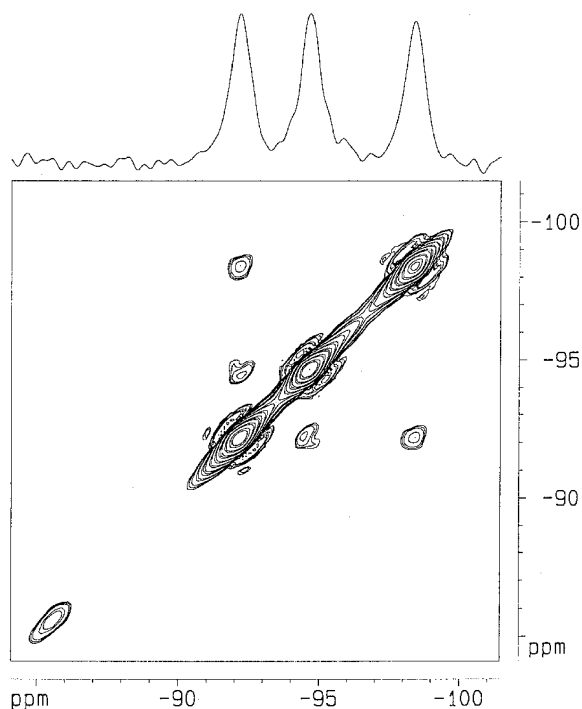


Figure 5. ^{29}Si COSY NMR spectrum of untreated sepiolite.

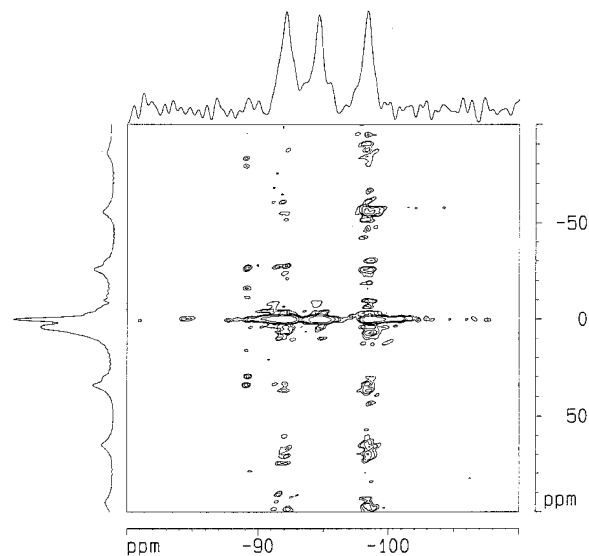


Figure 6. ^1H - ^{29}Si HETCOR NMR spectrum of untreated sepiolite.

Table 1. ^{29}Si NMR signals assignments for sepiolite.

Shift (ppm)	Barron and Frost (1985)	Komarneni <i>et al.</i> (1986)	d'Espinose de la Caillerie <i>et al.</i> (1994)	Aramendía <i>et al.</i> (1997)	Shore <i>et al.</i> (1998)	This work
-97.8	Edge	Center	Center	Center	Edge	Edge
-94.3	Center	n.a.	Edge	Edge	Center	Center
-92.0	Near edge	n.a.	Near edge	Near edge	Near edge	Near edge
-85	$\text{Q}^2(\text{Si}-\text{OH})$	$\text{Q}^3(\text{Si}-1\text{Al})$	$\text{Q}^2(\text{Si}-\text{OH})$	$\text{Q}^3(\text{Si}-1\text{Al})$	$\text{Q}^3(\text{Si}-1\text{Al})$	$\text{Q}^2(\text{Si}-\text{OH})$

n.a. – not applicable

HETCOR NMR spectrum of that sample is shown in Figure 7. There is a definite cross-peak linking the ^{29}Si resonance at -85 ppm with the upfield ^1H signal characteristic of the OH groups. This correlation provides strong evidence for the attribution of the -85 ppm signal to terminal $\text{Q}^2(\text{Si}-\text{OH})$ Si nuclei.

The ^{29}Si CP/MAS-NMR spectra of sepiolite samples that were partially dehydrated by heating in air to 120, 350 or 500°C are presented in Figure 4b, 4c and 4d. Our attempts to obtain two-dimensional NMR spectra using the partially dehydrated samples were not successful, and therefore it was not possible to assign the peaks to specific Si sites. Aramendía *et al.* (1997) and d'Espinose de la Caillerie and Fripiat (1994) have commented on the ^{29}Si MAS (and CP/MAS) NMR spectra of sepiolite that was heated to 120 and 500°C, but the spectrum for sepiolite after heating to 350°C (Figure 4c) has not been reported previously. The differences that are observed in the intensities and the chemical shifts of the peaks for the 350°C-heated samples compared to the 500°C-heated samples support the earlier claim by Nagata *et al.* (1974) that the former exist as distinct phases to be differentiated from that of the completely dehydrated state.

Rehydration of sepiolite clay previously heated to 120°C

Although there is no change in the unit-cell dimensions of sepiolite after the removal of the zeolitic water by heating to 120°C (Preisinger, 1959), the ^{29}Si CP/MAS-NMR spectrum does undergo a significant change (Figure 4b). The resonance at -92.7 ppm remains essentially unaffected. However, the other two resonances become coincident and produce a single resonance with twice the intensity of the original lines. This low-temperature structural change is almost completely reversible (Inagaki *et al.*, 1990; Rytwo *et al.*, 1998; Shariatmadari *et al.*, 1999) provided the thermal treatment temperature does not exceed ~250°C. In the current work we have successfully rehydrated sepiolite samples that were previously heated in air to 120°C by placing them in contact with water vapor or D_2O vapor for a period of up to 4 days at room temperature.

The ^{29}Si CP/MAS-NMR spectra of sepiolite heated to 120°C and of sepiolite- H_2O and sepiolite- D_2O are presented in Figure 8a, 8b and 8c, respectively. ^{29}Si CP/MAS-NMR is very sensitive to the slight change in the sepiolite structure that occurs when the zeolitic water is removed from the micropores. As is shown in Figure 8a,

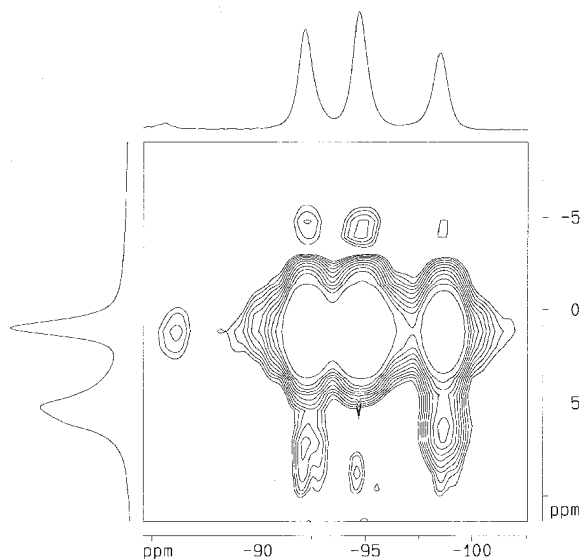


Figure 7. ^1H - ^{29}Si HETCOR NMR spectrum of sepiolite heated to 120°C and subsequently exposed to D_2O for three days.

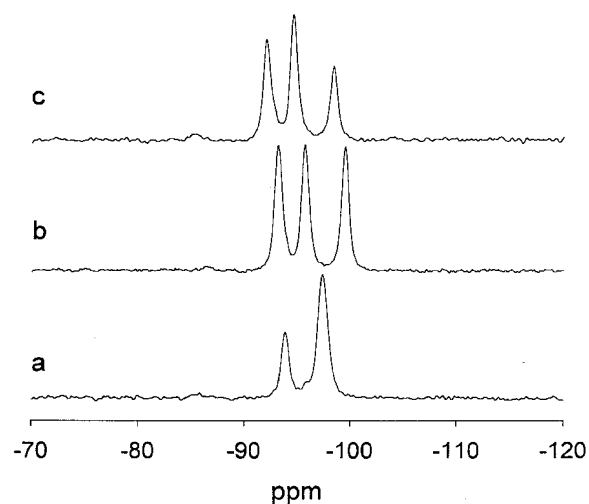


Figure 8. ^{29}Si CP/MAS-NMR spectra obtained at 25°C from (a) sepiolite heated to 120°C, (b) sepiolite heated to 120°C and subsequently exposed to H_2O vapor, and (c) sepiolite heated to 120°C and subsequently exposed to D_2O .

only two resonances are observed following the removal of the zeolitic water by low-temperature thermal treatment. Exposure to water vapor (room temperature, 3 days) fully restores the original sepiolite structure and the ^{29}Si CP/MAS-NMR spectrum that is obtained (Figure 8b) is indistinguishable from that of the original, untreated sepiolite sample (compare to Figure 4a). It is worth mentioning that exposure to some organic compounds, acetone for example, can also restore the original sepiolite structure, which encapsulates organic guests in the zeolitic channels (Weir *et al.*, 2000).

The spectrum that is presented in Figure 8c was obtained from a partially dehydrated sepiolite sample that was subsequently exposed to D_2O vapor under conditions identical to those that were used to rehydrate the sample in water. In this case, the structure of the partially dehydrated sepiolite has apparently been restored to that of sepiolite before thermal treatment since the three expected resonances are present in the ^{29}Si CP/MAS-NMR spectrum. The relative intensities of the peaks are not in the expected 1:1:1 ratio, and therefore the efficiency of the transfer of magnetization from the immobile protons to the different Si sites is no longer equal. This effect is caused by the presence of D_2O molecules inside the micropores, which undergo an exchange with the $\text{H}_2\text{O}_{\text{kr}}$ molecules or Mg-OH protons.

CONCLUSIONS

The assignment of the three main resonances in the ^{29}Si MAS-NMR spectrum of naturally-occurring sepiolite clay has been re-examined, using two-dimensional pulse sequences to aid in the interpretation of the spectrum. Each of the three main resonances at -92.1 , -94.6 and -98.4 ppm has been attributed to one of the three pairs of equivalent Si nuclei in the basal plane. The resonance at -92.1 ppm is unambiguously assigned to the intermediate, near-edge Si sites. The resonance at -94.6 ppm cross-polarizes almost entirely from the Mg-OH protons, and therefore is assigned to the central Si position. The remaining resonance at -98.4 ppm correlates strongly to the protons of the structural water molecules and therefore is assigned to the edge Si sites. The resonance at -85 ppm was attributed to $\text{Q}^2(\text{Si}-\text{OH})$ Si nuclei.

The ^{29}Si CP/MAS-NMR spectrum corresponding to the folded sepiolite structure in which approximately one half of the structural water has been removed by heating to 350°C is reported for the first time. The results support the earlier claim that sepiolite heated to $\sim 350^\circ\text{C}$ exists as a distinct phase to be differentiated from that of the completely dehydrated state.

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REFERENCES

- Aramendía, M.A., Jiménez, V.B.C., Marinas, J.M. and Ruiz, J.R. (1997) Characterization of Spanish sepiolites by high-resolution solid-state NMR. *Solid State Nuclear Magnetic Resonance*, **8**, 251–256.
- Barron, P.F. and Frost, R.L. (1985) Solid-state ^{29}Si NMR examination of the 2:1 ribbon magnesium silicates, sepiolite and palygorskite. *American Mineralogist*, **70**, 758–766.
- Corma, A. and Martín-Aranda, R.M. (1991) Alkaline-substituted sepiolites as a new type of strong base catalyst. *Journal of Catalysis*, **130**, 130–137.
- Damyanova, S., Daza, L. and Fierro, J.L.G. (1996) Surface and catalytic properties of lanthanum-promoted Ni/sepiolite catalysts for styrene hydrogenation. *Journal of Catalysis*, **159**, 150–161.
- Demirci, S., Erdogan, B. and Akay, Y. (1995) Removal of turbidity and color of sugar juices by using some Turkish bentonites and sepiolite. *Proceedings Euroclay'95, Leuven, Belgium*, pp. 158–159.
- d'Espinose de la Caillerie, J.-B. and Fripiat, J.J. (1992) Al-modified sepiolite as catalyst or catalyst support. *Catalysis Today*, **14**, 125–140.
- d'Espinose de la Caillerie, J.-B. and Fripiat, J.J. (1994) A reassessment of the ^{29}Si MAS-NMR spectra of sepiolite and aluminated sepiolite. *Clay Minerals*, **29**, 313–318.
- Galán, E. (1996) Properties and applications of palygorskite-sepiolite clays. *Clay Minerals*, **31**, 443–453.
- Inagaki, S., Fukushima, Y., Doi, H. and Kamigaito, O. (1990) Pore size distribution and adsorption selectivity of sepiolite. *Clay Minerals*, **25**, 99–105.
- Jiménez-López, A., López-González, J., Ramírez-Saenz, A., Rodríguez-Reinoso, F., Valenzuela-Calahorra, C. and Zurita-Herrera, L. (1978) Evolution of surface area in a sepiolite as a function of acid and heat treatments. *Clay Minerals*, **13**, 375–385.
- Komarneni, S., Fyfe, C.A. and Kennedy, G.J. (1986) Detection of nonequivalent Si sites in sepiolite and palygorskite by solid-state ^{29}Si Magic Angle Spinning-Nuclear Magnetic Resonance. *Clays and Clay Minerals*, **34**, 99–102.
- Le Van Mao, R., Rutinduka, E., Detellier, C., Gougay, P., Hascoet, V., Tavakoliyan, S., Hoa, S.V. and Matsuura, T. (1999) Mechanical and pore characteristics of zeolite composite membranes. *Journal of Materials Chemistry*, **9**, 783–788.
- Myriam, M., Suárez, M. and Martín-Pozas, J.M. (1998) Structural and textural modifications of palygorskite and sepiolite under acid treatment. *Clays and Clay Minerals*, **46**, 225–231.
- Nagata, H., Shimoda, S. and Toshio, S. (1974) On dehydration of bound water of sepiolite. *Clays and Clay Minerals*, **22**, 285–293.
- Pérez-Rodríguez, J.L. and Galán, E. (1994) Determination of impurity in sepiolite by thermal analysis. *Journal of Thermal Analysis*, **42**, 131–141.
- Preisinger, A. (1959) X-ray study of the structure of sepiolite. *Clays and Clay Minerals*, **6**, 61–67.
- Preisinger, A. (1963) Sepiolite and related compounds: its stability and application. *Clays and Clay Minerals*, **10**, 365–371.
- Rytwo, G., Nir, S., Margulies, L., Casal, B., Merino, J., Ruiz-Hitzky, E. and Serratosa, J. (1998) Adsorption of monovalent organic cations on sepiolite: experimental results and model calculations. *Clays and Clay Minerals*, **46**, 340–348.
- Serna, C., Ahlrichs, J.L. and Serratosa, J.M. (1975) Folding in sepiolite crystals. *Clays and Clay Minerals*, **23**, 452–457.
- Shariatmadari, H., Mermut, A.R. and Benke, M.B. (1999) Sorption of selected cationic and neutral organic molecules on palygorskite and sepiolite. *Clays and Clay Minerals*, **47**, 44–53.

- Shore, J.S., DePaul, S., Ernst, M. and Phillips, B.L. (1998) Double-Resonance and Two-Dimensional Silicon-29 NMR Spectroscopy of Minerals. Pp. 305–325 in: *Solid-State Nuclear Magnetic Resonance of Inorganic Materials* (J.J. Fitzgerald, editor). ACS Symposium Series, **717**, American Chemical Society, Washington, D.C.
- Sugiura, M. (1993) Removal of methanethiol by sepiolite and various sepiolite-metal compound complexes in ambient air. *Clay Science*, **9**, 33–41.
- Sugiura, M., Horii, M., Hayashi, H., Suzuki, T., Kamigaito, O., Nogawa, S. and Oishi, S. (1990) Deodorizing paper using β -sepiolite. Pp. 91–100 in: *Proceedings of the 9th International Clay Conference, Strasbourg, France*.
- Sugiura, M., Fukumoto, K. and Inagaki, S. (1991) Adsorption of odorous vapours by sepiolite in ambient air. *Clay Science*, **8**, 129–145.
- Vincente, M.A., López-González, J.D. and Bañares, M.A. (1994) Acid activation of a Spanish sepiolite: physicochemical characterization, free silica content and surface area of products obtained. *Clay Minerals*, **29**, 361–367.
- Wang, Q.K., Matsuura, T., Feng, C.Y., Weir, M.R., Detellier, C., Rutinduka, E. and Le Van Mao, R. (2001) The sepiolite membrane for ultrafiltration. *Journal of Membrane Science*, **184**, 153–163.
- Weir, M.R., Facey, G.A. and Detellier, C. (2000) ^1H , ^2H , and ^{29}Si solid state NMR study of guest acetone molecules occupying the zeolitic channels of partially dehydrated sepiolite clay. *Studies in Surface Science and Catalysis* (A. Sayari *et al.*, editors), **129**, 551–558.
- Weir, M.R., Rutinduka, E., Detellier, C., Feng, C.Y., Wang, Q., Matsuura, T. and Le Van Mao, R. (2001) Fabrication, characterization and preliminary testing of all-inorganic ultrafiltration membranes composed entirely of a naturally occurring sepiolite clay mineral. *Journal of Membrane Science*, **182**, 41–50.

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