

## NOTES

# DETECTION OF NONEQUIVALENT Si SITES IN SEPIOLITE AND PALYGORSKITE BY SOLID-STATE $^{29}\text{Si}$ MAGIC ANGLE SPINNING-NUCLEAR MAGNETIC RESONANCE

**Key Words**—Magic angle spinning-nuclear magnetic resonance, Nuclear magnetic resonance, Palygorskite, Sepiolite, Silicon sites.

Structural investigation of layer silicates or clay minerals by X-ray powder diffraction is a formidable task because of the similarity in scattering power of Si and Al and also because of the unavailability of single crystals. Spectroscopic techniques such as infrared and Raman have been of only limited value in the study of these minerals. The advent of solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy has given new impetus to the study of short-range order in fine-grained aluminosilicate minerals such as zeolites and clay minerals (Lippmaa *et al.*, 1980, 1981; Klinowski *et al.*, 1981; Fyfe *et al.*, 1982; Barron *et al.*, 1983; Thompson, 1984). The total range of  $^{29}\text{Si}$  chemical shifts in silicates is appreciable, from  $-60$  to  $-120$  ppm, and the shifts correlate with the type of silicon-oxygen tetrahedra and their linkage, the extent of Al substitution for Si (Lippmaa *et al.*, 1980), Si-Si bond lengths, and Si-O-Si bond angles (Smith and Blackwell, 1983). We report here what we believe to be the first  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS-NMR spectroscopic studies of sepiolite and palygorskite.

The structures of sepiolite and palygorskite are alike in that both contain continuous planes of tetrahedral basal oxygen atoms approximately  $6.5 \text{ \AA}$  apart (Brindley and Brown, 1980). The apical oxygens point alternately up and down relative to the planes of basal oxygens in a pattern such that the tetrahedra pointing in the same direction form tetrahedral ribbons that extend parallel to the length of the laths, i.e., along the X axis. The ribbons have an average width along Y of three linked pyroxene-like single chains in sepiolite and two linked chains in palygorskite. Ribbons with apices pointing up are linked vertically to ribbons with apices pointing down by forming octahedral coordination groups around Mg. The linked ribbons thus form a 2:1 layer that is continuous along X but of limited extent along Y. A limited number of exchangeable cations, zeolitic water, and structurally bound water are present in rectangular channels that lie between the backs of opposing 2:1 ribbons (Brindley and Brown, 1980).

Trioctahedral and dioctahedral 2:1 layer silicates, such as talc and pyrophyllite, have been independently

investigated using  $^{29}\text{Si}$  MAS-NMR by Lippmaa *et al.* (1980), Magi *et al.* (1984), and Smith *et al.* (1983). Talc, exhibited a single  $^{29}\text{Si}$  resonance at  $-98.1$  ppm which is in accord with the  $\text{Q}^3(0 \text{ Al})$  silicon environment, and pyrophyllite showed a single  $^{29}\text{Si}$  resonance at  $-95.0$  ppm which is also consistent with the  $\text{Q}^3(0 \text{ Al})$  silicon environment. The interpretation of the trioctahedral 2:1 sepiolite and palygorskite minerals investigated here is based on the above cited studies.

### MATERIALS AND METHODS

Sieved fractions ( $270 \times 400$  mesh) of one palygorskite and several sepiolites of different chemical composition (Table 1) from various sources were examined in this MAS-NMR study. X-ray powder diffraction analysis showed only trace quantities of quartz impurity in the various samples. The  $^{29}\text{Si}$  chemical shift of quartz occurs at  $-107.4$  ppm from tetramethylsilane (Lippmaa *et al.*, 1980) and does not affect the interpretation of the  $^{29}\text{Si}$  shifts of sepiolites and palygorskite. A high-resolution Bruker WH-400 narrow-bore commercial spectrometer with a home-built MAS broad-banded probe fitted with a standard Andrew-Beams spinning assembly (Fyfe *et al.*, 1982) was used to record  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS-NMR spectra.  $^{27}\text{Al}$  MAS-NMR spectra at ambient temperature were obtained at  $104.22$  MHz;  $^{29}\text{Si}$  MAS-NMR spectra were recorded at  $79.5$  MHz using the above spectrometer. Spinners made of Delrin had an internal volume of  $\sim 450 \mu\text{l}$  and were spun at  $\sim 3.5\text{--}4.0$  kHz with compressed air as the driving gas.  $^{27}\text{Al}$  chemical shifts were recorded with respect to  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  as an external reference, and  $^{29}\text{Si}$  chemical shifts were recorded with respect to tetramethylsilane (TMS). The spectra are presented with the appropriate line broadening without resolution enhancement.

### RESULTS AND DISCUSSION

$^{27}\text{Al}$  MAS-NMR spectra of three sepiolites and one palygorskite are presented in Figure 1. No  $^{27}\text{Al}$  resonance was detected in the sepiolite from Greece even after 30,000 scans under the same conditions as for the

Table 1. Quantitative chemical and spectrochemical analysis of sepiolites and palygorskite.

	Sepiolite, Greece (Courtesy, S. Augusti-this)	Sepiolite, Two Crows, Nevada (Courtesy, J. Post)	Sepiolite, Vallecas, Spain (Courtesy, G. W. Brindley)	Sepiolite, Ash Meadows, Nevada (Courtesy K. Papke)	Palygorskite, Florida <sup>1</sup> (Source Clays Repository, The Clay Minerals Society)
SiO <sub>2</sub>	51.1	53.7	58.1	55.0	65.23
MgO	23.3	23.2	21.1	20.6	7.44
Al <sub>2</sub> O <sub>3</sub>	0.09	0.61	2.89	3.07	8.82
Fe <sub>2</sub> O <sub>3</sub>	0.13	0.18	0.76	0.97	2.95
TiO <sub>2</sub>	0.02	0.02	0.10	0.20	0.64
MnO	0.003	0.007	0.009	0.015	0.09
Na <sub>2</sub> O	0.15	1.92	0.54	1.31	0.13
K <sub>2</sub> O	0.02	0.34	0.91	1.09	0.67
CaO	4.40	0.46	0.41	0.95	1.92
P <sub>2</sub> O <sub>5</sub>	0.02	0.02	0.04	0.05	—
CO <sub>2</sub>	6.23	0.02	0.01	0.62	1.25
SO <sub>3</sub>	—	1.9	—	—	0.09
Cl	—	1.0	—	—	—
H <sub>2</sub> O <sup>-</sup>	7.61	9.58	8.72	8.73	—
H <sub>2</sub> O <sup>+</sup>	6.62	6.36	6.05	7.11	11.07 <sup>2</sup>
Totals	99.69	99.32	99.37	99.72	100.3

<sup>1</sup> Average value of the chemical analyses from van Olphen and Fripiat (1979, p. 140).

<sup>2</sup> Ignition loss.

other samples. This result is consistent with the wet chemical analysis which showed only a trace amount of Al in this sepiolite (Table 1). The coordination of Al in sepiolites is mainly tetrahedral, and Al resonates between 56.6 to 58.4 ppm; however, minor octahedral Al ions are also present and resonate between 1.3 and 3.9 ppm (Figures 1a to 1c). On the other hand, the Al in palygorskite is mainly octahedral (4.1 ppm), with a trace of tetrahedral Al (55.7 ppm) (Figure 1d). The assignment of Al to tetrahedral or octahedral coordination is based on previous studies (Muller *et al.*, 1981; Fyfe *et al.*, 1983) which showed that Al<sup>3+</sup> ions when tetrahedrally or octahedrally surrounded by oxygen or hydroxyl ions resonate at 50 ± 20 ppm or 0 ± 10 ppm, respectively, with respect to [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>. Spinning side bands (SSB), clearly present in the spectrum of palygorskite, usually accompany the main resonances and are due to chemical shift anisotropy (Fyfe *et al.*, 1983). That the <sup>27</sup>Al MAS-NMR spectroscopic information is useful for the assignment of chemical shifts to various environments is discussed below.

Figure 2 shows the <sup>29</sup>Si MAS-NMR spectra of the four sepiolites and one palygorskite. All the sepiolites show at least four different <sup>29</sup>Si resonances; palygorskite gave three resonances. The spectrum of the Greek sepiolite which does not show any <sup>27</sup>Al MAS-NMR peak exhibits four different <sup>29</sup>Si resonances. The resolution of the spectrum is remarkable, and the spread of all the resonances is 9 ppm, whereas the spread of the three major resonances is only 5.7 ppm (Figure 2a).

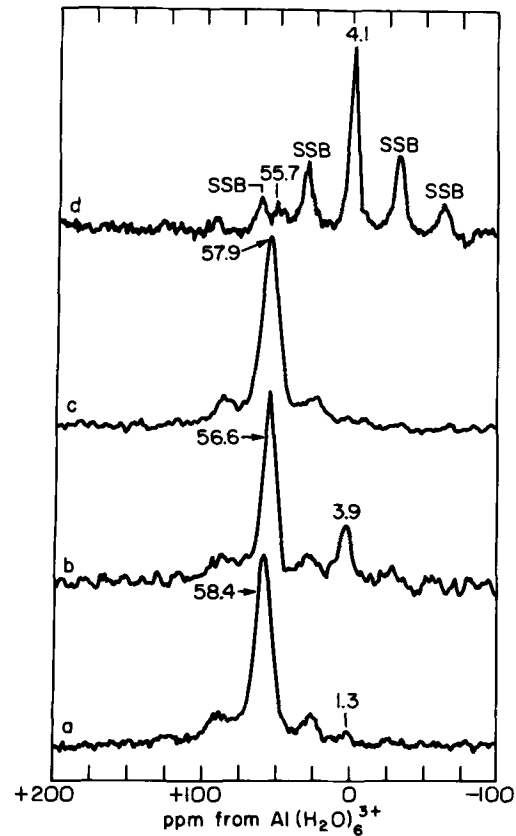


Figure 1. <sup>27</sup>Al magic angle spinning-nuclear magnetic resonance spectra of: (a) sepiolite from Two Crows, Nevada (SSB = spinning side bands); (b) sepiolite from Vallecas, Spain; (c) sepiolite from Ash Meadows, Nevada; and (d) palygorskite (=attapulgite) from Florida. No <sup>27</sup>Al peak was detected for sepiolite from Greece.

These multiple <sup>29</sup>Si resonances must arise from the crystallographically nonequivalent tetrahedral environments of the Q<sup>3</sup>(0 Al) sites inasmuch as little or no Al is present in this sepiolite. Two unequal Q<sup>3</sup>(0 Al) sites have been discovered in kaolinite, dickite, and nacrite (Barron *et al.*, 1983), whereas crystallographically different Si(4 Si) sites have been observed in silicalite (Smith and Blackwell, 1983; Fyfe *et al.*, 1982), other highly siliceous zeolites (Fyfe *et al.*, 1984a, 1984b, 1984c; Kokotailo *et al.*, 1984), and tridymite and holdstite (Smith and Blackwell, 1983) and have been correlated with mean Si-Si bond length and with mean Si-O-Si bond angle for the latter two samples. Inasmuch as the mean Si-Si bond lengths and Si-O-Si bond angles in sepiolites are not precisely known, it is premature to assign individual <sup>29</sup>Si signals to particular crystallographic sites. The Q<sup>3</sup>(0 Al) <sup>29</sup>Si resonances occurring between -97.6 to -98.1 in sepiolite coincide with that for talc (Magi *et al.*, 1984), thereby suggesting that the Si in the central 'pyroxene' chain of these minerals is in an environment similar to that of Si in

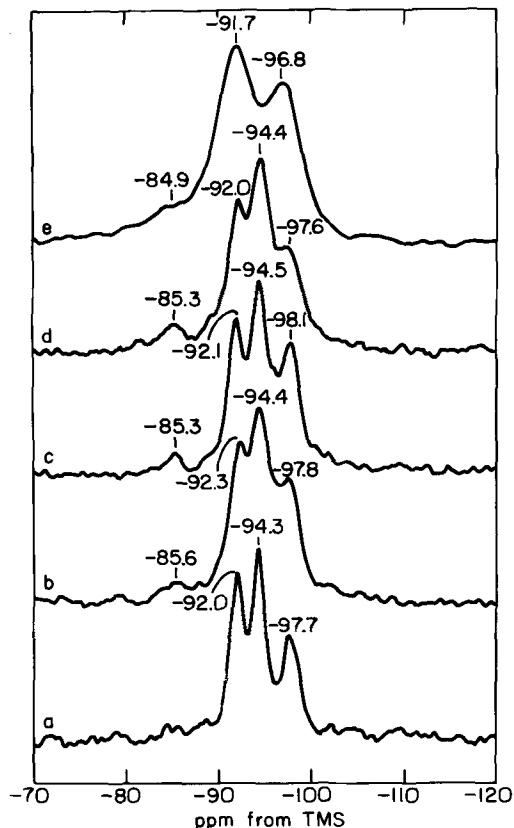


Figure 2.  $^{29}\text{Si}$  magic angle spinning-nuclear magnetic resonance spectra of: (a) sepiolite from Greece; (b) sepiolite from Two Crows, Nevada; (c) sepiolite from Vallecas, Spain; (d) sepiolite from Ash Meadows, Nevada; and (e) palygorskite (=attapulgite) from Florida.

tal. The other two  $^{29}\text{Si}$  resonances in sepiolite may be due to Si in the other two pyroxene chains. The  $^{29}\text{Si}$  resonance at  $-96.8$  in palygorskite may represent the Si in one pyroxene chain which is most like talc, whereas the  $-91.7$  resonance may suggest the Si in the other pyroxene chain.

The sepiolites from Two Crows, Nevada; Vallecas, Spain; and Ash Meadows, Nevada; having different amounts of Al substitution (Table 1) primarily in the tetrahedral sites (Figures 1a to 1c), also exhibit four  $^{29}\text{Si}$  resonances; however, the resonances are somewhat broad when compared to those of the Greek sepiolite. An extra  $^{29}\text{Si}$  resonance is present at about  $-85.3$  ppm in these three Al-substituted sepiolites in addition to the four  $^{29}\text{Si}$  resonances which are attributed to four distinct  $\text{Q}^3(0\text{ Al})$  sites, the latter as in the Greek sepiolite. These resonances at  $-85.3$  to  $-85.6$  ppm may be attributed to  $\text{Si}(1\text{ Al})$  tetrahedral environment because of the tetrahedral substitution of Al for Si (Figures 1a to 1c). This assignment is consistent with that of Magi *et al.* (1984).

Palygorskite, on the other hand, exhibits two broad

resonances at  $-91.7$  and  $-96.8$  ppm and a shoulder at  $-84.9$  ppm. The two broad resonances may be attributed to two specific  $\text{Q}^3(0\text{ Al})$  sites, whereas the shoulder at  $-84.9$  ppm may represent a  $\text{Si}(1\text{ Al})$  tetrahedral environment because this palygorskite contained a trace amount of tetrahedral Al (Figure 1d).

The results presented above show that at least three or four specific, crystallographically nonequivalent,  $\text{Q}^3(0\text{ Al})$  tetrahedral sites exist in sepiolites and that at least two such sites exist in palygorskite. It is impossible, at this stage, to assign individual  $^{29}\text{Si}$  resonances to specific crystallographic sites in these minerals because of the lack of precise information on the mean Si-Si bond lengths and the mean Si-O-Si bond angles. These results, however, demonstrate the value of solid-state NMR in the structural investigation of clay minerals. The information gained by the solid-state MAS-NMR when coupled with X-ray crystallography is invaluable in probing the structures of fine-grained layer silicates or clay minerals.

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