

# MECHANISMS OF Palygorskite and Sepiolite Alteration as Deduc'd from Solid-State $^{27}\text{Al}$ and $^{29}\text{Si}$ Nuclear Magnetic Resonance Spectroscopy

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**Abstract**—The mechanisms of palygorskite and sepiolite alteration to smectite under mild hydrothermal conditions were investigated by solid-state  $^{27}\text{Al}$  and  $^{29}\text{Si}$  magic-angle spinning-nuclear magnetic resonance (MAS-NMR) spectroscopy, X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). Palygorskite altered to smectite in the presence of NaOH at 150°C.  $^{27}\text{Al}$  MAS-NMR spectroscopy showed that the Al coordination changed from chiefly octahedral in palygorskite to chiefly tetrahedral in the smectite product.  $^{29}\text{Si}$  MAS-NMR spectroscopy showed that the nearest neighbor environment of Si also changed when palygorskite altered to smectite. The XRD data showed that the synthetic smectite is trioctahedral in nature with tetrahedral charge. The TEM results revealed that the needle-like morphology of palygorskite was preserved in the product smectite. The MAS-NMR results in conjunction with the above XRD and TEM studies suggest that the mechanism of palygorskite alteration was a dissolution and recrystallization process rather than a solid-state reorganization to form 2:1 layer silicate units from the preexisting chain structure. Sepiolite altered to smectite in the presence of 2 N salt solutions at 300°C. The trioctahedral nature of the product smectite as detected by XRD and the foil-like morphology of product smectite as shown by TEM suggest that the mechanism of sepiolite transformation to smectite was also a dissolution and recrystallization process. The tetrahedral Al coordination detected by  $^{27}\text{Al}$  MAS-NMR in the smectite altered from sepiolite corroborated the XRD and TEM results.

**Key Words**—Al coordination, Hydrothermal transformation, Nuclear magnetic resonance, Palygorskite, Sepiolite, Smectite, X-ray powder diffraction.

## INTRODUCTION

Experimental studies of hydrothermal alteration of minerals are useful in understanding their diagenesis and stability relations. The alteration of sepiolite, palygorskite and other clay minerals under hydrothermal conditions has usually been investigated by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and chemical analyses (Mumpton and Roy, 1956; Eberl *et al.*, 1978; Roberson and Lahann, 1981; Komarneni and Breval, 1985; Golden *et al.*, 1985; Bethke and Altaner, 1986; Whitney and Northrup, 1987). The advent of solid-state magic-angle spinning-nuclear magnetic resonance (MAS-NMR) spectroscopy has provided a new tool to experimental petrologists for the investigation of the alteration of minerals and especially the mechanisms of the alteration.  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS-NMR spectroscopy have been shown to be useful in determining the Al coordination and nearest neighbor environment of Si in aluminosilicate minerals (Lippmaa *et al.*, 1980; Muller *et al.*, 1981; Fyfe *et al.*, 1982; Komarneni *et al.*, 1986). The objective of the present study was to investigate the mechanisms of alteration of palygorskite and sepiolite to smectite under mild hydrothermal conditions using the data obtained from  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS-NMR and/or powder XRD and TEM analyses.

## MATERIALS AND METHODS

Palygorskite from Florida obtained from the Source Clays Repository of The Clay Minerals Society and sepiolite from Two Crows, Nevada (courtesy, J. Post), were used in the present study. The as-received palygorskite and the <325-mesh fraction of sepiolite obtained by sieving were treated under hydrothermal conditions. Five hundred milligrams of palygorskite was treated with 4 mmole of NaOH in 15 ml of water at 150°C for 24 hr in an acid digestion vessel, as described by Golden *et al.* (1985). Sepiolite was treated hydrothermally as follows: 50 mg of sample and 50  $\mu\text{l}$ iter of 2 N CsCl, CaCl<sub>2</sub>, or MgCl<sub>2</sub> solutions (pH ~6) were loaded in gold capsules and sealed by cold-welding (Komarneni *et al.*, 1979). The gold capsules were then held in cold-seal vessels at 300°C for 10 days under a confining pressure of 30 MPa. The gold capsules were checked for leaks by weighing before and after the hydrothermal treatments, and those that showed no leaks were further processed. The solid and solution phases from the hydrothermal runs were separated by centrifugation. The solid phases were characterized by MAS-NMR and/or powder XRD and TEM.  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS-NMR spectra were recorded with 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

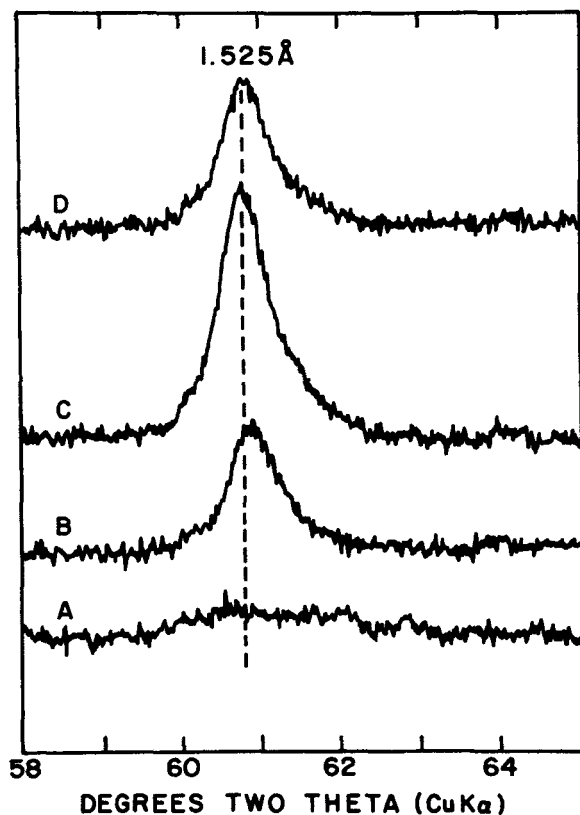


Figure 1. X-ray powder diffraction traces of 060 peaks of smectites formed under hydrothermal conditions from: (A) palygorskite at 150°C; (B) sepiolite in 2 N CsCl at 300°C; (C) sepiolite in 2 N MgCl<sub>2</sub> at 300°C; (D) sepiolite in 2 N CaCl<sub>2</sub> at 300°C.

assembly (Fyfe *et al.*, 1982). <sup>27</sup>Al and <sup>29</sup>Si MAS-NMR spectra were recorded at 104.22 and 79.5 MHz, respectively. <sup>27</sup>Al chemical shifts were recorded with respect to [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> as an external reference, and <sup>29</sup>Si chemical shifts were recorded with respect to tetramethylsilane (TMS). The as-recorded spectra are presented without resolution enhancement. XRD was carried out using a Philips APD-3600 diffractometer and graphite-monochromated CuK $\alpha$  radiation. A Philips 420 TEM was used for the morphology determinations.

The smectite solid phases were also characterized qualitatively for the magnitude and location of their layer charge and their di- or trioctahedral nature. The magnitude of the layer charge was deduced from K<sup>+</sup> saturation, ethylene glycolation, and XRD of oriented samples, as described previously by several investigators (Schultz, 1969; Howard, 1981; Komarneni and Breval, 1985). The expansion of the 001 spacing of smectite to 17 Å after K<sup>+</sup> saturation and ethylene glycolation indicated a small layer charge, whereas non-expansion to that spacing indicated a large layer charge. The location of the layer charge was detected by the Hofmann-Klemen and Greene-Kelley Li-test (Hof-

mann and Klemen, 1950; Greene-Kelley, 1955; Schultz, 1969; Howard, 1981; Komarneni and Breval, 1985) by Li<sup>+</sup> saturation, heat treatment at 250°C for 8 hr, glycerol solvation (glyceration), and XRD of oriented samples. The expansion of the 001 spacing to ~18 Å on Li<sup>+</sup> saturation, heat treatment, and glyceration indicated that the charge was located in the tetrahedral sheet, whereas non-expansion indicated that the charge was located in the octahedral sheet. The 060 XRD reflection of an unoriented sample was measured to determine the di- or trioctahedral nature of the smectite. A d(060) value of 1.53 to 1.55 Å indicated a trioctahedral smectite, whereas a spacing of 1.48 to 1.50 Å indicated a dioctahedral smectite (Brindley and Brown, 1980).

The concentrations ( $\mu\text{g/ml}$ ) of Si, Al, and Mg in the capsule fluids of some hydrothermal runs were determined by atomic emission spectroscopy (AES) using a Spectrametrics SpectraSpan III instrument and are presented as a percentage of their total amount in the sepiolite, the chemical composition of which is given elsewhere (Komarneni *et al.*, 1986).

## RESULTS AND DISCUSSION

### *Alteration of palygorskite in NaOH solution*

Powder XRD results showed that palygorskite was transformed to smectite under the hydrothermal, alkaline conditions, as reported by Golden *et al.* (1985). The Hofmann-Klemen Li<sup>+</sup>-saturation, heat treatment, and glyceration tests showed that the negative charge was located in the tetrahedral sheet, and the K<sup>+</sup>-saturation and glycolation test indicated, as expected from the chemical composition of palygorskite, that the smectite had a low charge density. The d(060) value of this smectite (Figure 1A) suggested that the smectite was trioctahedral and, hence, a saponite.

The XRD data on the location of the layer charge, the layer charge density, and the trioctahedral nature of the smectite were substantiated by the <sup>27</sup>Al and <sup>29</sup>Si MAS-NMR spectroscopy results. The <sup>27</sup>Al MAS-NMR spectra of palygorskite and the smectite transformed from palygorskite are given in Figure 2. As expected from the crystal structure of palygorskite (Brindley and Brown, 1980), the results show that Al in palygorskite was chiefly in octahedral coordination, along with a minor amount in tetrahedral coordination. The strong <sup>27</sup>Al resonance at 4.1 ppm from [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> indicates the presence of Al in octahedral coordination, and the minor resonance at 55.7 ppm (Figure 2) suggests the presence of a minor amount of tetrahedrally coordinated Al (Muller *et al.*, 1981). The smectite product from the palygorskite showed a strong <sup>27</sup>Al resonance at 58.2 ppm from [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> (Figure 2) which represents tetrahedrally coordinated Al. No resonance was detected at about 0 ppm, which indicates little or no octahedral Al in the smectite. Thus, the <sup>27</sup>Al MAS-

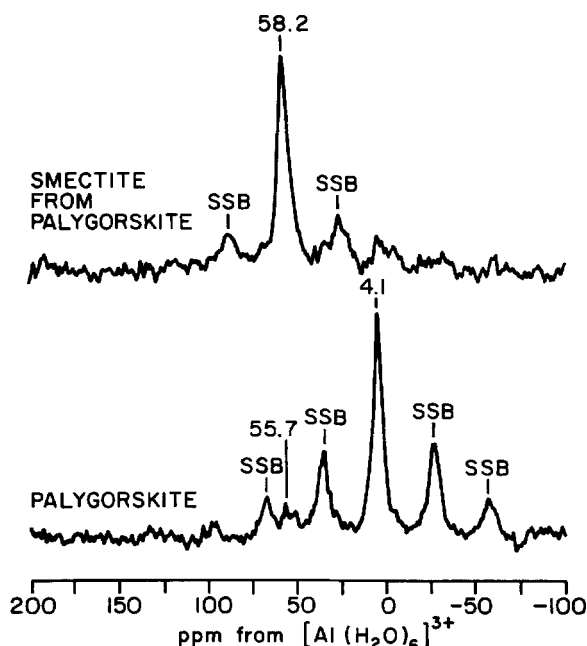


Figure 2.  $^{27}\text{Al}$  magic-angle spinning-nuclear magnetic resonance spectra of palygorskite and the smectite derived from palygorskite (SSB = spinning side bands).

NMR results showed that the coordination of Al changed from octahedral to tetrahedral during the transformation of palygorskite to smectite. These results are consistent with powder XRD results which showed a trioctahedral nature, i.e., a  $d(060)$  value of 1.525 Å for the smectite. These results also confirm the hypothesis of DeJong *et al.* (1982) that Al enters tetrahedral coordination in alkaline environments.

The  $^{29}\text{Si}$  MAS-NMR spectra of palygorskite and the smectite product from the palygorskite are shown in Figure 3. Palygorskite exhibited two broad resonances at  $-91.7$  and  $-96.8$  ppm from TMS, which were earlier attributed to two specific  $\text{Q}^3(\text{OAl})$  sites (Komarneni *et al.*, 1986), the  $\text{Q}^3$  sites being silicon atoms connected with three other tetrahedral silicon or aluminum atoms (Lippmaa *et al.*, 1980). The smectite product from the palygorskite showed two resonances at  $-93.2$  and  $-97.3$  ppm (Figure 1). The resonance at  $-97.3$  ppm may be due to talc-like layers  $\text{Q}^3(\text{OAl})$  (Magi *et al.*, 1984), whereas the  $-93.2$ -ppm resonance may be due to a  $\text{Q}^2(\text{1Al})$  environment. Thus, the talc-like regions in this smectite had little or no negative layer charge, whereas the regions showing  $\text{Q}^3(\text{1Al})$  had a negative layer-charge density approximately equivalent to standard smectites, as suggested by the  $\text{K}^+$  saturation and glycolation tests. Earlier studies with alkyl ammonium ions by Golden *et al.* (1985) suggested that the smectite transformed from palygorskite under similar conditions had two types of charge densities. The present  $^{29}\text{Si}$  MAS-NMR results support their finding.

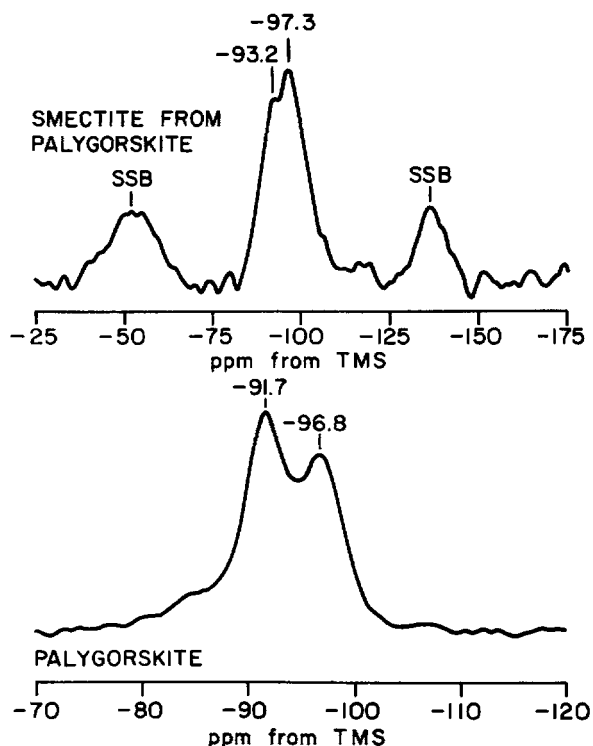


Figure 3.  $^{29}\text{Si}$  magic-angle spinning-nuclear magnetic resonance spectra of palygorskite and the smectite derived from palygorskite (SSB = spinning side bands).

#### Mechanism of palygorskite alteration

Two possible mechanisms for the transformation of palygorskite to smectite were offered by Golden *et al.* (1985): (1) dissolution and recrystallization, and (2) a breakdown of Si-O-Si bridges and recombination to form 2:1 silicate structural units of smectite (Güven and Carney, 1979). The  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS-NMR results presented here show that the coordination of Al changed from chiefly octahedral in palygorskite to chiefly tetrahedral in smectite, thereby suggesting a dissolution and recrystallization process. The nearest neighbor environment of Si also showed the presence of Al in the tetrahedral sheets of this smectite product. If the alteration were a simple breakdown and recombination of Si-O-Si bridges, the coordination of Al should not

Table 1. Percentage of elements remaining in solution after hydrothermal treatment of sepiolite at 300°C under a confining pressure of 30 MPa.

Sample	Element concentration in solution (g/100 g)		
	Si	Al	Mg
Sepiolite in 2 N CsCl	0.42	5.2	0.69
Sepiolite in 2 N $\text{MgCl}_2$	0.11	2.1	nd <sup>1</sup>
Sepiolite in 2 N $\text{CaCl}_2$	0.20	2.6	0.69

<sup>1</sup> nd = not determined because Mg remaining in solution from sample was expected to be very small compared to 2 N  $\text{MgCl}_2$  with which sample was treated.

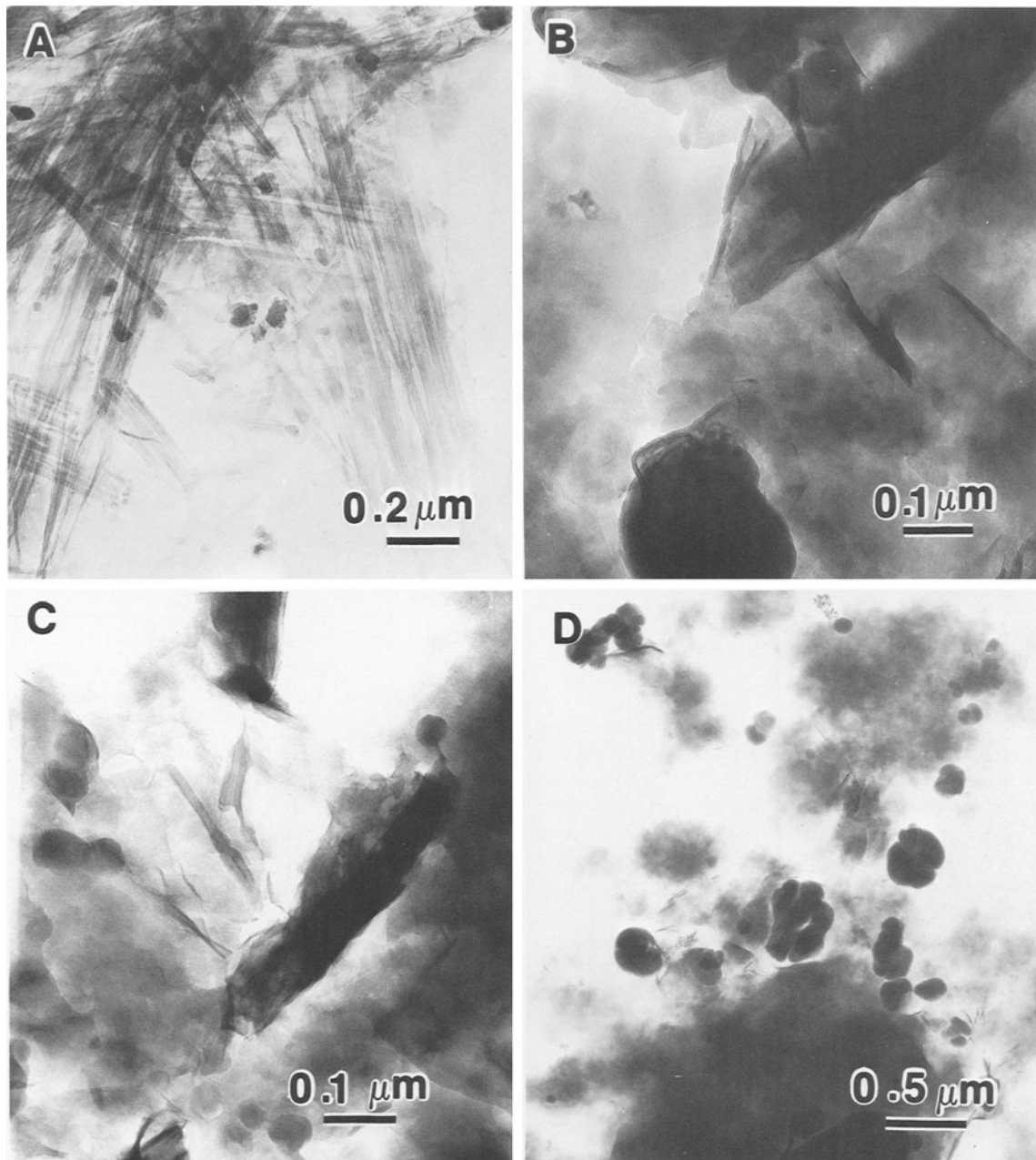


Figure 4. Transmission electron micrographs of smectites formed under hydrothermal conditions from: (A) palygorskite at 150°C; (B) sepiolite in 2 N CsCl at 300°C; (C) sepiolite in 2 N MgCl<sub>2</sub> at 300°C; (D) sepiolite in 2 N CaCl<sub>2</sub> at 300°C.

have changed during the transformation of palygorskite to smectite. Thus, the formation of smectite appears to have been a dissolution and recrystallization process, as was suggested earlier by Golden *et al.* (1985). Golden *et al.* (1985), however, suggested that partial breakdown and reorganization into smectite might also occur simultaneously with the dissolution and recrystallization process based on the lath-like morphology of the product smectite as revealed by TEM. In the

present study, the smectite formed from palygorskite also showed lath-like morphology (Figure 4A), which can be explained by a nucleation and epitaxial growth mechanism, i.e., the product smectite nucleated and grew on the surface of palygorskite remnants along the crystallographic axes. The above results on changes in nearest neighbor environment illustrate the value of <sup>27</sup>Al and <sup>29</sup>Si MAS-NMR in unraveling the mechanism of mineral alteration.

*Alteration of sepiolite in CsCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> solution*

Sepiolite transformed to smectite at 300°C in the presence of CsCl, MgCl<sub>2</sub>, and CaCl<sub>2</sub> solutions under a confining pressure of 30 MPa. The alteration occurred at a higher temperature but at lower pressure than that reported by Mumpton and Roy (1956). These authors reported sepiolite and palygorskite alteration to smectite at 200°C and 20,000 psi water pressure. Analyses of the product solutions (Table 1) showed that almost all of the principal constituents of the sepiolite were incorporated completely in the solid products. XRD data for the products after Li<sup>+</sup> saturation, heat treatment, and glyceration showed that these smectites were tetrahedrally charged. <sup>27</sup>Al MAS-NMR spectra (data not shown) of these smectite products showed that the Al is in fact in tetrahedral coordination just as in the original sepiolite (Komarneni *et al.*, 1986). XRD data on K-saturated, glycolated products showed that the magnitude of their layer charge was small. The d(060) values of these smectites clearly showed a trioctahedral nature (Figures 1B–1D), i.e., saponite. The morphology of these smectites, i.e., foliated aggregates (Figures 4B–4D), was different from that obtained from palygorskite under alkaline conditions (see above) and different also from the original sepiolite, which was needle-like. The nucleation and epitaxial growth mechanism which appears to have led to needle-like morphology for smectite formed from palygorskite was apparently not operating during sepiolite alteration to smectite. The reason for the above is unclear at present.

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