LOW-TEMPERATURE ALTERATION OF PALYGORSKITE TO SMECTITE

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Abstract—The feasibility of transforming palygorskite from two localities to smectite hydrothermally at temperatures ranging from 22° to 160°C was investigated in a series of laboratory experiments, in which alkalinity was maintained in the pH range of 11.4 to 12 by adding NaOH. The smectite formed was characterized by chemical, spectroscopic, and electron microscopic techniques. Smectite formed rapidly at >100°C; the transformation was slow, however, at 22°C. The introduction of $MgCO_3$ accelerated the alteration process, but changes in alkalinity at pH >12 and the difference in elemental composition of the palygorskite samples did not significantly affect the alteration. A pressure of one atmosphere and a temperature of 22°C were sufficient for some transformation to occur within a few months, provided the alkalinity was maintained close to pH 12. X-ray powder diffraction characterization of the product indicated a smectite, and infrared spectroscopy indicated saponite. The alteration to smectite was appreciable even at room temperature, which suggests that the reaction can take place without any external heating.

Key Words—Alkaline solution, Hydrothermal transformation, Palygorskite, Smectite, X-ray powder diffraction.

INTRODUCTION

Palygorskite, a fibrous clay mineral, is difficult to flocculate from suspension. Its bulk density is very low and it has a high water-holding capacity (Haden, 1963). These properties are due to its fibrous morphology and low cation-exchange capacity (10–17 meq/100 g; Singer, 1989). Although these properties can be used to advantage in certain industrial applications, such as stabilizing liquid fertilizer suspensions and deep-sea drilling fluids (Haden, 1963), they are detrimental in dewatering clay tailings from pebble phosphate mining and in reclaiming the waste clay ponds.

Palygorskite seems to be unstable in most soil environments and transforms to smectite (Bigham *et al.,* 1980). Under laboratory conditions, palygorskite can easily be transformed to smectite at 150°C under alkaline conditions (Golden *et al.,* 1985). Such a transformation, if possible at lower temperatures than 150°C, could be advantageous in reclaiming phosphatic clay-tailings ponds in Florida. The increase in cation-exchange capacity attending this transformation should facilitate phosphatic clay flocculation and reclamation. This report, in contrast to earlier work at 150°C by Golden *et al.* (1985), describes the transformation of palygorskite to smectite from 80° to 160°C at saturation water vapor pressure and at 22° and 80°C at atmospheric pressure. The effects of $CaCO_3$, $MgCO_3$, and $CaHPO_4$ also were investigated to determine the influ-

ence of other phosphatic clay constituents on the transformation.

MATERIALS AND METHODS

Samples

Two palygorskite clays were employed. One was from the Um Er Radhuma Formation, Saudi Arabia (PSA1) (Shadfan *et al.,* 1985), which was free of other minerals except for a trace of kaolinite. The second sample (F1) was taken from just below the pebble-phosphate beds near Bartow, Florida, in the Bone Valley Member of the Peace River Formation of the Miocene-Pliocene age Hawthorne Group.

Methods

X-ray powder diffraction and infrared analyses. An aqueous suspension of each sample was mounted on a glass slide, dried, and analyzed from 2° to 50°2θ by X-ray powder diffraction (XRD) using CuKα radiation at 30 kV and 18mA on a Philips Norelco diffractometer. Freeze-dried clay samples were examined by infrared spectroscopy (IR) as self-supporting films or as pellets of anhydrous KBr (0.75 mg clay/300 mg KBr) pressed at 1.38×10^5 kPa for 5 min. IR spectra were recorded using a Perkin Elmer 283 IR spectrometer equipped with a model 3500 data station.

Transmission electron microscopy. Transmission electron micrographs (TEM) were obtained with a Zeiss 10C instrument. The samples were washed 8–9 times in distilled water in 4-ml tubes using a refrigerated high-speed centrifuge. The final suspension was diluted with distilled water and sonicated prior to the depo-

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Table 1. Smectite produced in closed vessels from palygorskite (PSA1) in 24 hr as a function of temperature and NaOH concentration.[1]

NaOH (m)	pH	Temperature (°C)				
		80	100	120	140	160
0.05	11.3	ND[2]	10	20	56	92
0.10	11.7	ND	24	78	100	100
0.15	11.9	ND	35	96	100	100
0.20	12.0	tr[3]	45	100	100	100

[1] Percentage smectite estimated from X-ray powder diffraction (XRD) intensities of 10.4- and 14-Å peaks. 50 mg sample, 20 ml solution, 25 ml vessel.

[2] ND = not detected.

[3] tr = trace, small rise in XRD pattern at 14-Å position.

Table 2. Smectite formed from palygorskite (PSA1) in open vessels at 22° and 80°C in six months.

Treatment[1]	MgCO₃ added (mg/300 mg)	pH[2]	Clay	Smectite produced[3]	
				At 22°C (%)	At 80°C (%)
1	150	12	PSA1	3	70
2	150	12	PSA1	4	65
3	150	12	F1	7	100
4	150	12	F1	8	90
5	150	13	PSA1	3	65
6	150	13	PSA1	5	100
7	150	13	F1	8	100
8	150	13	F1	9	45
9	0	12	PSA1	5	5
10	0	12	PSA1	3	10
11	0	12	F1	5	25
12	0	12	F1	4	20
13	0	13	PSA1	2	10
14	0	13	PSA1	2	10
15	0	13	F1	6	30
16	0	13	F1	6	15

[1] Sample weight = 300 mg, volume = 100 ml.

[2] The pH was adjusted daily with 1 N NaOH.

[3] Smectite content estimated from X-ray powder diffraction data.

sition of drops on the microgrids (Fukami and Adachi, 1965).

Reaction procedure. Fifty-milligram portions of palygorskite clay (PSA1) were placed in four 25-ml, Teflon-lined, steel pressure vessels containing 20 ml of 0.05, 0.10, 0.15, and 0.20 M NaOH, respectively. The contents were sonicated briefly (20 s at 40 watts) to disperse the clay, and the vessels were closed airtight and heated in an oven at 80°, 100°, 120°, 140°, or 160°C under their own vapor pressure. These temperatures correspond to autogenous water vapor pressures of 0.5 to 6 bars at 80° and 160°C, respectively (Weast, 1989, p. 192). At the end of 24 hr, the vessels were removed from the oven and cooled in a refrigerator at 7°C. Contents were transferred to 40-ml centrifuge tubes and washed free of soluble materials. The supernatants were saved for chemical analysis. The residues were investigated using TEM, XRD, and IR.

The effects of phosphate (as CaHPO₄) and carbonate (as CaCO₃ or MgCO₃) in the amounts 0, 5, 10, 15, and 20 mg per 50 mg palygorskite clay were determined by heating the mixtures at 160°C in 20 ml 0.15 M NaOH for 24 hr in the digestion vessels described above. The products were freed of soluble materials by centrifuge washings and examined by XRD.

The effect of MgCO₃ on the alteration of palygorskite (PSA1) to smectite over extended time periods was tested under ambient conditions in open plastic containers, in which the water level was adjusted daily for evaporation. Two different palygorskite samples and two levels of pH were employed (Table 2). After 6 months, the yields of smectite were estimated by XRD analysis and were subjected to statistical analysis using General Linear Models Procedure (PROC GLM; SAS Institute, 1985). Selected treatments were continued for 10 months. A set of samples having a range of smectite contents for CEC analysis was prepared by treating palygorskite (100-mg samples) at pHs of 6, 10, 11, and 12 at room temperature and pressure for 2 weeks. Also, one sample was treated at 100°C in a closed Teflon-lined steel pressure vessel under its own

vapor pressure at pH 12 for 2 days. Final products were washed free of soluble materials and freeze dried, and CEC and XRD analyses were made. The amount of smectite was estimated from the increase in CEC after treatment.

Elemental analyses. Chemical analyses for Al, Mg, and Si in the starting clays and the transformation products were made using an HF-aqua regia digestion procedure (Bernas, 1968). The diluted digests were analyzed by atomic absorption spectrometry. Clear supernatant equilibrium solutions also were analyzed by atomic absorption spectrometry to determine the extent of dissolution at the end of the experiment.

Cation-exchange capacity (CEC). Fifty-milligram samples of freeze-dried, Na-saturated clays were placed into preweighed plastic centrifuge tubes. The clay samples were dispersed in 20 ml of 1 M KCl solution and shaken for 1 hr. The clay suspensions were centrifuged and the supernatants decanted. This process was repeated three times and followed by three washings with 20-ml portions of distilled, deionized water. The last washing was saved for analysis, and the centrifuge tube containing the clay and the entrained water was weighed and quick frozen in liquid nitrogen. Samples were dried in a freeze-drier and reweighed. The clay residues were dissolved while in the centrifuge tube by shaking in HF and aqua regia at room temperature for 24 hr, and the resulting solutions were mixed with 1.5 g boric acid and diluted to 100 ml. Potassium was analyzed by atomic absorption spectroscopy, and the cation-exchange capacity was calculated after adjusting for K in
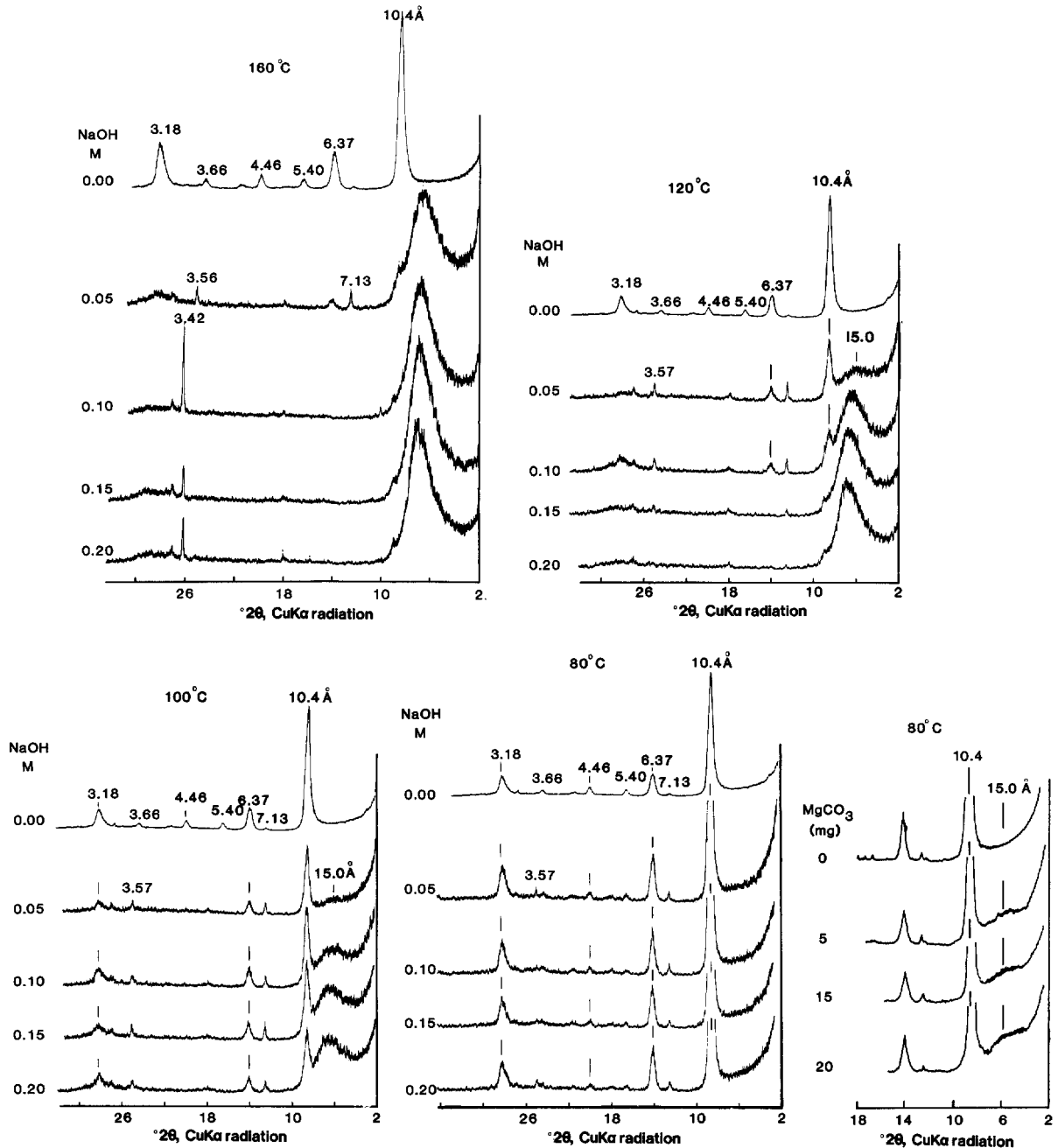
Figure 1.   X-ray powder diffraction patterns of samples of palygorskite (PSA1) digested at 160°, 120°, 100°, and at 80°C (a, b, c, and d, respectively), in closed vessels and at various concentrations of NaOH (a, b, c, and d) and in 0.15 M NaOH with MgCO₃ in indicated amounts (e).

the entrained solution and for any structural K (<0.1%) in the original sample.

RESULTS

Short-term (24 hr) experiments in closed vessels

The effect of heating on the palygorskite-to-smectite conversion was tested at various temperatures ranging

from 80° to 160°C. At 160°C, the reaction was about 90% complete after 24 hr, even in the 0.05 M NaOH solution (Table 1). The kaolinite, however, was relatively stable, as indicated by the persistence of the 7.13- and 3.56-Å XRD lines (Figure 1a). In the 0.10, 0.15, and 0.20 M NaOH solutions, however, the kaolinite dissolved, and analcime formed, as indicated by the appearance of a 3.42-Å peak. At 160° and 140°C (not
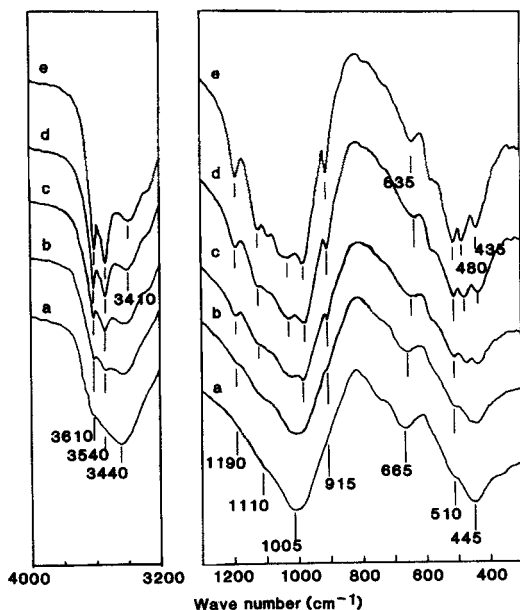
Figure 2. Infrared spectra of products obtained from palygorskite (PSA1) treated in closed vessels at (a) 160°, (b) 120°, (c) 100°, (d) 80°, and (e) 22°C in the presence of 0.15 M NaOH.

shown), palygorskite peaks at 10.4 and 6.4 Å were noted in the XRD patterns of 0.05 M NaOH solution. Kaolinite peaks were noted in the XRD patterns of 0.05 M NaOH addition; no analcime peaks were observed. The extent of transformation in 24 hr was less at 120° and 100°C (Figures 1b and 1c), as indicated by the increasingly intense 10.4-Å peak of unreacted palygorskite and the weaker smectite peaks at about 15 Å. At 80°C, no smectite peak was observed in the XRD pattern (Figure 1d), even after a reaction time of 48 hr (data not shown).

To test the influence of $MgCO_3$, incremental amounts were added to a mixture of a 0.15 M NaOH solution and palygorskite and heated at 80°C for 24 hr. The $MgCO_3$ appeared to accelerate the reaction, as evidenced by the broad 15-Å smectite peak that formed (Figure 1e). Thus, alkalinity and $MgCO_3$ both enhanced the palygorskite-to-smectite transformation.

As the palygorskite progressively altered to smectite, changes in the IR absorption bands of the sample were noted at 3610, 3540, and 3410 cm^{-1} (Figures 2a–2e). The intensity of the 3610- and 3410-cm^{-1} bands diminished, indicating a decrease in Al$_2$–OH bonded hydroxyls and coordinated water. The broad band at 3410 cm^{-1}, due to the zeolitic water in the palygorskite, disappeared upon alteration as the zeolitic water gave way to H-bonded interlayer water (3440 cm^{-1}).

The Si–O stretching band near 1000 cm^{-1} became broad, and the minor bands at 1190 and 1110 cm^{-1} of palygorskite (Figure 2e) disappeared altogether (Figure
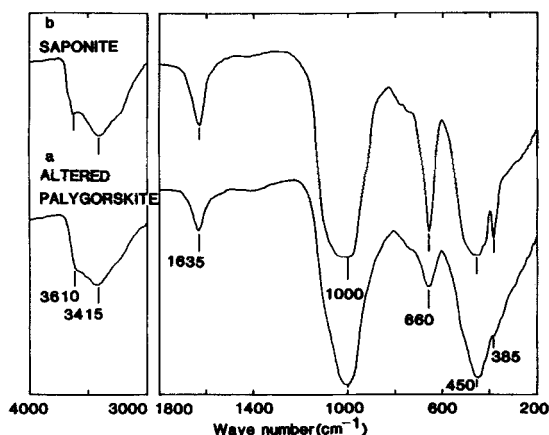
2a). The Al$_2$OH band at 915 cm^{-1} also disappeared as the transformation progressed. The Si–O bending vibration of palygorskite at 635 cm^{-1} shifted to 665 cm^{-1} (Figures 2a–2e), and the three bands at 510, 480, and 435 cm^{-1} (Figure 2e) merged to a broad peak at 445 cm^{-1} (Figure 2a).

The saponite-like product obtained as a result of the heat treatment at 160°C in a closed vessel had substantially the same IR pattern as the saponite control specimen (Figures 3a and 3b). The absorbances at 660 and 385 cm^{-1} were broader and weaker than corresponding absorbances for the saponite, suggesting fewer chemical bonds that absorb at these positions and thinner, more disordered crystals of the alteration product than the saponite reference (Figures 3a and 3b). Little evidence of other absorbances was noted to suggest other phases, such as montmorillonite, which typically absorbs at 3624, 1038–1026, and 915 cm^{-1} (van der Marel and Beutelspacher, 1976, p. 114).

Palygorskite mounted on holey carbon microgrids was examined by transmission electron microscopy (TEM). TEMs of the untreated specimen showed thick, blunt laths that were coarser than most palygorskites, which are typically acicular (Figure 4f). This specimen was chosen for its purity, but shows small amounts of smectite, as illustrated by the product after the 80°C heat treatment. Some sheets attributed to smectite were visible, and the palygorskite fibers showed blemishes due to solution etching or high susceptibility to electron beam damage (Figure 4e). At higher temperatures the transformation was more evident, as indicated by the larger size of the thin smectite sheets and the corresponding decrease in size of the palygorskite fibers. The presence of some laths even after 160°C heat treatment, where XRD and IR indicated relatively pure smectite, indicates the persistence of some morphological features characteristic of the original palygorskite, which deserve further study. A tentative interpretation is that

Figure 3. Infrared spectra of NaOH-treated palygorskite (PSA1) (a) and saponite (b).
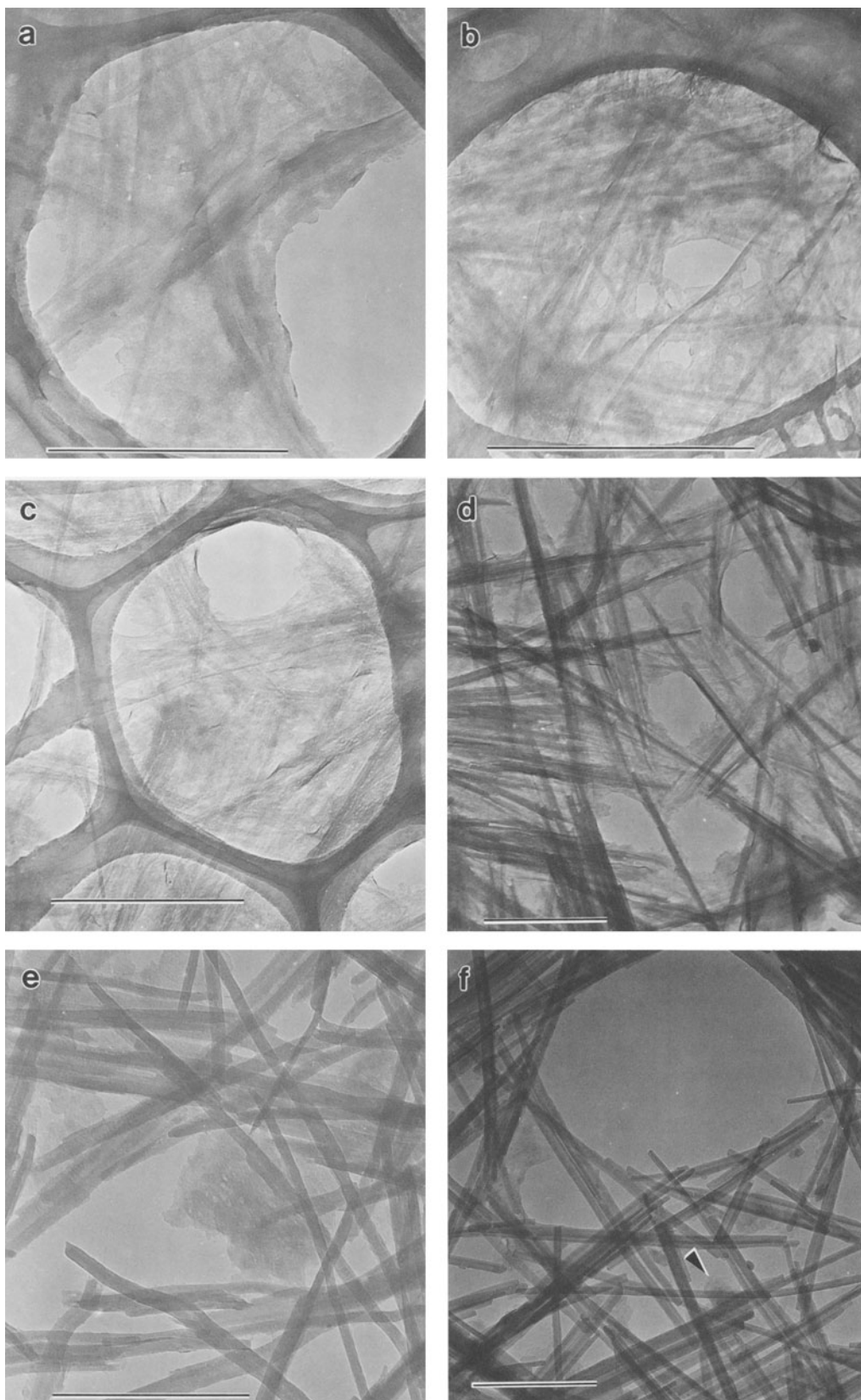
Figure 4.   Transmission electron micrographs of palygorskite (PSA1) NAOH treated in closed vessels at: (a) 160°, (b) 140°, (c) 120°, (d) 100°, (e) 80°C, and (f) untreated (bar represents 5000 Å).
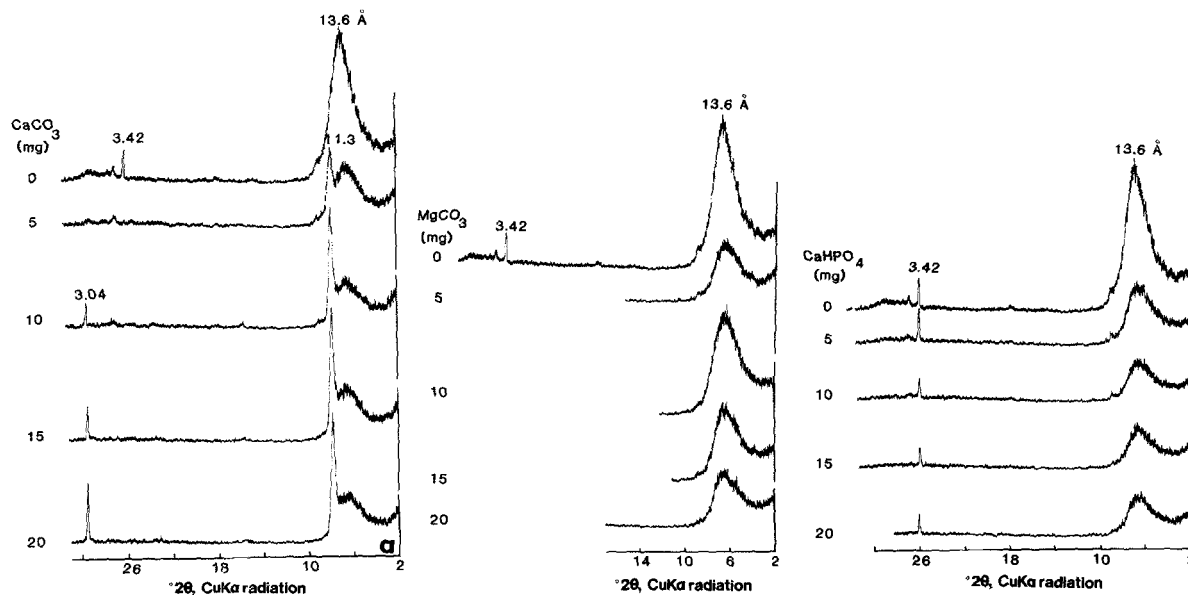
Figure 5.   X-ray powder diffraction patterns of samples of palygorskite (PSA1) treated in 0.15 M NaOH in closed vessels at 160°C with (a) $CaCO_3$, (b) $MgCO_3$, and (c) $CaHPO_4$.

some smectite formed on and in the palygorskite laths prior to their physical disruption, thereby producing a palygorskite pseudomorph composed of smectite.

Effect of $CaHPO_4$, $CaCO_3$, and $MgCO_3$ on palygorskite transformation

$CaCO_3$ and $CaHPO_4$ influenced the reaction rate of the palygorskite-to-smectite transformation (Figures 5a and 5b). The yield of smectite at 160°C decreased as the $CaCO_3$ content was increased (Figure 5a). The presence of Ca^{2+} contributed to the formation of a calcium silicate hydrate (11.3 Å; JCPDS, 1973) and reduced the smectite yield by depleting the silica in the system. The presence of $CaHPO_4$ or $MgCO_3$ apparently had no effect on the amount of smectite formed at 160°C (Figures 5b and 5c). The decrease in the XRD peak intensity of the smectite may have been due simply to dilution by the carbonate or phosphate and their reaction products.

Palygorskite conversion to smectite in open vessels

At 80°C, about 20% of the Florida palygorskite converted to smectite, and at 22°C only about 5% was converted after 6 months (Table 2). Magnesium carbonate had a pronounced effect upon the rate of reaction, as shown by the XRD data for the low-temperature samples after 10 months at a given temperature (Figure 6). The analysis of variance of the data in Table 2 (PROC GLM; SAS Institute, 1985) indicates that $MgCO_3$ (F = 64.35; df = 1,26; p < 0.0001), temperature (F = 109.16; df = 1,26; p < 0.0001), and the

$MgCO_3$ × temperature interaction (F = 56.36; df = 1,26; p < 0.0001) were highly significant. Although, not statistically significant, palygorskite F1 consisting of fine fibers (large surface area) produced more smectite than the coarse fibers of palygorskite PSA1 in 6 months (Table 2). Similar yields were recorded at both pH 12 and 13. The cation-exchange capacity of the smectite formed from palygorskite (CEC_s) was 75 meq/100 g; that of the original palygorskite (CEC_p) was 9.5 meq/100 g. The percentage of smectite in the reaction
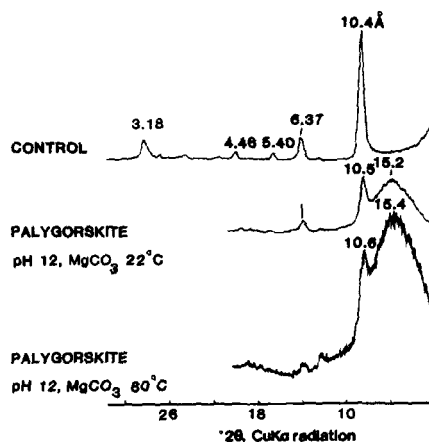

Figure 6.   X-ray powder diffraction of selected samples of alteration products of palygorskite (PSA1) and NaOH solution reaction after 10 months in open vessels at pH 12 in the presence of $MgCO_3$.

Table 3. Smectite content of products from NaOH treatment of palygorskite (PSA1) by cation-exchange capacity (CEC) and X-ray powder diffraction (XRD) procedures.

	Treatment			Smectite (%)	
pH	Temp. (°C)	Time (hr)	CEC (meq/100 g)	From CEC	From XRD
12	100	24[1]	17.3	12	5
12	22	336	12.5	5	ND[2]
11	22	336	11.2	3	ND
10	22	336	9.6	<1	ND
6[3]	22	336	9.4	0	ND

[1] At confined water vapor pressure; 50 mg sample, 20 ml solution, 25 ml vessel.
[2] ND = not detected.
[3] Control sample.

products was calculated using the formula:

$$\% \text{ Smectite} = (CEC_t - CEC_p) \times 100/(CEC_s - CEC_p),$$

where CEC_t is the CEC of the NaOH-treated sample. The samples from the low-temperature experiment, which showed little or no smectite by XRD, were investigated using the CEC procedure. The results (Table 3) indicate that smectite may have formed slowly at pH 10 and 11 at 22°C.

Chemical analysis of the supernatants of the palygorskite sample treated with NaOH at pH 12 after 50 days indicates that a substantial amount of Si and Al went into solution (Table 4). Relatively little Mg was solubilized. The solubility product of $Mg(OH)_2$, which determines the solubility of Mg^{2+} in this system, is small (5.61×10^{-12}) at 25°C compared with that of $MgCO_3$ (6.82×10^{-6}) at 25°C (Weast, 1989, p. B-207). Therefore, the precipitation of smectite was largely determined by the concentration of Mg^{2+}, which was controlled either by $Mg(OH)_2$ or $MgCO_3$.

DISCUSSION

Palygorskite fibers readily altered to smectite under alkaline conditions at 160°C and under autogenous water pressure in 24 hr. Some of the resulting smectite was lath-shaped. Lath-like morphology was reported by Güven and Carney (1979) for the stevensite produced by the hydrothermal transformation of sepiolite. The rate of alteration of palygorskite to smectite depended upon the temperature, as shown in Figures 1a–1e. Although the saturation vapor pressure of water in the pressure vessels ranged from 0.5 to 6 bar at 80° and 160°C respectively, the influence of pressure on the reactions was not considered. The apparent effect on $MgCO_3$ (Figure 1e) may have been to supply Mg^{2+} ions, which contributed to the formation of a Mg-rich smectite.

Although two mechanisms were proposed by Golden et al. (1985) for the alteration of palygorskite to smectite, a dissolution and reprecipitation mechanism was

Table 4. Chemical analysis of starting palygorskite samples and equilibrium supernatants after 50 days at pH 12 and 22°C.

Sample	Al (%)	Mg (%)	Si (%)	Al/Si (wt. ratio)	Mg/Si
Clays					
F1	1.91	4.10	14.92	0.128	0.275
PSA1	5.21	5.49	19.96	0.261	0.275
Supernatant					
F1	0.76	0.04	5.30	0.143	0.007
PSA1	0.90	0.01	4.66	0.192	0.002

favored by Komarneni (1986) from solid state nuclear magnetic responance data, which indicated the probable presence of tetrahedral Al atoms. The disappearance of Al_2OH-stretching and -bending IR bands upon alteration of palygorskite to smectite supports the formation of a Mg-rich smectite. Furthermore, the chemical analysis of the supernatant (Table 4) indicates that most of the initial Mg in palygorskite remained in a solid phase.

The alteration of palygorskite to smectite was dependent upon: (1) alkalinity, (2) temperature, (3) composition and surface area of the starting palygorskite, and (4) the presence or absence of $MgCO_3$. Of the factors mentioned, alkalinity, temperature, and the $MgCO_3$ concentration had the most profound influence on the rate of transformation (Table 2).

The CEC data (Table 3) suggest that the transformation of palygorskite to smectite under alkaline conditions took place at a slow rate (assuming all the CEC increase was due to smectite and not due to zeolites). Where smectite is the thermodynamically favored product (Elprince et al., 1979), palygorskite should transform to smectite under natural conditions; however, under some soil ionic conditions and at pH 7 to 8, palygorskite appears to be stable. Increased solubility of Al and Si under high pH favors the transformation of palygorskite to smectite.

The smectitic product of the dissolution of palygorskite at 160°C had properties of saponite, as indicated by XRD, IR, and chemical data on the product (Table 4). The broad absorption bands of the smectite (Figure 3a) indicate extensive substitution of Al for Si in the tetrahedral positions (Farmer, 1974). The IR peaks 445, 665, and 1005 cm^{-1} were characteristic of saponite.

In summary, the results obtained in this work strongly suggest that the alteration of palygorskite to smectite can be achieved at temperatures <100°C and at a pressure of 1 atmosphere, but at a slow rate. The development of appreciable cation exchange capacity, the reported presence of tetrahedral aluminum, and the presence of newly formed thin films of smectite-like material in the products suggest a dissolution and precipitation mechanism for smectite formation from palygorskite.

ACKNOWLEDGMENTS

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