PALYGORSKITE AND SEPIOLITE ALTERATION TO SMECTITE UNDER ALKALINE CONDITIONS

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Abstract—The instability of palygorskite and sepiolite under soil conditions was investigated to determine if these fibrous minerals transform directly to smectite under laboratory conditions. The treatment of 100 mg (0.12 mmole) of palygorskite with 1 mmole of NaOH solution (17 ml) at 150°C for 24 hr yielded a smectite. Analcime and smectite were formed when ≥ 3 mmole of NaOH was used. The addition of ≤ 6 mmole NaOH to sepiolite destroyed it gradually. On addition of ≥ 8 mmole NaOH, sepiolite altered to an X-ray amorphous material. In the presence of Al and Si, however, it transformed to smectite and analcime. Transmission electron microscopy, cation-exchange capacity, and X-ray powder diffraction studies of the products suggest that alteration was (1) via solution, or (2) by a structural reorganization wherein the basic 2:1 silicate structural units were unchanged.
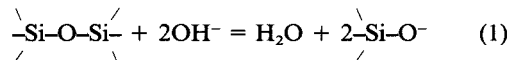
Key Words—Alteration, Analcime, Cation-exchange capacity, Palygorskite, Sepiolite, Smectite, Sodium hydroxide.

INTRODUCTION

Palygorskite and sepiolite occur in arid and semiarid soils. In reviewing the literature concerning the origin of these minerals Isphording (1973) concluded that both sepiolite and palygorskite normally form authigenically from marine and lacustrine waters. The stability diagram proposed for palygorskite (Elprince *et al.,* 1979) suggests a high pH, high Mg environment for the formation of palygorskite. Reduced OH and Mg activities probably contribute to the instability of these minerals in soil environments (Bigham *et al.,* 1980). Therefore, a possible transformation of palygorskite and sepiolite to more stable phases under soil conditions was predicted by Bigham *et al.* (1980) and Lee *et al.* (1983). Such a transformation to smectite was achieved hydrothermally for palygorskite and sepiolite at 200°C and 20,000 psi water pressure by Mumpton and Roy (1956). Sepiolite transformed to stevensite under similar conditions (Güven and Carney, 1979). These investigations indicate the relative instability of palygorskite and sepiolite with respect to smectite under elevated temperature and pressure conditions. The transformation under soil conditions, however, may involve rather sluggish kinetics as the rate of dissolution of these fibrous minerals and the rate of formation of smectite will be very slow.

Palygorskite may transform to smectite by (1) the breakdown of Si–O–Si bonds between 2:1 layer silicate units followed by reorganization to form a smectite-type structure, or (2) complete dissolution and reprecipitation. Both of these mechanisms involve the disruption of Si–O–Si bonds. The use of alkaline conditions should facilitate the breakdown of Si–O–Si bonds by the following reaction:

$$\overset{\textstyle\diagdown}{\underset{\textstyle\diagup}{-}}Si-O-Si\overset{\textstyle\diagup}{\underset{\textstyle\diagdown}{-}} + 2OH^- = H_2O + 2\overset{\textstyle\diagdown}{\underset{\textstyle\diagup}{-}}Si-O^- \qquad (1)$$

The aim of this study was to investigate the feasibility of a transformation of palygorskite and sepiolite at a relatively low temperature (150°C) and low pressure (69 psi). For this reason, alkaline conditions were employed to enhance the rates of reaction. The effect of the addition of $AlCl_3$, Na_2SiO_3, and $MgCl_2$ to the systems was also examined.

MATERIALS AND METHODS

Palygorskite (Gadsden County, Florida) and sepiolite (Vallecas, Spain) were obtained from Ward's Natural Science Establishment, Rochester, New York. The sepiolite was ground in an agate mortar in acetone and then treated with pH 5 sodium acetate to remove carbonate. The clay fraction ($< 2.0 \mu$m) was obtained using the procedure described by Jackson (1956). The final suspension was flocculated using NaCl to reduce the suspension volume and then washed free of NaCl and lyophilized. The palygorskite from Florida was found to contain a trace of quartz as an impurity. Oriented mounts of clay samples were prepared for X-ray powder diffraction (XRD) analysis using $CuK\alpha$ radiation.

Samples were saturated with Mg, solvated with glycerol, saturated with K, and heated to 300°C and subsequently to 550°C. Alkyl ammonium ion-saturation was accomplished by the method of Lagaly and Weiss (1976), as modified by Ruehlicke and Kohler (1981). Elemental compositions of the palygorskite, sepiolite,

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Table 1. Treatments of sepiolite[1] with NaOH, $MgCl_2$, $AlCl_3$, and Na_2SiO_3.

Treatment	Reactants
1	—
2	2 mmole NaOH
3	4 mmole NaOH
4	6 mmole NaOH
5	4 mmole NaOH + 0.5 mmole $MgCl_2$
6	4 mmole NaOH + 0.33 mmole $AlCl_3$
7	4 mmole NaOH + 0.5 mmole Na_2SiO_3
8	4 mmole NaOH + 0.17 mmole $AlCl_3$ + 0.25 mmole Na_2SiO_3

[1] 100 mg.

and the products obtained by various treatments were determined by the technique of Bernas (1968). Si determinations were made by the molybdenum blue colorimetric technique (Weaver *et al.,* 1968). Al, Mg, Na, and K were determined by atomic absorption spectrophotometry (Lee and Güven, 1975).
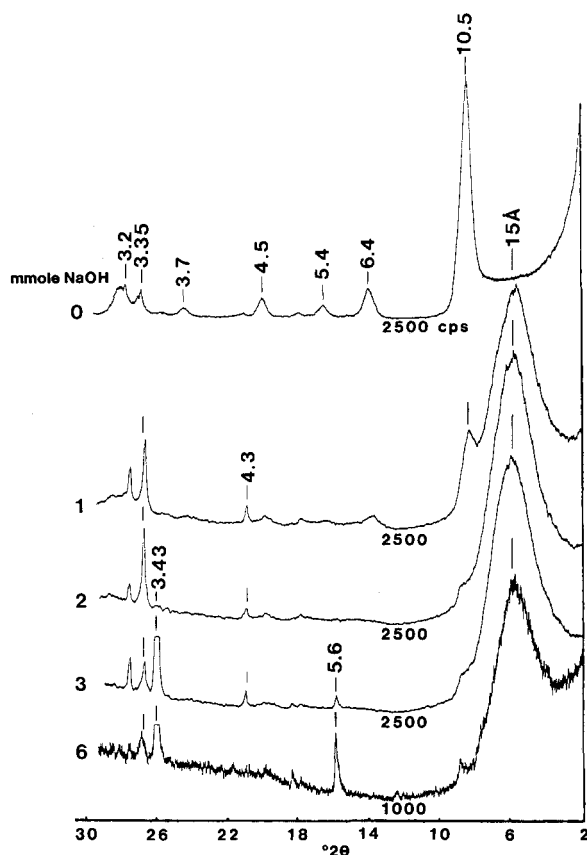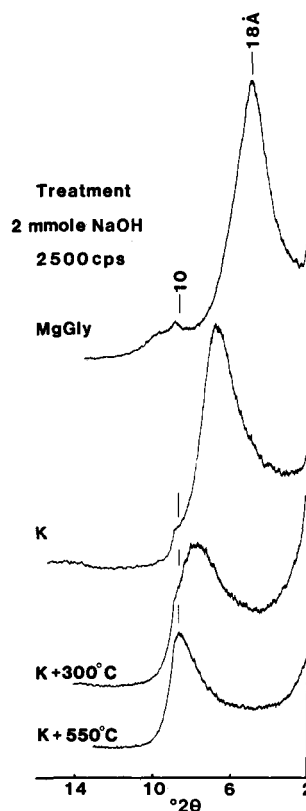

Figure 1. X-ray powder diffraction patterns of palygorskite treated with different concentrations of NaOH at 150°C for 24 hr. CuKα radiation.

Figure 2. X-ray powder diffraction patterns of palygorskite treated with 2 meq of NaOH showing peak positions on Mg-saturation, glycerol solvation, K-saturation, and K-saturation + heating to 300 and 550°C.

Alkali treatments

Palygorskite. Samples of palygorskite (100 mg) and a prescribed amount of NaOH (0–8 mmole) were placed in Teflon-lined digestion pressure vessels. After bringing the final volume to 17 ml with deionized-distilled water, the vessels were capped and placed in an oven at 150°C under their own vapor pressure for 24 hr. The vessels were cooled to room temperature, and the solutions were brought to pH 7 with 0.5 N HCl and washed with 1 N NaCl followed with water until all excess salt was removed. The final product was lyophilized and examined by XRD.

Sepiolite. Samples of sepiolite (100 mg) were treated similarly with varying amounts of NaOH plus 0.5 or 1.0 mmole of $MgCl_2$, $AlCl_3$, or Na_2SiO_3 (Table 1). The mixtures were held at 150°C for 72 hr and the products treated in a manner similar to that described above for the palygorskite samples. The reagent grade chemicals $MgCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$ and $Na_2SiO_3 \cdot 9H_2O$ were supplied by Matheson Coleman and Bell Manufacturing Chemists, Norwood, Ohio.
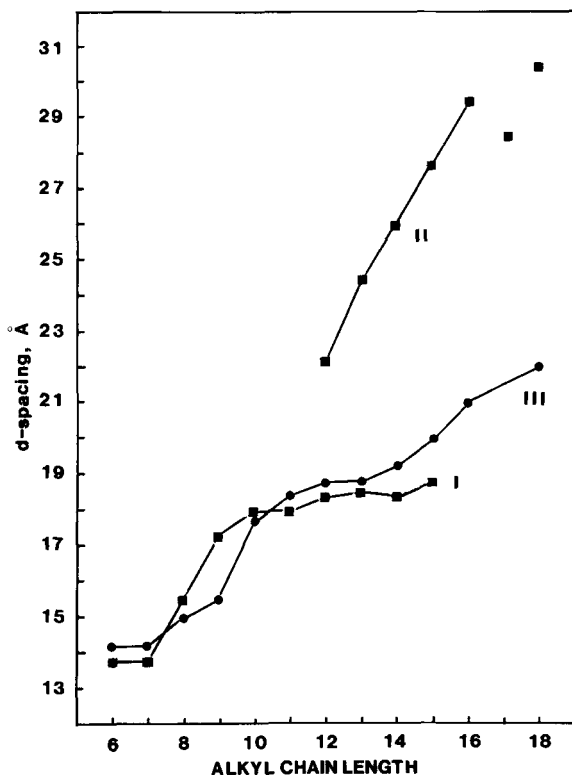
Figure 3. Variation of (001) spacing of the smectites from palygorskite (■) and from sepiolite (●) on saturation with alkyl ammonium ions with different chain lengths.
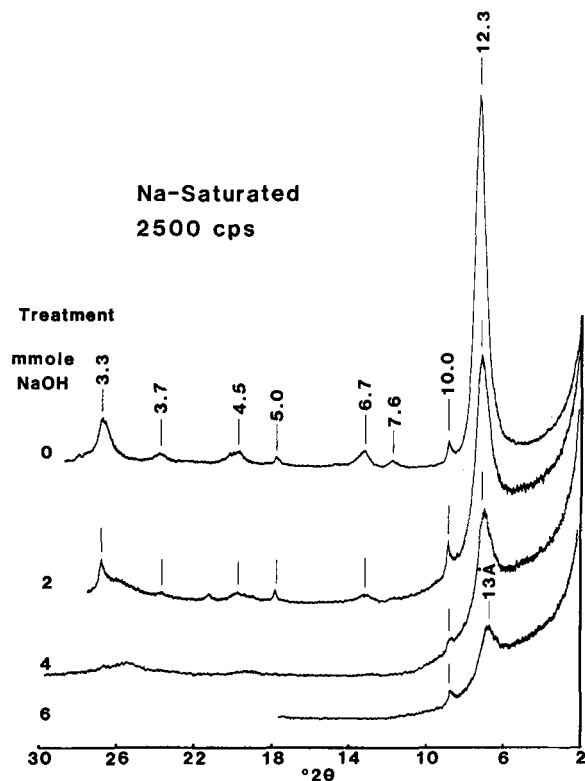

Figure 4. X-ray powder diffraction patterns of sepiolite treated with different concentrations of NaOH at 150°C for 3 days.

RESULTS AND DISCUSSION

Palygorskite treated with various amounts of NaOH was transformed to smectite and a zeolite in 24 hr at 150°C and 69 psi water vapor pressure. Figure 1 shows the XRD patterns of the products. Palygorskite heated in a similar fashion but without alkali addition showed no change. The NaOH treatment substantially changed the structure of palygorskite as shown by the reduction in intensity of the 110 reflection at 10.5 Å and the appearance of a smectite peak at 15 Å. The weak palygorskite diffraction peaks at 6.4, 5.4, 4.5, and 3.7 Å also decreased in intensity. As the amount of NaOH was increased, the peak intensities of the smectite increased at the expense of the palygorskite peaks. Maximum conversion was observed with the 2-meq-NaOH treatment. NaOH added in excess of 2 meq caused the formation of analcime (XRD reflections at 3.43 and 5.6 Å). This zeolite is a common alteration product of clay minerals in alkali soil systems (Baldar and Whittig, 1968). The present data indicate that in the presence of NaOH, the palygorskite-smectite conversion occurred at a lower temperature and pressure (150°C, 69 psi) and in a shorter time range (24 hr) than reported
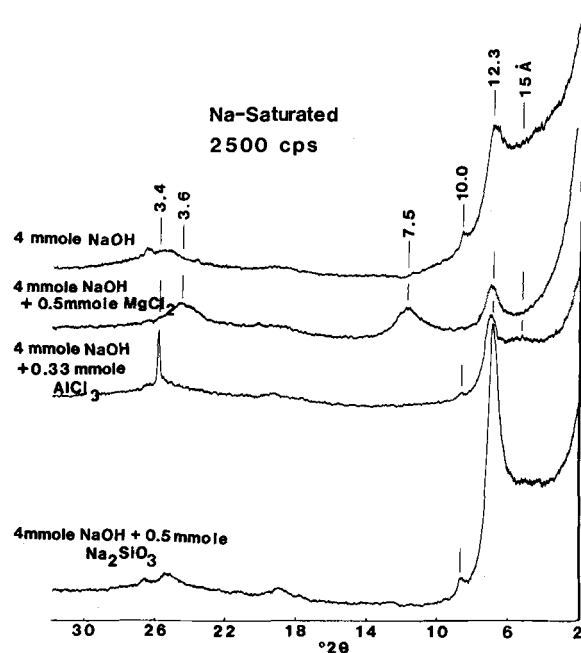

Figure 5. X-ray powder diffraction patterns of sepiolite treated with NaOH + MgCl₂, AlCl₃, or Na₂SiO₃ at 150°C for 3 days.
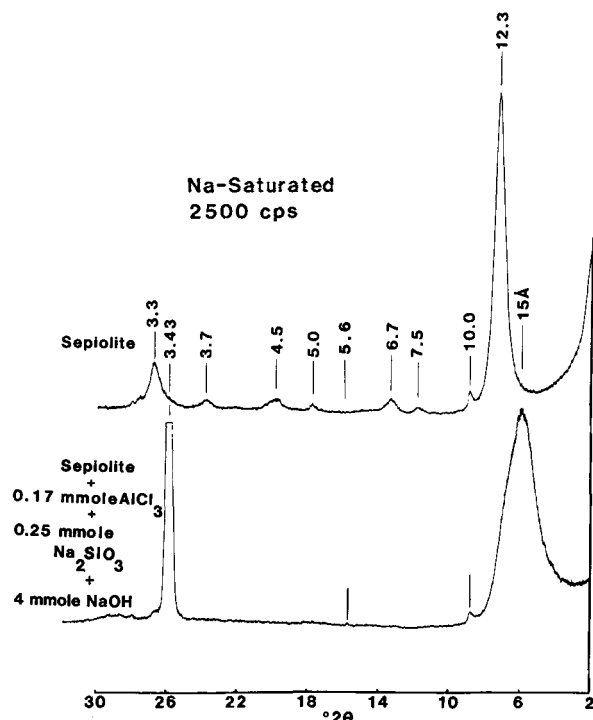
Figure 6.   X-ray powder diffraction patterns of sepiolite treated with a mixture of AlCl₃, Na₂SiO₃, and NaOH at 150°C for 3 days.

Table 2.   Ca-exchange capacity (Ca-CEC) and K-exchange capacity (K-CEC) of initial and treated clays.[1]

Sample	Ca-CEC (meq/100 g)	K-CEC (meq/100 g)
Palygorskite	19.7	17.4
Sepiolite	6.6	7.9
Treated palygorskite	74.1	58.2
Treated sepiolite	53.5	52.1

[1] For palygorskite, 2 mmole NaOH at 150°C for 24 hr; for sepiolite, 4 mmole NaOH + 0.17 mmole AlCl₃ + 0.25 mmole Na₂SiO₃ at 150°C for 3 days.

by earlier workers (Mumpton and Roy, 1956; Güven and Carney, 1979).

Smectite produced by the optimum NaOH treatment of palygorskite showed characteristic expansion to 18 Å on glyceration and collapse to 10 Å on heating at 550°C (Figure 2). On saturation with alkylammonium ion this smectite (Figure 3) showed the presence of two types of layer silicates: a smectite as shown by curve (I), where a distinct monolayer to bilayer transition that started at an alkyl chain length of 7 C atoms (13.8 Å) and a bilayer completion at a chain length of 13 C atoms (17.8 Å), and a layer silicate similar in charge to a vermiculite (curve II), which expanded in steps with an increase in alkyl chain length beyond 12 C atoms. No vermiculite was detected in the XRD pattern of the original palygorskite. Therefore, any mechanism proposed for the palygorskite-NaOH reaction must explain the formation of two types of smectite with different charge densities or of vermiculite + smectite.

The alkali treatment of sepiolite in the absence of added Al, Mg, or Si yielded different results than those reported above for palygorskite (Figure 4). Breakdown of the structure to form an X-ray amorphous material was observed when 8 mmole of NaOH was employed for a 3-day treatment (Figure 4); however, the effect of

prolonged treatment was not investigated. The reason for the slight shift of the 12.3-Å peak from 12.3 to 13.0 Å on NaOH addition (6 mmole) is not clear. The intensity of the 12.3-Å peak was diminished, and the peaks at 7.6, 6.7, 5.0, 4.5, 3.7, and 3.3 Å completely disappeared.

Upon MgCl₂ addition, only the diminished 12.3-Å peak and two broad peaks at 7.5 and 3.6 Å were observed. The weak peaks at 15 Å observed for the AlCl₃- and Na₂SiO₃-treated samples indicate the formation of a trace of smectite (Figure 5). A peak at 3.4 Å was observed in the AlCl₃-treated sample. The silicate-treated sample had a substantially stronger 12.3-Å peak, suggesting a lesser degree of NaOH attack. These experiments were replicated and yielded similar results.

When both aluminum chloride and sodium silicate were added with the NaOH (4 mmole) to sepiolite, the products obtained at the end of a 3-day incubation period were smectite + analcime (reflections at 15, 3.4, and 5.6 Å, Figure 6). The presence of smectite was confirmed by XRD data on Mg-saturated and glycerated samples. Upon saturation with alkylammonium ion the curve for peak shift vs. alkyl chain length was characteristic of a low-charge smectite (Figure 3, Curve III). Only a low-charge species was formed from the sepiolite, unlike the product of the treatment of the palygorskite (Figure 3, Curves I and II). These results were substantiated by cation-exchange capacity (CEC) determinations (Table 2). K-fixation was observed in the palygorskite treated with 2 meq NaOH, whereas the K-CEC and Ca-CEC values were equal for the smectite formed from sepiolite. The formation of a high-charge layer silicate can be explained by a mechanism similar to that proposed by Güven and Carney (1979) for the sepiolite to stevensite conversion (Figure 7). Here, the breaking of Si–O–Si bridges linking the 2:1 silicate structural units gives rise to a smectite-like structure on recombination (Figure 7). The NaOH favored the forward reaction by breakage of Si–O–Si bridges [reaction (1)] and also the removal of H₃O⁺ formed (Figure 8). The palygorskite used in this study had the following formula: $(OH_2)_4(OH)_2(Mg_{2.57}Al_{1.38}Fe_{0.34})(Si_{7.93}Al_{0.07})O_{20} \cdot 4H_2O$, which is closer to that of
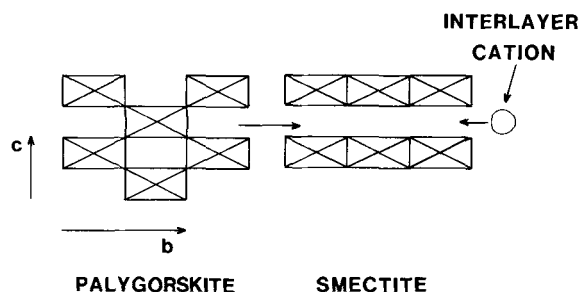
Figure 7. Schematic representation of the formation of smectite from palygorskite by structural reorganization.

a dioctahedral mineral as described by Serna *et al.* (1977). The acquisition of a layer-charge by this palygorskite after the NaOH treatment is shown in Figure 8, where the dioctahedral nature of the palygorskite is taken into consideration. Here also, Mg probably occupied the edge positions of octahedral sheets as suggested by Heller-Kallai and Rozenson (1981) for palygorskite from the same location. The resultant layer silicate on NaOH treatment resembled a dioctahedral smectite, in which Mg substituted for Al. Theoretically, the maximum charge created per formula unit (Si_4O_{10}) is 1.0 equivalent, but in practice some of the cations from the dissolved palygorskite probably fill octahedral vacancies, thereby lowering the charge. The product, therefore, should possess a charge similar to that of a high-charge smectite, whereas the low-charge smectite could either be produced by partial filling of the cation

vacancies in the high-charge smectite product or by the precipitation of a smectite from the dissolved palygorskite. When a mixture of Si, Al, and Mg equivalent to 100 mg of palygorskite (268 mg of $Na_2SiO_3 \cdot 9\ H_2O$, 34.5 mg of $AlCl_3 \cdot 6H_2O$, and 60 mg of $MgCl_2 \cdot 6H_2O$) was treated with NaOH and heated in a similar fashion to the palygorskite treatment discussed above, no crystalline material was detected by XRD. When 2 mg of palygorskite was added to the above mixture, however, substantial smectite was produced as estimated from the XRD peak intensity of smectite (data not shown), suggesting some form of nucleation.

The transmission electron micrographs of treated sepiolite (Figure 9 ST) showed numerous sheets growing from fiber axes, suggesting nucleation. Many of the fibers appear to be thinner than the parent material, as evidenced by their relative transparency to electrons. In the palygorskite treated with NaOH, large ragged bundles were noted (Figure 9 PT) which were not seen in the host material, indicating either growth or aggregation. Some smectite-like material less dense to electrons also was noted in the bundles with no apparent relation to the fibrous components. Only by mechanism (1) could the lath-like morphology be preserved because the rearrangement involves dislocations of 2:1 silicate units which are parallel to the fiber axis. The separate smectite-like product has no apparent growth relation to the parent fibers and probably formed by a solution-reprecipitation mechanism.

In conclusion, solution and reprecipitation seems to be a common process for the transformation of palygorskite and sepiolite to smectite; however, for paly-
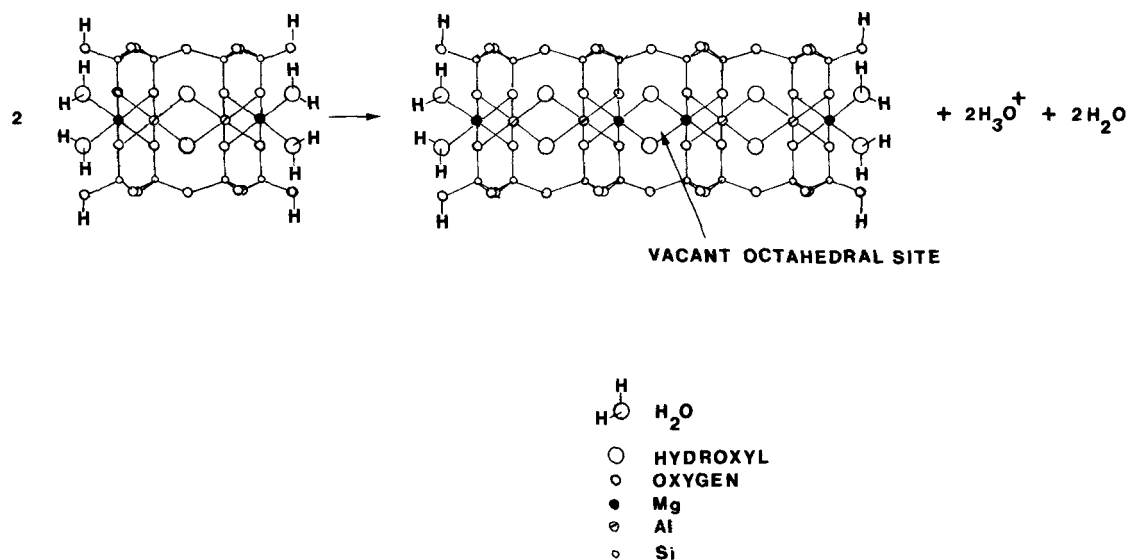

Figure 8. Creation of layer charge in rearranged palygorskite by elimination of hydronium ions and condensation of 2:1 silicate units.
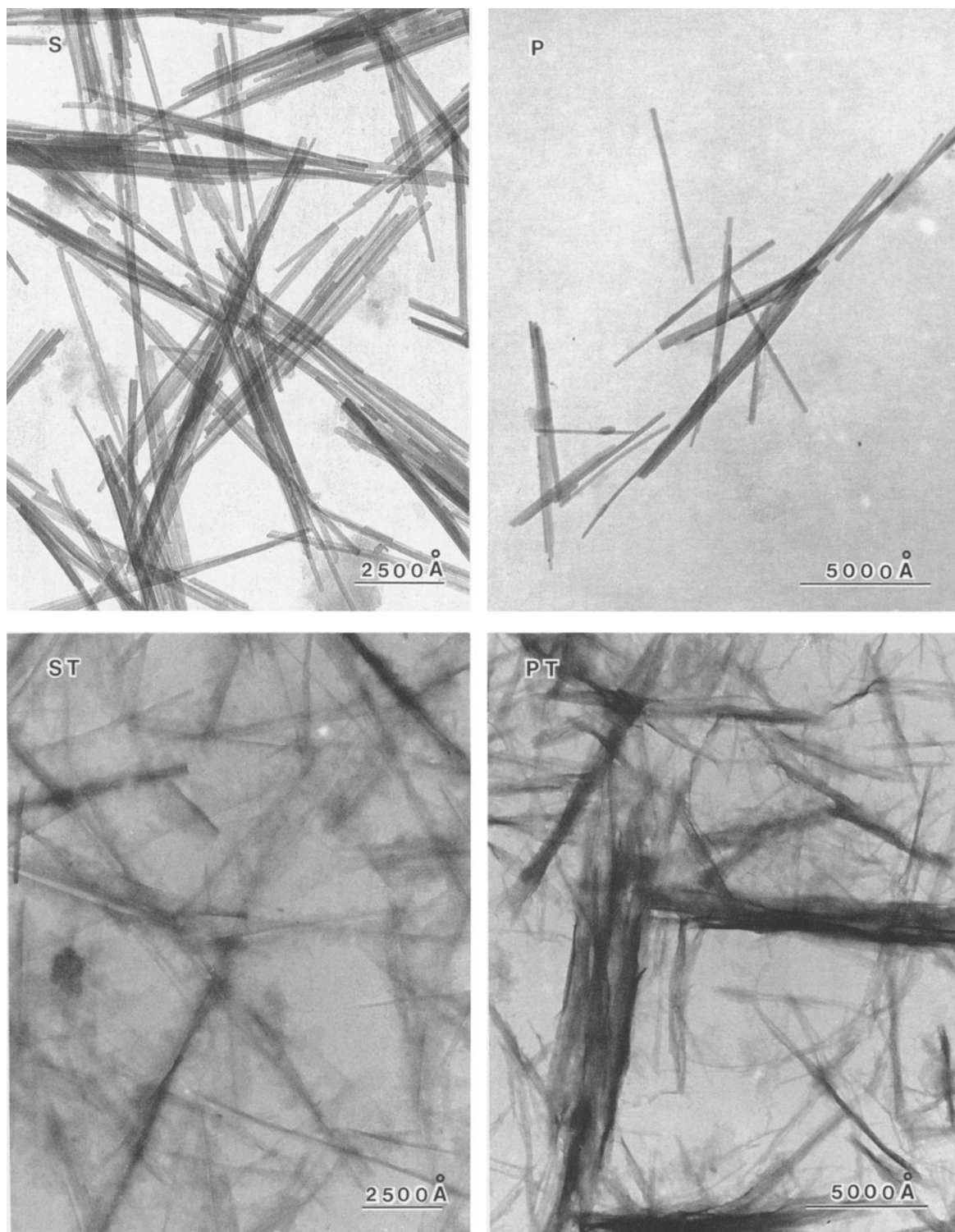
Figure 9.   Transmission electron micrographs of samples of palygorskite (P), sepiolite (S) and their NaOH-treated products (PT, ST).

gorskite, partial breakdown and reorganization seems to occur concurrently with precipitation.

ACKNOWLEDGMENTS

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Резюме—Исследовалась нестабильность палыгорскита и сепиолита в почвенных условиях для определения возможности прямой трансформации этих волоконных минералов в смектит в лабораторных условиях. Смектит являлся результатом обработки 100 мг (0,12 ммоля) палыгорскита 1 ммолем раствора NaOH (17 мл) в температуре 150°С через 24 часа. Анальцим и смектит формировались когда использовалось ≥3 ммоля NaOH. Добавление ≤6 ммолей NaOH к сепиолиту разрушало этот минерал постепенно. При добавлении ≥8 ммолей NaOH, сепиолит изменялся в аморфический (по рентгеновскому анализу) материал. Однако, в присутствии Al и Si, сепиолит изменялся в смектит и анальцим. Исследования путем электронной трансмиссионной микроскопии, катионо-обменной способности и порошковой рентгеновской дифракции этих продуктов указывают на то, что трансформация происходила (1) через раствор, или (2) путем структурной перестройки, во время которой основные структурные единицы 2:1 силикатов не изменялись. [E.G.]

Resümee—Die Instabilität von Palygorskit und Sepiolith unter Bodenbedingungen wurde untersucht, um festzustellen, ob diese faserigen Minerale sich unter Laborbedingungen direkt in Smektit umwandeln. Die Umwandlung von 100 mg (0,12 mMol) von Palygorskit mit 1 mMol NaOH-Lösung (17 ml) bei 150°C über 24 Stunden ergab einen Smektit. Analcim und Smektit wurden gebildet, wenn ≥3 mMol NaOH verwendet werden. Die Zugabe von ≤6 mMol NaOH zu Sepiolith zerstörte ihn allmählich. Bei der Zugabe von ≥8 mMol NaOH wandelte sich Sepiolith in ein röntgenamorphes Material um. Bei der Anwesenheit von Al und Si wandelte sich Sepiolith jedoch in Smektit und Analcim um. Transmissionselektronenmikroskopische, Kationenaustauschkapazitäts- und Röntgenpulverdiffraktometeruntersuchungen der Umwandlungsprodukte deuten darauf hin, daß die Umwandlung (1) über die Lösung oder (2) durch eine strukturelle Umordnung vorsich ging, wobei die grundlegenden 2:1 Silikatstruktureinheiten unverändert blieben. [U.W.]

Résumé—L'instabilité de la palygorskite et de la sépiolite sous des conditions de sol a été investiguée pour déterminer si ces minéraux fibreux se transformaient directement en smectite sous des conditions de laboratoire. Le traitement de 100 mg (0,12 mmole) de palygorskite avec 1 mmole de solution de NaOH (1,7 ml) à 150°C pendant 24 hr a produit une smectite. L'analcime et la smectite ont été formées lorsque ≥3mmole de NaOH ont été utilisées. L'addition de ≤6 mmole de NaOH à la sepiolite l'a petit à petit détruite. Lorsqu'on a ajouté ≥8 mmole de NaOH, la sépiolite s'est changée en un matériau amorphe aux rayons-X. En la présence d'Al et de Si, cependant, elle s'est transformée en smectite et en analcime. La microscopie à transmission d'électrons, la capacité d'échange de cations, et des études de diffraction des rayons-X de ces produits suggèrent que l'altération s'est produite (1) via une solution ou (2) par une réorganisation structurale dans laquelle les unites silicates de structure de base 2:1 n'ont pas changé. [D.J.]