EXPANDABLE PALYGORSKITE FROM THE CRETACEOUS-TERTIARY BOUNDARY, MANGYSHLAK PENINSULA, U.S.S.R.

Palygorskite, which expanded 0.5 Å in the x direction upon ethylene glycol solvation, was observed in the clay-size fraction of 11 marly limestones from the Soviet Union. The samples were taken from a stratigraphically continuous section of Upper Cretaceous and Lower Paleocene marls exposed on the Mangyshlak Peninsula, northeastern Caspian Sea. Naidin *et al.* (1982) described the lithology and paleontology of the section in detail. Expanding palygorskite (Watts, 1976) and sepiolite (Fleischer, 1972) have been reported previously, but their occurrence is rare. A detailed X-ray powder diffraction (XRD) investigation was undertaken to confirm, measure, and explain the expansion of the Mangyshlak palygorskite so that its value as a diagnostic criterion could be evaluated.

MATERIALS AND METHODS

A sample from just above the Cretaceous-Tertiary boundary horizon was selected for detailed study in the present investigation because the high relative intensity of its palygorskite XRD peaks minimized interference from the XRD patterns of other minerals.Whole-rock samples were pulverized, sieved through a coarse screen, and treated with buffered acetic acid solution (pH 4.0) for 4 hr to dissolve calcium carbonate (Jackson, 1956). The insoluble residue was dispersed in distilled water, and the <2-μm fraction was separated and concentrated by centrifugation. Solids were collected on 0.45-μm membrane filters and transferred by inversion onto glass slides. An aliquot of the <2-μm dispersion was dried and prepared as a random powder to minimize the intensities of basal XRD reflections of other clay minerals present.

XRD analysis was performed using a Siemens D-500 diffractometer equipped with a copper tube, 1° slits, and a graphite monochrometer. Oriented mounts were scanned at 2°2θ/min, and the random powder was scanned at 0.1°2θ/min. All samples were analyzed both after air-drying and after ethylene glycol solvation, which was accomplished by exposing the samples to the vapor at 60°C for at least 24 hr.

RESULTS

XRD patterns of the air-dried oriented aggregates show strong diagnostic 110, 200, and 400 palygorskite peaks at 8.5 (10.4 Å), 14.0 (6.34 Å), and 28.1°2θ (3.18 Å), respectively (Figure 1). The presence of illite is indicated by the 001 reflection at 8.8°2θ (10.0 Å), which

appears as a broadening of the high-angle side of the 110 palygorskite peak, and by the presence of the illite 002 and 003 reflections. Smectite, chlorite or kaolinite, quartz, and calcite peaks were also identified (Figure 1).

Upon glycolation, the 001 smectite peaks shifted as expected to 17 Å. In addition, the two low-angle palygorskite peaks shifted to 8.3° (10.7 Å) and 13.5° (6.59 Å) (Figure 1). On the basis of this apparent 0.5 Å expansion of the unit cell in the x crystallographic direction, new d-values for *hkl* reflections were calculated (Table 1), and further studies were conducted to identify and locate other shifted peaks. Calculations were based on an orthorhombic lattice for simplicity, although both monoclinic and orthorhombic palygorskites have been reported (Christ *et al.,* 1968). Values of β for monoclinic palygorskites are between 90° and 100° (Bailey, 1980), so $c \sin \beta$ is essentially equal to c for all samples.

All peaks whose shifts should have been observable were scanned to support the lattice-expansion hypothesis. Because of interferences from the XRD patterns of other minerals no precise measurements of shifts in 400, 600 and 121 peak positions could be made, but the qualitative results are in agreement with the calculated positions. The predicted position of the shifted palygorskite 400 peak at 26.9°2θ was masked by the strong 101 quartz peak at 26.65°2θ. A computer-generated synthetic quartz peak was subtracted from the XRD pattern of the glycolated sample to reveal the 400 palygorskite peak, which appeared as a shoulder at 26.9°2θ on the 3.26 Å illite peak at 26.7°2θ.The 600 peak of the glycolated sample was no longer observed at 42.9°2θ, having apparently shifted to 41–41.5°2θ, consistent with the predicted results. Moreover, the 121 peak, which was completely masked by the 100 quartz peak in the XRD pattern of the dry sample, may have shifted to its predicted position upon glycolation, as evidenced by the broadening of that composite peak.

The d-values of glycolated samples heated to 110°C returned to those found for the air-dried samples, indicating that no irreversible changes to the crystal structure had occurred. A standard palygorskite from Attapulgus, Georgia (obtained from Ward's Natural Science Establishment, Rochester, New York), was studied for comparison; sample preparation and chemical pretreatment were identical to those used for the Mangyshlak palygorskite. The XRD pattern of the At-
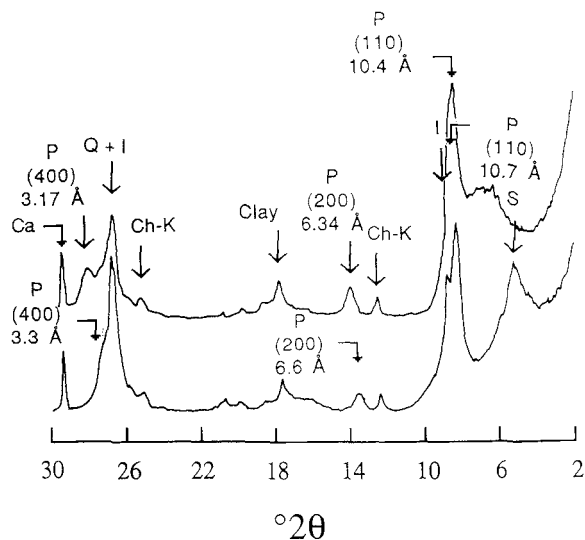
Figure 1.   X-ray powder diffraction patterns of air-dried (top) and ethylene glycol-solvated (bottom) oriented aggregates of <2-μm fraction of Mangyshlak marl insoluble residue showing principal peaks of smectite (S), illite (I), chlorite or kaolinite (Ch-K), quartz (Q), calcite (Ca) and palygorskite (P). d-values of 110, 200, and 400 palygorskite peaks given to illustrate shifts in positions upon glycolation. (CuKα radiation.)

Table 1.   Calculated d-values (Å) of Mangyshlak palygorskite[1] based on expansion of 100 spacing.

hkl	Air-dried sample observed	Ethylene glycol-solvated sample	
		Calculated	Observed
110	10.40	10.67	10.7
200	6.34	6.59	6.6
121	4.26	4.28	see text
400	3.17	3.29	3.3
600	2.11	2.19	see text

[1] a_0 = 12.67 Å dry, 13.17 Å glycolated; b_0 = 18.20 Å; c_0 = 5.24 Å.

tapulgus sample did not change with ethylene glycol solvation or with subsequent heating to 110°C.

DISCUSSION

The agreement between calculated and experimentally observed positions of XRD peaks of the glycolated samples clearly demonstrates that the Mangyshlak palygorskite expands from a_0 = 12.7 Å to 13.2 Å when saturated with ethylene glycol. Resolution of this expansion with the accepted structural schemes of palygorskite is rather straightforward.

Two substantially different structural varieties of palygorskite have been proposed. The structure determined in two dimensions by Bradley (1940) and refined to three dimensions by Preisinger (1963) and Drits and Aleksandrova (1966) incorporates 2:1 ribbons, each composed of two linked pyroxene-like chains (Figure 2). Micropores between the ribbons normally contain bound water, zeolitic water, and exchangeable cations. Gard and Follett (1968) proposed another structural type in which adjacent ribbons in the palygorskite structure have different widths. In their model, sepiolite-like ribbons (three linked pyroxene chains) alternate with single chains to produce approximately the same *b*-dimension as in the Bradley model. The Gard-Follett model implies that two different sizes of micropores exist, corresponding to the wide and narrow ribbons, having *b*-dimensions somewhat larger and smaller, respectively, than those of the Bradley structure.

These micropores, which parallel the long axis of the fibrous palygorskite crystals (the *c*-axis of the structure), are the only sites in the palygorskite structure which can possibly accommodate ethylene glycol molecules. The cross-sectional dimensions of the micropores are reported to be 3.7 Å × 6.4 Å for a monoclinic palygorskite having a_0 = 12.6 Å and b_0 = 18.2 Å (Ovcharenko, 1964). The van der Waals diameter of the CH_2 group (about 4.0 Å; Reynolds, 1965) appears to be the limiting factor in allowing the penetration of ethylene glycol molecules into the palygorskite structure.

The 200 spacing of the air-dried Mangyshlak specimen exceeds that of Ovcharenko's palygorskite by 0.05 Å. If this excess spacing is contained in the open channels of the structure, the small dimension of the channels is then 3.75 Å for the air-dried Mangyshlak palygorskite. The observed lattice expansion of 0.5 Å per unit cell (i.e., 0.25 Å per channel) provides the necessary room (4.0 Å) for ethylene glycol molecules to enter the palygorskite structure (Figure 2).

No constraints on the orientation of the ethylene glycol molecule in the palygorskite structure are implied beyond the restriction that the axis connecting the centers of the CH_2 groups in a single ethylene glycol molecule must be parallel to the 100 plane, and that the ethylene glycol molecule may not be rotated about this axis in such a way as to require an expansion of the channel greater than the observed amount. Inasmuch as the maximum dimension of the ethylene glycol molecule is about 6 Å, the "b" dimension of the channels does not appear to restrict its orientation.

The smaller micropores of the Gard-Follett palygorskite type (Figure 3b) are too small in the "b" dimension to accept ethylene glycol molecules; therefore, only the layers of larger micropores are expandable. Because the observed expansion of the Mangyshlak palygorskite was sufficient to allow accommodation of ethylene glycol molecules in all channels (i.e., 2 per unit cell), the palygorskite must be of the Bradley structural type (Figure 3a). If the Mangyshlak palygorskite were of the Gard-Follett structural type, only half of the observed expansion would be expected.

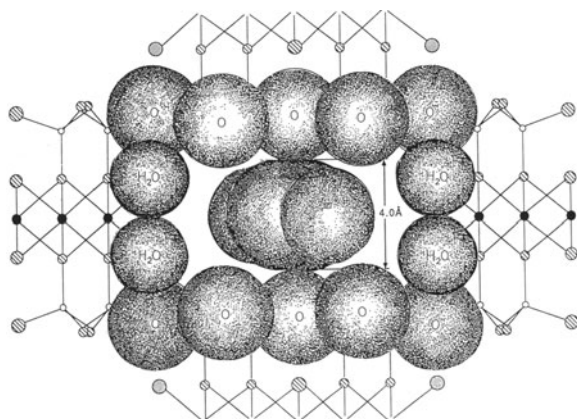The only probable change in the structure which

Figure 2. Palygorskite structure projected on (001), modified from Bradley (1940) to show proposed position of ethylene glycol molecule in a micropore. Oxygen, silicon, octahedral cations, and bound water shown by cross-hatched, open, solid, and shaded circles, respectively.

could cause the observed expansion is stretching or breaking of the bonds that join adjacent 2:1 ribbons in the palygorskite; because the expansion is reversible, the bonds are probably not actually broken. Why the Mangyshlak palygorskite expands and most samples from other localities do not, is not clear. The 200 spacing and the resulting minimum dimension of the open channels in the structure may be the most important factor. A critical range of 200 spacings probably exists, below which the ethylene glycol molecule cannot enter the structure, and above which it can enter without noticeable expansion of the lattice. The strength of the inter-ribbon oxygen bridges also may influence the expandability. While bond strength is in part related to the length of the bonds, and thus the unit-cell dimensions, it may also be a function of chemical composition, particularly octahedral Mg/Fe and tetrahedral Si/Al ratios.

CONCLUSIONS

The expandability of certain palygorskites may be diagnostic in distinguishing between the Bradley and Gard-Follett structural types. The distinction lies not in the presence or absence of expansion, but in the amount of expansion. Palygorskites that expand sufficiently to allow ethylene glycol penetration of all micropores must be of the Bradley type; lesser expansion is indeterminate. We were able to deduce that the Mangyshlak palygorskite is of the Bradley type on the basis of the observed 0.5-Å lattice expansion.

Palygorskites reported in the literature have a range of unit-cell dimensions. Ethylene glycol penetration of the palygorskite structure probably depends on the 200 spacing and the strength of the bonds joining the adjacent 2:1 ribbons; both of these factors are functions of chemical composition and crystallinity, both of which
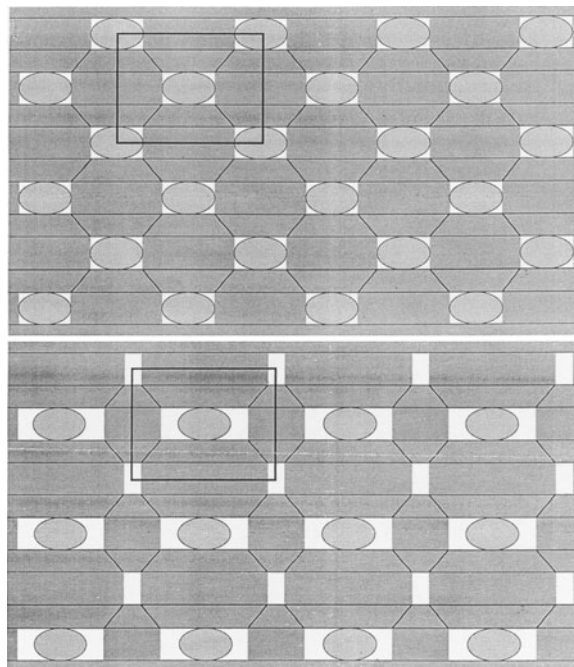

Figure 3. Schematic representations of palygorskite structural types, showing occupation of all available micropore sites by ethylene glycol molecules (shaded ovals). Unit cells outlined by bold rectangle. (001) projections. (a, upper) Bradley (1940) structural type, with 2 glycolated channels per unit cell. (b, lower) Gard-Follett (1968) structural type, with 1 glycolated channel per unit cell.

probably reflect the environment and mode of formation of the palygorskite. Some specimens of the Gard-Follett structural type might also expand, depending on their (200) spacing, in a manner analogous to the expanding sepiolite of Fleischer (1972). Clearly, more observations of expanding palygorskites and sepiolites are necessary before the exact mechanism of expansion can be determined.

Expansion of palygorskite and sepiolite suggests a mechanism by which the chain structure may be weakened or ruptured, allowing rearrangement into a sheet phyllosilicate, such as montmorillonite. Previous workers (Weaver and Beck, 1977; Singer, 1979) were unable to account for the high energy input required to invert silica tetrahedra in the palygorskite-to-montmorillonite reaction in natural systems; however, Ovcharenko (1964) referred to certain amines which entered the palygorskite structure and ruptured it along the inter-ribbon bonds. Interaction with organic constituents, particularly those containing ethylene glycol, may provide the catalysis necessary for the reaction to proceed in nature.

ACKNOWLEDGMENTS

thors are indebted to Michelle Hluchy and Kathleen Tellier for their assistance in the laboratory. Critical reviews by Emilio Galán, Necip Güven, and F. A. Mumpton greatly improved the manuscript.

Department of Earth Sciences   J. D. JEFFERS[1]
Dartmouth College   R. C. REYNOLDS, JR.
Hanover, New Hampshire 03755

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[1] Present address: Department of Geology and Geophysics, Rice University, Houston, Texas 77251.