and in some manner in combination with water causes the marked anlargement in *a*.

With heating to 775°C, total weight loss was 4 percent, and the sample decomposed to apatite plus whitlockite with the mixture containing 0.2 percent excess oxygen.

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ORIENTATION OF ETHYLENE GLYCOL MONOETHYL ETHER MOLECULES ON MONTMORILLONITE

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ABSTRACT

A study of the intensities of basal reflections from ethylene glycol monoethyl ether-montmorillonite indicates that the plane of symmetry of the aliphatic chain lies perpendicular to the clay oxygen surface. The complex appears to contain two layers, each of which has one-half the molecular density of ethylene glycol layers on montmorillonite. The value of $d(001) = 16.0$ Å makes this complex potentially useful for identification of expandable and mixed-layered expandable clays in cases where line interference is encountered on diffractograms from glycol or glycerine treated samples.

An X-ray diffraction study has been made of the ethylene glycol monoethyl ether[1]-montmorillonite complex $(d(001) = 16.0$ Å$)$. The complex should prove useful in the identification of monotmorillonite and mixed-layer illite-montmorillonite in cases where ethylene glycol or glycerol complexes produce diffraction maxima that are interfered with by contributions from other minerals in a mixed sample. An additional reason for interest in this reagent lies in its suggested use for the determination of surface areas of clays (Carter, Heilman, and Gonzalez, 1965).

[1] Available from Fisher Scientific Co.

Procedure

Clay Spur bentonite (A.P.I. 26) was dispersed in deionized water and settled to obtain the <2 μm fraction. The cation exchange complex of the clay was assumed to be sodium saturated (see Kerr *et al.*, 1950). The natural, <2 μm fraction was centrifuged onto a porous plate, dried at 110°C, and steeped in ethylene glycol monoethyl ether (EGEE). X-ray diffraction studies were performed with a General Electric XRD-5 spectrometer equipped with a copper target tube. Diffraction patterns were recorded at $2°$ 2θ/min. A 0.4° beam slit was used for the region between $2\theta = 5°$ and $2\theta = 18°$, and a 1° beam slit for the region above $2\theta = 15°$. Intensities were computed by multiplying peak heights times peak breadths at half-height. All peak intensties were put on the same basis by measuring the intensity of the 003 by both slit systems and calculating the appropriate intensity conversion factor. The intensity data were analyzed by computer methods described by Reynolds (1965).

In order to ascertain the uniformity of the complex over a range of montmorillonite types, values for $d(001)$ were obtained for EGEE-solvated samples of Umiat bentonite (Anderson and Reynolds, 1966), Santa Rita montmorillonite (A.P.I. 11), and Chambers montmorillonite (A.P.I. 23).

Results

Initial X-ray diffraction studies revealed anomalies in the EGEE-montmorillonite complex formation. Unlike the ethylene glycol complex, the EGEE complex required several hours to form when the reagent was applied to thick (1 mm) oriented aggregates of Clay Spur bentonite. Samples studied soon after the application of EGEE gave diffraction patterns that showed interstratified phases. However, after 17 hours in contact with EGEE, the thick montmorillonite aggregate showed a long (12) series of 00l reflections, indicating the presence of a well-ordered EGEE-montmorillonite complex. Based on values for the 006 through 00.12, $d(001) = 15.98 \pm 0.02$ Å. After obtaining detailed diffraction patterns, the sample was reimmersed in EGEE for two days. Patterns obtained at that time showed that no further change had occurred in the complex.

As a consequence of the relatively high volatility of EGEE, solvated aggregates showed a tendency to dry out during the recording of a long (45 minutes) diffraction run. It was found advisable to reapply EGEE at approximately 10-minute intervals.

The samples of Umiat, Santa Rita, and Chambers montmorillonites also gave $d(001)$ values of 16.0 Å, indicating that the configuration of the complex is not greatly influenced by exchangeable sodium or calcium. In addition, good agreement was obtained between observed and calculated diffraction profiles of EGEE-solvated mixed-layer illite-montmorillonite; these will be discussed in detail in a forthcoming publication.

Table 1 summarizes a structural model of an EGEE-montmorillonite complex that provided an acceptably low value for the reliability factor

TABLE 1. AN EXAMPLE OF A ONE-DIMENSIONAL MODEL OF A MONTMORILLONITE-
ETHYLENE GLYCOL MONOETHYL ETHER (EGEE) COMPLEX

Relative atomic positions[a]	Atoms		Remarks	Temperature factor B, in $Å^2$
0	1.54	Al		1.3
	0.16	Fe		
	0.33	Mg		
1.06	4	O	Montmorillonite structure	1.3
	2	OH		
2.70	4	Si		1.3
3.27	6	O		1.3
5.95	1	OH	OH and 2nd methylene group	7.5
5.95	1	CH_2		
6.15	1	$H_2O + Na^+$	Exchangeable cations and water	7.5
6.45	1	CH_2	3rd methylene group	7.5
7.27	1	CH_2	1st methylene group	7.5
7.32	1	O	Ether oxygen	7.5
7.99	1	CH_3	Terminal methyl group	7.5

[a] These values refer to projected positions of the atoms along a line normal to the (001). The center of the octahedral layer is taken as the origin. Distances are in Angstrom units.

(R). Table 2 compares observed structural amplitudes $|F_o|$ with F_c values calculated from the model described by Table 1.

DISCUSSION

Too few reflections were observed to define precisely the scattering centers within the EGEE molecules. A basal series extending to the 00.12 was obtained. Assuming that the absence of the 004 provides some information, independent parameters that could be isolated are therefore limited to 12. The amount of EGEE per unit cell was considered fixed by data of Carter *et al.*, 1965. This quantity was assumed to be two molecules per unit cell, or one molecule per unit cell per layer. The montmoril-

TABLE 2. A COMPARISON OF OBSERVED AND CALCULATED STRUCTURAL
AMPLITUDES, BASED ON THE MODEL OF TABLE 1

Basal series	$|F_o|$	F_o
001	62.4	64.0
002	13.6	15.7
003	43.4	−42.6
004	N.D.[a]	3.0
005	71.9	71.8
006	33.9	33.3
007	31.7	−31.6
008	37.3	−38.4
009	26.2	−26.5
00.10	15.0	13.4
00.11	30.0	30.5
00.12	24.0	22.7

[a] Not detected.

Relibility Factor, $R=3.29$; for this calculation, $|F004|$ was assumed to be one-half the minimum observable value, or $|F004| =6.2$.

lonite structure was also considered to be largely fixed. Therefore, the parameters which must be specified by the analysis are: (1) the location of six scattering centers within the EGEE molecule, the relative positions of which are limited by the constraints of molecular structure; (2) the location of the exchangeable cations and/or water molecules; (3) the amounts of water and exchangeable cations per unit cell; and (5) the values of three different temperature coefficients, namely, one for the silicate skeleton, one for the EGEE, and one for the water and exchangeable cations. This means that somewhat fewer than 11 independent parameters must be specified by the information contained in 11 to 12 equations (reflections). Such a low redundancy requires that only the general aspects of the proposed molecular orientation be considered as definite. For this reason, no interpretation is attempted of possible bond lengths and angles.

The data of Tables 1 and 2 are presented as an example of a model with acceptably low R. Variations also produced low R values, and these are not tabulated here. However, all low-R structural models had certain features in common, as follows: (1) a distribution of scattering centers indicating that the plane of symmetry of the aliphatic chain lies perpendicular to the clay oxygen surfaces; and (2) evidence of some scattering, presumably from water molecules and/or exchangeable sodium, near either 6.15 or 8.00 Å. It is assumed that the position near 6.15 is the valid

one (*Cf.* Bradley, Weiss and Rowland, 1963), because free space near 8.00 Å could not be generated by trial and error studies with dimensionally accurate models.

A synthesis of information derived from X-ray, chemical (Carter, *et al.*, 1965), and dimensioned model studies leads to the following possible molecular arrangement for EGEE-montmorillonite. EGEE forms a two-layer complex in which the plane of symmetry of the aliphatic chain lies perpendicular to the clay surface. Some compression of the organic layers is achieved by keying of the second methylene group of each molecule into a hexagonal site at the clay surface (*Cf.* Bradley, *et al.*, 1963; Reynolds, 1965). The complex contains one EGEE molecule per unit cell per half-layer, causing the molecules to be arrayed in rows, parallel to (010) or (110), that are separated by rows of blank positions. Keying of the second organic layer to the first is accomplished by a displacement, between the two layers, in a direction perpendicular to the long-dimension of the molecules. Water and/or exchangeable cations may be present at about 6.15 Å.

The proposed arrangement is somewhat similar to that of ethylene glycol-clay complexes (Brindley, 1956; Bradley *et al.*, 1963; Reynolds, 1965). Brindley and Hoffman (1962) have pointed out that aliphatic molecules that lack a strong polar group tend to assume orientations perpendicular to the clay surface (they designate this as the α_{II} orientation). Presumably, organic-organic interactions are responsible for this arrangement. It appears that the structure of EGEE-montmorillonite adds further confirmation to their conclusion.

Ethylene glycol monoethyl ether should prove to be a useful reagent for the determination of surface areas, and for X-ray diffraction studies of expandable clays. It forms a regular complex whose structure appears to be constant over a range of montmorillonite types. It requires greater equilibration times than ethylene glycol, and drying may be a problem during the recording of the diffraction pattern, but both of these difficulties may be easily circumvented.

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PALYGORSKITE FROM THE DEEP SEA: A DISCUSSION

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In an interesting paper E. Bonnati and O. Joensuu (1968) have recently reported the occurence of palygorskite (or attapulgite) in deep sea deposits of the Barracuda Escarpment.

They state, "Palygorskite has not been previously reported from the deep sea environment. It has been found to form in fresh water and lagunal sediments . . . or in shallow marine environment."

I think this statement too categorical, and I know, at least, one exception. B. C. Heezen *et al.* (1965) have reported, three years ago, the occurrence of attapulgite in deep sea deposits of North Indian Ocean (Aden Gulf) and Red Sea, between 1000 and 2500 meters below sea level.

Concerning the origin of this mineral various hypothesis can be put forward. It is possible that attapulgite was inherited from neighbouring lands where deposits of this mineral have been described (G. Müller 1961). It could also have been produced by hydrothermal reaction of the type discussed by Bonnati and Joensuu for the Barracuda Escarpment.

This second hypothesis is particularly attractive owing to the fractured nature of the sea floor in the North Indian Ocean and the Red Sea.

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