

ANOMALIES IN THE ETHYLENE GLYCOL SOLVATION TECHNIQUE USED IN X-RAY DIFFRACTION *

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ABSTRACT

X-ray diffraction results are presented to show that some montmorillonites will not retain two layers of ethylene glycol in the interlayer space when dried under atmospheric conditions. Diffraction data obtained from such samples of montmorillonite may erroneously be attributed to mixed layer minerals. Studies have shown however that this difficulty may largely be overcome by initially saturating the sample with ethylene glycol by the vaporization technique described, after which the sample is placed in a saturated atmosphere of ethylene glycol for a period of 12-24 hours to come to equilibrium and then irradiated.

INTRODUCTION

X-ray diffraction today is serving as a major tool in characterization studies of finely divided crystalline matter, particularly clays. Since its introduction in this capacity in 1930 by Hendricks and Fry (1930, p. 462) of the U.S.D.A. and Kelley *et al.* (1931, p. 31) of the California Agricultural Experiment Station, a great deal of time and effort has been spent in developing methods and techniques which would permit more positive identification and characterization of clay materials with X-ray diffraction. Many of the techniques which are being used today were developed prior to the advent of the X-ray spectrometer. In most cases sample preparation techniques are equally applicable whether the camera or the spectrometer arrangement is used. Recently, however, observations in this laboratory in connection with X-ray spectrometer results have shown that an interpretation of mixed layer minerals or interstratified minerals may be applied to the data unless certain precautions are taken in the preparation of samples containing montmorillonite. Therefore, the purpose of this paper is to point out the precautions found necessary in the preparation of such a sample for examination with the X-ray spectrometer arrangement as well as to illustrate the misleading type of data which may be obtained unless care is taken.

PREVIOUS WORK

Bradley (1945, p. 8) and MacEwan (1948, p. 352) found that if montmorillonite is treated with organic compounds such as ethylene glycol, glycol-

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erol and others, it will enter the interlayer space and replace the water. Furthermore these compounds enter into this position according to a definite pattern or arrangement. For example, their studies showed that two layers of glycerol were adsorbed by montmorillonite in the interlayer space which resulted in an (001) basal spacing of approximately 17.7 Å. Similarly two layers of ethylene glycol are adsorbed by montmorillonite resulting in an (001) basal spacing of 17.0-17.3 Å. This increase in basal spacing resulting from the adsorption of ethylene glycol or glycerol made it relatively easy to distinguish montmorillonite from vermiculite and chlorite which do not show a similar increase in the interlayer distance when treated with these compounds.

The technique employing glycerol and ethylene glycol was developed in connection with a diffraction camera arrangement, which involved a different type of sample mounting preparation for irradiation purposes than is generally used in connection with the X-ray spectrometer. MacEwan (1948, p. 352) sealed the sample of montmorillonite in a glass capillary with an excess of liquid; whereas Bradley (1945, p. 7) soaked the clay sample in the solvent, then washed the clay superficially by decantation and permitted it to air dry prior to irradiation. In some instances, however, he (1945, p. 7) mounted the clay on a blotting paper wick kept immersed in the organic liquid during exposure.

EXPERIMENTAL METHODS

Samples of soils and sediments from the Gulf of Mexico used in this study received a minimum of chemical treatment, which consisted of removal of the organic matter with hydrogen peroxide followed by dispersion with a solution of sodium hexametaphosphate (Calgon). The clay was separated by sedimentation, subsequently flocculated with magnesium acetate, transferred to a 250 ml. centrifuge tube and washed free of excess salt with several washings of distilled water. Approximately 100-150 mg. of clay were transferred to a 100 ml. centrifuge tube, 50 ml. of a 1.0 N magnesium acetate solution added and the sample boiled gently for ten minutes. After boiling, the sample was centrifuged, the supernatant liquid decanted, and the sample washed twice with 25 ml. of distilled water after which it was ready to be mounted.

To prepare oriented mounts, the samples were suspended in 10 percent and 50 percent aqueous solutions of ethylene glycol, the suspension placed on a glass slide and allowed to dry. Drying of samples was carried out at a temperature of $24^{\circ} \text{C} \pm 2^{\circ} \text{C}$ and a relative humidity of approximately 40 percent; a weak current of air was passed over the samples in order to speed up the drying process. All samples prepared with a 10 percent aqueous solution of ethylene glycol were initially allowed to dry for a period of 24 hours, irradiated, and allowed to dry for another 24-hour period and irradiated a second time.

Mounts prepared with the 50 percent aqueous solution of ethylene glycol were dried under the same conditions but required longer periods of time to dry. Some samples dried much more rapidly than others. After the initial irradiation, the samples were subjected to a second drying period and again irradiated.

Following the second irradiation, the samples were placed in small metal cans, 4 inches in diameter, which contained a small amount of ethylene glycol, the cover replaced and the can placed in an oven for an hour at 65° C. This temperature is high enough to vaporize the ethylene glycol and thereby effect a saturation of the sample.† After an hour the samples were removed from the can and placed in the oven at 65° C long enough to vaporize any large drops of ethylene glycol adhering to the sample. The samples must be checked every 5 to 7 minutes while drying in the oven in order to prevent excessive drying. The samples were then placed in a saturated atmosphere of ethylene glycol for a period of 12 to 24 hours and allowed to come to equilibrium after which they were irradiated.

The same samples were then placed in an oven at a temperature of 110° C to show the effect of heat on ethylene glycol retention in the interlayer space.

RESULTS AND DISCUSSION

Montmorillonite when saturated with ethylene glycol will give an (001) basal spacing of 17.0-17.3 Å. The (001) basal spacing for vermiculite and chlorite is approximately equal to 14 Å. In recent years the concept of mixed layer minerals has gained considerable acceptance among the clay mineralogists, and has frequently been used by them to explain or account for irregular basal spacings or basal spacings which could not be assigned to any single specific clay mineral. Using the concept of mixed layer minerals a basal spacing of 12 Å could be accounted for by interstratification of biotite and vermiculite in the ratio of 1 : 1. Similarly, assuming the sample has been treated with ethylene glycol, a 15.5 Å basal spacing could be interpreted as interstratification of montmorillonite and vermiculite in the ratio of 1 : 1. X-ray diffraction studies have shown, however, that irregular spacings of this type may also be shown by some montmorillonites if proper care is not taken in the preparation of the sample.

Figures 1 and 2 illustrate some of the irregular spacings which montmorillonites will give with improper sample preparation. Nos. 1-4 are typical patterns for montmorillonites extracted from soils while Nos. 5-8 are typical for montmorillonites separated from sediments in the Gulf of Mexico.‡ In the case of Figure 1 a 10 percent aqueous solution of ethylene glycol was used to mount the samples. After a drying period of 24 hours the (001) basal spacings for the samples of montmorillonite ranged from

† Brunton, G. D., Shell Exploration and Development Laboratories is credited with the idea of saturating the clay sample with ethylene glycol vapors.

‡ Grant Whitehouse of the Oceanography Department, Texas A. and M. College, provided the samples from the Gulf of Mexico.

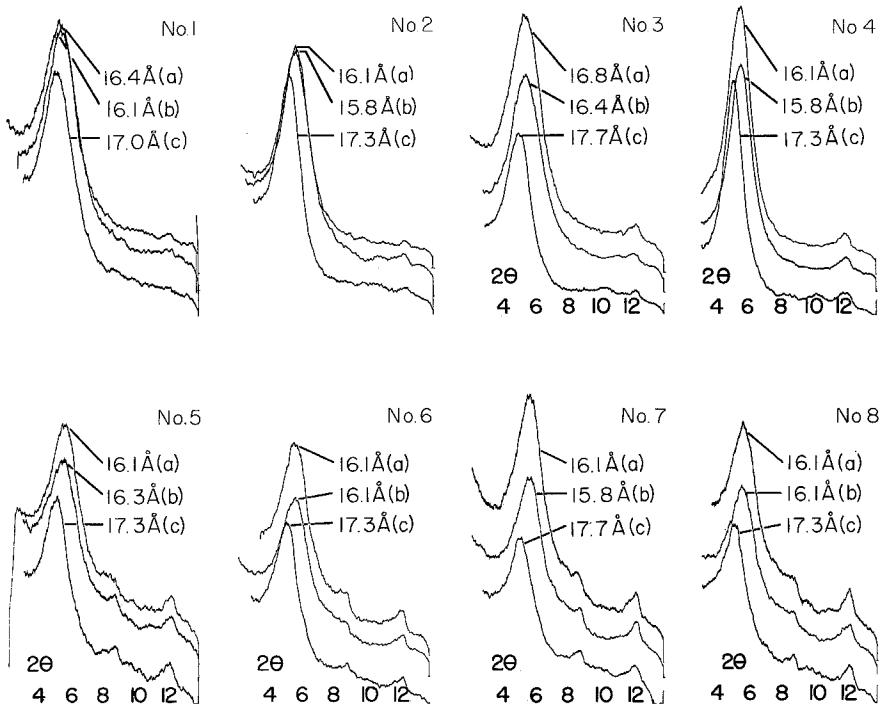


FIGURE 1. — X-ray diffraction patterns of clays ($< 2 \mu$) showing the effect of drying on ethylene glycol (10% aqueous solution) treated samples. Samples were dried for the following periods of time and then irradiated: Series "a"—24 hrs., series "b"—48 hrs., series "c"—saturated by vapors of ethylene glycol and allowed to come to equilibrium. Nos. 1-4 are representative of soil clays, while Nos. 5-8 are representative of clays from the Gulf of Mexico.

16.1 to 16.8 Å. After a drying period of 48 hours the minimum basal spacing observed was 15.8 Å, all of which are irregular spacings and could very easily be attributed to interstratification of montmorillonite with some other 14 Å, 2:1 lattice type mineral. However, when the same sample was resaturated with ethylene glycol by the vaporization technique described earlier and the sample placed in a saturated atmosphere of ethylene glycol for 12 to 24 hours to attain equilibrium, typical montmorillonite patterns were obtained as illustrated by the "c" series of patterns in Figure 1.

Figure 2 shows the results obtained for the same material initially mounted with a 50 percent aqueous solution of ethylene glycol. The samples were much slower to dry; however, upon drying they showed the same irregular spacings as were shown by the samples prepared with the 10 percent aqueous solution of ethylene glycol. Also upon resaturating the samples with ethylene glycol by the vaporization technique and then allowing them to come to equilibrium in a saturated atmosphere of ethylene glycol typical

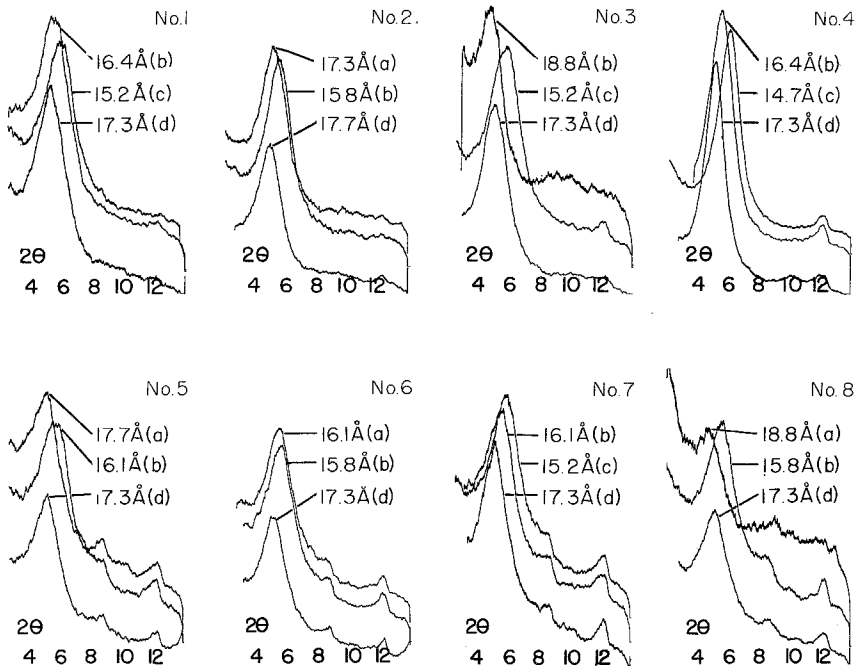


FIGURE 2. — X-ray diffraction patterns of clays ($< 2 \mu$) showing the effect of drying on ethylene glycol (50% aqueous solution) treated samples. Samples were dried for the following periods of time and then irradiated: Series "a"—36 hrs., series "b"—60 hrs., series "c"—75 hrs., series "d"—saturated by vapors of ethylene glycol and allowed to come to equilibrium. Nos. 1-4 are representative of soil clays, while Nos. 5-8 are representative of clays from the Gulf of Mexico.

montmorillonite spacings were obtained, as illustrated by the "d" series of curves in Figure 2.

Observations have shown that some samples of montmorillonites mounted on glass slides will lose upon exposure to the atmosphere sufficient ethylene glycol in an hour to give misleading X-ray diffraction data.

The initial diffraction patterns obtained for samples Nos. 3 and 8, shown in Figure 2, are in excess of the 17.0-17.3 Å (001) basal spacing characterizing ethylene glycol treated montmorillonite. Sample No. 3 appeared dry while sample No. 8 was still visibly moist during the initial irradiation. These results further emphasize the need for careful sample preparation in order to obtain reliable diffraction data for ethylene glycol treated montmorillonite.

Figure 3 illustrates that essentially the same results are obtained whether the sample is dried under atmospheric conditions or whether the drying process is speeded up by heating the sample in an oven. In both cases there is a loss of ethylene glycol from the interlayer space resulting in irregular spacings which could very easily be attributed to mixed layer minerals.

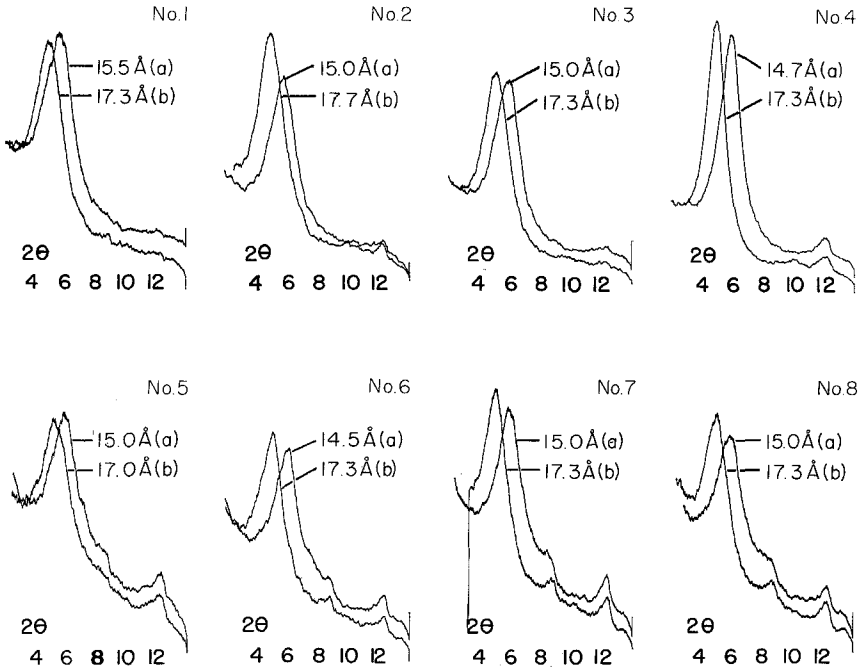


FIGURE 3.—X-ray diffraction patterns of clays ($< 2 \mu$) showing the effect of heat on ethylene glycol treated samples. Samples of series "a" were heated for two hours at 110°C ; samples of series "b" unheated. Nos. 1-4 are representative of soil clays, while Nos. 5-8 are representative of clays from the Gulf of Mexico.

In view of these results, surface area measurements which utilize ethylene glycol retention (1950, p. 421; 1952, p. 342) as the means for determining the area need to be used with discretion.

REFERENCES

- Bower, C. A., and Gschwend, F. B. (1952) *Ethylene glycol retention by soils as a measure of surface area and interlayer swelling*: Soil Sci. Soc. Amer. Proc., vol. 16, No. 4, pp. 342-346.
- Bradley, W. F. (1945) *Molecular associations between montmorillonite and some poly-functional organic liquids*: Jour. Amer. Chem. Soc., vol. 67, No. 6, pp. 5-12.
- Dyal, R. S., and Hendricks, S. B. (1950) *Total surface of clays in polar liquids as a characteristic index*: Soil Sci., vol. 69, pp. 421-432.
- Hendricks, S. B., and Fry, W. H. (1930) *The results of X-ray and microscopical examinations of soil colloids*: Soil Sci., vol. 29, pp. 457-479.
- Kelley, W. P., Dore, W. H., and Brown, S. M. (1931) *The nature of base exchange material of bentonite, soils and zeolites as revealed by chemical investigation and X-ray*: Soil Sci., vol. 31, pp. 25-55.
- MacEwan, D. M. C. (1948) *Complexes of clays with organic compounds. I. Complex formation between montmorillonite and halloysite and certain organic liquids*: Trans. Fara. Soc., vol. 44, Part 6, pp. 349-367.