

METHODS OF PREPARATION AND CONTROL OF CLAY MINERAL SPECIMENS IN X-RAY DIFFRACTION ANALYSIS

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ABSTRACT

The determination of the clay minerals present in mixtures by x-ray diffraction examination of oriented aggregates on glass slides becomes more reproducible and more conclusive when the relative humidity of the air in contact with the specimen is controlled during the recording of the diffraction pattern. The basal diffraction peaks of expanding and partially expanding clay minerals vary considerably in spacing and intensity with normal variations of relative humidity. These variations may be eliminated by the application of a simple modification to standard x-ray equipment. This modification is useful in maintaining a constant relative humidity at values between <1 and 100 percent. Dry air is used to maintain the effects of dehydration by heat and, in many cases, may be used as a substitute for heat treatment. This is especially true for mixed-layer minerals, which give more intense and more reproducible diffraction effects in dry air. Wet air is better, in many instances, than glycerol or ethylene glycol in resolving the basal reflections of montmorillonite and illite in mixtures. More information can be obtained from preparations of mixed-layer minerals and mixtures of clay minerals by recording the diffraction pattern at various stages of hydration.

INTRODUCTION

The study of clay minerals in soils and sedimentary rocks by x-ray diffraction methods usually involves the examination of several preparations that have been subjected to various chemical or thermal treatments. Such procedures are time consuming and must be simplified as far as possible if clay mineral studies are to be carried out in sufficient volume to be practical in characterizing environments or formations.

The methods of disaggregation and separation of clay materials from the coarser constituents of samples are well developed and need not be discussed. The use of oriented films of the separated clays on glass slides is also a common technique when the x-ray diffractometer is used. At this point the objective of x-ray diffraction study must involve both identification of minerals and the quantitative analysis of the clay mineral assemblage in a specimen. It is important, therefore, to obtain diffraction records which are reproducible in both spacing and intensity of diffraction peaks. Many variable factors can influence the spacing and intensity measurements of diffraction peaks from oriented slides containing expanding clay minerals. However, it is obvious that one of the most important variables is the degree of hydration of the expanding minerals in the sample. We have attempted to improve the reliability of diffraction spacing and intensity measurements of these minerals by a simple method of controlling the humidity of the air in contact with the sample while the x-ray diffraction

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pattern is being recorded. We have also attempted to increase the amount of information obtainable from a single sample preparation by recording the diffraction pattern of the sample equilibrated with air of different humidities.

THERMAL DEHYDRATION AND HUMIDITY CONTROL

Heat treatment in conjunction with x-ray diffraction measurement is a valuable technique in the identification of clay minerals. Oriented slides are commonly heated in a furnace and transferred to the x-ray diffractometer for recording of the diffraction pattern. There is always a possibility, especially when temperatures of less than 300° C are involved, that the dehydration effect produced by heat may be lost or modified by rehydration during the recording of the diffraction pattern. The simple modification illustrated in Figure 1, by means of which a stream of dry air is passed over the sample while it is being x-rayed, was designed to prevent the rehydration of heated samples. The modification requires only the attachment of an entry tap to the scatter shield of the diffraction apparatus and a piece of cellophane tape over the slot of the shield. Dry air is then passed into the enclosed space at approximately one liter per minute and escapes from the slotted edge of the shield where it is fitted to the

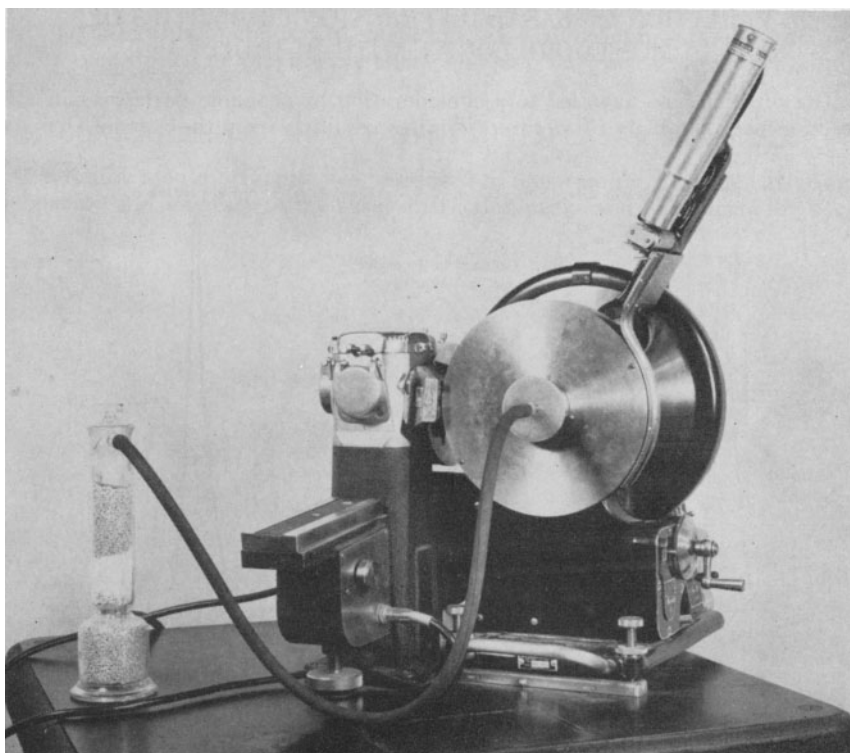


FIGURE 1. — Modified x-ray diffraction apparatus.

goniometer head. By passing through columns of Drierite and magnesium perchlorate, the laboratory air supply is dried to <1 percent relative humidity (hereafter simply called "humidity"). Under these conditions the rehydration of samples is negligible during the x-ray procedure.

The value of this method of control is illustrated by diffraction records from a sample of calcium-saturated montmorillonite from Clay Spur, Wyoming. This sample was x-rayed in equilibrium with air at 85 percent humidity, dried for several hours at 125° C in vacuum and re-run in dry air. The sample was then exposed to laboratory air for five minutes and x-rayed again. A final diffraction record was obtained after the sample had been equilibrated again with air at 85 percent humidity. The high humidity conditions were obtained by bubbling air through water before passing it into the scatter shield. The diffraction records of the low-angle region for each stage are reproduced in Figure 2. It will be noticed that a collapsed basal spacing of 9.8Å is maintained under dry air conditions but rapid expansion to 13.6Å occurs as a result of a five-minute exposure to laboratory air having humidity of 50 percent. It is evident also that the intensity of the 001 peak varies according to the state of hydration. The sample can be returned to its original state, with the same basal spacing and peak intensity, by rehydration under the original conditions.

VARIATION OF BASAL DIFFRACTION PROPERTIES OF MONTMORILLONITE WITH HUMIDITY

The observations have led to a consideration of probable variations in diffraction peak intensity of montmorillonites resulting from the normal changes

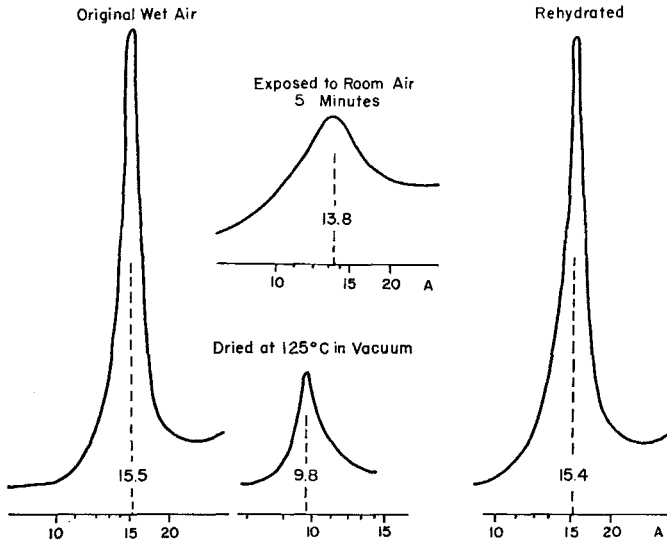


FIGURE 2. — Basal diffraction peak showing effect of rehydration after heat treatment. Calcium-saturated montmorillonite, Clay Spur, Wyoming; 0.2 to 0.05 micron.

of humidity that are encountered in the laboratory during the year. Measurements of temperature and humidity carried out over the past year have indicated that our laboratory air conditions vary from 50-60 percent humidity at 80° F, or greater, during the summer months to 15-20 percent humidity at 80° F during the winter months. The effects of such variations on the spacing and peak height of the 001 diffraction from an oriented slide of a calcium-saturated montmorillonite from Clay Spur, Wyoming, are indicated in Figure 3. The patterns obtained at 28 and 46 percent humidity represent actual laboratory conditions, while the <1 percent and 85 percent humidity conditions were produced artificially by passing dry air or air bubbled through water over the specimen. Equilibrium of the specimen with respect to its diffraction properties at any humidity is attained in a few minutes. The peak-intensity changes can be explained on the basis of the structure of the mineral, but it is more important at this stage to realize that large changes in peak height can be expected within a normal range of 15 to 60 percent humidity. The example given is that of a calcium-saturated montmorillonite in which the degree of hydration of the mineral varies between one and two layers of interlayer water. The same changes can be obtained from the magnesium-saturated montmorillonite. Hydrogen- and sodium-saturated montmorillonites are more stable, containing one layer of water over a fairly wide range of humidity conditions, but they can be expanded to two water layers at 85 percent and collapsed essentially at <1 percent humidity. We have often found it convenient to work with calcium-saturated samples and to record diffraction patterns under high and low relative humidity conditions.

CONTROLLED HUMIDITY WITH MIXED-LAYER MINERALS

Bentonitic montmorillonite has been used to illustrate the possible variations in spacing and intensity of the basal diffraction peaks and to indicate the need

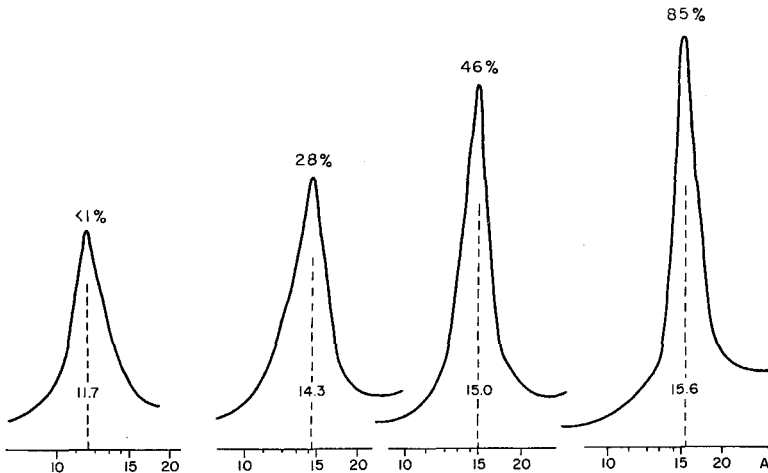


FIGURE 3. — Variation of basal diffraction peak of montmorillonite with humidity at 82° F. Ca-saturated montmorillonite, Clay Spur, Wyoming; 0.2 to 0.05 micron.

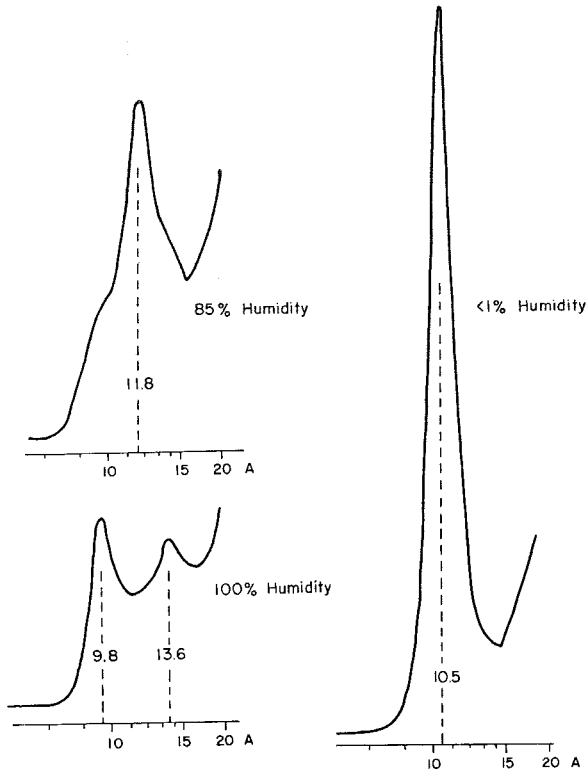


FIGURE 4. — Variation of basal diffraction peak of Ca-saturated potash bentonite (High Bridge, Kentucky) with humidity; 0.3 to 0.2 micron fraction; 80° F.

for control of humidity. Controlled humidity also has been used in the study of mixed-layer clay minerals which contain some expanding layers. It is possible to obtain several sets of diffraction data from the same oriented preparation and as a result interpret the mixed-layer structure more precisely.

Figure 4 shows the low-angle diffraction records of a calcium-saturated potash bentonite from High Bridge, Kentucky. The first diffraction peak occurs at 11.8Å at 85 percent humidity and has been interpreted as resulting from a mixed-layer structure, composed of 10.0Å and 15.4Å units in a ratio of approximately 2:1. The sample under <1 percent humidity conditions shows a drop in basal spacing to 10.5 Å and a remarkable increase in the height of the diffraction peak. It is apparent that this results from a partial dehydration of the expanded layers. When the sample is equilibrated with air of 100 percent relative humidity, a diffraction pattern with peaks at both 9.8Å and 13.6Å is obtained, as illustrated in the third part of Figure 4. Since it has been determined that a calcium-saturated montmorillonite under these conditions will expand to 13.9Å, indicative of three layers of water, it is suggested that these peaks probably

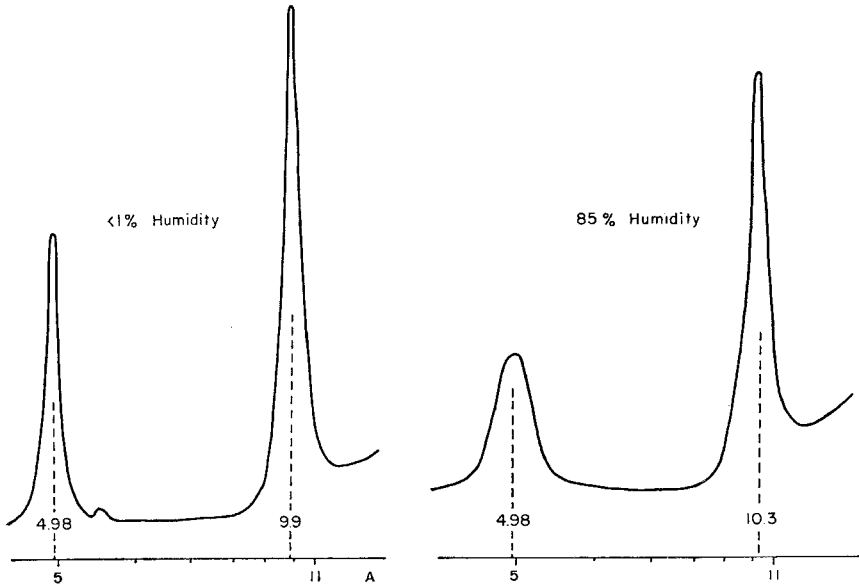


FIGURE 5.—Variation of basal diffraction peaks of Ca-saturated potash bentonite (no. N1, Oak Hall Quarry, Pennsylvania) with humidity; 0.2 to 0.05 micron fraction; 85° F.

result from 10.0A and 18.9A layers interstratified in the approximate ratio of 2:1. The remarkable increase in peak height obtained under humidity conditions of <1 percent may be used advantageously when it is desired to increase the sharpness of the diffraction from poorly diffracting mixed-layer minerals.

An example of the improvement of diffraction peaks by drying under <1 percent humidity conditions is the increase in peak height and sharpness shown in Figure 5. This sample is a potash bentonite from Oak Hall Quarry in central Pennsylvania. As described (Weaver, 1953), it contains 25 percent expanding layers in random interstratification with 10A layers. The partial diffraction records in this figure show that, when the sodium-saturated sample is collapsed at <1 percent humidity, the 001 and 002 peaks are much higher and sharper than those obtained at 40 percent humidity.

Another illustration of the improvement of diffraction patterns is given in Figure 6, in which a sample of Paleocene glauconite from California is compared at 20 percent and at <1 percent humidity. The 001 spacing shows only a small change from 10.5 to 10.4A, but the shape of the peak is changed considerably with an increase in peak height under the dry conditions. An Upper Cretaceous glauconite from Venezuela is also shown in Figure 6 under conditions of 20 percent and <1 percent humidity. In this glauconite there is no measurable change in the spacing, which, under both conditions, indicates very little expansion, but a small increase in diffraction intensity is evident at <1 percent humidity.

The effects of drying at room temperature and low humidity can also be produced by heating the sample. However, the same information can be ob-

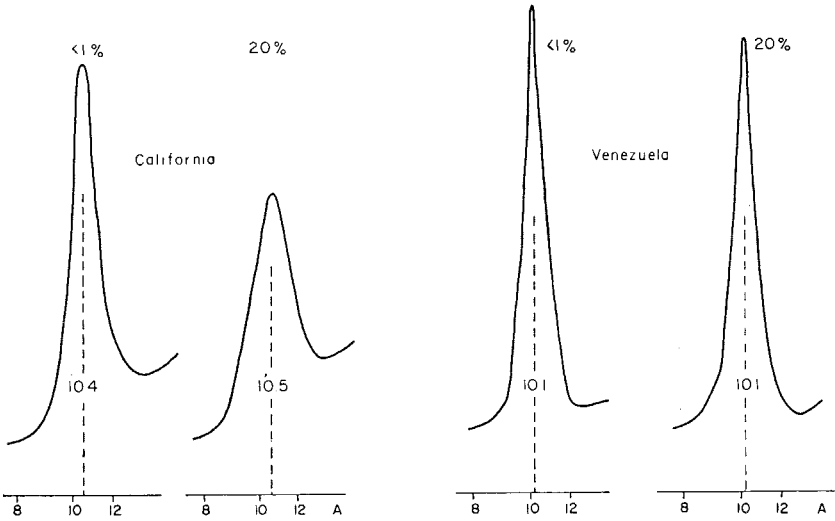


FIGURE 6.—Variation of basal diffraction peaks of glauconites with humidity, at 85° F.

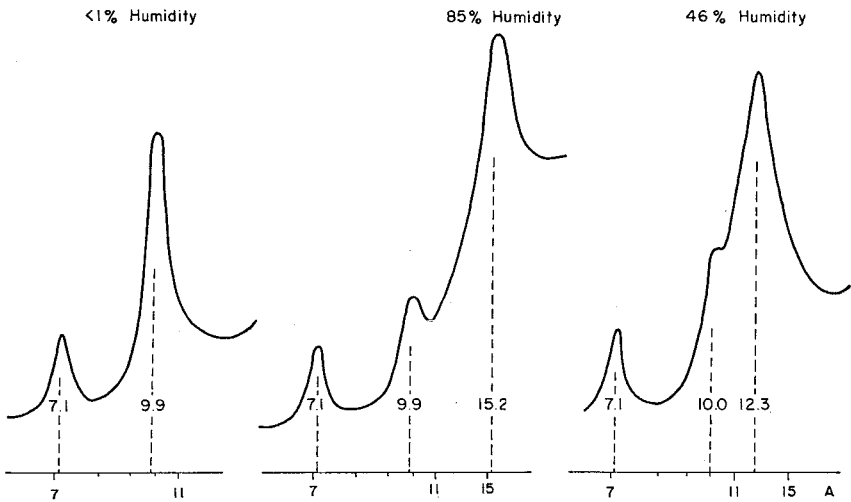


FIGURE 7.—Variation of basal diffraction peaks of clay-mineral mixture with humidity. Typical Recent mud (no. 5375), Na-saturated, 0.5 to 0.2 micron fraction; 77° F.

tained in a shorter time, and without any permanent alteration of the specimen, by the use of dry air.

CONTROLLED HUMIDITY WITH CLAY MINERAL MIXTURES FROM SEDIMENTS

In most sediment and soil samples, several clay minerals may be present in the same slide preparation. The diffraction record of a mixture of montmorillonite, illite, and kaolinite from a recent sediment is illustrated in Figure 7. The basal diffraction peaks of the illite and montmorillonite in this sodium-saturated sample overlap somewhat under conditions of 46 percent humidity. However, by expanding the montmorillonite to a basal spacing of 15.2Å at 85 percent humidity, a better resolution of the two diffraction peaks is obtained. A pattern obtained from the sample at <1 percent humidity, in which the illite and montmorillonite peaks are superimposed, is shown also in Figure 7. The use of glycerol in such a mixture will expand the montmorillonite to a basal spacing of 17.7Å and the second order of this spacing will then interfere with the first-order basal diffraction of illite.

REPRODUCIBILITY OF DIFFRACTION INTENSITY RATIOS WITH CONTROLLED HUMIDITY

Some reproducibility experiments have been carried out with a synthetic mixture of montmorillonite from Clay Spur, Wyoming, and kaolinite from Macon, Georgia. This mixture, which was known to contain equal quantities of the two minerals by weight and was composed of particles having an equivalent spherical

TABLE 1.—REPRODUCIBILITY TESTS. X-RAY DIFFRACTION DATA FOR 1:1 MIXTURE OF MONTMORILLONITE, CLAY SPUR, WYOMING, AND KAOLINITE, MACON, GEORGIA

Group	Slide	Montmorillonite		Kaolinite		Ratio	Average ratio of group	Percent standard deviation	Av. of group av.	Percent standard deviation
		dÅ	I	dÅ	I	$\frac{I(001) \text{ mont.}}{I(001) \text{ kaol.}}$				
A	1	15.2	81	7.1	57	1.43	1.49	4.8		
	2	15.2	94	7.1	64	1.47				
	3	15.2	94	7.1	60	1.57				
B	1	15.2	110	7.1	72	1.53	1.56	2.7		
	2	15.2	118	7.1	76	1.55				
	3	15.2	106	7.1	66	1.61				
									1.52	4.6
C	1	15.2	116	7.1	74	1.57	1.59	1.1		
	2	15.2	96	7.1	60	1.60				
	3	15.2	96	7.1	60	1.60				
D	1	15.2	122	7.1	86	1.42	1.43	2.2		
	2	15.2	108	7.1	74	1.46				
	3	15.2	112	7.1	80	1.40				

Slide preparations of Ca-saturated 0.5-0.2 micron fraction; scale factor = 16 and scan speed = 2° per minute; 60 percent relative humidity at 75° F

diameter ranging from 0.5 to 0.2 micron had been sodium saturated, dispersed together to assure intimacy of mixing, and supercentrifuged. Several portions of this mixture were calcium saturated, and from each portion three oriented slides were prepared. Diffraction records were made from each slide under 85 percent humidity conditions. The ratio of the peak height of the montmorillonite 001 diffraction over the peak height of the kaolinite 001 diffraction has been calculated for each preparation, and the assembled data are shown in Table 1. Although the intensity values of the 001 diffraction peaks vary considerably with each preparation, the ratios of the peak heights are reasonably constant, as indicated by the standard deviations.

REFERENCE

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