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HUMIDITY AND TEMPERATURE INTERACTION WITH RESPECT TO K-SATURATED EXPANDING CLAY MINERALS[1]

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In the identification of clay minerals by *x*-ray diffraction, collapse of the d_{001} spacing from about 14 Å with Ca or Mg saturation to about 11.5 Å or less with K saturation is diagnostic for the expanding lattice minerals (Brown, 1961). Montmorillonite is expected to have d_{001} of about 11.5 Å, nontronite and beidellite d_{001} of about 10.5 Å, and vermiculite d_{001} of about 10.3 Å after K-saturation and heating, commonly at about 150° C. Diffraction measurements on K-saturated samples are generally made without regard to atmospheric humidity even though humidity effects on Ca and Mg-saturated clay are well known.

The effect of humidity on the d_{001} spacing of K-saturated clay minerals was investigated using 2 to 0.2 μ samples of smectites (montmorillonite group) (Brown, 1961) and silt size samples of one vermiculite. The smectites included 17 montmorillonites, one beidellite, and one nontronite. These samples were pretreated to remove acid soluble material, organic matter, iron oxides, and alkali soluble material and dispersed with sodium carbonate. The vermiculite was treated with NaCl to convert interstratified biotite to vermiculite. Air of controlled relative humidity was circulated past the sample during *x*-ray diffraction. Relative humidity of about 1% was produced by passage of air through a column of Drierite. Passage over a container of saturated $(MgNO_3)_2 \cdot 6H_2O$ solution provided air of 55% relative humidity. Some of the principal results are shown in Table 1.

It is apparent that the lattice spacing of K-saturated clays is affected by changes in relative humidity to a greater extent than has been generally recognized. Unheated smectite samples exhibit d_{001} spacing of about 10.5 Å in controlled atmosphere of 1% relative humidity (Table 1). The complete reversibility of this collapse is indicated by d_{001} spacings from 11.8 to 12.4 Å in controlled atmosphere of 55% relative humidity. The vermiculite collapsed to a d_{001} spacing of 10.3 Å with K saturation regardless of the humidity level.

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Table 1. Basal Spacings of K-saturated Clay Minerals with Relative Humidity Levels as Indicated

Samples Source	Unheated[1] and analyzed at 1% R.H. (Å)	Heated 65° C. and analyzed at 55% R.H. (Å)	Heated 550° C. and analyzed at 55% R.H. (Å)
Vol Clay, Bentonite Panther Creek American Colloid Co.	10.4	11.8	9.8
Vol Clay, Bentonite SPV American Colloid Co.	10.4	12.1	12.1
Montmorillonite 21 Polkville, Mississippi	10.4	12.3	9.9
Montmorillonite 24 Otay, California Ward's Natural Sci., Inc.	10.5*	12.4	10.1
Montmorillonite S44-4 Colorado State University	10.4	12.3	10.0
Montmorillonite S34-6 Colorado State University	10.5*	12.4	10.2
Montmorillonite S34-1 Colorado State University	10.6	12.4	10.1
Montmorillonite S49-8 Colorado State University	10.5	12.4	12.3
Montmorillonite S79-1 Colorado State University	10.5	12.3	10.3
Montmorillonite S00-3 Colorado State University	10.5	12.4	10.3
Montmorillonite 30a Bayard, New Mexico Ward's Natural Sci., Inc.	10.5*	12.1	—
Montmorillonite 23 Chambers, Arizona Ward's Natural Sci., Inc.	10.5	12.3	10.1
Montmorillonite 26 Clayspur, Wyoming Ward's Natural Sci., Inc.	10.4	12.4	12.3
Montmorillonite 20 Polkville, Mississippi Ward's Natural Sci., Inc.	10.4	12.4	10.0
Montmorillonite 27 Belle Fourche, South Dakota Ward's Natural Sci., Inc.	10.5	12.1	10.0
Montmorillonite 32 Pioche, Nevada Ward's Natural Sci., Inc.	10.5	12.4	10.3

TABLE 1 (*continued*)

Samples Source	Unheated* and analyzed at 1% R.H. (Å)	Heated 65° C. and analyzed at 55% R.H. (Å)	Heated 550° C. and analyzed at 55% R.H. (Å)
Montmorillonite 11 Santa Rita, New Mexico Ward's Natural Sci., Inc.	10.5	12.3	10.6
Nontronite 33A Garfield, Washington Ward's Natural Sci., Inc.	10.5	12.4	—
Beidellite, R4762 Black Jack Mine U. S. National Museum	10.4*	11.8	—
Vermiculite, African Perlite Co., Portland	10.3	10.3	—

[1] Heated to 65 C.

Heat treatments below 550° C. had little effect on the ability of the montmorillonite clays to dehydrate or rehydrate. Control of humidity was the dominant factor on observed basal spacings. In addition to the results shown in Table 1, diffraction measurements were made at 1% relative humidity on smectite samples heated at 65 and 100° C. The total range in d_{001} at 1% relative humidity was from 10.3 to 10.6 Å. At 55% relative humidity, samples pre-heated at 100, 200, and 300° C. had d_{001} spacings ranging from 11.5 to 12.4 Å. Even after heating at 300° C. and hydration at 55% relative humidity, no sample had d_{001} more than 0.5 Å smaller than those shown in table 1 for samples heated at 65° C. On the other hand, after heating at 550° C., and subsequent hydration at 55% relative humidity, 13 out of 16 samples had much reduced spacings (Table 1).

The d spacing for any given smectite sample without humidity control during diffraction ranged between the d_{001} spacings observed with 1% and 55% relative humidity. With the regular scanning procedure where humidity is not controlled, the number of samples with d_{001} near 10 Å increased with increasing temperature of the heat treatment (Table 2). Diffraction immediately after removal from the oven resulted in d_{001} near 10 Å for more of the samples than diffraction after cooling in a desiccator containing Drierite. Results for nontronite and beidellite were similar to those shown for montmorillonite but were not included in every treatment because of shortage of material. The entire group of samples had d_{001} spacings ranging from 11.8 to 12.3 Å when heated at 65° C. and

TABLE 2. NUMBER OF THE 17 MONTMORILLONITE SAMPLES WITH d_{001} SPACING OF 10.6 Å OR LESS WITHOUT HUMIDITY CONTROL DURING DIFFRACTION

Heat treatment (° C.)	Cooled in desiccator	*X*-rayed directly
Unheated	0	0
65	0	0
100	1	6*, 13*
200	6	14
300	16	17
550	17	17

* Diffraction on different days.

cooled in a desiccator. They collapsed to spacings between 10.0 and 10.5 Å when heated to 300° and *x*-rayed directly. The d_{001} spacings for single samples heated at 100° C. were observed to vary from day to day, presumably with change in relative humidity.

The results discussed above indicate that smectite samples after heating and which were collapsed to spacings near 10 Å, tend to re-expand to spacings near 12 Å upon exposure to the atmosphere. This is true even for samples taken directly from the oven to the *x*-ray machine and scanned at one degree per minute starting at 14 degrees 2 θ. Thus, even scanning time required to reach the angular position of the d_{001} peak, about 5 minutes, is sufficient for re-expansion. To test the effect of time, samples heated at 65° C. were removed from the oven one by one and scanned immediately from 9 to 7 degrees 2θ without humidity control. The d_{001} spacings were within 0.2 Å of those for diffraction at 1% relative humidity.

Without humidity control, the d_{001} spacing of K-saturated smectite has been shown to be subject to two major variables. These are relative humidity of the atmosphere and rate of rehydration as affected by temperature of preheating. The increasing number of samples with d_{100} spacing near 10 Å with increasing temperature of heating, and without control of relative humidity during diffraction (Table 2), indicates that the rate of rehydration is reduced by heating. The rate of both dehydration and hydration was shown to be rapid for the montmorillonite samples heated to 65° C. by the following procedure. The d_{001} peak of the hydrated sample was found and locked on the goniometer. Then, air of 1% relative humidity was introduced. In all cases, the diffraction intensity began dropping almost immediately and reached equilibrium within one minute (Fig. 1). This indicated that, with dehydration, the diffraction peak had shifted completely away from its original position. The flow of dry

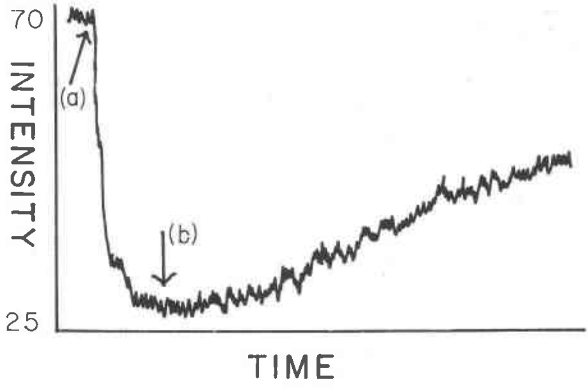

FIG. 1. Change of x-ray diffraction intensity of a hydrated K-saturated clay with time at 2θ equivalent to 12.4 Å: upon (a) dehydration by introduction of air at 1% relative humidity, and (b) rehydration upon exposure to room condition.

air was then discontinued and the sample was allowed to rehydrate in the atmosphere of the room. The diffraction intensity began to increase within one minute and continued to rise over a period of 8 to 10 minutes.

Figure 2 illustrates how control of relative humidity increases the sharpness of the d_{001} diffraction peak.

The sensitivity of d_{001} of K-saturated smectite to relative humidity emphasizes rates of rehydration in study of the interrelationships of micas, vermiculites and smectites. Diffraction patterns of K-saturated clay without humidity control are ambiguous. The position and broadness of peaks can be misinterpreted in clay identification and in studies of clay properties. Broadness of the peak due to partial expansion by ir-

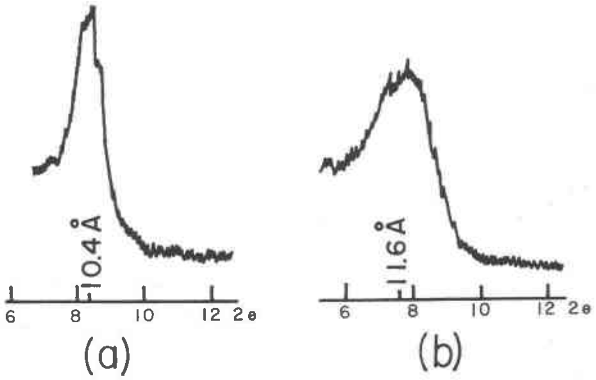

FIG. 2. X-ray patterns of a K-saturated clay: (a) under 1% relative humidity, (b) under uncontrolled humidity conditions.

regular rehydration even after heating could be taken as evidence for presence of interlayered material or some other imperfection. Control of humidity makes diffraction studies independent of atmospheric conditions and offers the possibility of more accurate and definite results.

REFERENCE

BROWN, G. (1961) *The X-ray Identification and Crystal Structures of Clay Minerals.* The Mineralogical Society, London.

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COMPUTER PROGRAM FOR NORM CALCULATION

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A program written for the IBM 650 digital computer permits the calculation of the norm of igneous rocks by the molecular norm method of Barth (1931, 1955).

A flow diagram[3] was first prepared outlining the step-by-step procedure. This formed the basis for the symbolic optimum assembly program which consists of (1) a program deck containing the instructions for the computer and the equivalent molecular weights for SiO_2, $AlO_{3/2}$, $FeO_{3/2}$, FeO, MgO, CaO, $NaO_{1/2}$, $KO_{1/2}$, TiO, MnO, $PO_{5/2}$, CO_2, S, H_2O-, H_2O+; and (2) a set of three data cards containing the chemical analysis of each of the rocks to be computed.

Once the program has been put into the computer, any number of analyses may be supplied for recasting to the norm. The saving in time over hand calculation is considerable. The actual machine time for the calculation, from start to punchout, averages six seconds per analysis. The results of the calculations consist of the percentages of the cations used in the calculation and the percentages of the normative minerals. They are punched out in a series of five cards which can be printed out as desired. The computer states the results in eight figures, using the floating decimal system. These figures must, however, be rounded off.

Although originally designed to deal only with analyses of relatively unaltered rocks, the program is flexible and can be adjusted to handle

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[3] A small supply of copies of the flow diagram is available. A copy may be obtained from the senior author.