THE NATURE OF THE SYNTHETIC CRYSTALLINE BASIC ALUMINIUM SULPHATES AS COMPARED WITH BASALUMINITE[1]

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ABSTRACT

Basaluminite, $Al_4(OH)_{10}SO_4.5H_2O$ from Northamptonshire and Kansas showed reversible expansion and contraction equivalent to 1 layer of interlayer adsorbed water between 100% and 0% (over P_2O_5) relative humidity. This characteristic supports the previous suggestion that the crystalline basic aluminium sulphate formed upon aging the partially neutralized solution of $Al_2(SO_4)_3$ in the presence of montmorillonite was basaluminite.

In the absence of clay, the crystalline basic aluminium sulphates that formed at 50°C, had compositions, thermal analysis features and solubility products similar to basaluminite but had a slightly different crystalline form.

INTRODUCTION

The naturally occurring basic aluminium sulphate, basaluminite $Al_4(OH)_{10}SO_4.5H_2O$ was first described by Hollingsworth & Bannister (1950) and more recently it was reported in sedimentary rocks in Kansas (Tien, 1967). The highly hydrated hydrobasaluminite—$Al_4(OH)_{10}SO_4.36H_2O$—which was found in the moist samples reverted irreversibly to basaluminite on air-drying. Further dehydration at 150°C produced metabasaluminite—$Al_4(OH)_{10}SO_4$ (Hollingsworth & Bannister, 1950).

Basic aluminium sulphates with compositions similar to basaluminite have been synthesized in the presence of clays (Singh & Brydon, 1967) and in the absence of clays (Bassett & Goodwin, 1949; Hsu & Bates, 1964). A variety of *x*-ray diffraction patterns were obtained showing differences from those published by Hollingsworth & Bannister (1950). One difference (Singh & Brydon, 1967) was the reversible contraction and expansion of the basal spacing with change in relative humidity.

Singh and Brydon (1968) have described the preparation and solubility characteristics of several crystalline basic aluminium sulphates. The nature and properties of these materials are described in this paper and compared with those of basaluminite. To provide a direct comparison, we obtained through the courtesy of the British Museum a specimen of basaluminite from the Lodge Pit, Irchester Ironstone Company, North-

[1] Contribution No. 268.

amptonshire, the same source of the sample used by Hollingsworth & Bannister. A specimen of the Kansas sample was kindly supplied by Dr. Pei-lin Tien after most of the experimental work had been done.

MATERIALS AND METHODS

The three synthetic samples 43, 36 and 44 were prepared by adding $Ca(OH)_2$ to a solution of $Al_2(SO_4)_3$ so that the OH/Al ratio was 1.6, 2.2 and 2.5, respectively (Singh & Brydon, 1968). The suspensions were aged at 50°C for a period of 180 days and the precipitates were recovered by centrifuging the suspensions, washing once with water and freeze-drying.

X-ray powder patterns of specimens mounted in 0.2 mm capillary tubes were obtained with 114.7 mm cameras, using Fe-filtered Co radiation. The differential thermal analysis and thermogravimetric analysis data were obtained with equipment and procedures outlined by Brydon & Kodama (1966).

Oriented aggregate specimens for *x*-ray diffraction were prepared by allowing 1 ml of a suspension containing 20 mgm of sample to sediment and dry on one-half microscope slides. The relative humidity of the specimen chamber of a Philips diffractometer was controlled by flushing it with premixed moist and dry air. The driest operating condition (referred to as zero R.H.) was obtained by mounting a small vessel of P_2O_5 below the specimen in the closed specimen chamber. Following heat treatments at various temperatures for 30 minutes, the specimens were *x*-rayed at 100% relative humidity after a steam treatment and then at 0% relative humidity.

RESULTS AND DISCUSSION

X-ray diffraction

The specimen of Northamptonshire basaluminite consisted of air-dry chalky aggregates with some dark-coloured impurities which could not be identified. The dark material settled during sedimentation in water but the *x*-ray diffraction patterns (basaluminite) of the sediment and suspension were identical. The bulk specimen contained 0.6% Fe_2O_3. The powder pattern, (only the forward reflection region is given in Table 1) except for several additional weak reflections, matched that published by Hollingsworth & Bannister (1950). The patterns of the synthetic basic aluminium sulphates were rather similar to that of basaluminite and showed a match for some of the weak reflections not given by Hollingsworth and Bannister. Some of the variation in the low angle region among the samples was resolved by a consideration of the

TABLE 1. *X*-RAY POWDER DATA FOR BASALUMINITE AND VARIOUS SYNTHETIC BASIC ALUMINIUM SULPHATES

Basaluminite†		Basaluminite		44		36		43		Basaluminite 150°C	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
		10.32	1½	10.27	5	10.37	10	10.4	10		
9.4	vs	9.38	10	9.09	2	9.17	6	9.01	5	9.09	1½
		8.71	f*	8.22	10					8.25	10
		7.84	1			7.85	f	7.82	f	7.56	f
7.18	vvw	7.32	4	7.34	f	7.27	f			6.93	2
6.73	w	6.88	3	6.72	½b	6.47	f			6.76	4
				6.16	f	6.11	2	6.18	2	6.31	f
5.92	m	5.93	5	5.92	2	5.88	3	5.93	4	5.93	3
				5.52	3						
5.27	m	5.35	3			5.29	½b	5.27	f	5.48	f
		5.21	2								
		5.01	1	5.05	1½	5.08	3	5.07	4	4.99	2
								4.82	4	4.84	1½
4.68	s	4.69	7	4.69	2½	4.68	3½			4.71	2
		4.54	2½			4.54				4.54	f
		4.41	2½	4.41	4		2b	4.43	3vb	4.41	4½
		4.25	1			4.31				4.30	5
		4.15	½							4.14	4
		3.94	1	4.07	4	4.03	1½	4.02	2	4.02	½

3.87	m	3.86	2	3.84	2	3.83	4	3.85	4½	3.91	f
3.68	ms	3.69	4	3.70	2			3.64	f	3.69	2
		3.62	3								
3.44	m	3.44	3	3.46	4½	3.53	1	3.52	f	3.46	2
						3.39	1	3.39	2	3.35	2
3.20	vw	3.23	1			3.26	½	3.24	½	3.24	2
		3.13	1					3.11	½	3.13	f
		3.08	½	3.10	½	3.09	½				
		3.02	½							3.04	2
		2.95	2	2.96	1	2.95	2	2.96	2	2.97	1
										2.91	f
2.90	w	2.93	2	2.90	f	2.88	½	2.89	2	2.88	3
		2.84	3	2.83	1						
2.82	w			2.81	1	2.80	1	2.81	2	2.75	½
2.71	mw	2.72	4	2.73	1	2.72	f	2.71	f	2.70	f
		2.63	1	2.61	1	2.60	1	2.62	1	2.65	1
		2.58	f								
		2.55	½	2.55	f						
		2.50	½	2.51	2½	2.52	½	2.54	½	2.55	1
		2.47	2½			2.46	½	2.46	½	2.47	½
2.45	mw	2.44	1							2.45	2

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*f—faint, just detectable.

†taken from Hollingsworth and Bannister, (1950).

diffractometer patterns obtained from oriented specimens of the materials as shown in Figs. 1 and 2.

At room temperature and relative humidity, the basaluminite specimen showed two major peaks at 9.36 Å and 4.68 Å (Fig. 1, left) which were identical to the reflections which Hollingsworth & Bannister indexed as basal spacings of a hexagonal cell. Moistening the specimen gave no change in the diffraction pattern but exposing it to dry air shifted the basal spacing to 8.07 Å and 3.96–4.02 Å. The shift on drying and moistening was completely reversible up to a temperature of 100°C. A gradual change from the 8.0 Å phase to an 8.3 Å phase took place upon heating between 120°C and 150°C (Fig. 1, right). The basal spacings of the latter material were unaffected by moisture and gave a powder pattern similar to that of the metabasaluminite of Hollingsworth & Bannister. The metabasaluminite reflections disappeared between 250°C and 300°C. The Kansas sample showed the same characteristics.

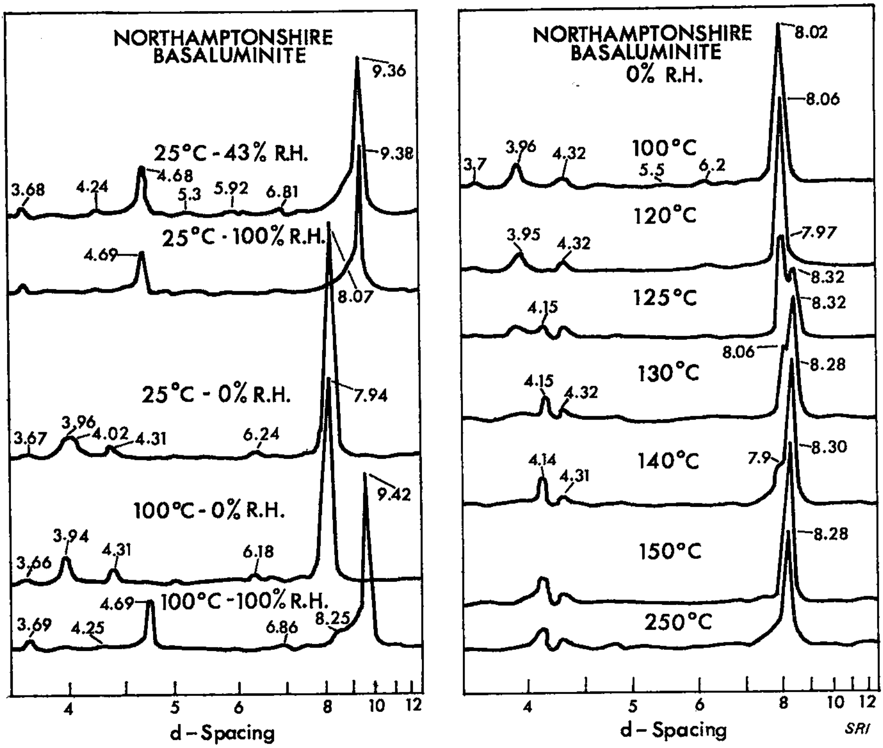

FIG. 1. X-ray diffraction patterns of oriented specimens of basaluminite from Northamptonshire at various relative humidities (left) and at zero relative humidity after successive 30-minute heat treatments (right).

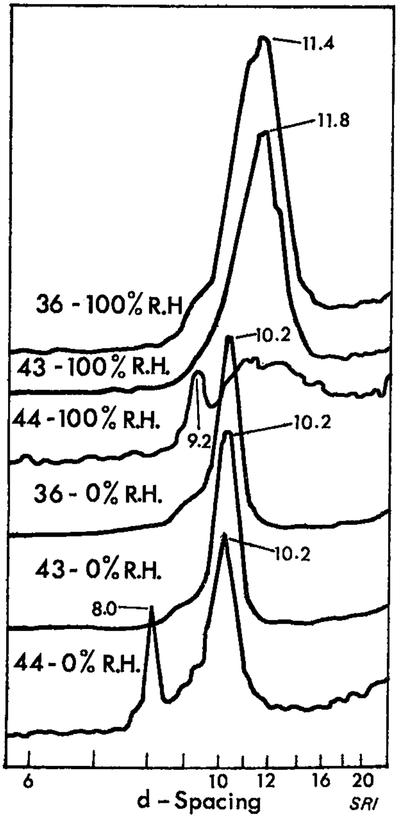

FIG. 2. X-ray diffraction patterns of the three synthetic basic aluminium sulphates at zero and 100% relative humidity and at room temperature.

X-ray diffraction patterns of the various synthetic precipitates obtained at the end of the reaction periods showed the presence of two different materials (Fig. 2). A portion of sample 44 was similar to basaluminite, i.e., the main peak shifted from 9.2–9.4 Å when moist to 8.0 Å when dry. The remaining portion of sample 44 and all of samples 36 and 43 gave a broad reflection at 11.4–11.8 Å when moist which shifted to a sharp reflection at 10.2 Å when x-rayed at zero R.H.

Thermal analysis

The Differential Thermal Analysis curves for the basaluminite specimens from Kansas and Northamptonshire were very similar (curves a and b, Fig. 3, left). The curves show a variety of features which depended

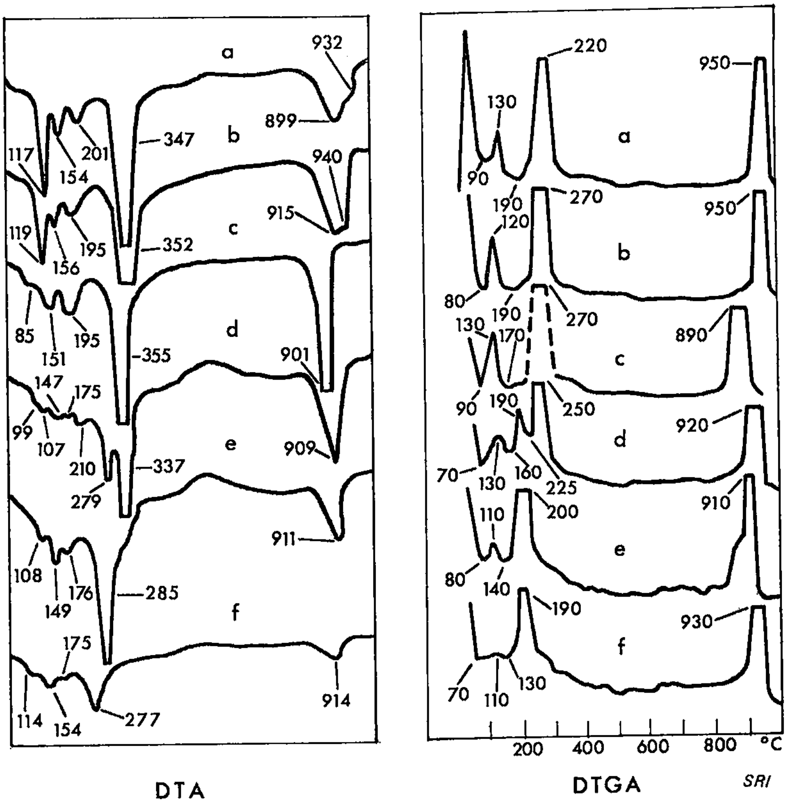

FIG. 3. Differential thermal analysis curves (left) and differential thermogravimetric analysis curves (right) a) basaluminite, Kansas; b) basaluminite, Northamptonshire, natural; c) basaluminite, Northamptonshire, suspended and freeze-dried; d) 44; e) 43; f) 36.

upon whether the specimen was run in the natural condition (curve b) or after sedimentation and freeze-drying (curve c). The major dehydroxylation peak at 355°C and the low temperature peaks at 155°C and 195°C were common to both specimens. The untreated material showed a sharp peak at 119°C which was not shown by the freeze-dried material and it showed a high temperature double endotherm at 915°C and 940°C as compared with a single large sharp peak at 901°C with the freeze-dried material. No reason can be offered for these differences.

The synthetic samples, which had been freeze-dried, did not have a 120°C endotherm and had a single high-temperature endotherm at 910°C. The curves for samples 36 and 43 were similar but their major dehydroxylation peak at 280°C and the minor peak at 175°C occurred at lower temperatures (curves e and f) than the corresponding peaks shown by basaluminite (curve c). The curve for sample 44 appeared to be a composite of the curves of basaluminite (peaks at 337, 210, 147, 99°C) and sample 43 (peaks at 280, 175, 107°C) with a single high-temperature endotherm at 909°C.

The Differential Thermogravimetric Analysis curves (Fig. 3, right) show the same general features and differences as the DTA curves. The two basaluminite curves are very similar (a and b). The freeze-dried specimen (curve c) showed the loss of SO_3 at 890°C which was 60°C below that of the natural specimens. Samples 36 and 43 gave a lower dehydroxylation temperature than basaluminite and the curve of sample 44 (curve d) appeared to be a composite of the curves for sample 36 and basaluminite.

TABLE 2. ALLOCATION OF WEIGHT LOSS INCREMENTS FOR BASALUMINITE AND VARIOUS SYNTHETIC BASIC ALUMINIUM SULPHATES

	Al_2O_3[1]	SO_3[2]	H_2O[3]
Air-dry weight			
Ideal $Al_4(OH)_{10}SO_4.5H_2O$	44.0	17.2	38.8
basaluminite (ref. 4)	43.5	17.4	39.1
basaluminite—Kansas	48.0	17.2	34.9
basaluminite—North.	49.9	15.8	34.1
basaluminite—North.—freeze-dried	51.1	18.6	30.4
Oven-dry weight[4]			
Ideal $Al_4(OH)_{10}SO_4$	54.5	21.4	24.1
basaluminite—Kansas	54.2	19.4	26.6
basaluminite—North.	56.0	17.7	26.2
basaluminite—North.—freeze-dried	53.9	19.6	26.5
44	51.9	19.8	28.3
43	47.3	23.3	29.4
36	49.6	21.1	29.2

[1] Calculated as the residue weight at 1000°C.
[2] Calculated as the loss in weight 500–1000°C.
[3] Calculated as the loss in weight up to 500°C.
[4] The sample weight corresponding to the first minimum on the DTGA curve.

The well-defined DTA and DTGA features can be allocated as a first approximation to the loss of adsorbed water (<100°C), the loss of water of crystallization (100–200°C), the dehydroxylation (200–350°C) and the decomposition of sulphate (900–950°C) leaving a pure Al_2O_3 residue (Davey *et al.*, 1963). The respective losses are given in Table 2 on the air-dry weight basis and on an "oven-dry" basis, i.e., the weight corresponding to the first minimum (70–90°C) on the DTGA curve. It is obvious that the air-dry materials had less than the ideal $5H_2O$. No attempt was made to control the relative humidity but it varied from 20–30% at the time the specimens were run. When the dry temperature at the second DTGA minimum was used, the results were not consistent and departed further from the ideal values (data not shown). A further anomaly is shown in Fig. 3. It can be seen that the main DTA dehydroxylation peak was approximately 80°C higher than the corresponding DTGA peak whereas the sulphate decomposition occurred in most cases at a lower temperature in DTA than in DTGA. There is commonly a consistent lag in the temperature of reactions in DTA due to a faster heating rate and difference in sample mass and geometry (Brydon & Kodama, 1966) but this cannot explain a lag for one reaction and a gain for another.

Davey *et al.* (1963) have indicated several complicating reactions during the thermal decomposition of a basic sulphate of different Al:OH:SO_4 ratio: 1. Equilibrium was difficult to attain and the various stages of decomposition overlapped. 2. A small amount of residual OH remained beyond 600°C and was associated with SO_4 decomposition. 3. The sulphate was decomposed to give H_2SO_4, SO_3, SO_2 and O_2, the proportions of which depended upon temperature and partial pressure of oxygen. 4. Prolonged heating at 1000°C or heating to a much higher temperature was required to remove the last 1% SO_3. They also showed that the shapes, areas and positions of the peaks on the DTA and DTGA curves varied considerably with operating techniques. Some combination of these factors is undoubtedly responsible for the variations in allocated weights (Table 2) as well as the differences in the DTA and DTGA curves in Fig. 3.

Dehydration of basaluminite

The data presented above show several characteristics of basaluminite not previously known. The Kansas and Northamptonshire specimens had both apparently dried irreversibly from hydrobasaluminite (Hollingsworth & Bannister, 1950) to basaluminite prior to receiving them. Oriented specimens of basaluminite showed basal spacings of 8.0 Å when dry and 9.4 Å when moist and complete reversibility unless heated to 120°C. Using indices proposed by Hollingsworth & Bannister, the corresponding *c* dimensions would be 16.0 Å and 18.8 Å. The difference, 2.8 Å, is approximately the thickness of a single layer of water molecules. The reversible expansion and contraction below 100°C reinforces the statement of Hollingsworth & Bannister that the properties of basaluminite are similar to those of some of the clay minerals.

Above 100°C metabasaluminite forms irreversibly with an increase in basal spacing and accompanied by a partial loss of OH as indicated by thermal analysis. The metabasaluminite decomposes to an amorphous aluminium oxide-sulphate near 300°C and the sulphate is largely decomposed near 900°C giving γ Al_2O_3.

Synthetic basic aluminium sulphates

Singh & Brydon (1967) showed that aluminium hydroxide, when precipitated from an aluminium sulphate solution, entered the interlayer space of Wyoming bentonite and gradually changed to a basic aluminium sulphate. This phase had a composition similar to basaluminite. Because it showed reversible expansion and contraction from 9.4 Å when wet to 8.0 Å when dry and because basaluminite has been shown here to have the same characteristics (Fig. 1), it can be concluded that the synthetic basic aluminium sulphate formed in those clay suspensions was synthetic basaluminite.

In the absence of clay (Singh & Brydon, 1967), a basic aluminium sulphate precipitated and aged in the same way as with the clay suspensions remained amorphous indefinitely although it had a similar composition to basaluminite. When the temperature of aging was increased, crystallinity developed. However, just as Bassett & Goodwin (1949) and Tanabe (1957) obtained a variety of crystalline forms in their synthesis experiments, the crystalline materials formed in the present experiments varied. Samples 36 and 43 showed basal spacings of 10 Å when dry whereas sample 44 was a mixture of the "10 Å" basic sulphate and basaluminite. The chemical composition of the three samples (Singh & Brydon, 1968) were very close to the ideal basaluminite composition $Al_4(OH)_{10}SO_4.5H_2O$; the SO_3 content was 0.2 to 0.8% higher and the hydroxyl water content was 0.2 to 0.4% lower. Thermal analysis showed the main dehydroxylation of the "10 Å" material (samples 36 and 43) to occur 50–60°C lower than with basaluminite whereas the sulphate decomposition occurred at the same temperature. Furthermore, the solubility products $(Al)^4(OH)^{10}(SO_4)$ of the three samples were relatively constant and similar to that of the synthetic basaluminite formed in the presence of clay (Singh & Brydon, 1968).

With the exception of the experiment of Hsu & Bates (1964) whose basic aluminium sulphate gave a diffuse diffraction pattern with some similarities to basaluminite, the authors do not know of any other successful synthesis of basaluminite in pure solutions. On the other hand aluminium hydroxide absorbed on Wyoming bentonite slowly changed in sulphate solutions to form synthetic basaluminite under a variety of conditions (Singh & Brydon, 1967, 1968).

ACKNOWLEDGMENTS

Since the manuscript was submitted, the papers by Pei-Lin Tien (1968), and C. Frondell (1968), have reported occurrences of basaluminite and associated basic aluminium sulphate minerals, and some analytical data. Our paper complements the others; it elucidates the reversible expansion and contraction of the basaluminite layer structure at normal temperatures and shows the difficulties in accurately interpreting the thermal analysis data.

The authors acknowledge the technical assistance of N. M. Miles and G. C. Scott.

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Manuscript received June 20, 1968, emended October 15, 1968

CORRECTION

On page 472, vol. 9, part 4, the formula of Weloganite appears as $5SrCO_3.Zr_2O_3(OH)_2.3H_2O$. This should read:

$$5SrCO_3.Zr_2O_3(OH)_2.4CO_2.3H_2O$$

There was also omitted from the list of references:

CLARK, T. H. (1952): Montreal Area, Laval and Lachine map-area, *Que. Dept. Mines Geol. Rept.* 46.