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Hydrobasaluminite and basaluminite from Chickerell, Dorset

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SYNOPSIS

HYDROBASALUMINITE and basaluminite, two hydrated basic aluminium sulphate minerals have been found in the weathering zone of the Oxford Clay at Crook Hill Brickyard, Chickerell, near Weymouth, Dorset. Hydrobasaluminite occurs as a reaction rim surrounding carbonate concretions, and is believed to have resulted from the neutralization of aluminium-bearing acid sulphate solutions formed by oxidation of pyrite and subsequent leaching of clay. Basaluminite is found only on concretions that have fallen to the floor of the pit, suggesting that it is formed as a dehydration product of hydrobasaluminite.

Chemical analysis of hydrobasaluminite yields the composition $2Al_2O_3 \cdot SO_3 \cdot 20H_2O$, although this almost certainly includes substantial amounts of adsorbed water. Chemical analysis of basaluminite gives the composition $2Al_2O_3 \cdot SO_3 \cdot 9H_2O$, which is equivalent to a formula of $Al_4SO_4(OH)_{10} \cdot 4H_2O$ if it assumed that water is present only as water molecules or hydroxyl ions. The sulphate ions are readily exchangeable. Electron-optical and X-ray powder diffraction data show the minerals to be monoclinic rather than hexagonal as previously reported. Indexed X-ray powder patterns give unit-cell parameters of $a = 14.911(5)$ Å, $b = 9.993(2)$ Å, $c = 13.640(5)$ Å, $\beta = 112.40(4)°$ for hydrobasaluminite and $a = 14.857(3)$ Å, $b = 10.011(3)$ Å, $c = 11.086(7)$ Å, $\beta = 122.28(3)°$ for basaluminite. The specific gravity of basaluminite is found to be 2.10 and $Z = 4$.

Hydrobasaluminite dehydrates irreversibly to basaluminite under normal laboratory conditions, but can be preserved indefinitely at high relative humidity. A study of the dehydration of basaluminite using a diffractometer heating-stage shows the presence of three further distinct hydration states as well as interstratified intermediates. The dehydrations occur topotactically and involve major changes in the c^* direction only. DTA and TGA curves can be interpreted in terms of progressive dehydration.

It is suggested that the minerals possess a layer structure, probably containing gibbsite-like double-hydroxide layers with interlayer sulphate ions and water molecules. The data also seem to show a close structural relationship between basaluminite and the hydrated basic aluminium carbonate mineral, scarbroite.

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[*Note*. After submission of this paper, a paper by Brindley (*Mineral. Mag.* **43**, 615-18) was published, giving new dehydration data for scarbroite and proposing a similar structural arrangement to the one postulated here.]

HYDROBASALUMINITE AND BASALUMINITE FROM CHICKERELL, DORSET

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Hydrobasaluminite and basaluminite, two hydrated basic aluminium sulphate minerals were reported first by Bannister and Hollingworth (1948) as occurring in fissures in the Northampton Ironstone (Inferior Oolite) at Lodge Pit, Irchester, Northamptonshire. In a later article, the same authors (Hollingworth and Bannister, 1950) described the minerals more fully. Subsequently, several other occurrences have been reported including Milton et al. (1955), Fominykh (1965), Frondel (1968), Tien (1968), Sunderman and Beck (1969), Ball (1969), Srebrodol'skiy (1969), Mitchell (1970) and Wieser (1974). The minerals invariably occur in the weathering zone, usually as a consequence of the oxidation of pyrite, and are commonly associated with gypsum, allophane, gibbsite and iron oxides. The present investigation describes hydrobasaluminite and basaluminite from a new locality at Chickerell, near Weymouth, Dorset.

Bannister and Hollingworth (1948) found that hydrobasaluminite was unstable under normal laboratory conditions and that it dehydrated irreversibly to form basaluminite. They showed, however, that it could be preserved indefinitely if kept in contact with moisture. Other phases, which occur when basaluminite is heated, have been reported by Hollingworth and Bannister (1950) and Brydon and Singh (1969). These were studied at room temperature after cooling. Because of the rapid rehydration of some of the phases, the full complexity of the dehydration was not appreciated. In the present investigation, a diffractometer heating-stage was used which enabled the phases to be studied at their temperatures of formation.

In all occurrences recorded to date, the minerals have been found to be extremely fine grained and usually admixed with varying amounts of impurities. These factors, combined with the ease of dehydration, make chemical analysis rather difficult. This is particularly true for the water content, since it is difficult to differentiate between the adsorbed and combined states. Chemical analyses of hydrobasaluminite reported to date have given compositions ranging from $2Al_2O_3.SO_3.17H_2O$ to $2Al_2O_3.SO_3.41H_2O$, whilst chemical analyses of basaluminite have given compositions ranging from $2Al_2O_3.SO_3.8.3H_2O$ to $Al_2O_3.SO_3.10H_2O$. If the assumption is made that H_2O is present only as molecular water or hydroxyl ions, these would correspond to chemical formulae between $Al_4SO_4(OH)_{10}.12H_2O$ and $Al_4SO_4(OH)_{10}.36H_2O$ for hydrobasaluminite and between $Al_4SO_4(OH)_{10}.3.3H_2O$ and $Al_4SO_4(OH)_{10}.5H_2O$ for basaluminite.

Because of the fine-grained nature of the minerals, no detailed optical or single crystal X-ray diffraction studies have been made. Hollingworth and Bannister (1950) provisionally indexed the X-ray powder pattern of basaluminite on the basis of a hexagonal unit cell with lattice parameters of $\underline{a}$ = 22.56 Å and $\underline{c}$ = 18.72Å. Electron micrographs obtained by Tien (1968) showed the existence of thin rhombic plates with internal angles of 65½° and 114½°. This suggested that hexagonal symmetry was unlikely. Sunderman and Beck (1969) reported that a selected-area electron diffraction pattern obtained perpendicular to the plates was orthogonal, but they were unable to relate it to the X-ray powder data.

Bassett and Goodwin (1949) in an extensive investigation of the system $Al_2O_3 - SO_3 - H_2O$ at room temperature synthesized many basic aluminium sulphates but were unable to synthesize either hydrobasaluminite or basaluminite. They suggested that the minerals were stable only over a very small compositional range in the vicinity of the water corner. Hsu and Bates (1964) reacted sodium hydroxide with aluminium sulphate and obtained an amorphous precipitate containing sulphate ions when the OH/Al ratio was less than 2.7. Below an OH/Al ratio of 2.1 the composition of this precipitate was approximately $Al(OH)_{2.2}(SO_4)_{0.4}$, whilst between 2.1 and 2.7 a continuous compositional range from $Al(OH)_{2.2}(SO_4)_{0.4}$ to $Al(OH)_{2.7}(SO_4)_{0.15}$ was obtained. These precipitates were readily soluble in dilute HCl. On ageing the $Al(OH)_{2.2}(SO_4)_{0.4}$ for a period of one year, material which dissolved only partially to give a residue of composition $Al(OH)_{2.58}(SO_4)_{0.21}$ was obtained. This residue gave an X-ray powder pattern with broad peaks which the authors suggested bore some resemblance to that of basaluminite. Brydon and Singh (1969) claimed to have synthesized basaluminite by reacting calcium hydroxide with aluminium sulphate in the presence of Wyoming bentonite. They obtained similar results in the absence of clay by ageing at 50°C. Although the chemical compositions of these products are very close to that of basaluminite, the X-ray powder patterns do not correspond to any of those obtained during the present study. Adams and Rawajfih (1977), using similar methods, also claimed to have synthesized basaluminite but again the X-ray diffraction evidence cannot be regarded as satisfactory. Adams and Rawajfih (1977) also suggested that the formation of basaluminite might be an important factor in the retention of sulphate in acid soils.

Bassett and Goodwin (1949) suggested that the crystal structures of the more basic aluminium sulphates were probably related to those of the various aluminium hydroxides, and that establishment of the appropriate hydroxide arrangement was the principal difficulty in their synthesis. They postulated that the crystal structures of hydrobasaluminite and basaluminite were related to that of gibbsite. Hsu and Bates (1964) suggested that precipitation of basic aluminium sulphates occurred as a result of the linking together of large positively-charged ions of the type $Al_m(OH)_n^{3m-n}$ by negatively-charged sulphate ions. The amorphous nature of the precipitate was considered to be due to the variety of polynuclear ions existing at the time of precipitation. Hayden and Rubin (1974) showed that the principal species present in aqueous aluminium solutions at a pH of between 4.5 and 5 was probably the hydroxo-aluminium (III) species $Al_8(OH)_{20}{}^{4+}$. Their results seemed also to suggest that sulphatohydroxo-aluminium (III) ions were present in acid sulphate solutions, but they were unable to identify individual species.

Crystal structure analyses of basic aluminium sulphates that have been performed to date confirm the existence of polynuclear ions. The crystal structure of the synthetic basic aluminium sulphate $13Al_2O_3.6SO_3.79H_2O$ (Johansson, 1963) shows the presence of the large complex ion $Al_{13}O_4(OH)_{25}(H_2O)_{11}{}^{6+}$ containing aluminium in both four and six coordination. The crystal structure of aluminite $Al_2SO_4(OH)_4.7H_2O$ (Sabelli and Ferroni, 1978), a mineral sometimes found in association with basaluminite, shows the presence of the complex ion $Al_4(OH)_8(H_2O)^{4+}$. This consists of aluminium ions octahedrally coordinated to hydroxyl ions and water molecules to form a cluster of four edge-sharing octahedra. These clusters are linked together to form chains. On the basis of their work, Sabelli and Ferroni (1978) suggest that hydrobasaluminite and basaluminite also possess structures containing some type of polynuclear complex ion.

Occurrence. The minerals were found in the *athleta* Zone of the Oxford Clay at Crook Hill Brickyard, Chickerell, near Weymouth, Dorset (National Grid map reference SY644797). The pit, now abandoned, exhibits about thirty metres of pyritic bituminous shales and clays containing several horizons with large septarian concretions. Full stratigraphic details are given by Arkell (1947) and details of the mineralogy and geotechnical properties of the clays are given by Jackson (1973).

FIG. 1. Basaluminite associated with gypsum surrounding calcareous septarian concretion.

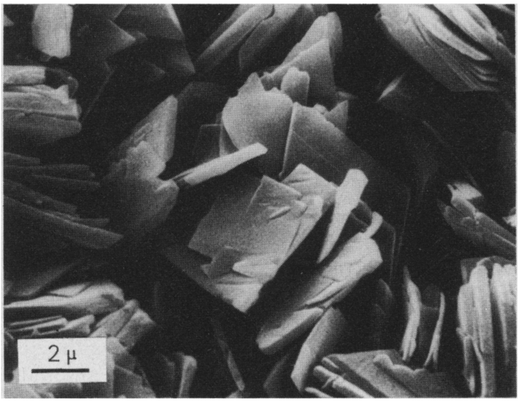

FIG. 2. Scanning electron micrograph of basaluminite from Chickerell.

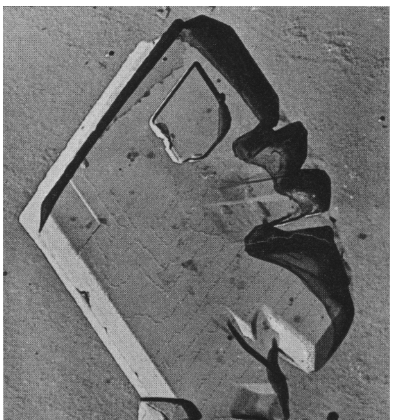

FIG. 3. Transmission electron micrograph of carbon replica of basaluminite crystal.

The upper five metres of the pit lie within the weathering zone. Septarian concretions below this zone are unaltered and consist principally of grey argillaceous limestone. Within the weathering zone two horizons of concretions can be observed. The upper horizon is situated approximately one metre from the top of the pit, and here the concretions have weathered brown with a yellow-brown crust of limonite and jarosite. In the lower horizon, situated approximately two metres below the upper horizon, the concretions have also weathered brown but possess a rim up to five centimetres wide (fig.1). The rim consists of crystals of gypsum, mainly of lenticular habit, the spaces between these crystals being filled with a white plastic fine-grained material which on X-ray examination proved to be hydrobasaluminite. The material was kept in sealed jars to prevent dehydration. Basaluminite was not observed in situ, but only in concretions that had fallen to the floor of the pit, suggesting that it is formed only as the dehydration product of hydrobasaluminite.

The field evidence thus suggests that the formation of hydrobasaluminite and basaluminite is controlled by weathering. The unweathered clay contains abundant pyrite and within the weathering zone this is oxidised and hydrolysed to produce acid sulphate solutions with sufficiently low pH to mobilize aluminium from the clays. The calcareous septarian concretions act as a geochemical barrier to such solutions, neutralizing them and precipitating gypsum at the reaction interface. The aluminium can no longer be held in solution at the higher pH, and is precipitated either directly as hydrobasaluminite or as an amorphous gel which subsequently ages to hydrobasaluminite.

Electron microscopy. Basaluminite was examined using both scanning and transmission electron microscopy. The scanning electron micrograph (fig.2) shows that the crystals consist of thin plates possessing rhombic outlines with dimensions of the order of a few microns. In the case of transmission electron microscopy, the crystals were examined both directly and as replicas. Replicas were prepared by evaporating a film of carbon onto the crystals and shadowing with gold at an angle of 45°. A typical electron micrograph of a replica is shown in fig. 3. Close examination of the scanning electron micrographs and the replicas, using the shadowing to distinguish between features not in the same plane, indicates that the majority of the crystals possess the habit idealized in fig.4. Although accurate measurements of the angles between the faces of the crystals cannot be made, the most likely interpretation of the morphology is that the crystals are monoclinic, point group 2/m, with the unique two-fold axis of symmetry coincident with the intermediate dimension of the crystal. Using the conventional choice of crystallographic axes in the monoclinic system this will be referred to as the b axis. The choice of the other two axes in the monoclinic system is somewhat arbitary but, since the crystals invariably occur as thin plates, a convenient choice would be to make the a crystallographic axis parallel to the long dimension of the crystal. This would make the large faces of the crystal {001}, and the direction normal to them would be c*. Determination of the axial ratio a/b from the replica on the assumption that the inclined faces are of type {hhℓ}, where ℓ may be zero, gives a value of 1.48.

Electron diffraction. Selected-area electron diffraction patterns were obtained for crystals which had been deposited onto aluminium-coated carbon grids. The aluminium produced rings of known d-spacing which acted as a calibration standard. Electron micrographs of the crystals producing the patterns were also obtained. After correction for rotation of the electron beam, the relative orientation of the diffraction pattern to the crystal morphology was established. Because of the presence of a vacuum and the heating effect of the electron beam, it was difficult to be sure which of the dehydration states was actually being examined. Selected-area diffraction patterns were obtained for crystals of basaluminite that has been heated to 160°C and allowed to rehydrate. The patterns showed no change in the positions of the spots but a more uniform distribution of intensities was observed. This shows that crystallographic continuity is retained and that dehydration and rehydration do not involve any major structural changes in the ab plane. A typical selected-area electron diffraction pattern is shown in fig.5 along with the orientation of the crystal from which the pattern was obtained. It can be seen that the reflections lie on a primitive rectangular net with spacings of 14.8Å and 10.0Å. The former corresponds to the long direction of the crystal whilst the latter corresponds to the intermediate direction. Such an arrangement is consistent with the proposed monoclinic symmetry. The spacing of 14.8Å is thus coincident with the proposed a crystallographic axis and the spacing of 10.0Å is coincident with the proposed b crystallographic axis. Since the electron beam is parallel to c*, these spacings represent actual lattice parameters along the a and b axes. Hence a = 14.8Å and b = 10.0Å. This gives an axial ratio a/b of 1.48 which is identical to that obtained from the crystal morphology.

X-ray diffraction. X-ray powder patterns were recorded for hydrobasaluminite and basaluminite and their various dehydration states using a diffractometer with an attached heating-stage. This enabled the phases to be studied at their temperatures of formation and avoided any problems due to premature rehydration. In every phase encountered during the study, the X-ray intensities were dominated by the reflection of largest d-spacing. This was always accompanied by an intense reflection at approximately half this spacing. Material which had been oriented by deposition from suspension gave X-ray patterns showing considerable enhancement of these reflections. It was thus concluded that they corresponded to basal reflections from lattice planes parallel to the large crystal faces. These would be indexed as 00ℓ if the assignment of the a and b axes described above was accepted.

The most highly hydrated state encountered was the mineral hydrobasaluminite. It was unstable under normal laboratory conditions, dehydrating irreversibly to form basaluminite. It could be preserved indefinitely, however, in the presence of moisture. Because of this instability, hydrobasaluminite was studied only as a random powder and was always kept moist. Four orders of basal reflection were observed over the range scanned, possessing d-values of 12.59Å, 6.30Å, 4.21Å and 3.15Å. As was observed previously by Sunderman and Beck (1969), the transformation of hydrobasaluminite to *basaluminite* was found to be discontinuous, no intermediate basal spacings being recorded. It was marked by a distinct change in the physical properties of the material, going from a dull-white plastic state to a chalky-white brittle state. Basaluminite possessed basal spacings of 9.36Å and 4.68Å, no third or fourth order reflections being observed. The mineral was stable indefinitely under normal laboratory conditions, although Brydon and Singh (1969) have shown that it is unstable at 0% relative humidity.

In preliminary heating experiments, an oriented smear slide of basaluminite was prepared and mounted on the diffractometer heating-stage. The temperature was raised in steps of approximately 10°C and held at each new temperature for at least four hours. The basal spacings were recorded, and if any change was observed the temperature was held constant for a further sixteen hours. After any major change the sample was allowed to cool to room temperature in order to establish whether the change was reversible. No attempt was made to control the humidity but it was monitored during the experiments.

Basaluminite was found to dehydrate at a temperature of approximately 40°C at a relative humidity of between 55% and 65%. The initial product of dehydration was somewhat sensitive to the relative humidity but at 65% humidity it possessed broad basal reflections with d-spacings of 8.29Å and 4.08Å. Both reflections showed considerable asymmetry towards higher d-spacings. This asymmetry, coupled with the non-integral nature of the basal spacings, suggested that some type of interstratified species was present. No superlattice reflections indicative of regular ordering were observed. As the temperature was increased the reflections became sharper and less asymmetrical and their d-spacings gradually contracted. At 90°C they had reached maximum sharpness and possessed basal spacings of 7.92Å and 3.96Å which can be seen to show an integral relationship to each other. This fully contracted phase will be referred to as basaluminite dehydrate (I). On cooling, the *contraction* was reversed and basaluminite was reformed. Intermediate interstratified species were also observed. These possessed the same range of d-spacings observed on heating, but lack of humidity control made it impossible to establish whether equilibrium was reached at any given temperature. The TGA curve (fig. 7) described below shows that the dehydration does not take place as a single continuous event, but consists of a discontinuous weight loss followed by a continuous one. This suggests that the first part of the dehydration consists of the production of a relatively stable interstratified species, which subsequently dehydrates via a continuous series of interstratified species containing fewer and fewer water layers. The more highly dehydrated end-member of the interstratified species need not be basaluminite but could be

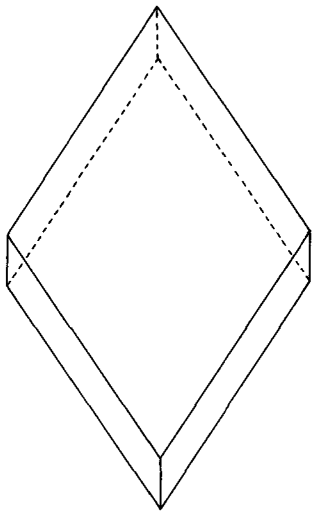

FIG. 4. Idealized habit of basaluminite crystals.

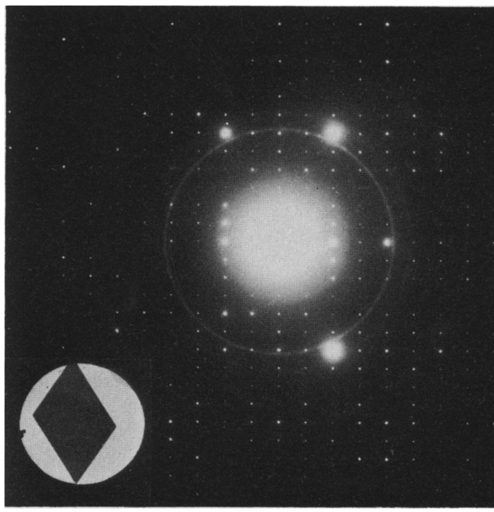

FIG. 5. Selected-area electron diffraction pattern of basaluminite crystal.

TABLE I. X-ray data

Hydrobasaluminite

I	d_{obs}	d_{calc}	hkl
100	12.59	12.611	001
3	8.08	8.091	110
1	7.81	7.832	011
2	7.62	7.629	111
10	6.30$_{o}$	6.305	002
3	6.21^{o}	6.208	111
9	5.91	5.915	211
		5.906	202
3	5.67^{o}	5.674	210
4	5.62^{o}	5.620	112
8	5.33	5.333	012
10	5.26	5.263	201
1	5.00	4.996	020
11	4.693$_{o}$	4.697	120
2	4.656^{o}	4.657	211
		4.652	302
		4.645	021
1	4.601	4.602	121
		4.595	300
3	4.511	4.509	112
1	4.420	4.413	203
9	4.205$_{o}$	4.204	003
3	4.169^{o}	4.175	310
3	4.127	4.130	221
		4.127	113
1	4.044	4.045	220
11	3.960	3.961	202
4	3.877	3.875	013
		3.869	301
11	3.681^{b}	3.703	401
		3.682	212
		3.669	402
1	3.523	3.523	321
4	3.472$_{o}$	3.472	411
1	3.437^{o}	3.446	400
		3.444	412
		3.430	113
2	3.404	3.405	322
1	3.361	3.365	104
		3.356	123
3	3.218	3.220	031
		3.217	214
		3.217	023
1	3.192^{o}	3.191	413
		3.189	114
2	3.152	3.153	004
3	3.094	3.093	323
4	3.061	3.059	321
2	3.033	3.033	231
		3.031	312
1	3.000$_{b}$	2.999	230
3	2.948^{b}	2.953	404
		2.948	123
		2.945	032
1	2.910$_{o}$	2.911	411
1	2.831^{o}	2.832	414
2	2.813$_{o}$	2.815	231
1	2.745^{o}	2.748	513
1	2.727	2.728	205
1	2.700	2.697	330
1	2.660	2.659	233
		2.658	510
1	2.635	2.635	223
1	2.558$_{b}$	2.557	522
3	2.539^{b}	2.545	412
		2.544	514
		2.543	333
		2.542	424
1	2.483	2.485	602
		2.481	523
1	2.452	2.451	041
1	2.430	2.430	601
		2.427	511
1	2.416	2.414	520
4	2.383	2.383	141
1	2.364$_{b}$		
1	2.335^{b}		
1	2.300		
1	2.274$_{o}$		
1	2.257^{o}		
2	2.240^{o}		
1	2.226^{o}		
1	2.211^{o}		
1	2.197^{o}		
2	2.186		
1	2.158		
1	2.116		
2	2.088		
3	2.064		
1	2.040$_{b}$		
1	2.020^{b}		
1	2.002		
1	1.955		
1	1.878		

a = 14.911(5)Å

b = 9.993(2)Å

c = 13.640(5)Å

β = 112.40(4)°

Basaluminite

I	d_{obs}	d_{calc}	hkl
100	9.36	9.373	001
2	7.82	7.829	110
6	7.32	7.334	201
		7.327	111
7	6.84	6.842	011
13	5.91	5.916	211
8	5.32	5.320	210
5	5.22	5.215	111
6	5.00$_{o}$	5.006	020
20	4.723^{o}	4.737	212
27	4.681	4.686	002
5	4.536	4.538	121
5	4.418	4.420	311
		4.415	021
5	4.242	4.244	012
2	4.135	4.134	221
5	3.924	3.926	211
5	3.870	3.872	121
10	3.687	3.692	203
		3.685	122
5	3.617$_{o}$	3.615	401
5	3.464^{o}	3.464	213
9	3.445	3.442	412
4	3.400	3.400	411
4	3.224$_{o}$	3.225	130
1	3.184^{o}	3.187	131
4	3.142	3.144	031
		3.140	400
3	3.079	3.077	311
3	3.020$_{o}$	3.016	122
4	2.957^{o}	2.958	422
5	2.923^{o}	2.922	212
8	2.835	2.835	232
		2.834	501
10	2.720	2.724	513
		2.723	423
		2.723	204
		2.718	032
4	2.692^{o}	2.692	332
5	2.660	2.660	420
3	2.625	2.627	214
2	2.595	2.596	414
2	2.554$_{o}$	2.555	522
2	2.502^{o}	2.503	040
		2.501	132
6	2.464	2.466	521
		2.464	523
		2.463	602
4	2.440	2.442	333
		2.438	141
2	2.390	2.392	224
		2.392	612
3	2.321^{o}	2.322	331
7	2.300	2.300	421
10	2.275$_{b}$	2.274	142
3	2.245^{b}	2.245	520
3	2.209	2.211	405
		2.210	622
		2.208	042
7	2.195	2.197	623
		2.194	342
1	2.157	2.159	415
		2.159	241
		2.159	533
		2.156	501
2	2.133	2.134	402
		2.131	334
2	2.108^{b}	2.110	234
		2.110	104
		2.108	621
		2.107	511
3	2.092	2.093	434
		2.093	600
3	2.072	2.074	624
		2.074	713
		2.072	243
4	2.037	2.036	303
		2.036	143
1	1.997	2.000	615
		1.995	313
2	1.975	1.976	525
3	1.964	1.964	225
		1.963	422
12	1.888	1.890	204
		1.888	625
1	1.862		
6	1.842		
1	1.809		
2	1.787		
5	1.773		

a = 14.857(4)Å

b = 10.011(3)Å

c = 11.086(7)Å

β = 122.28(3)°

Basaluminite dehydrate (I) at 90°C

I	d_{obs}	d_{calc}	hkl
100	7.92	7.923	001
7	6.66	6.649	200
9	6.21	6.206	011
12	5.53	5.534	210
5	4.994$_{b}$	4.992	020
6	4.690^{b}	4.673	120
15	4.383^{o}	4.366	311
27	4.322	4.320	121
		4.311	202
5	4.224	4.223	021
5	4.053$_{b}$	4.051	310
22	3.964^{b}	3.962	002
		3.958	212
11	3.919^{o}	3.927	211
16	3.681	3.682	012
		3.679	401
16	3.453	3.452	411
4	3.320	3.324	400
		3.314	320
2	3.263	3.263	222
11	3.100	3.105	131
		3.103	022
11	3.072	3.072	322
		3.068	031
3	2.984	2.980	231
3	2.782	2.785	212
		2.781	422
5	2.760	2.762	313
		2.759	321
4	2.734$_{b}$	2.734	512
4	2.626^{b}	2.634	232
		2.625	231
		2.615	413
2	2.591	2.591	411
2	2.528	2.531	332
		2.526	521
20	2.470	2.470	522
15	2.395	2.397	141
15	2.363^{o}	2.363	421
		2.361	432
4	2.217^{b}	2.220	523
		2.220	341
		2.216	322
		2.216	600
15	2.182^{o}	2.183	622
		2.179	613
		2.178	621
15	2.163^{o}	2.164	123
		2.164	142
		2.164	610
		2.161	532
2	2.110	2.112	042
		2.109	213
		2.107	414
3	2.065	2.065	441
7	2.040	2.038	623
7	1.962	1.963	422
		1.962	713
		1.961	632
20	1.898	1.900	700
		1.899	541
		1.898	313
		1.898	243
2	1.872	1.873	143
10	1.809	1.810	233
		1.809	434
		1.809	812
		1.809	251
15	1.802	1.803	323
		1.800	621
		1.797	432

a = 14.717(3)Å

b = 9.983(3)Å

c = 8.769(4)Å

β = 115.37(2)°

Basaluminite dehydrate (II) at 160°C

I	d_{obs}	d_{calc}	hkl
100	7.56	7.553	001
2	6.99	6.993	200
10	6.17	6.171	201
6	6.05^{o}	6.095	111
		6.012	011
2	5.88^{o}	5.923	101
5	5.23	5.242	211
15	4.958	4.967	020
14	4.683	4.680	120
50	4.482$_{b}$	4.486	201
6	4.208^{b}	4.222	311
		4.220	310
		4.177	121
8	4.080^{b}	4.088	211
20	3.776$_{b}$	3.776	002
3	3.584^{b}	3.598	212
3	3.504^{o}	3.511	301
		3.497	400
8	3.401	3.410	411
		3.400	321
		3.399	320
4	3.330^{b}	3.329	221
2	3.104$_{b}$	3.100	122
3	3.023^{b}	3.032	031
4	2.947	2.947	412
2	2.860	2.859	420
3	2.663	2.664	231
1	2.521	2.527	521
		2.518	003
		2.513	232
8	2.438	2.440	013
		2.437	520
14	2.394	2.393	501
1	2.355	2.358	522
		2.354	103
10	2.278	2.285	323
		2.283	322
		2.271	612
3	2.210^{b}	2.207	232
14	2.173	2.173	241
14	2.155	2.156	521
3	2.074	2.075	042
6	2.014	2.014	613
		2.013	611
4	1.973	1.974	502
		1.974	303
4	1.903	1.903	242
		1.900	623
3	1.854	1.855	014
		1.854	720
		1.853	504
6	1.830	1.835	522
		1.835	323
		1.832	801
		1.828	351
		1.828	350
2	1.814	1.818	124
		1.816	251
		1.815	802

a = 14.709(6) Å

b = 9.933(4)Å

c = 7.943(5)Å

β = 108.03(3)°

Basaluminite dehydrate (III)

I	d_{obs}	d_{calc}	hkl
100	8.31	8.307	002
8	6.92	6.924	200
16	6.76	6.751	111
10	5.96	5.952	211
4	5.01	5.004	020
6	4.850	4.846	013
		4.839	302
5	4.723	4.728	213
16	4.420	4.420	311
28	4.309	4.308	204
24	4.150$_{o}$	4.154	004
4	4.047^{o}	4.056	220
		4.034	313
1	3.902	3.896	122
3	3.703$_{o}$	3.702	402
3	3.482^{o}	3.489	213
		3.478	322
3	3.449^{o}	3.462	400
		3.439	411
3	3.361^{o}	3.360	413
3	3.323^{o}	3.330	115
		3.330	215
		3.322	124
2	3.265^{o}	3.271	031
		3.265	224
3	3.234	3.234	131
1	3.153	3.154	015
		3.151	315
2	3.046	3.051	324
		3.041	231
1	2.975^{o}	2.976	422
6	2.920^{o}	2.925	106
		2.916	313
12	2.886	2.886	322
		2.880	231
4	2.853	2.853	402
1	2.763	2.762	331
		2.758	424
2	2.660	2.660	333
3	2.553	2.557	515
		2.551	522
		2.550	226
5	2.477^{o}	2.478	422
5	2.455^{o}	2.455	524
3	2.403	2.403	142
1	2.354	2.354	035
		2.353	335
		2.353	240
2	2.215^{o}	2.214	308
		2.210	622
8	2.178	2.180	144
		2.178	624
2	2.149^{o}	2.152	522
3	2.080	2.080	424
1	2.017	2.017	626
12	1.912	1.912	326
		1.912	542
		1.912	246
3	1.898	1.899	528
		1.896	153
2	1.855	1.857	540
		1.856	046
		1.856	717
		1.855	524
		1.854	351
		1.854	711
2	1.842	1.843	137
		1.841	726
		1.840	720

a = 14.835(3)Å

b = 10.007(2)Å

c = 17.800(7)Å

β = 111.02(2)°

b = broad

o = overlapped

an unstable intermediate hydrate. A further study of this dehydration using a controlled-humidity cell is needed.

From 100°C to 120°C the intensities of the basal reflections decreased slightly, accompanied by a slight contraction of the basal spacings. At 130°C a completely new X-ray diffraction pattern was observed. The initial product had basal reflections with basal spacings of 7.60Å and 3.78Å, both showing slight asymmetry towards higher d-spacings. By 160°C these peaks reached a maximum sharpness and possessed spacings of 7.54Å and 3.77Å. This phase will be referred to as basaluminite dehydrate (II). Unlike the previous dehydration, no evidence of a two-step reaction was observed in the TGA curve. It was concluded that the intermediate spacings correspond to interstratifications of basaluminite dehydrate (I) and basaluminite dehydrate (II) which occur as a result of incomplete dehydration. This could be due to layer inhomogeneity or to difficulties in removing residual isolated pockets of water. At higher temperatures the intensities of the peaks decreased without further contraction of the d-spacings and by 200°C they had completely disappeared, leaving an amorphous residue.

The dehydration of basaluminite dehydrate (I) to basaluminite dehydrate (II) was not reversible. When cooled at room temperature in the presence of moisture, basaluminite dehydrate (II) rehydrated to form a new phase which will be referred to as basaluminite dehydrate (III). This phase possessed basal spacings of 8.31Å and 4.15Å and was identical to the phase described as metabasaluminite by Hollingworth and Bannister (1950). On reheating basaluminite dehydrate (III) a slight contraction of the basal spacings was observed to occur at about 100°C. At 110°C it decomposed to give an initial product with basal spacings of 7.64Å and 3.79Å showing pronounced asymmetry towards higher d-spacings. These reached maximum sharpness at 160°C, giving basal spacings of 7.54Å and 3.77Å corresponding to basaluminite dehydrate (II). As with the dehydration of basaluminite dehydrate (I) to basaluminite dehydrate (II), no evidence of a two-step reaction was observed, and the intermediate spacings were taken to be due to interstratified basaluminite dehydrate (III) and basaluminite dehydrate (II).

Intensities and d-spacings were recorded for random-powder mounts of hydrobasaluminite at 23°C, basaluminite at 23°C, basaluminite dehydrate (I) at 90°C, basaluminite dehydrate (II) at 160°C and basaluminite dehydrate (III) at 23°C. Silicon powder (a = 5.4308Å) was used as an internal standard. The change in lattice parameter of silicon over this temperature range was considered to be negligible. Scans were made over the angular range 2° to 50° (2θ) at an angular velocity of 1/4° (2θ) per minute using Ni-filtered Cu-Kα radiation. Intensities were measured in terms of peak heights. Because of the platy nature of the crystals, preferred orientation was impossible to eliminate, and the intensities are not exactly reproducible. The results are given in Table I.

Indexing of the X-ray powder patterns. Since approximate values for the a and b unit-cell parameters had already been determined by electron diffraction, only values of c and β remained to be determined if, in fact, the unit cell was monoclinic. The strong reflections with d-spacings of 9.36Å and 4.68Å, considered to represent lattice planes parallel to the large crystal faces of basaluminite, were provisionally indexed as 001 and 002 respectively. This gave a value for $c \sin\beta$ of 9.36Å and determination of either c or β would automatically give the other. A trial and error method for the determination of β was used. The first twenty possible d-spacings were calculated for unit cells having the parameters already determined and β angles ranging from 90° to 135° in steps of 1°. Inspection showed that the only reasonable fit with the observed spacings was obtained when β was equal to 122°. Using this value, a full set of possible reflections was calculated and as many reflections as possible were indexed. A new set of more accurate unit-cell parameters was calculated using a least-squares procedure. This was repeated until all the reflections had been indexed. No reflections present in the powder pattern remained unaccounted for. The principal difficulty was the usual ambiguity in indexing at low d-spacings. Only peaks that could be uniquely indexed and were free from overlap were used in the final determination of the unit-cell parameters.

It would seem that the deduction of monoclinic symmetry for basaluminite made from the crystal morphology is justified by the fitting of a monoclinic unit cell to the X-ray powder pattern. It is still possible that the mineral might be triclinic, but no transformed cell of higher symmetry could be found. Because of the difficulty of recognising weak reflections in X-ray powder patterns, the possibility of a larger monoclinic unit cell cannot be discounted.

In the other phases, there was no difficulty in recognising 001 and 002 reflections equivalent to those of basaluminite. However, there were no distinct non-basal reflections that could be traced unambiguously from phase to phase. This made it necessary to repeat the indexing procedure described above for each of the phases. This was successful with hydrobasaluminite and basaluminite dehydrate (I) where excellent fits were obtained. In the case of basaluminite dehydrate (II), line broadening, particularly of the non-basal reflections, led to a greater number of overlapping reflections. This made indexing more difficult and less reliable and the fitted unit cell should be regarded in this light. In the case of basaluminite dehydrate (III), it proved impossible to fit a unit cell using the parameters obtained above. If the value of $c \sin\beta$ was doubled, however, it became possible to index the pattern. All reflections could be accounted for by indices that satisfied the criterion $k + \ell = 2n$ which suggests that an A-centered cell is present. It seems, therefore, that the dehydration of basaluminite dehydrate (III) to basaluminite dehydrate (II) involves a translation of $b/2$ between adjacent layers.

Table I gives the indexed powder patterns of the five phases determined along with their respective unit-cell parameters. It can be seen that as well as major contractions in the c^* direction, dehydration is accompanied by slight shrinkages in the a and b directions. Since individual non-basal reflections were not followed from phase to phase, the true relative orientations of the unit cells of the various dehydration states are not known. This means that true translations, rather than just shrinkages in the c^* direction, cannot be unambiguously determined. It also means that reflections from structurally equivalent lattice planes do not necessarily have the same ℓ index. Nevertheless, it can be seen that the indexed patterns show considerable similarities. In particular, the relatively frequent occurrence of reflections of type 52ℓ and 62ℓ at higher angles should be noted.

Chemical Analysis. Small uncontaminated aggregates were removed from the concretions and gently ground to pass a 100 mesh sieve. The resulting powder was examined for impurities. No impurities were revealed by X-ray diffraction, although optical examination revealed the presence of a small quantity of gypsum. The powder was air-dried over a period of several months in an atmosphere whose relative humidity was maintained at around 55%.

The principal difficulties in the chemical analysis of basaluminite were caused by the low temperature of dehydration of the mineral. This meant that removal of adsorbed water by drying at 110°C was not possible, and hence the estimate of H_2O necessarily includes adsorbed water.

Table II. Chemical composition of basaluminite from Chickerell

	1	2	3	4
Al_2O_3	44.75	0.439	0.439	1.98
CaO	0.20	0.004		
SO_3	18.10	0.226	0.222	1.00
H_2O	35.60	1.976	1.969	8.87
Insoluble residue	0.72			
	99.37			

1. Chemical analysis in weight percent
2. Molecular proportions
3. Molecular proportions recalculated after removal of gypsum
4. Recalculated molecular proportions normalized to SO_3 = 1

Also, since the analysis of each constituent was performed on a different portion of material, it was necessary to keep the amount of adsorbed water constant. For this reason the material was stored and also weighed at a constant relative humidity.

A rapid analysis by X-ray spectrometry showed that the only cations present in amounts greater than 0.1% were aluminium and calcium. Infrared gas analysis showed the carbonate content to be insignificant. Thus the calcium can be regarded as present as gypsum contamination. Determinations were made of the five components Al_2O_3, CaO, SO_3, H_2O and insoluble residue on separate portions of material. The basaluminite was taken into solution using concentrated hydrochloric acid, excess acid being removed by evaporation.

The insoluble residue was removed by filtration and the weight recorded. Al_2O_3 was determined gravimetrically as alumina after ignition of aluminium hydroxide precipitated by ammonium hydroxide. CaO was determined by atomic absorption spectrometry and SO_3 was determined gravimetrically as barium sulphate after precipitation by barium chloride. Water was determined by weight loss at 550°C. It has been shown by Davey et al. (1963) that the last traces of water are difficult to remove from compounds of this type, and it is likely that the water determination is slightly too low. The chemical analysis of basaluminite is shown in Table II. Column 1 gives the weight percentages, column 2 the molecular proportions and column 3 the molecular proportions after the removal of all the CaO as gypsum. Column 4 shows the resulting molecular proportions recalculated to an SO_3 value of 1. The chemical composition of basaluminite can thus be represented as $2Al_2O_3.SO_3.8.9H_2O$, giving a formula of $Al_4SO_4(OH)_{10}.3.9H_2O$ if it is assumed that H_2O is present only as water or hydroxyl ions. This makes the number of water molecules one less than previously reported analyses, although Brydon and Singh (1969) report analyses consistent with a water content of around $9H_2O$ and Srebrodol'skiy (1969) obtained a value of $8.3H_2O$. In view of the low temperature of dehydration of basaluminite and the interstratified nature of the initial product, it is possible that significant numbers of dehydrated layers could be present in basaluminite without being detected by X-ray diffraction. This would make the water content somewhat low and also temperature and humidity dependent. Nevertheless, the closeness of the obtained value to an integral number suggests that the ideal water content is $9H_2O$ and that previous analyses have included substantial amounts of adsorbed or impurity water.

Specific gravity. Specific gravity was determined for basaluminite by pycnometer and gave a value of 2.10. This compares with the values of 2.08, 2.10 and 2.12 obtained by Sunderman and Beck (1969), Tien (1968) and Hollingworth and Bannister (1950) respectively. On the basis of a chemical composition of $2Al_2O_3.SO_3.9H_2O$, a value of Z = 4 and a calculated specific gravity of 2.12 was obtained. This gives a composition of $8Al_2O_3.4SO_3.36H_2O$ for the unit cell of basaluminite which would be equivalent to a formula of $Al_{16}(SO_4)_4(OH)_{40}.16H_2O$.

Differential thermal analysis. Differential thermal analysis of basaluminite was performed over the range 20°C to 800°C in a nitrogen atmosphere at a heating rate of 10°C per minute. The resulting curve is shown in fig.6a. It is virtually identical with those obtained by Brydon and Singh (1969) for basaluminite from Kansas and Northamptonshire. It possesses endotherms at 121°C, 157°C, 202°C and 344°C. By halting the runs before and after each endotherm and examining the products by X-ray diffraction, it was found possible to assign the various transformations. It should be noted that there is the usual lag between the temperatures of reaction determined by X-ray diffraction and those determined by DTA, in this case approximately 80°C. The endotherm at 121°C corresponds to the initial dehydration of basaluminite. The product observed by X-ray diffraction was an interstratified phase. The second endotherm at 157°C corresponds to the dehydration of this interstratified phase to basaluminite dehydrate (I). Thus the DTA data seem to confirm the two-step nature of the transformation between basaluminite and basaluminite dehydrate (I). The third endotherm at 202°C corresponds to the irreversible dehydration of basaluminite dehydrate (II). The final large endotherm at 344°C represents the dehydroxylation of basaluminite dehydrate (II). Brydon and Singh (1969) observed further endotherms corresponding to the loss of sulphate, but these were not studied during the present investigation. DTA of basaluminite dehydrate (III) which was prepared by the rehydration of basaluminite dehydrate (II) showed the presence of only two major endotherms (fig.6b). The first at 196°C corresponds to the dehydration of basaluminite dehydrate (III) to basaluminite dehydrate (II). No evidence of a two-step reaction was observed in this case, the very small endotherm at 120°C being attributed to residual basaluminite. The second endotherm at 333°C corresponds to the dehydroxylation of basaluminite (II) described previously.

Weight-loss studies. In order to establish the number of water molecules associated with each of the phases encountered during dehydration and rehydration, weight-loss determinations were made using both static and dynamic methods. In the case of the transformation of hydrobasaluminite, the weight loss was recorded after dehydration at room temperature for several months. The relative humidity was maintained at around 55%. A weight loss of 31.4% was recorded. On the basis of a basaluminite composition of $2Al_2O_3.SO_3.8.9H_2O$, this would be equivalent to the loss of 11.3 water molecules and would give a chemical composition of approximately $2Al_2O_3.SO_3.20H_2O$ for hydrobasaluminite. This would correspond to a formula of $Al_4SO_4(OH)_{10}.15H_2O$ if only hydroxyl ions and water molecules were present. Comparison of this composition with the composition of $2Al_2O_3.SO_3.41H_2O$ obtained by Hollingworth and Bannister (1950), the composition of $2Al_2O_3.SO_3.33H_2O$ obtained by Tien (1968) and the composition of $2Al_2O_3.SO_3.17H_2O$ obtained by Sunderman and Beck (1969) emphasises the difficulty involved in differentiating between adsorbed and structural water in these minerals.

The weight changes associated with the transformations between basaluminite and its dehydration products were investigated by thermogravimetric analysis. Fig.7a shows the curve obtained from air-dried basaluminite heated at a rate of 5°C per minute in a flow of nitrogen. Fig.7b shows the curve obtained from basaluminite dehydrate (III) which had been formed by heating basaluminite to 160°C and allowing to cool in air. Even at the slowest heating rate, it was considered unlikely that maximum weight loss has been reached at any given temperature, and the results were supplemented by static weight-loss determinations at specific temperatures.

The weight loss corresponding to the transformation of basaluminite to basaluminite dehydrate (I) can be seen to occur in two steps. The first step appears to be discontinuous and occurs at around 55°C. This corresponds to the discontinuous transformation of basaluminite to an interstratified phase observed to occur at 40°C by X-ray diffraction. The second step appears to be continuous over the temperature range 65°C to 100°C, the TGA trace being virtually a straight line. This corresponds to the continuous contraction of the basal spacings observed by X-ray diffraction over the temperature range 60°C to 90°C. This can be explained in terms of dehydration via a continuous series of interstratified species containing fewer and fewer water layers. The total weight loss involved was found to be 10.7%, which corresponds to the loss of 2.7 water molecules on the basis of a basaluminite composition of $2Al_2O_3.SO_3.8.9H_2O$. This would give a chemical composition of $2Al_2O_3.SO_3.6.2H_2O$, which would be equivalent to a formula of $Al_4SO_4(OH)_{10}.1.2H_2O$. It is most likely that the true formula of basaluminite dehydrate (I) is $Al_4SO_4(OH)_{10}.H_2O$, the excess water being due to either incomplete dehydration or retention by adsorption. Because of the consecutive nature of the two steps involved in this dehydration it is difficult to separate them. The point of inflection on the TGA curve corresponds to a weight loss of 6.4% which would be equivalent to the loss of $1.6H_2O$. This would give a composition of approximately $Al_4SO_4(OH)_{10}.2.3H_2O$ for the intermediate phase.

The next weight loss at 150°C corresponds to the dehydration of basaluminite dehydrate (I) to basaluminite dehydrate (II) observed to occur at 130°C by X-ray diffraction. The actual weight loss was found to be 4.5% which is equivalent to $1.1H_2O$. This gives a chemical composition of $2Al_2O_3.SO_3.5.1H_2O$ for basaluminite dehydrate (II) which corresponds to $Al_4SO_4(OH)_{10}.0.1H_2O$. It is almost certain that the ideal loss of water should be $1H_2O$ and that the true formula of basaluminite dehydrate (II) is $Al_4SO_4(OH)_{10}$. This was the most highly dehydrated phase encountered without breakdown of the structure.

The decomposition of basaluminite dehydrate (II) observed to occur at around 270°C is accompanied by a weight loss of 20.4%, which is equivalent to the removal of the remaining 5.1 molecules of water to leave an amorphous residue of $2Al_2O_3.SO_3$.

The TGA curve of basaluminite dehydrate (III) shows a slight gradual weight loss up to 120°C followed by a more rapid weight loss. The total weight loss was found to be 8.7% which is equivalent to $2H_2O$ on the basis of a composition of $2Al_2O_3.SO_3.5H_2O$ for basaluminite dehydrate (II). As before, it is not possible to determine how much of this, if any, is adsorbed water. If it is assumed that all the water present is structural water, this would give a formula of $Al_4SO_4(OH)_{10}.2H_2O$ for this phase.

Discussion. The platy habit of the crystals, the retention of structural continuity during dehydration, and the existence of interstratified species, all suggest that hydrobasaluminite and basaluminite possess some type of layer structure. If the hypothesis of Bassett and Goodwin (1949), that the structures are related to that of gibbsite, is adopted, then the simplest structural arrangement would be based on the assumption that no O^{2-} ions are present and that all the hydroxyl ions are held in a close-packed double-hydroxide layer. Sulphate ions and water molecules would occupy an 'interlayer' situated between the double-hydroxide layers. Aluminium would occupy up to four-fifths of the available octahedral sites rather than two-thirds as gibbsite, although the possibility of some in the interlayer would not be excluded. Support for the presence of relatively free sulphate ions is given by the fact that they can be exchanged for other anions when basaluminite is suspended in appropriate salt solutions. An investigation of these anion-exchange products is in progress. By considering the packing geometry of the double-hydroxide layer, it is possible to find a layer repeat unit with dimensions close to the a and b parameters of hydrobasaluminite and basaluminite that would accommodate all 40 hydroxyl ions present in the unit cell. This repeat unit and its relationship to the unit cell of gibbsite is shown in fig.8. Using the unit-cell parameters for gibbsite, the repeat unit can be calculated to have dimensions of approximately 14.4Å and 10.1Å. These are reasonably close to the values of the a and b parameters of 14.9Å and 10.0Å respectively, which were determined for hydrobasaluminite and basaluminite. Some support for this type of arrangement is given by the X-ray powder intensities, insofar as reflections of type 52ℓ and 62ℓ which are fairly prominent in the powder patterns for all the phases, would be parallel or sub-parallel to planes of hydroxyl ions in the structure. Reflections of this type also appeared to be intense in the electron diffraction patterns, although lack of specimen tilting facilities prevented a systematic study of reciprocal space. It would seem, however, that the value of the basal spacing of 7.5Å obtained for the most highly dehydrated phase, basaluminite dehydrate (II), is too small to accommodate both a double-hydroxide layer and a separate layer containing sulphate ions. This means that either the layer structure is more complicated than that described above or that the sulphate ions are somehow incorporated into the layer. One possibility might be that one or more of the oxygen atoms present in the sulphate tetrahedron replace hydroxyl ions in the layer. This would leave the rest of the tetrahedron 'protruding' from the layer, and would allow collapse of the layers such that protruding sulphate ions from adjacent layers could be accommodated in approximately the same plane. The existence of protruding sulphate ions might also provide an explanation for the formation of the A-centred monoclinic cell of doubled c spacing that was obtained for basaluminite dehydrate (III). This might occur by displacement of alternate double layers as a result of the attached sulphate ions moving to a more favourable position within the interlayer on rehydration. Some support for the incorporation of sulphate ions is given by the fact that they are no longer exchangeable once the irreversible transformation to basaluminite dehydrate (II) has taken place. In view of the rather complex units found in the structures of basic aluminium salts determined to date, however, it seems that little progress towards the true structures of these minerals will be made until material suitable for single-crystal analysis becomes available.

The physical properties described above for basaluminite show many similarities to those of scarbroite, a basic aluminium carbonate mineral described by Duffin and Goodyear (1960). Scarbroite is a fine-grained, white compact mineral found associated with gibbsite in fissures in sandstone at South Bay, Scarborough. The chemical composition was determined to be $Al_2(CO_3)_3.12.9Al(OH)_3.15.6H_2O$ which is almost exactly equal to $Al_5CO_3(OH)_{13}.5.2H_2O$. Although no other phases were detected by X-ray diffraction, the chemical analysis contained several percent of unexplained impurities including 3.2% SiO_2 and 1.8% SO_3. The SiO_2 was attributed to free quartz, but as none was detected by X-ray diffraction it is quite possible that it is present as an amorphous or poorly crystalline alumino-silicate. The SO_3 could be present as sulphate substituting for carbonate in the mineral. Also, as the authors admit, there is the possibility of contamination by small amounts of gibbsite, which is found in association with the mineral. The effect of any of these would be to reduce the aluminium content in the formula unit. It would seem , therefore, that a chemical formula of $Al_4CO_3(OH)_{10}.nH_2O$ analogous to that of basaluminite or one of its dehydration products would not be impossible.

The electron micrograph and electron diffraction pattern of scarborite shown by Brindley and Comer (1960) bear a remarkable similarity to those recorded for basaluminite during this study. Brindley and Comer (1960), however, interpret the electron diffraction pattern as representing a section in a*b* reciprocal space and obtain values of d_{100} = 9.90Å and d_{010} = 14.67Å. This would be true only if the electron beam were parallel to the c axis of the crystal. In fact the electron beam is perpendicular to the large faces of the crystal and can be regarded as

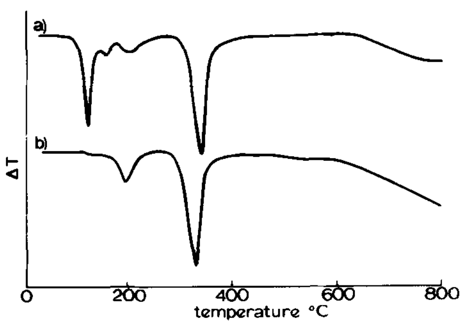

FIG. 6. DTA curve of: (a) basaluminite; (b) basaluminite dehydrate (III).

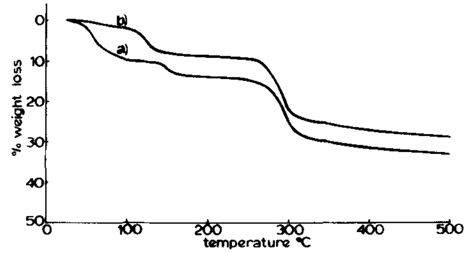

FIG. 7. TGA curve of: (a) basaluminite; (b) basaluminite dehydrate (III).

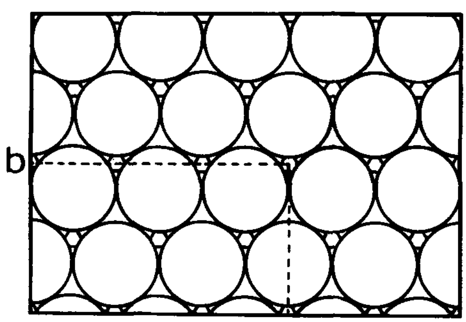

FIG. 8. Possible double-layer arrangement of hydroxyl ions in the unit cell of basaluminite (solid line) and its relationship to the unit cell of gibbsite (dashed line).

being parallel to c*. This means that the spacings obtained from the electron-diffraction pattern give unit-cell parameters a and b, not d_{100} and d_{010}. This casts some doubt on the rather large triclinic unit cell fitted by Duffin and Goodyear (1960) on the basis of these values. Nevertheless, it can be seen that the spacings obtained from the electron diffraction pattern are very close to, although slightly smaller than, those obtained for basaluminite.

The dehydration behaviour of the mineral is similar, but not identical, to that of basaluminite, showing various dehydration states whose powder patterns are dominated by strong basal reflections. Because all the powder patterns were recorded at room temperature it is difficult to relate the phases directly to those obtained in this study, although it is apparent that the basal spacings are generally smaller than those obtained for basaluminite. Treatment of basaluminite with 1M sodium carbonate yields a phase possessing an X-ray powder pattern with d-spacings very close to those of scarbroite. It is thus apparent that scarbroite and basaluminite are very closely related, although the possibility that they represent different hydration states must be borne in mind. A reinvestigation of scarbroite is being undertaken in order to clarify this relationship and perhaps also to provide more information as to the structural characteristics of these minerals.

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