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Basaluminite and hydrobasaluminite, two new minerals from Northamptonshire.

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Introduction.

A WHITE mineral coating joint-faces in quarries in the Northampton ironstone (Inferior Oolite) was long ago recorded as allophane. W. D. Herman who determined the mineral from the surface of a sandstone rock in a quarry opened in 1871 also analysed an unnamed white earthy mineral from crevices in the ironstone and obtained a composition close to that of fully hydrated halloysite.

During the six-inch geological survey of that ironstone field in 1939-44 the occurrence of similarly situated white incrustations and joint infillings was found to be widespread especially in the shallow workings where the ferrous minerals chamosite and chalybite have been oxidized to produce a limonitic ore. In the large Lodge pit of the Irchester Ironstone Company, two miles south of Wellingborough the development of white mineral was much greater than had been observed elsewhere. Fissures up to one foot in width were largely filled with secondary white minerals and rock fragments. A preliminary optical examination by Dr. J. Phemister and X-ray photographs by Dr. G. Nagelschmidt had suggested the presence of more than one mineral in the white portion of the infilling.

A preliminary note recording the presence of two new minerals from Irchester was published in 1948. They are now described in more detail and compared with related species in the British Museum. One of us (S. E. H.) has also added an account of the field relations and possible mode of origin.

GEOLOGICAL OCCURRENCE.

The Irchester pits lie in the south-eastern part of the ironstone field which includes the mines and quarries of the Finedon-Irthlingborough area to the north of the river Nene. This part of the field is the type area for the full lithological succession of the 'eastern type' of ironstone development (Hollingworth and Taylor, 1946). It has also provided much of the material on which recent advances in our knowledge of the petrology of the ironstone seam, and particularly of the lower and upper chamosite-kaolinite groups, have been made (Taylor, 1949). Amongst the changing physical and physico-chemical conditions during deposition that are revealed by variations in lithology and mineral content there is abundant evidence of penecontemporaneous secondary changes such as oxidation of ferrous minerals to limonite, of leaching processes, and of carbonatization. The formation of secondary sphaerosiderite, usually in the upper part of the seam and below a leached zone characterized by rootlets passing down from the overlying Lower Estuarine Series, may be mentioned.

The hydrated silicates and sulphates of aluminium which make up the white mineral of the Irchester fissures will be generally accepted as the products of oxidation and hydrolysis that are part of the weathering processes.

As they are found in the ironstone at Irchester beneath a cover of 60 feet or more of newer strata which includes impervious clays, the possibility arises that they may have been formed during a phase of weathering related to a Jurassic land surface. There is, however, as will be seen later, no evidence to support this view.

The present lie of the Northampton ironstone and overlying rocks on this part of Northamptonshire is attributable to two major factors: (i) the gentle regional dip, a fraction of one degree to the south-east, upon which has been superimposed, (ii) a pronounced local tilting of the strata that is closely related to the form of the ground and represents valleyward down-warping (cambering) or sagging of the strata. Concurrently with these movements new joint patterns were developed and subsidiary faulting occurred ('gulls' and 'dip and fault' structure). These movements have produced marked changes in the dip and altitude of the strata that locally completely mask the effects due to

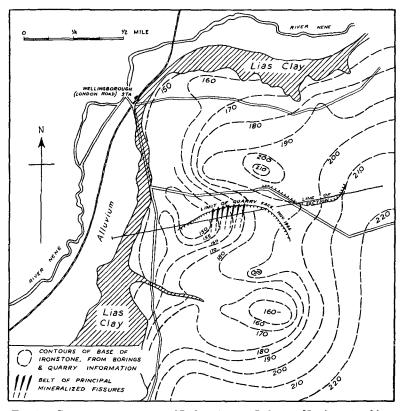


Fig. 1 α . Structure-contour map of Lodge pit area, Irchester, Northamptonshire.

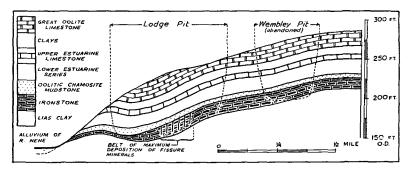


Fig. 1 b. Section across Lodge pit area.

the regional dip. The general principles that appear to apply to these movements have already been described (Hollingworth, Taylor, and Kellaway, 1944), and have been attributed to the valleyward flow of Lias clay causing disruption of the overlying massive beds from the Northampton Sand up to and including the Great Oolite limestone.

In some areas this valleyward down-warping is extremely uniformly developed on the valley side, with increasing inclination on the lower slopes. At other places, however, it is irregular in its development, due, perhaps, to strongly localized outflow of the Lias towards the valley (Hollingworth and Taylor, 1946, p. 229). Excellent examples of the structures produced by such movements are found in the Irchester area in the region that has been extensively bored and subsequently quarried by the Irchester Ironstone Company.

Fig. 1 shows the results of such movements as revealed by the structure contours drawn on the base of the Northampton Sand in the neighbourhood of Lodge pit. Somewhat elongated trough-like depressions opening out towards the valley, and with a rounded closed head towards the plateau are clearly displayed. In one case at least there is a strong suggestion that the depression or sag is an enclosed basin of small extent at its lowest point. The location of the infilled fissures which contain the minerals described below is indicated on this map. The possible significance of the location of these exceptional deposits of hydrated aluminium silicate and sulphate in this basin-shaped structure will be discussed later.

THE DEPOSITS.

The mineral assemblage, including the two new minerals, occurs along joints as a coating on the wall-rock and as filling narrow fissures, or as matrix to the infilling in which there are variable amounts of broken or brecciated rock. Their occurrence compares with that of the mineralized fracture or lode which is typical of many metallic and non-metallic ore-bodies, and they show comparable evidence of a sequence of deposition and of movement along the fractures during the process of infilling. They clearly die out downwards, and were filled in from above (cf. some haematite ore-bodies). At Lodge pit the more important and wider fissures trend approximately N.–S. more or less normal to the working face as seen during the years 1941–8. Other open joints trending E.–W. have coatings of white mineral.

The greatest development of white minerals occurred in N.-S. fissures for some 300-400 yards east from the site of Little Irchester Lodge, the

buildings of which have since been obliterated by the northward advance of the quarry face. In this advance during 1945–8 the width of the fissures gradually decreased and their changing width is illustrated diagrammatically on fig. 1.

Fig. 2 is a composite sketch of a typical major N.-S. fissure. The fissures may be up to one foot wide, but seldom reach down to the base of the ironstone. In this aspect they contrast with the typical silt-filled fissures or 'gulls' described from the Pitsford ironstone quarry (Hollingworth, Taylor, and Kellaway, 1944).

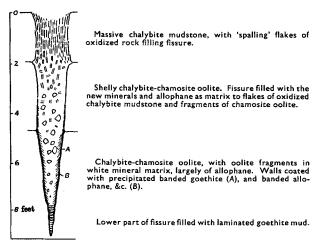


Fig. 2. Diagrammatic section of typical fissure in ironstone.

The uppermost bed of the ironstone is a massive chalybite mudstone which weathers by the spalling off of thin plates, $\frac{1}{8} - \frac{1}{4}$ inch thick, of limonitized chalybite. This appears to have taken place as the fissure opened so as to occupy the space formed, for there is little infilling from above, and only thin coatings of white mineral on the major joints.

In the underlying shelly chalybite-chamosite onlite weathering has oxidized much of the massive joint blocks to ochreous brown limonitic stone with surviving cores of fresh green carbonate stone. An outermost skin to the joint blocks consists of dense dark brown limonite, clearly a secondary enrichment. Deposited on the latter where it forms the wall of a fissure there is usually a thin layer of fairly compacted brown goethite, $\frac{1}{8}$ — $\frac{1}{4}$ of an inch thick, which becomes less prominent in the upper part of the fissure. This goethite shows a banded depositional

structure with minor unevenness due to development of small scale mamillation.

Following this goethite outwards is a second layer. This is usually fairly hard white and yellowish allophane, with well-defined banding consisting of fine alternation of translucent and opaque porcellaneous bands which are nearly vertical adjoining the goethite, but become less inclined away from it, dipping towards the centre of the fissure as if developing a catenary form of lamination. This deposit may be up to an inch thick, but is usually less. Its inner surface is frequently highly indented with small downwardly inclined projections resembling minute stalactites. Secondary fibrous gypsum, presumably of later date, is in places found between this deposit and the rock-wall. Calcite in masses the size of a small pin head, aragonite needles, and long hair-like gypsum crystals all occur locally as a later deposit on the 'allophane' in open fissures.

In some of the larger fissures goethite appears not only on the walls, but also as a finely laminated goethite clay filling the lower part of the fissure. It is a soft inconsolidated greasy clay, but may be contemporaneous with that higher up on the walls.

The central part of the infilling below the chalybite mudstone is a breccia of fragments of the wall-rock in a white matrix consisting of the new minerals basaluminite and hydrobasaluminite associated with allophane. In the upper part fragments are mostly limonitized chalybite mudstone, and in the lower part brown oolitic ironstone. Massive halloysite occurs immediately below the chalybite mudstone. There is some evidence that this assemblage is a late stage in the infilling which is usually preceded by the deposition of (1) goethite, (2) banded allophane.

DESCRIPTION OF THE MINERALS. (F.A.B.)

The white infilling of the ironstone fissures includes a white compact mineral with conchoidal fracture and a white plastic clay-like mineral. The latter rapidly loses water in air and crumbles to a fine powder which does not regain its plastic character when wetted. For this reason several specimens were collected in damp cloths and kept in their original plastic condition by standing them in the upper chamber of a desiccator containing water. Associated minerals from the joints and fissures of the ironstone are gypsum, aragonite, halloysite, and a black manganese oxide gel mineral, an X-ray photograph of which shows only weak haloes, approximate spacings in Å.: 4·7, 3·12, 2·36, 2·20, 1·92, 1·62, 1·41.

Those specimens of the white plastic mineral which were allowed to dry at room-temperatures broke up and revealed inclusions of a compact pale yellow gel mineral identified as allophane with refractive index close to 1.48. The air-dried material is a fine-grained, powdery to compact substance consisting of minute birefringent plates or fibres with mean refractive index 1.519 and specific gravity 2.12. Powder

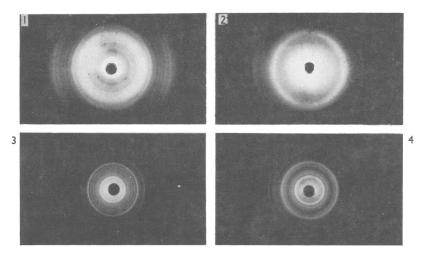


Fig. 3. X-ray powder photographs of: 1, hydrobasaluminite in a sealed lithium glass capillary tube; 2, allophane; 3, basaluminite; 4, metabasaluminite. Taken with filtered copper radiation, $\lambda 1.5418$ Å. in a cylindrical camera 6 cm. diameter.

photographs of a large number of air-dried samples containing the white mineral sometimes showed the presence of allophane haloes (fig. 3, no. 2; approximate spacings in Å.: 3·44 vs, 2·28 s, 1·86 w, 1·40 m, 1·23 w) and all gave the same line-rich pattern excepting for a marked variation in the intensity of the innermost line 12·6 Å. (see table I, cols. 1 and 2; fig. 3, no. 3). Specimens dried in air after powdering for longer periods yielded the same pattern, but with the 12·6 Å. line either very weak or completely missing. These preliminary photographs suggested that at least two minerals are present in the original samples, one of which in the moist state gives a strong X-ray diffraction that disappears when the mineral is dried in air.

A small quantity of the plastic material kept moist in saturated water vapour as described above was quickly packed into a fine capillary of lithium glass both ends of which were then plugged with wax. The capillary was then mounted vertically and the powder photograph obtained (table I, col. 1; fig. 3, no. 1) was found to be quite different from that of the air-dried mineral (table I, col. 2; fig. 3, no. 3). It is above all characterized by the strong diffraction at 12.6 Å. The glass capillary was then unplugged and the plastic contents allowed to dry in air. A further X-ray powder photograph showed the pattern of the air-dried mineral and the pattern of the moist mineral had disappeared.

Table I. X-ray powder data for aluminium sulphate miner	als.
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1		2		3		4		5	
Hydr	0-			Met	a-				
basalum	inite.	Basalun	ainite.	basalum	inite.	Felsőbár	nyite.	Alumin	ite.
12·6 Å.	vvs	9·4 Å.	vs	8·5 Å.	vvs	4·58 Å.	m	9·0 Å.	s
8.08	m	7:18	vvw	6.90	ms	4.24	m	7.8	s
6.18	8	6.73	w	5.97	m	3.58	m b	6.33	$\mathbf{m}\mathbf{s}$
5.29	s	5.92	m	4.90	ms	$3 \cdot 1$	ms b	5.4	\mathbf{m}
4.70	8	5.27	m	4.36	vs	2.68	vw	$5\cdot 2$	$\mathbf{v}\mathbf{w}$
4.23	$\mathbf{m}\mathbf{s}$	4.68	8	4.14	$\mathbf{m}\mathbf{s}$	2.50	w	4.96	\mathbf{m}
4.00	ms:	3.87	m	3.72	vw	2.33	m b	4.7	$\mathbf{m}\mathbf{s}$
3.73	s	3.68	ms	3.46	$\mathbf{m}\mathbf{w}$	2.22	m b	4.18	m b
3.43	m	3.44	m	3.20	w	$2 \cdot 10$	vw	3.72	s
3.21	\mathbf{w}	3.20	vw	2.92	ms	2.00	$\mathbf{v}\mathbf{w}$	3.54	$\mathbf{v}\mathbf{w}$
3.07	S	2.90	\mathbf{w}	2.76	\mathbf{w}	1.910	$\mathbf{m}\mathbf{w}$	3.41	m
2.83	mw	2.82	\mathbf{w}	2.68	\mathbf{w}	1.734	\mathbf{w}	3.31	w
2.57	m	2.71	$\mathbf{m}\mathbf{w}$	2.54	$\mathbf{v}\mathbf{w}$	1.729	$\mathbf{v}\mathbf{w}$	3.16	w
$2 \cdot 41$	\mathbf{m}	2.45	$\mathbf{m}\mathbf{w}$	2.48	m	1.685	$\mathbf{v}\mathbf{w}$	3.06	$\mathbf{m}\mathbf{w}$
2.25	\mathbf{m}	2.38	$\mathbf{v}\mathbf{w}$	2.42	$\mathbf{m}\mathbf{w}$	1.625	$\mathbf{m}\mathbf{w}$	3.01	$\mathbf{m}\mathbf{w}$
2.22	\mathbf{w}	2.26	\mathbf{m}	2.30	$\mathbf{v}\mathbf{v}\mathbf{w}$			2.86	w
$2 \cdot 10$	ms	2.18	$\mathbf{m}\mathbf{w}$	2.19	m			2.68	$\mathbf{m}\mathbf{w}$
2.06	\mathbf{w}	2.06	\mathbf{w}	$2 \cdot 10$	$\mathbf{v}\mathbf{w}$			2.60	vw
1.96	$\mathbf{m}\mathbf{w}$	2.02	w	2.02	vw			2.49	$\mathbf{v}\mathbf{w}$
1.835	$\mathbf{m}\mathbf{s}$	1.958	$\mathbf{v}\mathbf{w}$	1.921	s			2.38	$\mathbf{v}\mathbf{w}$
1.793	\mathbf{m}	1.880	ms	1.851	\mathbf{w}			$2 \cdot 32$	$\mathbf{v}\mathbf{w}$
1.729	$\mathbf{m}\mathbf{w}$	1.835	$\mathbf{m}\mathbf{w}$	1.753	\mathbf{w}			$2 \cdot 19$	$\mathbf{m}\mathbf{w}$
1.680	vw	1.762	$\mathbf{m}\mathbf{w}$	1.689	$\mathbf{m}\mathbf{w}$			$2 \cdot 13$	vw
1.625	$\mathbf{m}\mathbf{s}$	1.678	$\mathbf{v}\mathbf{w}$	1.665	\mathbf{w}			2.08	$\mathbf{v}\mathbf{w}$
1.560	vvw	1.616	$\mathbf{m}\mathbf{w}$	1.602	$\mathbf{m}\mathbf{w}$			2.048	$\mathbf{v}\mathbf{w}$
1.500	W	1.601	\mathbf{w}	1.560	\mathbf{w}			1.960	$\mathbf{m}\mathbf{w}$
1.445	m	1.462	$\mathbf{v}\mathbf{w}$	1.518	w			1.908	$\mathbf{v}\mathbf{w}$
1.408	$\mathbf{v}\mathbf{w}$	1.448	$\mathbf{v}\mathbf{w}$	1.485	vw			1.879	$\mathbf{v}\mathbf{w}$
1.382	vw	1.433	m	1.458	ms			1.840	vw
1.349	vw	1.414	vw	1.426	ms			1.810	$\mathbf{v}\mathbf{v}\mathbf{w}$

^{1.} Hydrobasaluminite, Al₄SO₄(OH)₁₀.36H₂O: white plastic clay-like material from Lodge pit, Irchester, Northamptonshire. A portion of this specimen dried in air yielded basaluminite (no. 2 following).

^{2.} Basaluminite, $Al_4SO_4(OH)_{10}.5H_2O$ (analyses 1 and 2, table II): white, powdery to compact substance consisting of minute birefringent plates or fibres with mean refractive index 1.519 and specific gravity 2.12. These data are also given by basalu-

minite from Épernay, Marne, France (analysis 3, table II) and by the same mineral from Clifton Hill, Brighton.

- 3. Metabasaluminite, $Al_4SO_4(OH)_{10}$: produced by heating hydrobasaluminite or basaluminite at 150° C. n 1·523, sp. gr. 2·20.
- 4. Felsőbányite: yellowish concretions on stibnite, Felsőbánya, Szatmár, Hungary (= Baia Sprie, Romania).
 - 5. Aluminite: grey-white nodular massive, Newhaven, Sussex.

The above data were obtained from X-ray photographs of powdered specimens 1–5 with filtered cobalt radiation λ 1·7902 Å. in a cylindrical camera, 6 cm. diameter. Relative intensities are given as: vs very strong, s strong, ms medium strong, m medium, mw medium weak, w weak, vw very weak, vvw very very weak. See also fig. 3 for reproductions of powder photographs.

X-ray powder spacings given for basaluminite from Irchester by Bassett and Goodwin (1949, p. 2278) correspond to a mixture of hydrobasaluminite and basaluminite.

Air-dried material was then selected for chemical analysis. Both microscopic and X-ray examination were carried out to check that allophane was absent. Mr. Harvey's analyses of two separate portions, table II, cols. 1 and 2, show that it is difficult to select a sample quite free from small amounts of allophane and no doubt traces of other minerals may also be present. The results of chemical analysis show that the principal mineral constituent is a basic aluminium sulphate with composition close to 2Al₂O₃.SO₃.10H₂O. X-ray powder spacings (table I), chemical analyses (table II), refractive index, and specific gravity distinguish the mineral from aluminite Al₂O₃.SO₃.9H₂O. It can also be distinguished from other known minerals of similar composition. In order to convey an idea of its chemical nature and at the same time to differentiate it from aluminite, the name basaluminite is proposed for the air-dried mineral and hydrobasaluminite for the fully hydrated plastic mineral (table I, col. 1).¹

Attempts to obtain dehydration data for the hydrobasaluminite were not completely successful. Portions of the mineral were kept at 16° C. in air of known water-vapour pressure until constant in weight by placing the mineral under cover with a beaker containing sulphuric acid of known dilution. It was found difficult to achieve equilibrium and bring samples to constant weight in a reasonable time. The outer layers of less hydrated material appear to form impermeable crusts which hinder the dehydration of the interior. The following measurements

 1 In the preliminary account of both minerals, already published, the values quoted for the longest spacings, 12.9 Å. for hydrobasaluminite and 9.2 Å. for basaluminite, are in error. More accurate measurements give 12.6 ± 0.2 Å. and 9.4 ± 0.1 Å. respectively. F. A. Bannister and S. E. Hollingworth, Nature, London, 1948, vol. 162, p. 565.

	TABLE II.	Chemical	analyses	of	basal	luminite.
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	1.	la.	2.	2 a.	3.	4.	5.
SiO_2	$2 \cdot 4$		3.6	_			_
SO ₃	15.6	$17 \cdot 4$	14.2	16.9	20.06	17.2	23.37
Al_2O_3	43.0	43.5	41.3	$42 \cdot 2$	39.70	44.0	29.87
Fe_2O_3	0.3		0.2	_	_		_
P_2O_5	\mathbf{trace}		1.0	-			
H ₂ O	(38.7)	$39 \cdot 1$	(39.7)	40.9	39.94	38-8	46.76
	100.0	100.0	100.0	100.0	99.70	100.0	100:00
Sp. gr.	$2 \cdot 12$		$2 \cdot 12$		1.670		1.7054

1 and 2. Air-dried samples of basaluminite from Lodge pit, Irchester, Northamptonshire, containing up to 15 % allophane. Analysed by Mr. C. O. Harvey, Geological Survey Chemical Laboratory; water content by difference. Nature, London, 1948, vol. 162, p. 565. [M.A. 10-452.]

- l a and 2 a. Recalculated excluding allophane.
- 3. Basaluminite, Mount Bernon, Épernay, Marne, France. Analysed by J. L. Lassaigne who determined each constituent separately and also found 0.30 % of calcium sulphate. Ann. Chim. Physique, Paris, 1823, ser. 2, vol. 24, p. 97.
 - 4. Calculated for 2Al₂O₃.SO₃.10H₂O.
- 5. Aluminite, Newhaven, Sussex, analysed by F. Stromeyer who determined each constituent separately and corrected for a small amount of admixed gypsum. Untersuchungen über die Mischung der Mineralkörper. Göttingen, 1821, p. 99.

were made, showing that the approximate composition of the fully hydrated hydrobasaluminite is $2Al_2O_3.SO_3.41H_2O$.

Total loss	Temperature	Duration	
of weight.	degrees C.	hours.	Mineral present.
0	16	_	hydrobasaluminite
$52 \cdot 9$	16	120	basaluminite
54	16	24 0	basaluminite

No further loss in weight could be detected for the mineral at 16° C., but on raising the temperature further loss of water occurred and powder photographs were taken of the products obtained:

$65 \cdot 1$	150	2	metabasaluminite
$72 \cdot 4$	500	2	amorphous
73.6	750	2	amorphous
77-9	920	2	unidentified

No change in the powder pattern of basaluminite could be detected in samples heated to 105° C., but at 110° C. a change in pattern was observed that is apparently complete at 150° C. when the pattern remains constant and the chemical composition corresponds to Al₄SO₄(OH)₁₀ (table I, col. 3; fig. 3, no. 4). No further change in the powder pattern occurred when samples were heated to 200° and 300° C. At the latter temperature, however, the pattern begins to fade away and at 500° C. completely disappears, the material having become amorphous. The product

obtained by heating basaluminite to 750° C. is also amorphous and X-ray photographs show only haloes; approximate spacings in Å. 3·7 s, 2·18 w, 1·46 w. When the amorphous product obtained at 750° C. is heated to 920° C. further loss in weight takes place possibly due to evolution of sulphur trioxide as well as water vapour and the X-ray photograph no longer shows haloes but powder lines flecked with spots, none of which can be attributed to either α - or γ -alumina. So far this recrystallized material has not been identified.

An X-ray examination has also been made of samples of the white minerals collected from Irchester by Dr. G. Nagelschmidt in 1943 and kindly lent to us for study. Most of them prove to be mixtures of basaluminite and allophane, but a few samples have been encountered which yield unidentified X-ray patterns suggesting the presence of additional, possibly undescribed, minerals that need further study.

Basaluminite yields a powder photograph with sharp, well-defined lines showing that the average crystal size is less than $5 \mu = 5 \times 10^{-4}$ cm. So it is not surprising that the optical data are meagre and that no optic picture can be obtained to show whether the mineral is uniaxial or biaxial. An attempt, however, has been made to index the first twelve lines of the basaluminite pattern, table I, col. 2, by using charts of the Hull-Davey type prepared by C. W. Bunn who has plotted values of log d for each possible crystal plane against log c/a for tetragonal, hexagonal, and rhombohedral substances. A satisfactory 'fit' could be obtained by using an hexagonal chart for an axial ratio c/a 0.8318:

d.	$\log d$.	Indices.	d.	$\log d$.	Indices.
9·4 Å.	0.9722	0002	3.87	0.5877	$41\overline{5}2$
7.18	0.8501	$11\overline{2}2$	3.68	0.5658	$10\overline{1}5, 42\overline{6}0, 33\overline{6}1$
6.73	0.8280	$20\overline{2}2$	3.44	0.5366	$42\overline{6}2,51\overline{6}1$
5.92	0.7723	$10\overline{1}3$	3.20	0.5051	$60\overline{6}1, 43\overline{7}0, 33\overline{6}3$
5.27	0.7218	$20\overline{2}3$	2.90	0.4624	$42\overline{6}4$
4.68	0.6702	$0004, 31\overline{4}2$	2.82	0.4502	$44\overline{8}0, 30\overline{3}6$

This possible solution should not be taken too seriously, neither can we regard it as a proof that the symmetry of basaluminite is hexagonal. It is now possible to calculate the unit-cell dimensions and contents, but we must again emphasize that they are reported here only as a possible solution. The spacings of the two lines $44\overline{80}$ and 0004 yield values of a 22.56, c 18.72 Å and this hexagonal rhomb-based unit cell would contain $22.72[2Al_2O_3.SO_3.10H_2O]$. It is always difficult to measure accurately the specific gravity of a porous fine-grained mineral and the approximate value 2.12 obtained during this work by immersion in a mixture of methylene iodide and benzene containing indicators of

known specific gravity is probably low. If it be assumed that the unit cell really contains an integral number of formula weights consistent with hexagonal symmetry, i.e. $24[2Al_2O_3.SO_3.10H_2O]$, the calculated specific gravity would be $2\cdot23$. The powder pattern of hydrobasaluminite is more complex than that of basaluminite, so that still less reliance could be placed on a graphical method of indexing its powder pattern.

Mention has already been made of the difference in chemistry, optical properties, and powder patterns of the new minerals from Irchester and aluminite proper. During the comparison of basaluminite with all possibly related aluminium sulphate species in the British Museum collections it was soon discovered that those specimens labelled aluminite revealed considerable variation in external characters, and X-ray photographs grouped them into three divisions each corresponding to a specific powder pattern:

- 1. Aluminite: grey-white, finely fibrous, nodular groups and masses (table I, 5). Localities represented: Halle, Germany; Newhaven, Sussex.
- 2. Basaluminite: white, powdery to compact, sometimes nodular (table I, 2) from Irchester, Northamptonshire, and Clifton Hill, Brighton, Sussex; also as white pellets up to 5 mm. long in a matrix of metahalloysite and fine-grained quartz from Épernay, Marne, France.
- 3. Gibbsite+allophane: white, compact nodules consisting of an intimate mixture of the two minerals, from Clifton Hill, Brighton, Sussex. So-called collyrite from Hove, Brighton, should also be included here. A polished specimen in the British Museum collections showing concentric zones yields a sharp pattern due to gibbsite with a background of haloes due to allophane. It is of interest that the chemical analysis by J. H. and G. Gladstone corresponds, as J. D. Dana pointed out, to a composition equivalent to a mixture of equal parts of gibbsite and allophane.

The powder patterns of basaluminite from Irchester, Épernay, and Brighton are identical. This fact is good evidence that the pattern itself corresponds to one single mineral species. The 12.6 Å. line of hydrobasaluminite appearing on powder photographs of imperfectly dried basaluminite also appears on photographs of the interior of the white pellets from Épernay. Thus the outer crust of basaluminite can effectively

¹ A duplicate specimen of gibbsite, probably from Brighton, but incorrectly labelled aluminite, Newhaven, was used for the data on aluminite supplied to the American Society for Testing Materials for the first supplementary card file of X-ray data, 1944. A.S.T.M. II–356.

seal up the more hydrated mineral hydrobasaluminite for a long time. Table II, col. 3 shows the analysis of the Epernay mineral studied by J. L. Lassaigne. He pointed out the higher alumina and lower sulphate contents compared with aluminite specimens from Halle and Morl, but did not apparently suspect that he had analysed a new mineral species. So far this is the only known occurrence of basaluminite free from allophane. It would not, however, be easy to isolate sufficient white pellets for chemical analysis. Basaluminite from Clifton Hill, Brighton, formerly labelled aluminite, is, like the mineral from Irchester, frequently associated with allophane. No chemical analysis of the Brighton mineral has yet been published and its identification with basaluminite depends entirely upon X-ray photographs.

The relationship of the new minerals hydrobasaluminite and basaluminite to the doubtful species felsőbányite and paraluminite is still uncertain. No paraluminite from Halle is available for comparison, but the optical properties reported by Larsen (1921) do not suggest identity with basaluminite. The only specimens of felsőbányite in the British Museum that were not wrongly labelled are almost amorphous and yield only weak patterns quite different in spacings and relative intensities from the patterns for the two new minerals (table I, col. 4).

In a recent study of the basic aluminium sulphates by H. Bassett and T. H. Goodwin attempts to prepare basaluminite and hydrobasaluminite have failed. Their experiments were carried out at 25° C. or higher temperatures, and it is possible that attempts made at lower temperatures might be more successful. They have also published (1949, p. 2265) analyses of two specimens of basaluminite supplied by us from Northamptonshire and obtained a formula for basaluminite close to $2Al_2O_3$.SO₃.10H₂O. Bassett and Goodwin (p. 2265) state correctly that 'aluminite has not, so far, been found in the Northampton deposits'. They are in error, however, in stating (pp. 2252, 2265) that basaluminite is associated with aluminite on many specimens of that mineral: I have not detected it on any of the British Museum specimens of aluminite Al_2O_3 .SO₃.9H₂O from Halle or Newhaven (p. 12).

Although both the new minerals are basic aluminium sulphates, not aluminosilicates, they nevertheless show some relationship to members of the clay family: the difference in their longest powder spacings is 3.2 Å. and possibly corresponds as in halloysite and metahalloysite to the thickness of a water-layer in their layer structures. Fully hydrated halloysite with its longest spacing close to 10 Å, is more frequently encountered in the clay deposits of northern Europe,

whereas metahalloysite with composition close to that of kaolinite and longest spacing 7 Å. is the more usual form recorded in warmer climates. Halloysite readily passes into metahalloysite by heating to 70° C. Hydrobasaluminite is an example of a plastic mineral which can only be preserved indefinitely in a moist environment; and it may well be, if suitable precautions are taken in the collection and preservation of clays and other clay-like substances, that new hydrated forms of known minerals may be discovered.

CONDITIONS OF FORMATION.

It is generally accepted that the breakdown of complex aluminosilicates by hydrolysis takes place in the zone of weathering, and the mobility of alumina and silica which is required for the transport of the constituents of the white mineral assemblage may be assigned wholly or in part to some such chemical breakdown. Although the presence of kaolinite in unweathered ironstones should not be overlooked, the association of the white mineral assemblage with the zone of weathering (but well below the present surface) is too intimate to be fortuitous. Sulphates of aluminium suggest the solution of alumina by acid waters derived from the oxidation of pyrite which is a widespread constituent of the unweathered ironstone. Pyrite is in places concentrated at the base of the upper chamosite-kaolinite group, and also occurs as a secondary deposit below the leached zone associated with the Lower Estuarine seat-earth.

It is not to be expected that the acidity or alkalinity of solutions derived from the zone of weathering will necessarily survive unmodified during their movement downward through varying environments. In particular, contact of acid alumina-bearing solutions with alkaline waters (e.g. of calcium bicarbonate derived from calcium carbonate in the ironstone or indirectly from the Great Oolite limestone) could lead to a precipitation of gypsum and then of alumina and silica gel (Clarke, 1920, p. 495). It has also been suggested by van Bemmelen (1904; Robinson, 1936, p. 45) that the colloidal sols of electro-negative silicic acid and electro-positive alumina and iron may cause mutual precipitation, first as adsorption compounds of indefinite composition giving rise later to crystalline compounds with definite composition. The general character of the central infilling—the halloysite-allophane-hydrobasaluminite assemblage—is not inconsistent with crystallization from such an adsorption complex.

It is, however, difficult to visualize the accumulation of such large

quantities of material from presumably dilute solutions except under some specially favourable conditions. The basin-like structure suggested by fig. 1 would not sufficiently restrict circulation for continued precipitation. There is, however, some probability of a special combination of circumstances which could have produced unusually favourable conditions. This seems an appropriate place to mention these.

There are various facts, which it is hoped to describe in detail elsewhere, that point to an intimate, probably causal, relation between cambering and its associated superficial structures, and the abnormal conditions of the glacial climate of the Pleistocene. The suggestion that the partial or complete thawing of a deep zone of 'permanently frozen' ground could produce conditions favourable to development of superficial disturbances has already been made (Hollingworth, Taylor, and Kellaway, 1944, footnote p. 18). This receives support from the observations of Záruba-Pfeffermann (1943) in Czechoslovakia. Deeply frozen ground in the peri-glacial areas of southern Britain is favoured by Dr. A. J. Bull to account for the shattering of chalk, without appreciable mass movement, so as to preserve the lines of flint nodules such as he has observed in the Beachy Head area (personal communication), and can be well seen at Freshwater Bay in the Isle of Wight.

With these preliminary remarks we may refer to observations of Livingston Wernecke (1932) in the Yukon Territory where mining operations have proved frozen ground to a depth of more than 400 feet. Small ice veins (frozen ground-water) are abundant in the rock, and ice-rock breccia provides evidence of the splitting off of fragments from the walls of joints. Mine water contains 178 parts per million of solids mostly CaCO₃.

'When the underground water froze, the calcium carbonate seems to have segregated and precipitated in spots as a soft, white, pulverulent (when dry) mass on the walls of the fractures. When wet, this substance is a soft, pasty mass. Some of this material was observed included as small irregular-shaped masses in the ice, but the greater portion was on the edges of the ice. The carbonate was pronounced in the ice in the siderite veins, and not evident in the ice surrounded by slate or quartzite. In the last instance, a very thin coating of limonite has precipitated on the slate or quartzite walls.' (Wernecke, 1932, p. 43.)

This description of the occurrence of calcium carbonate has a striking resemblance to the occurrence of 'rock-rulk', a soft deposit of fine-grained white calcium carbonate that is frequently found coating the joints in Jurassic limestones of the Cotteswolds and elsewhere.

Of the Chipping Norton limestone, H. B. Woodward wrote (1894, p. 149):

'In many quarries the exposed faces of the beds become lime-washed or incrusted with a calcareous coating. This is the "Rock Milk" (*Lac Lunae*) of old mineralogists, sometimes also termed the "Agaric Mineral" from its supposed resemblance to fungoid growth. The beds are often much shattered, and the "rifts" or "swillies" are filled with clay and débris from the overlying Great Oolite Series.'

Weaver (1824) wrote:

'Inferior oolite; traversed by fissures of variable width, the walls of which are frequently coated with rock-milk. . . .'

Wernecke's record of precipitated limonite is of particular interest in view of its occurrence in the fissures in the ironstone. We envisage a deeply-frozen ground in Northamptonshire during cold phases of the Pleistocene, with probably major and minor oscillations in the lower limit of freezing.

At the Lodge pit site the geological conditions are particularly favourable to the sealing up of a considerable volume of ground-water as freezing proceeded from above downwards. Freezing to a depth of say 10–15 feet would seal off the route of possible valleyward escape of ground-water on the valley sides, by freezing the ironstone outcrop down to the Lias clay, as may be seen from a consideration of fig. 1. At this stage ground-water could continue to feed down dip into the 'basin' area for some time with consequent accumulation and concentration of the silicates and sulphates of alumina, &c., as freezing proceeded. It is probable that the zone of frozen ground extended downwards through the ironstone into the Lias below.

The distribution of minerals in the fissures is suggestive of a precipitation succession—limonite, allophane, hydrobasaluminite; a sequence which may perhaps be regarded as a natural one.

One result of the weathering of the chalybite-chamosite ironstone is an increase in the silica-alumina ratio in the weathered rock (after allowance is made for free quartz originally present) (Taylor, 1949, pp. 55-56). It seems probable that the alumina-rich minerals of the fissure infilling represent nature's trapping of the soluble products of weathering. If this is so it would appear to provide useful information on the nature of the solutions derived from the weathering process in this particular environment, but the alumina/silica ratio of the deposit is much higher than is considered normal for the mobile products of weathering.

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Postscript.—The thin plates or fibres of basaluminite from Irchester have negative elongation and refractive indices in sodium-light n_1 1·517, n_2 1·521, yielding the average value 1·519 given above (pp. 7–8). The same mineral from Épernay and Brighton yields less distinct fibres and the mean refractive index recorded for sodium-light is 1·515. Preparations of metabasaluminite retain the fibrous appearance and negative elongation of basaluminite and have n_1 1·521, n_2 1·524, yielding the mean value 1·523 as given on p. 9.