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A thermal and X-ray investigation of scarbroite.

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Summary.—Scarbroite, a fine-grained but compact deposit obtained from fissures in the sandstone on the north Yorkshire coast, is shown by chemical analysis to have an idealized formula $Al_2(CO_3)_3.12Al(OH)_3$. X-ray and electron diffraction data indicate a triclinic cell with a 9·94 Å., b 14·88 Å., c 26·47 Å., α 98·7°, β 96·5°, and γ 89·0°. A layer structure consisting of gibbsite-type sheets of $Al(OH)_3$ and sheets of $Al_2(CO_3)_3$ is proposed. The structure is stable from room temperature to about 125° C.

IN a preliminary report (Duffin and Goodyear, 1957), the authors described an aluminous mineral obtained from vertical fissures in the sandstone in South Bay, Scarborough. In spite of some quantitative difference between the properties of this mineral and those of scarbroite as first announced by Vernon (1829), some later measurements on specimens of the original material by Melmore (1930) show excellent agreement with the corresponding data in this paper (p. 354): there seems no doubt that the two are identical.

There appear to have been no other investigations of the mineral, although the American Petroleum Institute research project no. 49 on clay minerals (1951) states, without evidence, that it is probably a mixture of clays. The present paper is an extension and amplification of the preliminary report, and confirms Vernon's hypothesis that scarbroite is a mineral in its own right.

Occurrence and appearance. Specimens appear to be localized in a small cove just south of South Bay, where vertical fissures in the sandstone are occasionally lined with dark brown and grey materials between which the scarbroite is sandwiched. Many specimens of scarbroite are veined with light-brown material, which is largely gibbsite, and most of them also contain varying amounts of quartz. It has proved possible, however, to obtain specimens from layers about ½ inch thick that show no impurity lines in X-ray photographs, although inevitably some quartz and possibly gibbsite may be present. The darker materials sandwiching the scarbroite are largely discoloured quartz, although the grey material contains some kaolinite and calcite, and X-ray photographs of it show a few lines that are not identifiable.

The scarbroite itself, when relatively pure, is white and compact, but most samples are soft and easily crumbled into a very fine-grained powder. The ease with which the mineral crumbles may be due to continual wetting by surface water from the cliff top, since a few dryer specimens are much harder.

Physical and chemical data. Scarbroite is too fine-grained for detailed optical study, but a mean refractive index of 1·509 was obtained. Melmore (1930) states that the refractive index is less than 1·509 and very slightly greater than 1·502. Determinations of the specific gravity in the lump, both by pycnometer and displacement methods, yielded variable results whose mean was 1·85. Using powdered material to eliminate entrapped air as far as possible, a partially evacuated pycnometer gave 2·03, while flotation in a methylene iodide–ethyl iodide mixture gave 2·01 ± 0·01, a result which is probably the most reliable. These results are in good agreement with Melmore's value of 2·05 determined by flotation.

The particle size of the material as found is sufficiently small to give continuous X-ray powder reflections, and electron micrographs (see following note by G. W. Brindley and J. J. Comer) show that the crystallites have a plate-like habit and average about 1 μ across their basal planes.

A chemical analysis was carried out by Dr. R. A. Chalmers of the University of Aberdeen, and gave: SiO_2 3·2 %, Al_2O_3 45·7 %, MgO 0·1 %, Na_2O 1·7 %, K_2O 0·2 %, H_2O 37·9 %, SO_3 1·8 %, CO_2 7·9 %, total 98·5 %. In three analyses Melmore found SiO_2 6·48, 5·69, 5·88 %, Al_2O_3 44·19, 44·32, 44·02 %. The only cation present in amounts sufficient to be associated with the CO_2 is Al^{3+} and this suggests that the mineral is a basic aluminium carbonate. If the silica is attributed to free quartz and the minor constituents (each contributing less than 2 %) are associated with contaminants then the empirical formula would be $Al_2(CO_3)_3.12{\cdot}9\ Al(OH)_3.15{\cdot}6\ H_2O$. The 15·6 H_2O in the formula amounts to 17·0 % of the original material and accounts for the loss in weight when a sample is heated to about 100° C. without a noticeable structural change as revealed by X-ray powder data. It is also possible that a

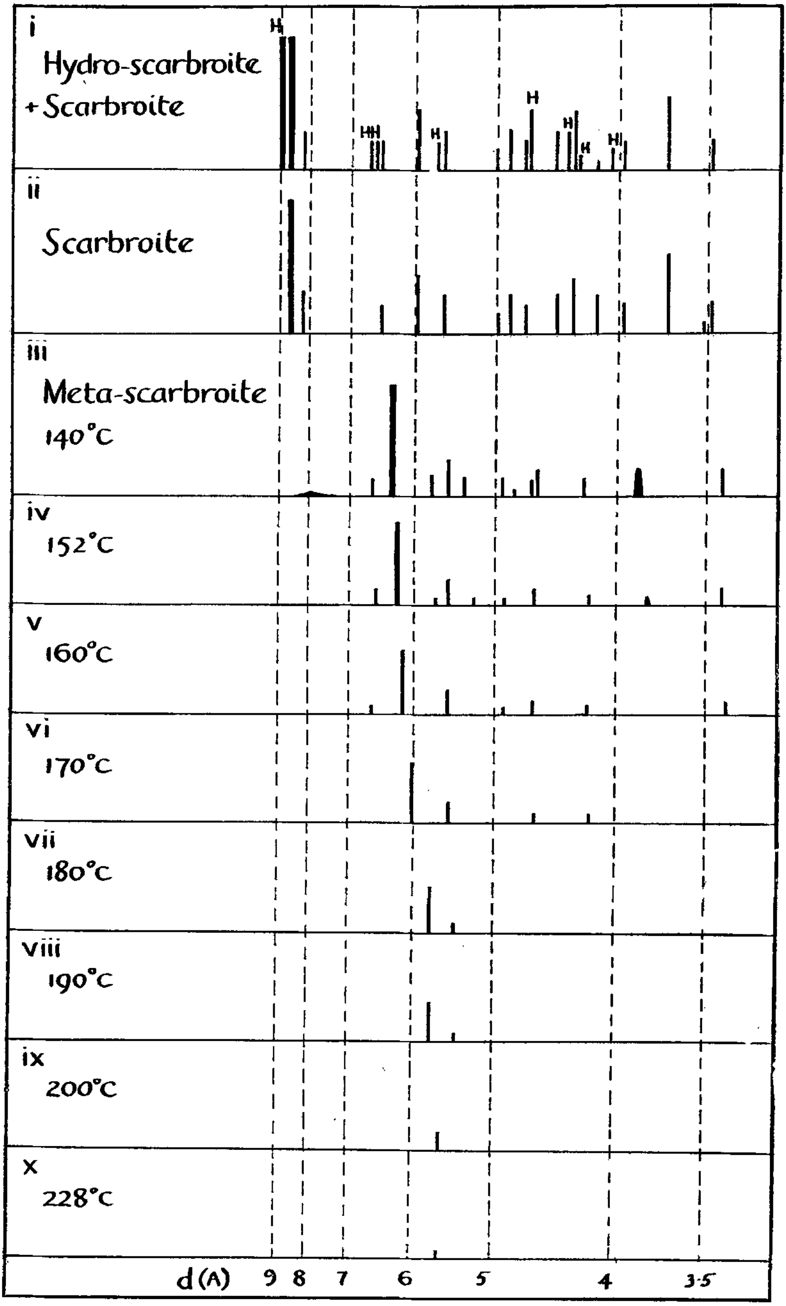

FIG. 1. X-ray powder patterns of hydroscarbroite, scarbroite, and metascarbroite. Heights of lines represent relative intensities estimated visually (compare Tables I and II).

small amount of gibbsite impurity was associated with the sample that was analysed, even though no gibbsite reflections were recorded in its X-ray powder pattern. If an allowance were made for this, the idealized formula of the material in equilibrium with the atmosphere in the range room temperature to 100° C. (see p. 358) may well be $Al_2(CO_3)_3.12\ Al(OH)_3$.

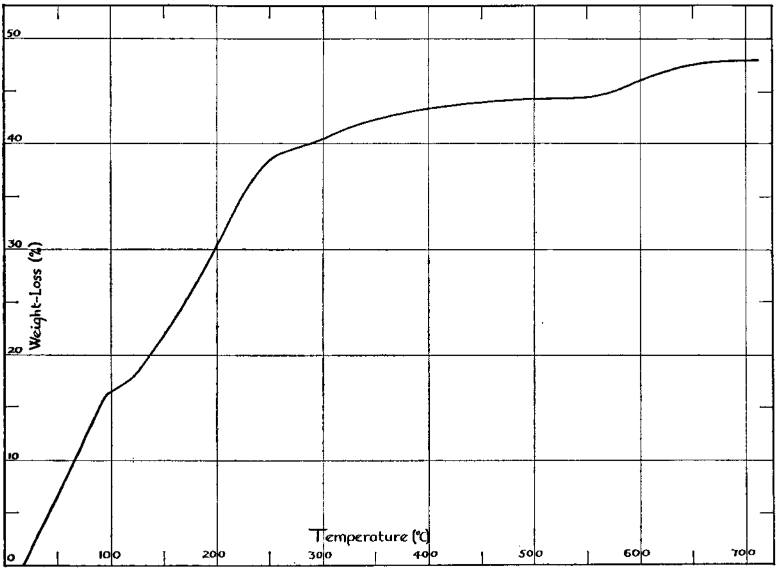

FIG. 2. Weight-loss curve for scarbroite.

Thermal and X-ray data. The effect of heat-treatment on scarbroite was studied by heating a sample to constant weight at predetermined temperatures and taking X-ray powder photographs of the material after it had cooled quickly to room temperature. The weight-loss curve obtained is shown in fig. 2, the loss being expressed as a percentage of the material as found. The X-ray photographs were taken with monochromatized Cu-$K\alpha$ radiation, mostly with a Guinier-type transmission camera of effective diameter 22·9 cm.; calibration was effected by mixing aluminium powder with the specimen to be X-rayed.

Prior to any heat-treatment, when a lump of scarbroite was lightly crushed and an X-ray photograph taken immediately, the diffraction pattern obtained was that shown in table I, column i, and in fig. 1, i. The reflections marked H in the figure varied in their intensity from specimen to specimen, but if the powder was left exposed to the atmo-

TABLE I. Powder patterns of scarbroite and hydroscarbroite.

i		ii		i		ii		i		ii	
Hydroscarbroite +scarbroite.		Scarbroite.		Hydroscarbroite +scarbroite.		Scarbroite.		Hydroscarbroite +scarbroite.		Scarbroite.	
I.	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.
vvs	9·00			wm	3·005	vw	3·011	vw(b)	1·984	w	1·994
vvs	8·74	vvs	8·66	m(b)	2·981	wm	2·986	f	1·969	w(b)	1·969
wm	8·35	m	8·34	w(vb)	2·922					vw	1·945
wm	6·77			vw	2·864	w	2·864	vw	1·932	w	1·929
wm	6·69			tr	—	w	2·823	f	1·914		
wm	6·59	wm	6·56	tr	—			f	1·903	vw	1·903
w	5·99	ms	5·99	vw	2·801			f	1·873	w	1·871
wm	5·72			tr	—			w	1·855	w	1·852
vw	5·62	m	5·63	w	2·752	w(b)	2·750	vw	1·841		
wm	5·00	w	5·01	w	2·704	vw	2·703	w	1·825	wm	1·825
vw	4·900	m	4·906	w	2·674			w(b)	1·785	f	1·794
m	4·739	wm	4·747	tr		w(b)	2·632	vw	1·776	w	1·776
m	4·713			vw	2·602	vw	2·600	f	1·762	vw	1·760
ms	4·467	m	4·456	w(b)	2·552	w(b)	2·560	vw	1·746		
m	4·386			vw	2·501	vw	2·498	w(b)	1·698	f	1·703
m	4·349	ms	4·331	vw	2·477	vw	2·475	tr	—	vw	1·629
vw	4·291			m(b)	2·447	w	2·447			w	1·610
Tr	—	m	4·159	vw	2·426			tr	—	w	1·593
w	4·074			f	2·405			f	1·534	vw	1·560
m	3·985	wm	3·973	wm	2·365	wm	2·366	tr	—	f	1·484
ms	3·726	s	3·724	w	2·338			tr	—		
		vw	3·533			f	2·280	vw	1·471	w(vb)	1·474
m	3·482	wm	3·491	vw	2·226	w(b)	2·222	ms	1·452	m	1·452
w(b)	3·279	f	3·286	w	2·207	vw	2·162	m	1·437	vw	1·418
w(b)	3·253	w	3·252	vw	2·148	wm	2·149	vw	1·389		
tr	—	f	3·187	vw	2·138	w	2·137	f	1·380	w	1·381
wm	3·130	f	3·129	wm(b)	2·099	vw	2·089	tr	—		
vw	3·064	f	3·092	w(b)	2·075	w(b)	2·072	tr	—		
tr	—	w	3·039	f	2·053			m	1·167		

sphere for several weeks and then photographed the H-reflections were no longer recorded and the pattern was that displayed in fig. 1, ii, the reflections corresponding very closely to the unlabelled reflections of fig. 1, i. Powder patterns of the material at intermediate stages in the transition showed the process to be a continuous one, the H-reflections becoming fainter with a corresponding strengthening of the other reflections.

It thus appears that in the material as found two phases may exist, one (for which the name *hydroscarbroite* is proposed) spontaneously dehydrating to the other (scarbroite) when the material is left to come into equilibrium with the humid atmosphere at room temperature. The dehydration process can be hastened by heating the material; for example, hydroscarbroite can be completely transformed by heating at 40° C. for 1 to 2 hours. It seems that the change is completely irreversible since no specimens composed entirely of hydroscarbroite have been found, nor have attempts to transform scarbroite to hydroscarbroite been successful.

Fig. 2 shows that the loss in weight of the material varies uniformly with temperature up to 100° C., at which temperature the curve flattens out somewhat and then begins to rise steeply again at about 125° C. The X-ray powder pattern shows only very minor changes over this temperature range, suggesting a stable scarbroite phase from room temperature to 125° C. If the loss at 100° C., i.e. 16·5 %, is regarded as free water then the chemical formula for scarbroite is probably $Al_2(CO_3)_3.12\,Al(OH)_3$ as previously suggested.

At 130° C. the scarbroite powder pattern disappears, to be replaced by one completely different. This indicates a reconstruction of the crystal lattice to form a further modification for which the name *metascarbroite* is appropriate. At higher temperatures, up to about 230° C., the X-ray pattern shows a continuous shift of some lines to higher Bragg angles together with a progressive decrease in their intensity and a corresponding increase in their diffuseness. These changes in the powder pattern are illustrated in fig. 1, iii–x, and the spacings of the reflections given in columns iii to x in table II. Above 230° C. the

TABLE II. Powder patterns of metascarbroites.

iii		iv		v		vi		vii		viii		ix		x	
140° C.		152° C.		160° C.		170° C.		180° C.		190° C.		200° C.		228° C.	
28 hrs.		22 hrs.		24 hrs.		30 hrs.		3 days		3 days		2½ days		2 days	
I.	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.
f(b)	8·09														
vw	6·73	vw	6·62	f	6·72										
vs	6·41	s	6·25	ms	6·17	ms	6·04	m	5·76	wm	5·76	w	5·64	f	5·63
f	6·13														
w	5·77	f	5·71												
m	5·57	wm	5·54	wm	5·55	w	5·55	f	5·47	f	5·45				
w	5·38	f	5·23												
w	4·95	f	4·93	f	4·93										
f	4·84														
w	4·69	tr	—												
wm	4·65	w	4·64	w	4·66	f	4·64								
w	4·26	f	4·22	f	4·22	f	4·20								
wm(b)	3·89	f	3·83												
wm	3·45	vw	3·43	vw	3·41										
f	3·30														
vw	3·21														
f	3·17														
wm	2·96	f	2·95												
f(b)	2·78														
wm(b)	2·59	f	2·60												
wm	2·539	vw	2·529	wm	2·529	w	2·512	f	2·484	f	2·486	f	2·459		
f	2·475														
f	2·432														
w(b)	2·351														
s	2·199	m	2·192	m	2·192	m	2·181	w	2·164	w	2·164	vw	2·142		
f	2·128														
w(b)	2·031														
tr	—														
tr	—														
w	1·478	w	1·450												
ms(b)	1·441	m	1·439	m	1·434	wm	1·427								
m(b)	1·406	w	1·402												

X-ray pattern becomes so diffuse that no measurable lines remain, although at 900° C. a very diffuse pattern of γ-Al_2O_3 emerges.

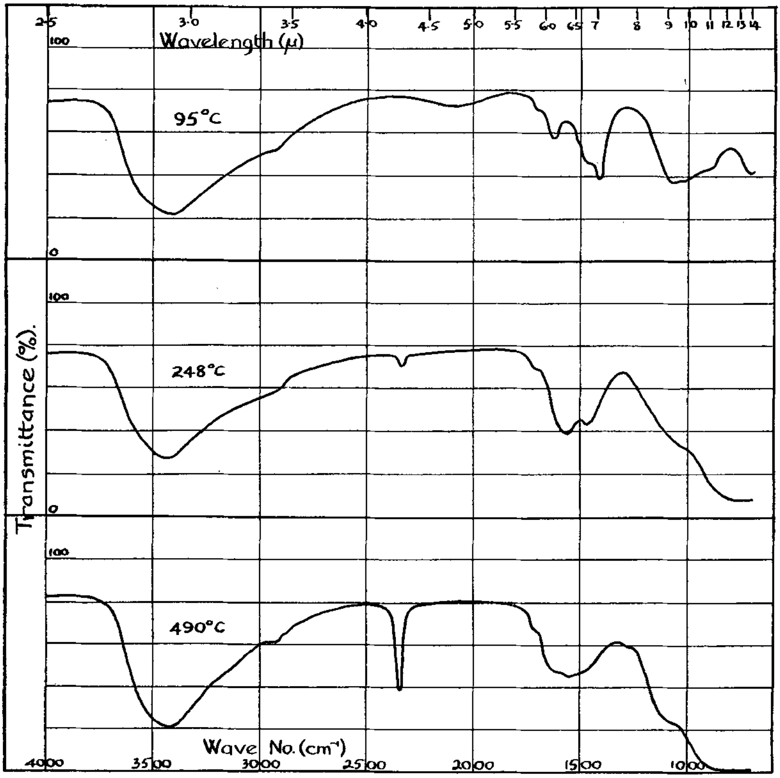

FIG. 3. Infra-red absorption curves for scarbroite after being heated at 95° C., 248° C., and 490° C. No precaution was taken to prevent water being adsorbed on the crystallite surfaces after the heat-treatment.

Immediately above 100° C. further loss in weight with increase of temperature is undoubtedly due to the loss of hydroxyl groups, and if this were the only change occurring, all the hydroxyl would have been lost at 245° C. In fact the weight-loss curve does flatten out at about this temperature. Any further loss at higher temperatures would then be due to the breakdown of the carbonate in the lattice with the evolution of CO_2. The loss of CO_2 is confirmed by infra-red absorption curves shown *in fig.* 3; these were taken for scarbroite which had been heated at 95° C., 248° C., and 490° C. At 490° C. the presence of a peak at

2350 cm.$^{-1}$ shows quite clearly the presence of molecular CO_2 occluded in the specimen, but the small peak in the trace from the specimen heated at 248° C. shows that a few carbonate groups had broken down even at this lower temperature. It is thus reasonable to suppose that the carbonate begins to break down at temperatures just below 250° C. and that the discontinuity in the weight-loss curve at about 250° C. marks the beginning of the loss of CO_2 by the specimen. At 500° C., when the curve flattens out again, the total loss is about 44 % compared with 45·8 % attributable to the H_2O and CO_2 in the analysis. The extra loss of 4 % on heating to even higher temperatures is probably due to the loss of CO_2 gas occluded in the specimen together with a breakdown of the sulphate impurity in the material.

Structural considerations. X-ray photographs of scarbroite, taken with a Brindley-type semi-focusing camera, of specimens oriented by deposition from suspension in water showed enhancement of the 8·66 Å. and 4·33 Å. reflections. These are clearly basal reflections and indicate that d_{001} is some multiple of 8·66 Å. In the absence of single crystal data an attempt was originally made to index the scarbroite powder pattern using a Bunn chart, and a relatively satisfactory fit could be obtained in terms of a large hexagonal cell with a 34·5 Å. and c 17·3 Å. (see Duffin and Goodyear, 1957).

Subsequently, electron diffraction photographs taken by Brindley and Comer (see following note) showed that the a^*–b^* plane of the reciprocal lattice was only pseudo-hexagonal and provided the following values for the parameters: d_{100} 9·90±0·02 Å., d_{010} 14·67±0·04 Å., and γ^* 90°±0·05°. This suggests that the unit cell is either orthorhombic or of lower symmetry. However, it was found impossible to explain the X-ray reflections with an orthorhombic cell with the values of a and b suggested by the electron diffraction data. Perhaps this was to be expected since if the structure of scarbroite is in some way related to that of gibbsite (which is reasonable in view of the close association of these minerals both in environment and composition) it seems unlikely that the presence of a small amount of $Al_2(CO_3)_3$ would raise the symmetry from monoclinic to orthorhombic.

In seeking a cell of lower symmetry to explain all the diffraction data two pieces of evidence proved invaluable: Diffractometer records of scarbroite (G. W. Brindley, private communication) showed a trace reflection at 27±1 Å., which suggests that the strong basal reflections at 8·66 Å. and 4·33 Å. are 003 and 006 respectively giving a d_{001} of 26 Å. And the ease with which clear and extensive electron diffraction patterns were obtained suggests that the *c*-axis is nearly perpendicular to the (001) face of the crystal.

Assuming initially $d_{001} = 26$ Å. together with the values of the reciprocal lattice parameters a^*, b^*, and γ^* found by Brindley and Comer and in the absence of a reasonable monoclinic fit, a triclinic cell was found which accounted very well for the X-ray diffraction data. The parameters of this cell are a 9·94 Å., b 14·88 Å., c 26·47 Å., α 98·7°, β 96·5°, and γ 89·0° and the values of the 100, 010, and 001 spacings are 9·88 Å., 14·71 Å., and 25·99 Å. respectively. Although slight adjustments had to be made to Brindley and Comer's values of a^* and b^*, the cell still explains the electron diffraction data within the expected limits of accuracy. The agreement between the Bragg angles of the observed X-ray reflections and those calculated for the above cell is shown in table III; for every reflection the discrepancy between the observed and calculated values of θ is within the limits of the experimental error.

TABLE III. Observed and calculated $\theta°_{\mathrm{Cu}}$ for scarbroite.

θ obs.	*hkl.*	θ calc.	θ obs.	*hkl.*	θ calc.
5·104°	003	5·104°	9·962°	202	9·970°
5·306	$10\bar{2}$	5·315	10·253	006	10·250
6·743	$11\bar{3}$	6·746	10·682	$20\bar{4}$	10·677
7·398	$\bar{1}13$	7·406	11·189	025	11·190
7·865	014	7·859	11·944	222	11·944
8·853	$1\bar{2}3$	8·861	12·604	$23\bar{1}$	12·592
9·041	030	9·044	12·757	$14\bar{2}$	12·756
9·345	201	9·333			

Assuming the chemical formula for scarbroite to be $Al_2(CO_3)_3 . 12\,Al(OH)_3$ and taking 4 molecules per unit cell, the calculated density is 2·03 as compared with an observed value of 2·17 for scarbroite after being heated to 100° C. to remove externally absorbed water. It is tempting to postulate a layer structure for scarbroite consisting of $Al(OH)_3$ layers as found in gibbsite between which are situated layers of $Al_2(CO_3)_3$. One gibbsite-type layer of area approximately equal to the (001) face of the scarbroite cell would contain 12 $Al(OH)_3$, so that four such layers would account for all the $Al(OH)_3$ in the cell. If these layers were parallel to the (001) face and were stacked as they are in gibbsite (Megaw, 1934) their total thickness would be $\sim$ 19·5 Å. leaving a space $\sim$ 6·5 Å. for two layers each consisting of 6 carbonate groups with the aluminium of the $Al_2(CO_3)_3$ accommodated interstitially. However, in the absence of sufficient intensity data for the 00*l* reflections, this model must remain purely hypothetical.

In conclusion, the X-ray data for hydro- and metascarbroites were not considered sufficiently detailed and precise for structural investigations of these phases. Nevertheless, the most prominent differences between their X-ray powder patterns and that of scarbroite appear to be associated with a change in the *c*-parameter of the scarbroite cell.

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References.

American Petroleum Institute Research Project 49. Reference Clay Minerals (Columbia University, New York, 1951).

Brindley (G. W.) and Comer (J. J.), 1960. Min. Mag., vol. 32, p. 363.

Duffin (W. J.) and Goodyear (J.), 1957. Nature, vol. 180, p. 977.

Megaw (H. D.), 1934. Zeits. Krist., vol. 87, p. 185.

Melmore (Sidney), 1930. Ann. Rept. Yorkshire Phil. Soc., 1930 (for 1929), Proc., p. 9 [M.A. 4–479].

Vernon, (W. V.), 1829. Phil. Mag., ser. 2, vol. 5, p. 178.