A hydrous mica from Yorkshire fireclay.

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RECENT investigations[1] into the mineralogical constitution of fireclays have revealed the presence of a micaceous mineral in all samples examined. Naturally-occurring clays may contain up to 30 % of this type of mineral, and exceptional concentrations have been found in the Yorkshire area. Tests on the purified mineral from this source have proved it to be a hydrous mica of an unusually large grain-size.

Method of separation.

Although a mica-type mineral has long been known as a constituent of most fireclays, the isolation of the pure mineral species has proved difficult. Samples have been isolated from only three clays, from the outcrop and drift mine workings of the Better Bed clay, near Leeds. A clay from an outcrop at Tong (G.M. Ref. $^{4}236^{4}315$ Sheet 77) was obviously rich in large particles of mica and it is from this source that the purest sample has been secured.

The clay was thoroughly dispersed in water with vigorous stirring. The suspension was then poured through a nest of sieves; the largest of which had apertures of $251\,\mu$ and the smallest apertures of $66\,\mu$. Each fraction was washed until free from adhering smaller particles.

There was obviously a concentration of mica flakes in the sample retained on the large aperture sieves, but admixed were sand and coal grains, and some undispersed clay. Further separation was achieved by rolling the mixture down a vibrating inclined ebonite board. The flat micaceous plates adhered, whilst the rounded quartz and coal particles rolled away. The final traces of impurity were removed by heavy liquid separation. It was only possible to separate about five grams of pure mineral from two kilograms of clay.

The above method was excellent for isolating mica particles of about

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[1] K. Carr, R. W. Grimshaw, and A. L. Roberts, Trans. Brit. Ceramic Soc., 1952, vol. 51, p. 334.

100μ, below this size heavy liquid separation was more effective, although really pure samples were difficult to obtain. The large-particled mica flakes were free from any quartz or coal contamination, and were silvery white in colour.

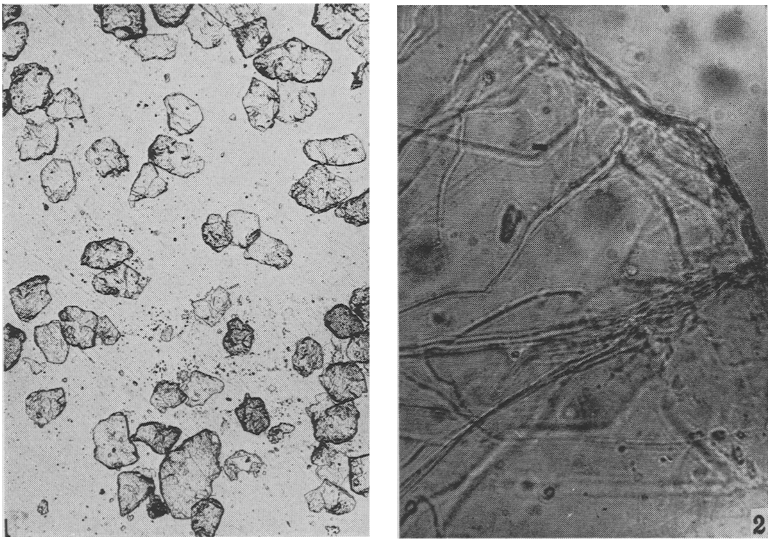

FIG. 1. FIG. 2.

FIGS. 1 and 2. Photomicrographs of micaceous flakes from fireclay. Fig. 1, ×5; fig. 2, ×300, showing fissures.

Properties of micaceous mineral.

Optical.—The mineral appeared to be typical of the mica family when observed under the microscope. Some of the flakes were hexagonal in shape, and cleavage was parallel to the basal section (fig. 1). Under high magnification, cracks could be seen in most of the plates, particularly at the crystal boundaries (fig. 2). Along these fissures were traces of an alteration mineral which absorbed the dyes suffranine and malachite-green, suggesting colloidal or clay material.

A negative biaxial interference figure was obtained on the large flakes, but it was not as distinct as would be expected from muscovite. This may be due to the degree of alteration. The 2V angle was small, being between 5° and 10°. The birefringence was low, and the refractive index 1·578. These optical data agree well with those of other hydrous micas or illites described in the literature.[1] The mica had a specific gravity of 2·913.

Chemical analysis.

Standard methods of silicate analysis were used. The results are shown in table I.

TABLE I. Chemical analyses.

	Micaceous mineral.	Muscovite (Jacob[2]).
SiO_2	46·75	44·85
TiO_2	1·15	trace
Al_2O_3	32·43	36·95
Fe_2O_3	2·98	1·54
FeO	n.d.	1·36
MgO	1·00	0·00
CaO	1·04	0·00
Na_2O	0·94	1·78
K_2O	5·72	9·13
H_2O+	8·01	4·08
H_2O-	0·04	0·00
	100·06	99·69
SiO_2/R_2O_3 molecular ratio	2·31	1·91
Molecular proportion of alkali	0·76	1·25

The SiO_2/R_2O_3 ratio of 2·31:1 is greater than that for ideal mica of 2:1. The loss on ignition is considerably higher than that of muscovite, whilst the alkali content is not as great.

Differential thermal analysis.

The characteristic thermal curve given by the micaceous mineral is shown in fig. 3, along with a curve for muscovite mica. A comparison record of the original Tong clay is also shown. There are three well-defined endothermic peaks, observed in all tests on the purified mineral, none of which are shown in the thermal curves of micas of the muscovite or biotite type. The first peak at 570° C. may be caused by the alteration product, which cannot be removed entirely, although its magnitude can be influenced by the degree of purification. The other two endo-

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[1] R. E. Grim, R. H. Bray, and W. F. Bradley, Amer. Min., 1937, vol. 22, p. 813. [M.A. 7–12]. G. Nagelschmidt and D. Hicks, Min. Mag., 1943, vol. 26, p. 297. E. Maegdefrau and U. Hofmann, Zeits. Krist., 1937, vol. 98, p. 31; Sprechsaal, 1941, vol. 74, p. 369. T. F. Bates, Amer. Min., 1947, vol. 32, p. 625 [M.A. **10**–365].

[2] J. Jakob, Zeits. Krist., 1925, vol. 62, p. 443 [M.A. **3**–81].

thermic effects at 625° C. and 660° C. are probably characteristic of the mineral.

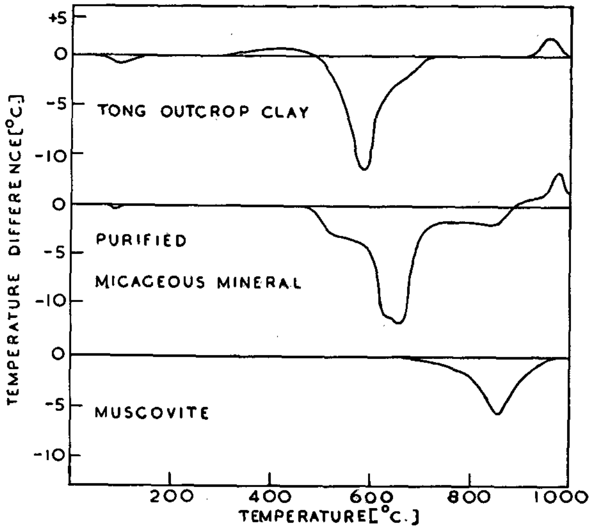

FIG. 3. Differential thermal analysis curves.

X-ray analysis.

Powder photographs of the micaceous mineral give spacings as shown in table II. Also shown are the spacings for muscovite and kaolinite. The lines are in agreement with those of Nagelschmidt, Grim, and others for hydrous mica, except for the additional lines at 7·18 and 3·57 Å., which are possibly due to a kaolin alteration mineral. On heating to 500° C., the 10 Å. line is unchanged in sharpness or position. Furthermore the 060 line is at 1·50, thus indicating a micaceous mineral of the dioctahedral series. Single crystal photographs have been taken, but the complete analysis has not yet been accomplished.

Structure of the mineral.

The mineral is of the micaceous type, but with a higher SiO_2/R_2O_3 ratio, less alkali, and more lattice-held water than true muscovite. Similar minerals have been described by Grim et al., Nagelschmidt, Maegdefrau and Hofmann, Bates, and by Brammall, Leech, and Bannister,[1] and ascribed the name 'illite' or 'hydrous mica'. No previous author, however, has been able to isolate the mineral in such

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[1] A. Brammall, J. G. C. Leech, and F. A. Bannister, Min. Mag., 1937, vol. 24, p. 507.

TABLE II. X-ray spacings.

Micaceous mineral.		Muscovite.		Kaolinite.	
d (Å.).	Int.	*d* (Å.).	Int.	*d* (Å.).	Int.
9·98	s	10·16	s	—	—
7·18	vs	4·98	s	7·14	vs
4·97	w	4·49	s	4·46	vs
4·44	w	4·31	vw	4·17	s
4·09	vw	4·17	vw	3·86	m
3·83	vw	3·92	w	3·58	vs
3·73	vw	3·77	w	3·36	w
3·57	s	3·52	w	2·57	s
3·50	vw	3·33	vs	2·50	s
3·31	vs	3·19	fw	2·36	s
3·19	w	3·12	vw	2·30	s
2·96	fw	2·99	m	2·00	m
2·84	w	2·85	fw	1·953	w
2·76	w	2·78	fw	1·848	w
2·54	m	2·57	w	1·794	w
2·47	vw	2·55	s	1·670	s
2·37	fw	2·48	w	1·623	m
2·31	fw	2·46	w	1·547	w
1·976	m	2·38	w	1·493	s
1·503	w	2·23	vw		
1·500	w	2·19	vw		
		2·12	w		
		1·984	vs		

a pure state, or of such large particle size. The hydrous mica from Yorkshire fireclays closely resembles that isolated from South Wales shales and also from Sarospatak, Hungary.

Recent work by Brown and Norrish[1] suggests that hydroxonium ions can replace potassium in the muscovite lattice, and they classify hydrous micas on this basis. By applying similar calculations, the

TABLE III. Atomic cell configuration.

	Micaceous mineral from Tong.		Hydromuscovite A (Brammall, Leech, and Bannister).		Illite 2 (Grim, Bray, and Bradley).	
Si ...	6·163	8·00	6·1183	8·00	6·7495	8·00
Al ...	5·040	—	5·6467	—	4·0237	—
Ti ...	0·114		—		0·0522	
		3·96		3·97		4·02
Fe ...	0·295		0·1108		0·6419	
Mg ...	0·196	—	0·0981	—	0·5572	—
Ca ...	0·147	—	0·0309	—	0·0230	—
Na ...	0·233		0·1171		0·0427	
		2·20		1·99		1·85
K ...	0·962		1·3547		1·0226	
H ...	7·029	4(OH)	5·5423	4(OH)	6·2714	4(OH)
O ...	25·005	20(O)	24·5159	20(O)	24·7566	20(O)

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[1] G. Brown and K. Norrish, Min. Mag., 1952, vol. 29, p. 929.

structure of the Yorkshire hydrous mica can be adduced. Table III gives the atomic configuration of the mineral in comparison with other hydrous micas.

In calculating the above formula for the micaceous mineral, better agreement is given by attributing the Ca ions to the dioctahedral layer rather than to the alkali or hydroxonium ion grouping.

Possible mechanism of formation.

The mechanism of formation of hydrous mica is still a matter for conjecture. The mineral may be produced as a result of diagenic or authigenic processes. The micaceous minerals in the Yorkshire fireclays appear to be diagenic in character, i.e. arising from the breakdown of true mica. Close examination of the clay in bulk indicated that the thin mica flakes were oriented along the bedding planes, implying that the mineral was deposited in a similar form to its present state, and not formed in situ. There is always the possibility, however, that the mineral may have been formed authigenically at some geological period prior to its deposition in the Lower Coal Measures.

Conclusions.

The micaceous mineral isolated from a Yorkshire fireclay has been shown to be a hydrous mica. Other samples of fireclays from many localities contain a similar mineral. Separation of these minerals is being effected and it is hoped to compare the properties of these hydrous micas from different geological horizons and at various positions along the same seam.

Single crystal X-ray photographs are now being examined with a view to the complete elucidation of the structure.