

*The illite in some Old Red Sandstone soils and sediments.*

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*Summary.* An illite separated from an Upper Old Red Sandstone sediment at Denholm Hill Quarry, Roxburghshire, when examined by optical, X-ray, and chemical methods, appeared to be closely similar to Fithian illite. Its composition was  $1.96 M^+ (Al_{2.86}Fe_{0.31}^{3+}Fe_{0.09}^{2+}Mg_{0.68})(Si_{6.92}Al_{1.08})O_{20}(OH)_4$ , where  $M^+$  for the Ca-saturated sample was  $[(H_2O)_{0.55}Ca_{0.10}Na_{0.06}K_{1.12}]$ . The differential thermal curve showed two peaks: one at 550° C. and the other at 600° C. (i.e. somewhat intermediate between the Fithian and Ballater illites). The dehydration curve was also intermediate. Electron-microscope examination showed rather better crystallization than in Fithian illite. The possible reasons for variation of the illite peak temperature are discussed.

EARLIER thermal studies have shown that the illite in soils developed on Old Red Sandstone till is 'abnormal', in the sense that the main endothermic peak on the differential thermal curve is at 580–600° C. instead of at 550° C. (Mackenzie, 1954, 1956); the peak is thus not additive with the kandite one and the curve obtained for such soil-clays is reasonably characteristic (fig. 1).

It has also been noted that the soils derived from Upper Old Red Sandstone in Roxburghshire differed from those derived from Middle Old Red Sandstone material in Aberdeenshire in that the 580–600° C. peak is less sharply defined (and perhaps rather smaller) for the former than for the latter (cf. figs. 1*a* and 1*b*). The reason for this difference is not known; it might be due to different weathering conditions, or, if the illite is inherited from the parent rock, to differences in the age or the parent material of the sediment.

The fact that this type of illite has so far been observed only in soils derived from the Old Red Sandstone formation suggested that the illite was inherited from the rock; examination of the clay fraction of several samples of Old Red Sandstone sediments confirmed this view. One of the samples so examined—namely, one from Denholm Hill Quarry, Roxburghshire, grid reference NT/572171—had an illite content of about 90% and it was found possible to purify this sample by size fractionation

using sedimentation and the Sharples supercentrifuge. Thus, the  $0.4\text{--}0.2\ \mu$  fraction appeared from X-ray examination to be pure illite with only a trace of kandite and with some contaminating iron oxide; the  $< 0.2\ \mu$  fraction also appeared relatively pure, although some scattering at low angles rendered this less certain. On removal of free iron oxide from the  $0.4\text{--}0.2\ \mu$  fraction by the method of Mitchell and Mackenzie (1954) a creamy-coloured illite of excellent purity was obtained.

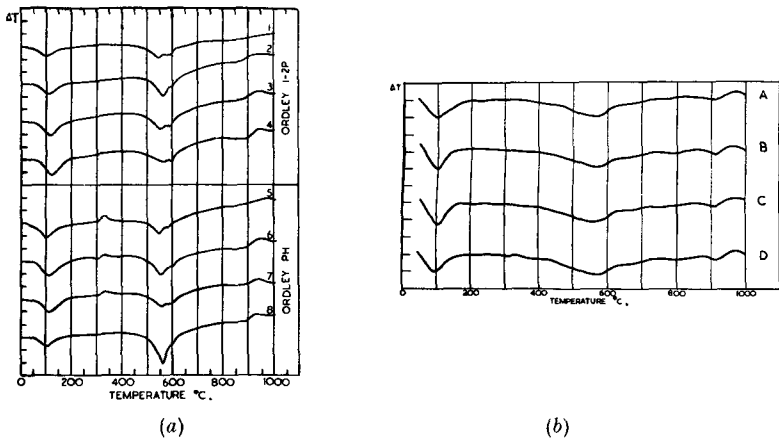


FIG. 1. Differential thermal curves for clays from soils developed on till derived from Old Red Sandstone sediments: (a) Middle Old Red Sandstone, Ordley, Aberdeenshire (1-2 P, freely drained; PH, poorly drained); (b) Upper Old Red Sandstone, Belling Hill, Roxburghshire.

*X-ray data.* The spacings obtained from the X-ray powder diffraction pattern are given in table I, together with, for comparison, those for single-layer, monoclinic (1M) illite, disordered 1M (1Md) illite (Levinson, 1955), and illite from Fithian, Illinois, U.S.A. From these data it will be seen that both the Denholm Hill and the Fithian samples examined are dioctahedral illites and satisfy the criteria given by Levinson (1955) for the 1Md structure. The lattice parameters for the Denholm Hill material are  $a = 5.16\ \text{\AA}$ ,  $b = 9.02\ \text{\AA}$ ,  $c = 9.99\ \text{\AA}$ .

*Thermal data.* Since the X-ray examination revealed no obvious differences between the Denholm Hill and the Fithian illites, the thermal data are of considerable importance. It is particularly interesting that removal of the kandite from the total clay fraction (curve A, fig. 2) does not remove completely the  $550^{\circ}\text{C}$ . peak (curves B and C, fig. 2)—and this peak is too large to be attributed to the trace of kandite remaining.

Thus, the illite does not have a single peak at about 600° C., as was originally envisaged, but has a double peak system with one peak at 550° C. and the other at 600° C. In the 0.4–0.2  $\mu$  fraction both peaks are about the same size, but in the < 0.2  $\mu$  fraction the first peak is larger

TABLE I. X-ray data for illites.

1M illite.*		1Md illite.*		Fithian.		Denholm Hill.	
<i>d</i> , Å.	<i>I</i> .	<i>d</i> , Å.	<i>I</i> .	<i>d</i> , Å.	<i>I</i> .	<i>d</i> , Å.	<i>I</i> .
10.1	vs	10.1	s	10.2	vs	10.14	vs
4.98	m	4.98	w	4.98	m	4.98	w
4.50	s	4.48	s	4.49	s	4.50	vs
4.35	vw	—	—	—	—	—	—
4.10	vw	—	—	—	—	4.12	vvw
3.85	vw	—	—	3.90	vvw	—	—
3.62	ms	—	—	3.73	vvw	3.72	vvw
—	—	—	—	3.52	vw	3.53	vvw
3.32	s	3.33	s	3.34	ms	3.33	vs
3.08	ms	3.07	vw	3.01	w	2.99	vvw
2.89	mw	2.85	vw	2.87	vvw	—	—
—	—	—	—	2.80	vvw	2.81	vw
2.67	w	—	—	—	—	—	—
2.57	vs	2.57	vs	2.58	s	2.58	vs
2.47	w	2.46	w d	2.46	w	2.44	vvw
2.38	m	2.38	w d	2.395	mw	2.40	vw
2.25	mw	2.25	w d	2.253	vw	2.255	vvw
2.14	m	2.14	w d	2.145	m	2.136	vvw
1.99	s	1.99	w d	1.995	w	1.992	m
—	—	—	—	—	—	1.891	vvw
1.71	vw	—	—	1.703	w	1.702	vvw
1.65	m d	1.65	w d	—	—	1.647	vvw
1.58	vvw	—	—	—	—	—	—
1.50	s	1.50	s	1.505	ms	1.504	m
—	—	—	—	—	—	1.453	vvw
1.38	vvw	—	—	—	—	—	—
1.34	w d	1.34	w d	—	—	1.344	vvw
1.30	m	1.30	mw	1.295	m	1.293	vw
1.25	w	1.25	w	—	—	1.250	vw

\* After Levinson (1955); 1M illite, St. Austell, Cornwall; 1Md illite, Fithian, Illinois, U.S.A.

than the second, with the result that this curve is nearer to that for the Fithian illite (curve *D*, fig. 2). In the coarse fraction containing the bulk of the kaolinite it would be expected, therefore, that the illite 600° C. peak would be slightly larger than the 550° C. one. Thus, there appears to be a variation in the ratio of the size of the two peaks, a conclusion which helps to explain this difference in the soil clays referred to in fig. 1, since it might be considered that the Aberdeenshire soil contained an

illite with a better defined and larger 600° C. component. An X-ray photograph with normal exposure taken after heating the illite to 575° C. (i.e. beyond the first peak) showed no difference in the diffraction pattern, either in position or in intensity of the lines, thus confirming that the two peaks belong to the same material.

The dehydration curve shows no definite break corresponding to dehydroxylation in two steps, unless the inflexion commencing at about

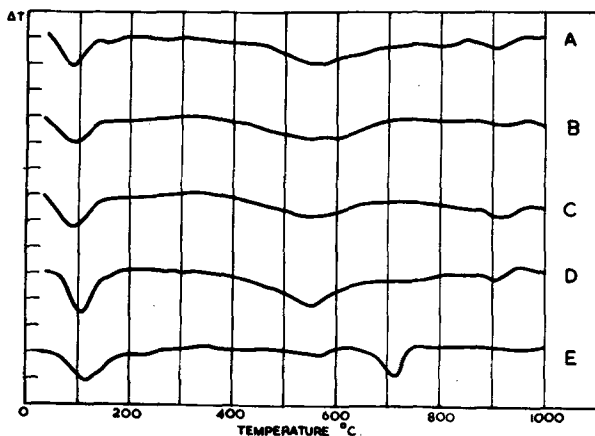


FIG. 2. Differential thermal curves for: *A*, total clay fraction of Old Red Sandstone rock, Denholm Hill, Roxburghshire; *B*, deferrified 0.4–0.2  $\mu$  fraction of same; *C*, deferrified < 0.2  $\mu$  fraction of same; *D*, illite Fithian, Illinois, U.S.A.; *E*, illite, Ballater, Aberdeenshire. (Curve *E* after Mackenzie, Walker, and Hart, 1949.)

300° C. represents the first (fig. 3). This is not improbable, as the near-equilibrium nature of the dehydration curve lowers all temperatures by about 100° C., at least, compared with the differential thermal curve.

From the appearance of both the differential thermal and the dehydration curves the Denholm Hill illite appears to be somewhat intermediate between the Fithian and the Ballater illites.

*Optical data.* The optical data, together with those for some other illite samples, are given in table II. The Fithian illite may have been either the 2M or the 1Md polymorph, while the South Wales and the Ballater illites have the 1Md and 3T structures, respectively (Levinson, 1955). The Denholm Hill material was biaxial negative and appears optically to be virtually identical with Fithian illite, bearing out the close similarity revealed by other data.

*Chemical data.* The chemical composition, as indicated by the analysis

and the ionic formula calculated by the method of Brown and Norrish (1952) (table III), is also remarkably similar to that of Fithian illite. The cation-exchange capacity of 23.2 m.e. per 100 g. is virtually identical with that of the Fithian material of 23.5 m.e. per 100 g. Thus, the only significant difference is the iron content: the difference in CaO content is due to

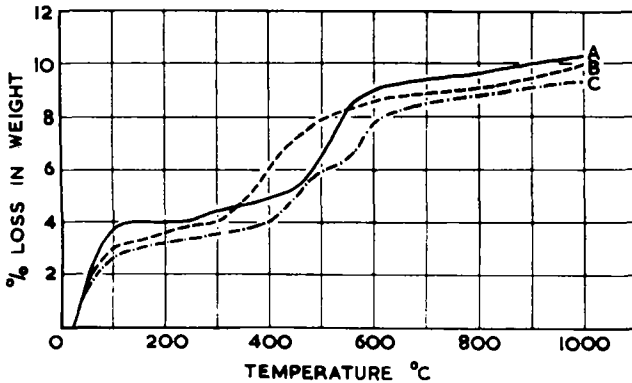


FIG. 3. Dehydration curves for illites from: A—Denholm Hill, Roxburghshire; B—Fithian, Illinois, U.S.A.; C—Ballater, Aberdeenshire.

TABLE II. Optical data for illites.

	1.	2.	3.	4.
$\alpha$ ...	1.555	1.555	1.572	1.568
$\beta$ ...	1.571	—	1.587	1.590
$\gamma$ ...	1.586	1.588	1.600	1.593
$\gamma - \alpha$ ...	0.031	0.033	0.028	0.025
2 V ...	very small	small	small	large*

1. Denholm Hill Quarry, Roxburghshire.
2. Fithian, Illinois, U.S.A (after Grim, Bray, and Bradley, 1937).
3. South Wales (after Nagelschmidt and Hicks, 1943).
4. Ballater, Aberdeenshire (after Mackenzie, Walker, and Hart, 1949).

\* Re-examination revealed an error in the original measurement.

the fact that the Denholm Hill material was Ca-saturated before analysis. The South Wales illite, however, has an even lower iron content (Nagelschmidt and Hicks, 1943) than the Denholm Hill sample and yet gives a peak at 550° C. (Mackenzie, Walker, and Hart, 1949); it seems therefore that the difference between the thermal reactions of the Denholm Hill and Fithian illites cannot be explained on a compositional basis.

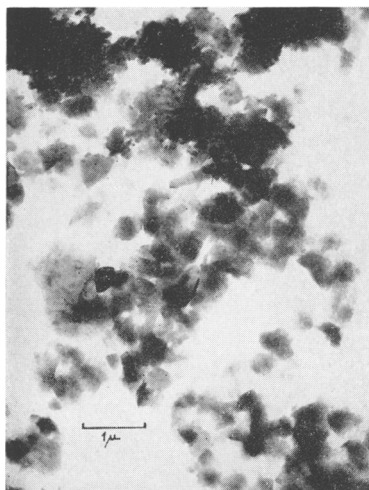
The lattice parameter  $b$  calculated from the composition by the method of Brindley and MacEwan (1953) is 9.03 Å., compared with the value of 9.02 Å. derived from the X-ray data.

TABLE III. Chemical data.

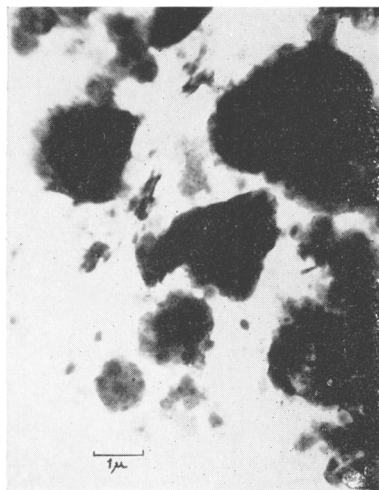
	Fithian.*	Denholm Hill.†	Ionic formula.			
			Fithian.		Denholm Hill.	
SiO <sub>2</sub> ...	51.22%	49.85%	H <sub>3</sub> O <sup>+</sup> ...	0.76		0.58
TiO <sub>2</sub> ...	0.53	0.62	Ca/2 ...	0.06	} 1.88	0.20
Al <sub>2</sub> O <sub>3</sub> ...	25.91	24.16	Na ...	0.04		0.06
Fe <sub>2</sub> O <sub>3</sub> ...	4.59	2.96	K ...	1.02		1.12
FeO ...	1.70	0.80				
CaO ...	0.16	0.65	Si ...	6.75	} 8.00	6.92
MgO ...	2.84	3.27	Al ...	1.25		1.08
MnO ...	—	tr.				
Na <sub>2</sub> O ...	0.17	0.21	Al ...	2.77		2.86
K <sub>2</sub> O ...	6.09	6.31	Fe <sup>3+</sup> ...	0.45	} 3.97	0.31
H <sub>2</sub> O+ ...	7.14	6.22	Fe <sup>2+</sup> ...	0.19		0.09
H <sub>2</sub> O- ...	—	4.75	Mg ...	0.56		0.68
Σ	100.35	99.80				

\* After Grim and Rowland (1941).

† J. B. Craig, analyst.



(a)



(b)

FIG. 4. Electron micrographs of illites: (a) Denholm Hill, Roxburghshire; (b) Fithian, Illinois, U.S.A.

*Electron-microscope data.* The Denholm Hill illite, under the electron microscope (fig. 4a), appears to be rather better crystallized than the Fithian material (fig. 4b), crystals of which have rather indeterminate fluffy edges. Shadow-casting showed both samples to consist of very thin platelets (about 200–400 Å. thick, or less).

*Discussion.* The data presented show that the illite from Denholm Hill, which, so far as is known, is the only illite as yet separated in a virtually pure state from Old Red Sandstone sediments, differs significantly from the Fithian material only in its thermal reaction. Since this difference cannot be associated with compositional differences it must be micro-structural, but it must be sufficiently slight not to show up on the X-ray diffraction pattern.

The thermal data, in effect, indicate that *some* of the hydroxyl groups of the illite are more tightly bound than in the normal type—i.e. they require a greater energy input before they can condense to evolve water. The most straightforward mechanism for this seems to be the following.

In the dioctahedral series only two out of every three octahedral positions are filled, and these positions are not all equivalent with respect to the hydroxyl groups in the oxygen-hydroxyl sheets above and below. It might be considered, therefore, that in a normal illite, such as the Fithian material, the octahedral ions are distributed largely around the oxygen ions and away from the hydroxyl ions. On the other hand, in Ballater illite, which may be regarded as the other end-member, the octahedral ions are distributed largely around the hydroxyl ions giving a tendency to stronger binding and in addition perhaps necessitating an alteration in the position of the octahedral ions before the hydroxyl groups on opposing sheets can condense. The greater energy required for such a system is reflected in the higher peak temperature for the dehydroxylation peak. The Denholm Hill material seems to be intermediate, in that part, roughly half, of the octahedral ions are in the positions occupied in normal illite while the remainder are rather more closely associated with hydroxyl groups—although not so closely associated as in Ballater illite. The two different arrangements could quite easily occur in the same sheet, and interlayering of sheets of two different types is not necessary. This view would tend to be supported by the X-ray evidence for the material heated to 575° C. Variation in the relative positions of the oxygen-hydroxyl sheets above and below the octahedral ions might also influence the result. No information regarding this hypothesis could be obtained from infra-red absorption spectra since the bands which would be affected were outside the range studied. The infra-red spectrum was, with small differences that cannot at present be definitely explained, similar to that for Fithian illite. No comparable system could operate with trioctahedral minerals, and it is significant that trioctahedral minerals, in which octahedral ions are necessarily in close contact with hydroxyl ions, generally have a much higher

dehydroxylation temperature than their dioctahedral analogues (cf. saponite and montmorillonite).

The arrangement visualized above is somewhat similar to that proposed by Jonas and Grim (1957) to explain lowering of the peak temperature of montmorillonite on rehydroxylation, and can equally be used to explain the existence of the 'normal' and 'abnormal' montmorillonites of Cole (1955). It seems preferable to the vague 'order-disorder' suggestion of Cole (1955)—who may, however, have had something of this nature in mind (see Cole and Hosking, 1957)—and in addition does not require the corollary that normal illites alter to abnormal montmorillonites and vice versa (Cole and Hosking, 1957). This corollary is particularly difficult to justify for Ballater illite since it tends to contradict field evidence.

The only other illite known to the author which gives a peak at about 600° C. is that described by Carr, Grimshaw, and Roberts (1953) from some fireclay deposits, but for this material the peaks appear to be at slightly higher temperatures. The reason for the shift is presumably the same as in the Denholm Hill material, but the illite is a 2M polymorph and the chemical composition is quite different from that of the sample now described. The reason why this structure should form, so far as is known, only in Old Red Sandstone sediments and in some fireclays is not clear. It suggests that the prevailing conditions imposed a certain structural order upon the clay mineral being formed, or that the primary minerals in the parent material of the sediments played a significant part (since the fireclay illite occurs in fairly large sheets its structure may easily reflect that of a mica from which it was formed). Further work is at present in progress to investigate how widespread is the occurrence of this illite in Old Red Sandstone sediments, and whether it occurs in the Lower as well as the Upper and Middle beds. A differential thermal curve for a clay from a Devonian deposit in Russia (Frank-Kamenetsky, 1954) appears to show only one peak at about 550° C., although in the absence of the peak tip it is difficult to be sure.

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