NOTES

INTERSTRATIFIED ILLITIC CLAY IN ORDOVICIAN
ASH FROM CONWAY, NORTH WALES

Introduction

A section in Ordovician sedimentary rocks temporarily exposed in 1959 at Town Ditch, Conway, Caernarvonshire (O.S. grid ref. SH781777) included (Wood & Harper, 1962) shaly flags of the Upper Ash group (of possible upper Longvillian (mid-Caradoc) age). Interbedded with the flags over a stratigraphic distance of 9 m were eleven thin clay seams which averaged 1–3 cm in width. The most clearly defined clay seams had central sections of a uniform pale grey-coloured clay, soft and plastic when wet, but darker in colour and hard and moderately massive on drying. A type seam (Sample No. 392) reported in Wood & Harper (1962, p. 180) to be composed of an illitic clay has now been further studied.

Results

X-ray diffraction. Powder photographs (Phillips PW 1008 generator, Co Kα radiation, 11·48 cm powder cameras) were obtained from material mounted as Durofix-cemented spindles. A diffractometer trace was also obtained for the <2 μ fraction, by Mr G. Morris, Department of Physics, University College of North Wales, Bangor. Comparisons of the total clay seam and the <2 μ fraction (Table 1) showed these to be essentially identical and illitic in composition. Wood & Harper (1962) reported muscovite, chlorite, quartz and soda felspar in less pure clay seams, and small quantities of leucoxene as always present.

Basal spacings are greater than in a simple clay mica (10·0–10·2 Å, Mackenzie, 1957; Bradley & Grim, 1961). Several of the Conway clay seams gave either a broad (c. 10–11 Å) band which did not permit accurate measurement or a sharper but still broad line at 10·5 Å. The diffractometer peak at 10·4 Å though clear, was also broad and asymmetric, tailing-off towards higher spacings. With the exception of the high basal spacing, the powder patterns are comparable to those given for the 1d Md polymorph of illite (Levinson, 1955; Bradley & Grim, 1961, Fig. V5). The spacing at 5 Å absent on the diffractometer trace but present on powder photographs was more strongly developed on photographs of oriented flake specimens.

Treatment with glycerol gave a sharp reflection at 9·8 Å in place of the broad line at 10·5 Å, no higher spacing lines being seen. This anomalous contraction with glycerol may be explained if the 9·8 Å line is an order of a larger spacing not detected, either because of its low intensity, or because it is above the camera cut-off limit. Heating to 400° C also sharpened the basal spacing, giving a smaller reduction to 10·2 Å. These results show a proportion of interstratified expanding layers.
**Table 1. X-ray powder data. Illite, Conway**

<table>
<thead>
<tr>
<th>Total clay seam (sample N 392)</th>
<th>10·5</th>
<th>5·0</th>
<th>4·48</th>
<th>3·52</th>
<th>3·35</th>
<th>2·57</th>
<th>2·45</th>
<th>2·39</th>
<th>2·25</th>
<th>2·14</th>
<th>1·90</th>
<th>1·70</th>
<th>1·67</th>
<th>1·50</th>
<th>1·30</th>
<th>1·27</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder photograph*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;2 ( \mu ) clay fraction,</td>
<td>10·4</td>
<td>—</td>
<td>4·46</td>
<td>3·50</td>
<td>3·34</td>
<td>3·30</td>
<td>2·55</td>
<td>—</td>
<td>2·37</td>
<td>2·34</td>
<td>2·24</td>
<td>2·14</td>
<td>2·03</td>
<td>1·90</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Diffractometer*</td>
<td>(10)</td>
<td>(10)</td>
<td>(3)</td>
<td>(2)</td>
<td>(2)</td>
<td>(9)</td>
<td>(2)</td>
<td>(1)</td>
<td>(1)</td>
<td>(2)</td>
<td>(4)</td>
<td>(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Spacings in Å, intensities on diffractometer trace as peak heights. Diffractometer trace by G. Morris, Dept of Physics, U.C.N.W., Bangor.

**Table 2. Chemical Analysis, Illite, Conway**

<table>
<thead>
<tr>
<th></th>
<th>( \text{SiO}_2 )</th>
<th>( \text{Al}_2\text{O}_3 )</th>
<th>( \text{TiO}_2 )</th>
<th>( \text{Fe}_2\text{O}_3 )</th>
<th>( \text{FeO} )</th>
<th>( \text{MgO} )</th>
<th>( \text{Na}_2\text{O} )</th>
<th>( \text{K}_2\text{O} )</th>
<th>( \text{H}_2\text{O}^+ )</th>
<th>( \text{H}_2\text{O}^- )</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis, weight % &lt; 2 ( \mu ) fraction*</td>
<td>47·55</td>
<td>32·49</td>
<td>2·55</td>
<td>0·40</td>
<td>0·32</td>
<td>0·88</td>
<td>0·83</td>
<td>6·35</td>
<td>6·14</td>
<td>2·04</td>
<td>99·55</td>
</tr>
<tr>
<td>Analysis 'adjusted' for structural formulae calculation</td>
<td>49·79</td>
<td>34·0</td>
<td>0·58</td>
<td>0·42</td>
<td>0·34</td>
<td>0·92</td>
<td>0·87</td>
<td>6·65</td>
<td>6·43</td>
<td>—</td>
<td>(100)</td>
</tr>
</tbody>
</table>

* Analyst: J. H. Scoon, Department of Mineralogy and Petrology, University of Cambridge.
Differential thermal analysis. D.T.A. (Netzsch equipment, 10° C/min heating rate) gave a trace of the general type recorded for illites (Taboadela & Ferrandis, 1957) having endotherms at 180–200° C and 600–620° C. Additional peaks were a small endotherm at 290° C and a small exotherm at 740° C, the former comparable to one present on curves for illite-montmorillonite mixed-layer systems given by Bradley & Grim (1961, Fig. V, II).

Chemical analysis. Analysis of the <2 μ fraction, after dithionite treatment for removal of any ‘free’ iron oxides, was made by Mr J. H. Scoon, Department of Mineralogy and Petrology, University of Cambridge, and is reported in Table 2. The TiO₂ content, higher than typically found in illites (c. 0·5%) has been attributed to finely divided anatase or rutile (‘leucoxene’). A composition ‘adjusted’ to 100% after subtraction of 2% TiO₂ and 2·04% H₂O⁻ has therefore been used to calculate structural formula for the clay mineral, on the assumption of a single mica-type structure. Although this assumption is not correct, Hower & Mowatt (1966) concluded that until the nature of mixed layering is better understood, a single ‘mean’ structural formula is the most useful that can be given for the composition of a mica-clay. Alternative methods employed here for calculation of the structural formulae are: (a) that of Foster (1960) after Marshall, and (b) that of Brown & Norrish (1952) employing the correct equations for calculation of structure factors given in Mankin & Dodd (1963). The derived formulae are:

(a) \( M + [(Si_{6.56}Al_{1.44})_{3}^{1.44}(Al_{1.34}Fe_{0.04}^{3+}Fe_{0.04}^{2+}Mg_{0.18}Ti_{0.08})_{4.16}O_{20}(OH)_{4}]^{1.12} \)

In this, the charge deficit is only approximately balanced by \( M + = (Na_{0.22}K_{1.12})^{+1.34} \)

(b) \( M + [(Si_{6.44}Al_{1.56})_{3}^{1.56}(Al_{1.34}Fe_{0.04}^{3+}Fe_{0.04}^{2+}Mg_{0.18}Ti_{0.06})_{3.96}O_{20}(OH)_{4}]^{1.86} \)

In this, the charge balance is obtained by inclusion of interlayer oxonium ions as \( M + = (Na_{0.22}K_{1.12}(H_{2}O)_{0.82})^{+1.86} \). No clear cut preference can be given to either of the calculated formulae. In comparison with other illites, such as those studied by Hower & Mowatt (1966) or that from Old Red Sandstone sediments in Roxburghshire described by Mackenzie (1957) the Conway mineral has higher Al and lower Fe contents.

Discussion

X-ray and D.T.A. results identify the clay mineral of the Conway clay seams as consisting of an illite with a proportion of randomly interstratified expanding layers. The basal spacings and a consideration of Fig. 7 of Hower and Mowatt (1966) which plots percentage expanded layers against fixed interlayer (K + Na) indicate a proportion of about 10% expanding layers.

It was reported by Wood & Harper (1962) that the clay seams contained fragments of pumice. Because of their sharp mineralogical, chemical and morphological distinction from the surrounding flags they were interpreted as individual ash showers. The alteration of volcanic ash in situ to a montmorillonite clay gives materials termed bentonites. By analogy, ash materials of illitic composition have
been termed K-bentonites or meta-bentonites. Hower & Mowatt (1966) have concluded that it is not necessary to postulate a montmorillonitic stage followed by alteration in a K-rich environment (such as the sea) to produce K-bentonites. Weaver & Bates (1952) have studied K-bentonites in the Ordovician of central Pennsylvania which they described as occurring in bands from 1 to 25 cm thick, composed of an illitic clay with (00l) from 10-2 to 10-6 Å and (060) at 1-50 Å. They suggested that volcanic glass fragments laid down in a marine environment would alter over a long period, in the presence of available K, to an illitic clay.

The study of this clay supports the suggestion of Wood & Harper (1962) that the clay seams at Conway represent individual ash falls in a sedimentary sequence. They appear essentially similar to the K-bentonites described by Weaver & Bates (1952). They do however differ mineralogically from the simple illites with basal spacing of 10-10-2 Å found to be characteristic (unpublished) of thick rhyolitic ash beds and from the chlorites (Ball, 1966) characteristic of the more basic volcanic ashes in the Ordovician of Snowdonia. How far original variation in volcanic glass composition, depositional conditions, or post-depositional history are responsible for these differences is a large topic worthy of study.

I am grateful to Dr D. A. Jenkins, Department of Biochemistry and Soil Science, U.C.N.W., Bangor, who made arrangements for the chemical and diffractometer analysis of the Conway illite in connection with its use in other research studies.

D. F. Ball

The Nature Conservancy,
Penrhos Road,
Bangor,
Caernarvonshire.
23 October 1967.

A STRUCTURAL SCHEME FOR Palygorskite

Published unit cell dimensions for sepiolite and palygorskite approximate to the following:

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(β)</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sepiolite</td>
<td>5·3</td>
<td>27·0</td>
<td>13·4 Å</td>
<td>90°</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Palygorskite</td>
<td>5·2</td>
<td>18·0</td>
<td>12·8</td>
<td>95° 50′</td>
<td>monoclinic</td>
</tr>
</tbody>
</table>

Following Zvyagin, Mischenko & Shitov (1963), the axes used here conform to the orientation in other clay minerals, and (a) is the fibre direction. Two structural schemes have been proposed for sepiolite, with space groups \( A2/m \) (Nagy & Bradley, 1955) and \( Pnna \) (Brauner & Preisinger, 1956), and one for palygorskite, with space group \( A2/m \) (Bradley, 1940). Projections of these structural schemes, which contain linked talc-like ribbons, have been compared by Caillère & Hénin, 1961a). Electron-diffraction patterns which we have recorded, and those already published (Brindley, 1959; Zvyagin, 1964, 1967), all have extinctions in accord with the space group \( Pnna \). The oblique textured patterns of Zvyagin et al. (1963) also indicated this space group. The available data all confirm the Brauner-Preisinger model, but not the Nagy-Bradley model, which must therefore be discarded. The X-ray powder data (Brindley, 1959; Caillère & Hénin, 1961a) are incorrectly indexed in some respects; the 2·825 Å spacing, for example, should be indexed 411, not 081.

Published analyses of palygorskite, reviewed by Drits & Aleksandrova (1966) show that an average of four out of five octahedral cation sites are occupied. Oblique textured electron-diffraction patterns of palygorskite (Levando's specimen No. 3/3) were partly indexed by Zvyagin et al. (1963), who found the space group to be \( P2/a \), not \( A2/m \), suggesting that Bradley's model may be incorrect in detail. In an attempt to decide between these space groups, electron-diffraction patterns were recorded from single fibres of palygorskite from Attapulgus, Georgia, U.S.A. (de Lapparent, 1935), and from Cabrach, Aberdeenshire, Scotland (Heddle's 'pilotite', 1879). The Attapulgus fibres gave rotation patterns, indicating bundles with random orientation around (a), but a tubular morphology seems unlikely, as there is no streaking of reflections along the layer lines. The Cabrach specimen comprised single crystals which were too sensitive to the electron beam for thorough exploration of the reciprocal lattice, and further work will be deferred until an image intensifier is available. In common with Brindley's (1959) patterns for sepiolite, the strongest reflections in the \( hko \) zone lie on a centred grid corresponding to \( (a)=5·3, (b)=9·0 \) Å, as would be expected from talc-like sheets. The space group \( P/2a \) (Zvyagin et al., 1963) is probably correct, at least for the specimen which they investigated, as a much weaker electron beam is necessary for polycrystalline patterns. In the octahedral layers, the (a)-glide would require an equal number of cation sites in each row parallel to (b), and the primitive lattice would also require that adjoining talc-like ribbons differ in width. The only structural scheme of this
type which fulfils both of these conditions is shown in Fig. 1 (a–d), in which pyroxene chains are linked to ribbons similar to those in sepiolite, but with the cations in dioctahedral sites. Four of the five cation sites would thus be occupied, in agreement with the chemical analyses (Drits & Aleksandrova, 1966). The possible occurrence of chains of three fused pyroxenes in both minerals suggests that this configuration has a stability comparable with that of pyroxene and amphibole chains. The difference in relative orientations of adjacent octahedral layers in the two minerals may be significant, indicating the most stable states, but a hypothetical orthorhombic variation of palygorskite, with space group $Pmam$ (as in Fig. 1 e), and a monoclinic version of sepiolite, with space group $A2/a$ (as in Fig. 1 d), may

![Fig. 1. Idealized projections of a structural scheme for palygorskite, with the monoclinic space group $P2/a$. (a) Projection on (001) of the dioctahedral pyrophyllite-like ribbon; small dark circles, cations at $z = 0.5$; large circles, the lower layer of oxygen atoms, hydroxyl ions, and ‘bound’ water at $z = 0.41$; small broken circles indicate the layer of cations in the adjacent pyroxene chains. (b) The tetrahedral layer below (a). (c) [100] projection. (d) [010] projection. (e) [010] projection of a hypothetical orthopalygorskite. In (b)–(e); •, cations at $x = \frac{1}{4}, \frac{3}{4}$, respectively; ○, $\text{OH}^-$; ⊕, ‘bound’ water; ⊙, zeolitic water in the sites proposed by Brauner & Freisinger (1956) for sepiolite.]

be visualized. Should these variations be eventually identified with minerals, the prefixes ortho- and clino- are proposed, by analogy with the chrysotiles. The possibility of such structural variations makes more plausible the intergrowths postulated by Martín Vivaldi & Linares González (1962) to explain the anomalous
X-ray spacings observed in some specimens, and also the fringes, seen in electron micrographs, with spacings greater than the normal lattice periods. Such fringes could be moiré patterns; overlapping crystals of palygorskite lying on (001) and (010), for example, might give a fringe spacing of 44 Å. However, this was not the origin of the 45 Å fringes which we observed in a single fibre of Cabrach palygorskite. A possible explanation is that pyroxene chains inserted at regular intervals into an ortho- or clinosepiolite structure would have a lattice period of (13·5\(n+4·5\)) Å, i.e. 18·0 (palygorskite), 31·5, 45, 58·5, 72 Å, etc. Such polytypes should be detectable by electron diffraction of single fibres, but the fringes are often too faint to be seen on the viewing screen, and are revealed only after inspection of the photographic plates.

The palygorskite model proposed here would be difficult to test and refine, because of the lack of suitable material for X-ray rotation photographs, but the fibres are possibly thin enough for the use of electron-diffraction intensities. The ideal structural formula is \(\text{MgAl}_2\text{Si}_4\text{O}_{20}(\text{OH})_8(\text{OH}_2)_8 \cdot 4-5\text{H}_2\text{O}\), corresponding to losses of c 6·5 and 3·6% at temperature 250–400°C and above 400°C, respectively. The loss above 400°C would be higher than for Bradley’s model, but lower than most observed values (see Caillère & Hénin, 1961b); the deficit must be explained in terms of protons on some of the tetrahedral oxygen atoms.

Some of the work described here was done while one of us (E.A.C.F.) was at the Macaulay Institute for Soil Research. The authors wish to thank Dr R. C. Mackenzie for specimens of palygorskite and sepiolite, and Dr W. J. McHardy for assistance with the electron microscopy.

J. A. Gard
E. A. C. Follett

J.A.G.:Department of Chemistry,
University of Aberdeen,
Aberdeen,
Scotland.

E.A.C.F.:M.R.C. Experimental Virus Research Unit,
Institute of Virology,
Church Street,
Glasgow, W.1.

1 March 1968.

Under the auspices of the Organization for Economic Cooperation and Development (O.E.C.D.) a committee on Non-Metallic Minerals, under the chairmanship of Professor J. J. Fripiat, Institut des Sciences de la Terre, Laboratoire de Physico-Chimie Minerale, 42, de Croylaan, Heverlee, Louvain, Belgium, is at present making a collection of standard mineral specimens. These, after being homogenized, are to be characterized as fully as possible using all the techniques available in a number of cooperating laboratories. The committee will then receive and collate the analytical results and prepare reports on each of the samples. There will eventually be available on request for research purposes, bulk samples of well-characterized minerals along with copies of the analytical data. The samples will be stored and distributed by the suppliers and requests for further information on the scheme should be made to Mr G. Hausen, Materials Research Section, O.E.C.D., 2, Rue André Pascal, Paris 16e, France.

The following species are currently being characterized: montmorillonite (Camp-Berteaux), laponite, china clay (kaolinite), attapulgite, illite, chrysotile, crocidolite, talc, bayerite (? gibbsite), magnesite, calcite, gypsum and graphite. It is hoped that some materials, not represented in the above list, will be added later.

The Editor

21 February 1968