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S. Hillier wishes to dedicate this paper to Graham 'Jack' Hobbs (formerly St Joseph's High School, Newport, Gwent) Athro a chyfaill da.

Clay mineralogy of the Old Red Sandstone and Devonian sedimentary rocks of Wales, Scotland and England

S. HILLIER[1,*], M. J. WILSON[1] AND R. J. MERRIMAN[2]

[1] *Macaulay Institute, Craigiebuckler, Aberdeen AB15 8QH, UK, and* [2] *British Geological Survey, Keyworth, Nottingham NG12 5GG, UK*

ABSTRACT: The Devonian sedimentary rocks of the UK are made up of a continental red bed facies, the Old Red Sandstone (ORS), and sediments of a marine origin. The latter are confined to southwest England whereas the ORS occurs much more extensively, particularly in South Wales, the West Midlands, Northern England, the Midland Valley of Scotland and the Orcadian basin. The ORS also occurs extensively offshore where it contains important hydrocarbon reservoirs. Highly variable suites of clay mineral assemblages are characteristic of the ORS. In the West Midlands and Monmouthshire, the Downton Group is characterized by illitic, smectitic, and mixed-layer illite-smectite minerals. A tuff bed (Townsend Tuff) also contains expansible minerals but when the bed is traced westwards it is found that the clay mineralogy changes progressively to an illite-chlorite assemblage, suggesting the influence of diagenetic or metamorphic change. It is not known, however, whether such a transformation is typical of the Downton Group as a whole. The overlying Ditton Group in its eastern outcrops contains a high-spacing mineral identified as tosudite, together with regularly interstratified illite-smectite and well crystallized kaolinite. Further west this assemblage gives way to illite and chlorite, with the latter being trioctahedral or dioctahedral, while in Dyfed the Ditton Group may contain smectite and poorly crystallized kaolinite in addition to illite and chlorite. The geographical distribution of clay minerals in the Ditton Group may also be accounted for by progressive diagenetic to low-grade metamorphic reactions, although it is necessary to postulate retrogressive diagenesis to account for the smectite and kaolinite that occur in the Dyfed samples. The clay mineralogy of the overlying Brecon Group and the Upper ORS also consists of mixtures of illite and chlorite in the west and central parts of the region. No data are available for the Brecon Group in the eastern parts of the outcrop but the Upper ORS from around Monmouth and Portishead contains assemblages rich in kaolinite and mixed-layer illite-smectite with only minor amounts of chlorite. The distribution of clay minerals in the Upper ORS is again suggestive of a progressive westerly increase in the influence of diagenetic alteration, although the influence of provenance cannot be discounted.

In Scotland the clay mineralogy of the Lower ORS in the Midland valley is characterized by a variety of interstratified minerals, including regularly interstratified trioctahedral chlorite-vermiculite, a tosudite mineral similar to that described from South Wales and illite-smectite, as well as occasional illite, chlorite and smectite. The oldest Stonehaven Group is kaolinitic but in the younger groups kaolinite is either completely absent or present in only minor amounts. It is clear that detrital inputs, particularly from associated volcanic rocks, have contributed to the clay minerals found in these rocks, although the contribution could be indirect with diagenetic clay minerals forming from volcanic detritus after deposition. Diagenetic alteration may also be important,

* E-mail: S.Hillier@macaulay.ac.uk
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particularly with respect to the origin of the tosudite mineral. The Middle ORS lacustrine sediments of the Orcadian Basin of Scotland are characterized by mixtures of trioctahedral chlorite and dioctahedral illite, with interstratified chlorite-smectite, illite-smectite, kaolinite and occasional reports of minor montmorillonite. The most recent interpretations of the origins of the clay minerals in these rocks emphasize the role of progressive diagenetic and low-grade metamorphic reactions, based on correlations of clay mineral assemblages and parameters such as illite crystallinity with organic maturation data. This interpretation argues that the illite-smectite in the shales is derived largely from a precursor detrital smectite. However, the finding of two populations of morphologically and structurally distinct illite-smectite particles in the Middle and Upper ORS sandstones suggests a more complex picture involving different diagenetic episodes. In addition, the likelihood of a smectitic-rich detrital input to the ORS may also be a point of debate. The clay mineralogy of the North Sea offshore is also described briefly, in addition to the marine Devonian in southwest England. The latter is characterized by chlorite and illite assemblages of low-grade metamorphic origin, although smectite and kaolinite are also found occasionally in these rocks. The offshore ORS, however, contains a variety of clay minerals, including an assemblage similar to that found in the Lower ORS south of the Highland Boundary Fault and notably contains a tosudite-like mineral.

KEYWORDS: ORS, Old Red Sandstone, Devonian, clay mineralogy, illite, chlorite, kaolinite, illite-smectite, chlorite-smectite, tosudite, dioctahedral chlorite, sudoite, UK.

The Devonian sedimentary rocks of the UK consist of two main facies, the non-marine Old Red Sandstone and the marine Devonian. The more extensive of the two, the Old Red Sandstone (ORS), is a typical red-bed continental facies consisting of claystone, siltstone, sandstone and conglomerate deposited in fluvial, alluvial, lacustrinal and aeolian environments generally under oxidizing conditions. Fossils are relatively rare and biostratigraphical correlation is limited, being based mostly on fossil fish and more recently on palynology, though many schemes remain largely lithostratigraphic. House *et al*. (1977) give a detailed account of correlation and stratigraphy: more general accounts are given by Dineley (1992), Mykura (1991) and Cope *et al*. (1992). For the offshore areas, see Marshall & Hewett (2003) for a recent account of Devonian stratigraphy in the Northern North Sea. Most of the ORS is Devonian in age but in many areas Lower ORS sedimentation began in Silurian times and the Upper ORS frequently extends into the Carboniferous (Tournasian). Over this period the geography and climate of the region changed dramatically as the final stages of the Caledonian orogeny came to a close and as the resulting ORS continent drifted slowly northwards from tropical to more equatorial latitudes. The main onshore outcrops of the ORS are in South Wales and the Welsh Borderland, the Northumberland Trough, the Midland Valley of Scotland and the Orcadian Basin which includes northeast Scotland, Orkney and the Shetland Islands (Fig. 1). The ORS also occurs extensively in the North Sea where it has been penetrated in many exploratory wells.

Onshore Devonian sediments of marine origin are restricted to southwest England. They consist of turbiditic sand and mudstone with reef limestone, and are often interbedded with basaltic pillow lava and tuff and crosscut by minor intrusions of olivine basalt, dolerite, lamprophyre and picrite (Dewey & Flett, 1911; Dineley, 1992). These marine Devonian sediments were initially affected first by the compressional, deformational and regional metamorphic events associated with the Variscan (Hercynian) orogeny in Devonian and early Carboniferous times. Locally they were subsequently thermally metamorphosed adjacent to the post-orogenic intrusion of granite in SW England. The northern limit (or front) of Variscan deformation also affected the ORS of southwest Wales (Fig. 1)

The mineral detritus that makes up the ORS consists very largely of the erosional products stripped off the uplifted Caledonian Mountain Belts. These include Laurentian terranes north of the Highland Boundary Fault, uplifted in the Scandian Orogeny (~420–400 Ma), and those uplifted in the Acadian Orogeny that created a mid-Devonian (–400-375 Ma) unconformity across southern Britain (Soper & Woodcock, 2003). Subaerial volcanism was also widespread both in and surrounding many of the areas where the ORS

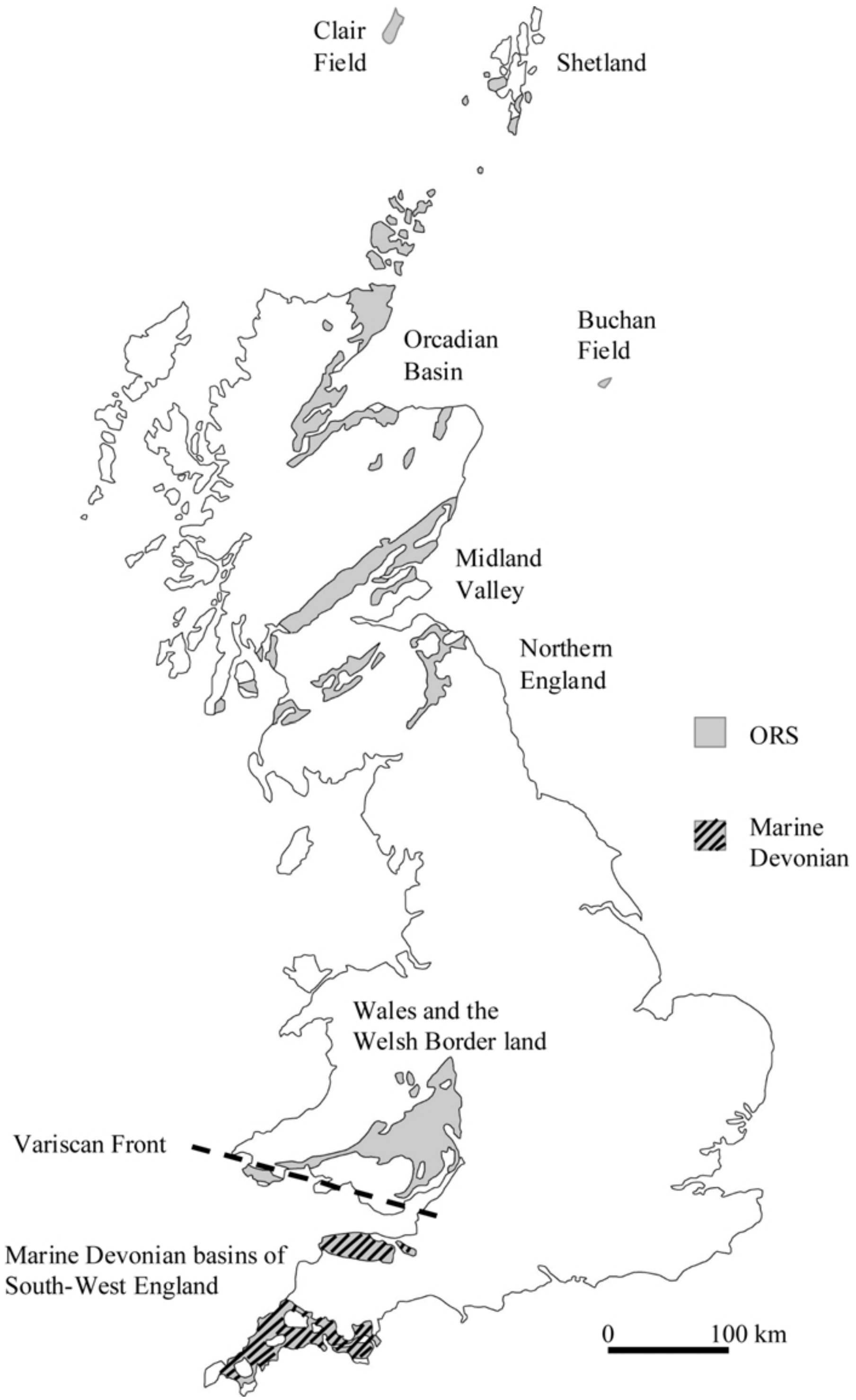

FIG. 1. Distribution of the Old Red Sandstone (ORS) and the marine Devonian in Great Britain. Approximate offshore locations of ORS reservoirs in the Clair and Buchan fields are also shown.

is preserved, and volcanic ash and the weathering of lavas must also have contributed considerably to the sediment and to the subsequent development of clay minerals during its burial history. There is also widespread evidence of soil formation in the alluvial ORS (Allen, 1986), but the extent to which primary minerals were weathered, and clay minerals formed by weathering processes acting on the Caledonian detritus is unknown. Much of the ORS has not been affected by regional metamorphic events. However, the Lower ORS has been folded and cleaved on Anglesey (N Wales) during the Acadian orogenic event, and similarly affected by the Variscan event in southwest Wales. More local thermal metamorphism is associated with granitic and other igneous intrusions (e.g. the newer granites of the Scottish Highlands; Cheviot granite of northern England) emplaced after the Caledonian Orogeny, and have affected in particular the ORS sediments in the Orcadian Basin and in the Northumberland Trough. A ubiquitous but no doubt regionally variable degree of diagenetic alteration of the ORS must also be assumed given its age and burial history beneath younger rocks.

The internal correlation and the stratigraphy of the ORS and the marine Devonian are limited by the generally unfossiliferous nature of the continental facies, poor preservation in the metamorphosed marine Devonian sediments and the absence of floral and faunal elements common to both facies. Traditionally the ORS is divided into Lower, Middle and Upper divisions. The Lower ORS is best developed in Wales and the Welsh Borderland and the Midland Valley of Scotland. The Middle ORS, of Middle Devonian age, is essentially present only in the Orcadian Basin, where it accounts for most of the succession. Elsewhere, all of Middle Devonian and much of Upper Devonian time, some 20 Ma, is represented by an unconformity between Lower ORS and Upper ORS strata, the latter being conformable with the overlying Carboniferous. In northern areas, ORS facies persisted longer into the Carboniferous than in southern regions. Offshore, important oil reservoirs in the ORS are generally in rocks that are tentatively correlated with the onshore Middle ORS and the Upper ORS. Locally, many different group and formation names are in use. Herein, mention is made only of a small selection of groups and formations that are either stratigraphically significant, or for which something is known about the clay mineral assemblages they contain (Fig. 2).

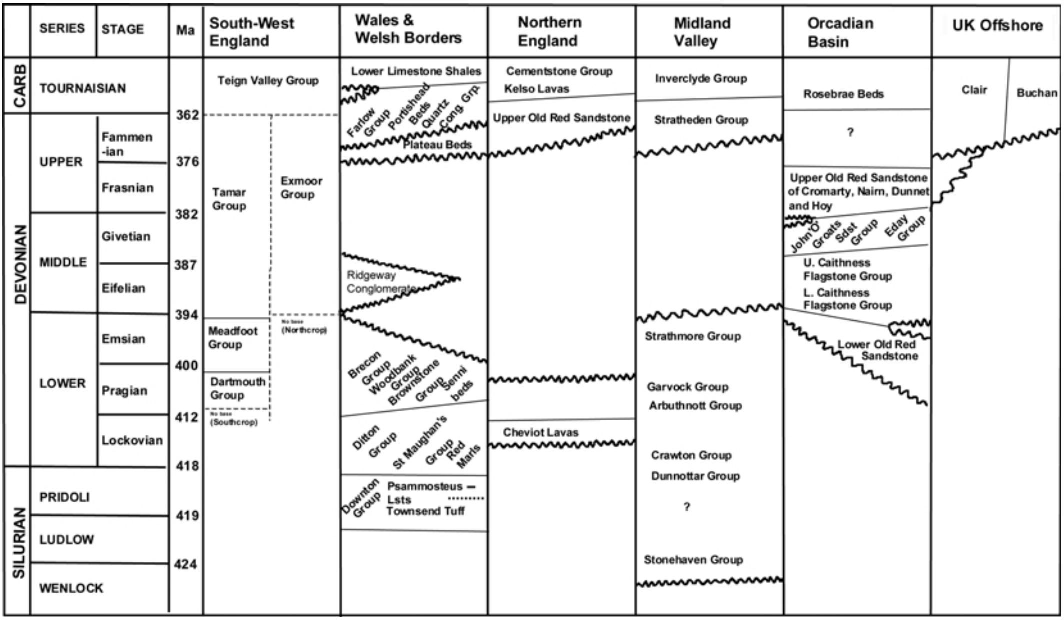

FIG. 2. Abbreviated stratigraphy of the ORS and marine Devonian in Great Britain. Note that parts of the Lower ORS are Silurian in age and parts of the Upper ORS are Carboniferous.

CLAY MINERAL ASSEMBLAGES OF THE ORS

Present knowledge on vertical and lateral variations in the clay mineral assemblages of the ORS is sparse, despite their extensive outcrop, stratigraphical thickness (up to 4000 m) and varied geological history. Prior to Perrin's (1971) compilation the only published works were those of Ferrero (in Burolett *et al*., 1969) and Wilson (1971) both concerned with parts of the ORS of Scotland. Subsequent publications include Parker *et al*. (1983), Hillier & Clayton (1989), Garvie (1992), Hillier (1993), Jeans (1995) and Pay *et al*. (2000). Unpublished clay mineral data on the ORS of South Wales are also found in theses by Watts (1977) and Maskall (1985), whilst that of Hillier (1989) is concerned with the ORS of the Orcadian Basin. In addition, in this review, we present data from a further 97 ORS samples mainly from Wales and the Welsh Borderland, a region where data were previously very limited. Details of these new samples are given in Appendix A.

The clay mineralogy of the ORS is diverse; indeed, in many respects the assemblages of clay minerals found in the ORS are among the most diverse of any geological division. On the one hand, one may encounter assemblages containing abundant smectite or abundant kaolinite. On the other hand, assemblages consisting only of well crystallized illite and chlorite are commonplace and similar to those found in the low-grade metamorphic terrains of the Lower Palaeozoic. Some of this diversity might be explained in terms of spatial variation in patterns of burial diagenesis and low-grade metamorphism, but other aspects of ORS clay mineralogy may be related to differences in provenance, such as the importance or otherwise of syn-depositional volcanism or of low-grade metamorphic rocks as a source of detritus. This account of the clay mineralogy of the ORS is organized along traditional regional lines. For each region its stratigraphy is outlined. This is followed by an attempt to present the available clay mineralogy data in relation to this stratigraphic framework, and the genesis of the clay mineral assemblages are discussed and interpreted.

In the parts of the ORS that have been studied in detail, the signatures of diagenesis are clear. In other parts of the ORS, so little is known about the clay mineral assemblages observed that important questions remain over the relative importance of provenance and diagenetic factors. In our following attempts to interpret the observed patterns we have tried to carefully consider the various possible explanations on the basis of the balance of the available evidence. The questions that this leaves open are many and, just like Perrin (1971), we can only hope that by pointing out the gaps and where uncertainty exists more research will be stimulated.

WALES AND THE WELSH BORDERLAND

Stratigraphy and sedimentology

The Devonian of this region comprises the Lower ORS and Upper ORS separated by a regional unconformity, and apart from the Ridgeway Conglomerate the Middle ORS is absent. The Lower ORS (2000–4000 m) is divided into the Downton, Ditton and Brecon Groups. The Downton Group is in places conformable with the underlying marine Silurian and over much of the region the transition is represented by the Ludlow Bone Bed, a condensed sequence of shelly and phosphatic material. The succeeding deposits are of marginal marine facies and pass gradually upwards into continental coastal facies. Mid-Wales was more persistently influenced by marine conditions and here the Ludlow bone bed is absent. Important marker horizons in the Downton Group include the Psammosteus Limestone and the Townsend Tuff (Allen & Williams, 1981). The Psammosteus Limestone represents a well developed fossil caliche or calcrete soil profile, modern analogues of which develop under semi-arid seasonal climates. Less well developed calcretes are common throughout the Lower ORS (Allen, 1986). The sediments of the succeeding Ditton Group are generally dominated by igneous and sedimentary detritus, in contrast to the dominantly metamorphic detritus of the Downton Group. The sediments of the Downton Group and the basal part of the Ditton Group are of late Silurian age (Fig. 2; Cope *et al*., 1999).

The sediments of the Ditton Group consist of fluvial sandstone, siltstone and mudstone arranged in fining-upward cycles (Allen, 1985). The overlying Brecon Group also shows fining upward cycles of similar fluvial sediments containing many clasts of Lower Palaeozoic formations from the Welsh area.

The Upper ORS of Wales and the Welsh Borderland (up to 300 m) is developed mainly in a marginal marine facies. The earliest deposits, the Plateau Beds of central south Wales, are composed of conglomerate, sandstone and mudstone of probable late Frasnian to Fammenian age. They are overlain disconformably by the Grey Grits consisting mostly of quartz pebble conglomerate and quartzite, a facies that was widely developed across the region at this time (the Quartz Conglomerate Group). Indeed, the sandstones of the Upper ORS are generally much more mature than those of the Lower ORS. In most areas the upper parts of the Upper ORS are of Early Carboniferous (Tournaisian) age and pass conformably into the Carboniferous Lower Limestone Shales.

Clay mineral assemblages of the Lower ORS

Downton Group. All of the data compiled by Perrin (1971) for the Lower ORS are from mudstones or marls of the Downton Group from the easternmost outcrop areas of the West Midlands, the Welsh Borderland and Monmouthshire. These assemblages are described as being dominated either by micaceous or by smectitic minerals, with subordinate chlorite. Kaolinite is reported in the tabulated analyses but is described as 'uncertainly present'. A notable feature is the identification of some samples that are exceedingly rich in smectite or randomly interstratified illite-smectite (I-S), which may account for 90% of the clay fraction. In the introduction to Perrin (1971), these samples are referred to as 'bentonitic clay' but it is not clear if this term is used simply because of the high smectite content (*sensu* Grim & Güven, 1978) or if there is other evidence (unpublished) for bentonites in the sense of altered volcanic ash. Indeed, the latter seems quite possible since the Downton contains a group of prominent volcanic tuff deposits, known as the Townsend Tuff, which can traced throughout Wales and the Welsh Borderland (Allen & Williams, 1981). Furthermore, reports of tuffs are quite common in the Lower ORS of Wales and the Welsh Borderland, details of which were summarized by Allen & Williams (1981). The clay mineralogy of the Townsend Tuff was subsequently studied in some detail by Parker *et al*. (1983) and by Maskall (1985). Parker *et al.* (1983) identified five different clay mineral assemblages that characterize the tuff in different regions (Fig. 3). Essentially, the assemblages change from east to west across the ORS outcrop. The sequence of changes range from highly smectitic and/or kaolinitic (regions I and II), through an assemblage with major I-S, low chlorite and no kaolinite (region III), to an assemblage with small amounts of I-S and large amounts of illite and chlorite (region IV), and finally to an assemblage with only illite and chlorite (region V). Parker *et al*. (1983) concluded that this variation was probably related to the pattern of increasing diagenetic grade from east to west, presumably due to the general increase in the depth of burial of the ORS in this direction, with the additional effects of Variscan tectonism in the most westerly occurrences of the tuff. Maskall (1985) came to similar conclusions, although he identified only two clay assemblages from the Townsend Tuff, namely, (1) illite, I-S and chlorite, and (2) illite, I-S and kaolinite, the kaolinite being confined to the region of the Forest of Dean. The first of Maskall's assemblages effectively lumped together assemblages I, III, IV and V of Parker *et al*. (1983) as a continuum varying only in the proportion of discrete illite and proportion of illite in the mixed-layer I-S. The percent smectite in I-S was shown by Maskall (1985) to vary progressively westwards from samples near end-member smectite, such as at Hope Gutter Shropshire, right through to end-member illite in the most westerly localities. At some localities where the tuff changes back to normal sediments, Maskell identified illite and chlorite which he interpreted as a background detrital input.

It may be noted that the interstratified mineral, interpreted by Parker *et al*. (1983) as representing I-S, is characterized by a large spacing peak at ~29 Å in the air-dried state that expands to 31.5 Å after glycolation. These spacings may be accounted for by R1 ordered interstratified I-S, with a composition of ~30% smectite layers. However, the large-spacing peaks are rather well defined, and a contribution from a mixed-layer chlorite-smectite, or chlorite-vermiculite, may be suspected. In other words there may be two interstratified phases in samples with these characteristics. As will be seen in the following discussion of the clay mineralogy of the Ditton Group based on newly collected material, this is a common occurrence.

Ditton Group. There are few published analyses ascribed to rocks belonging to the Ditton Group in Wales and the Welsh Borderland. Perrin (1971) recorded clay mineral analyses from two samples (from south Shropshire), containing large amounts

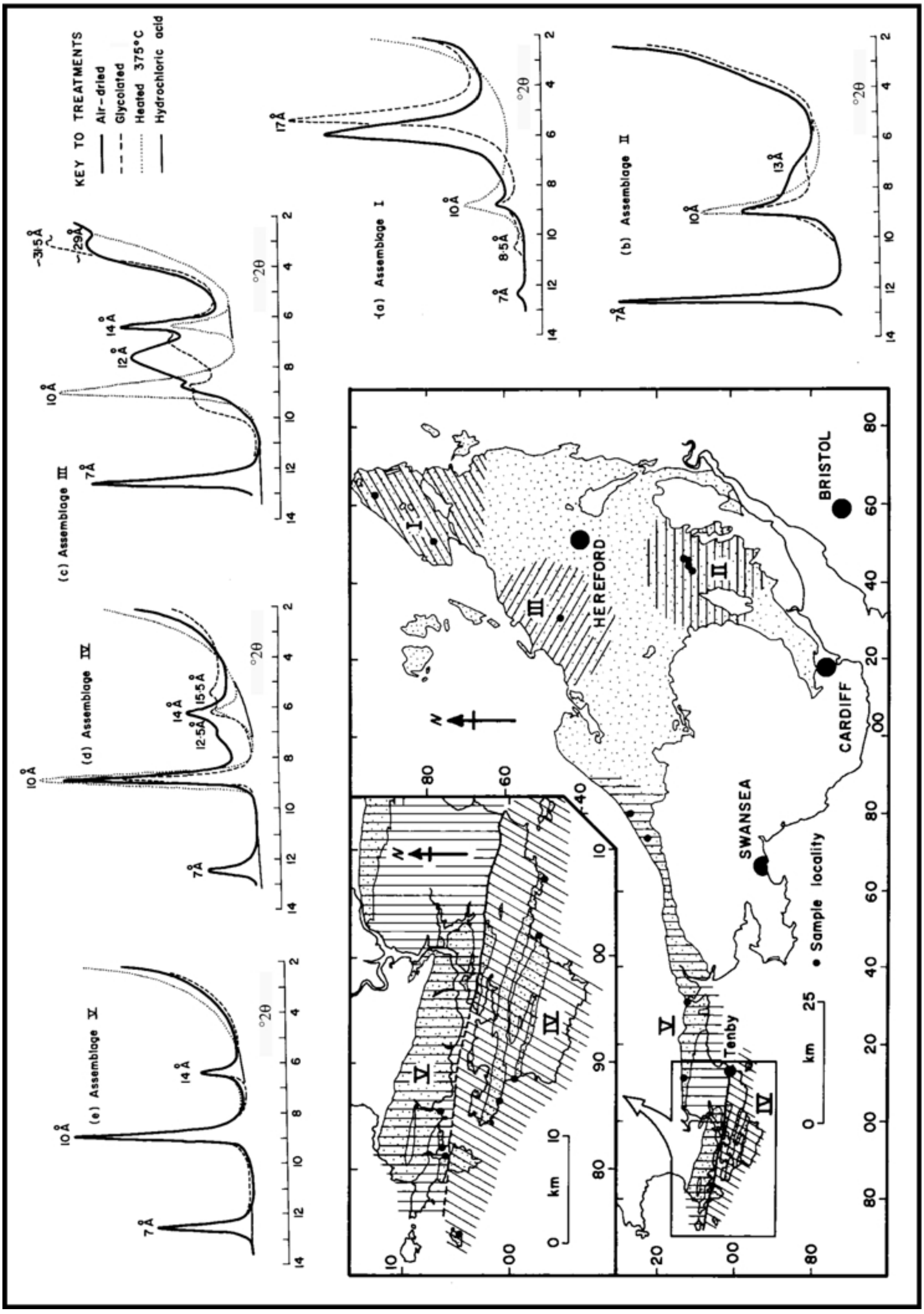

FIG. 3. Clay Mineralogy of the Townsend Tuff Bed, and distribution of the five clay mineral zones identified by Parker *et al.* (1983) (modified from Parker *et al.* (1983, their figs 4 and 5).

of mica and chlorite, respectively. Other phases recorded in these samples include interstratified vermiculite/talc and boehmite, but these are of doubtful authenticity. Watts (1977) studied the clay mineralogy of two calcretes in the Lower Ditton group and concluded that the typical assemblage consisted of illite, I-S, smectite, Fe-rich chlorite and minor kaolinite. Textural evidence suggested to Watts (1977) that most of these clays were detrital in origin, although smectite and I-S could be either detrital or authigenic. Recently, Garvie (1992) reported the occurrence of tosudite (regularly interstratified R1 dioctahedral chlorite/dioctahedral smectite) from the St Maughan's Group, at Lydney Harbour, in the Forest of Dean (SO 655021). It occurs in fluvial, fine to medium grained, micaceous sandstones, together with some kaolinite, illite and dioctahedral chlorite, and is characterized by a large spacing of ~29 Å in the untreated state, expanding to ~31 Å after glycolation. The 060 reflection at 1.507 Å proves the mineral's dioctahedral nature (Fig. 4). Garvie (1992) mentions that X-ray diffraction analysis (XRD) examination of different size fractions, and of the intact sample by scanning electron microscopy (SEM), indicates that the tosudite occurs predominantly in the fine clay fraction and that kaolinite is present mostly in the coarser clay in its common 'book' or 'accordion-like' form.

Because of the paucity of information on the clay mineralogy of the Welsh Dittonian sequence in general, new samples were collected by the authors

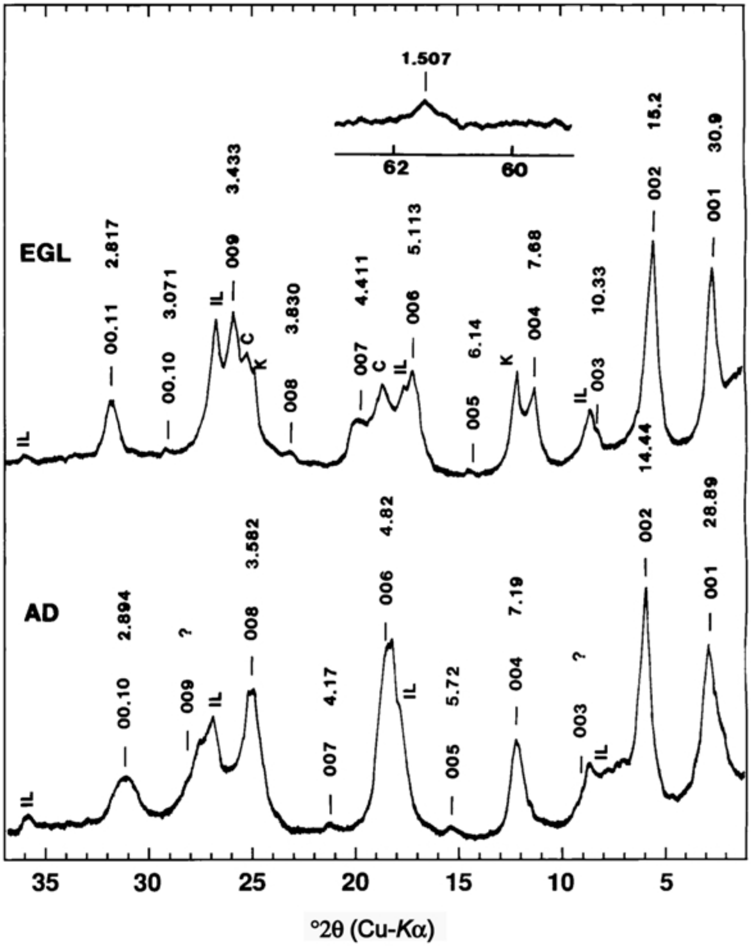

FIG. 4. XRD patterns of tosudite from the St Maughan's Group, Forest of Dean after Garvie, 1992. AD = air-dried, EG = ethylene glycol solvated, insert shows '060' region.

and analysed by XRD. Selected samples were also analysed by Fourier Transform Infrared (FTIR) spectroscopy and by SEM. Altogether, 39 new Dittonian samples were investigated comprising: six samples from a road cutting in presumed Dittonian strata (DEV16), collected during construction of the A4042 at Newport; 12 samples from alongside the A40 between Monmouth and Ross; 12 samples from Freshwater West in Pembrokeshire; and nine samples from scattered localities in Herefordshire and the West Midlands. In addition, 11 samples were investigated from ORS outcrops that were located near the Dittonian/Breconian boundary but whose exact attribution is unknown. Sample details are given in Appendix A and results from this new sampling campaign as described below.

Two of the six samples (DEV5 and DEV6) from the Newport area yielded an XRD pattern characterized by a large spacing peak at ~ 29 Å expanding to ~31 Å after glycolation (Fig. 5a) similar to the tosudite described by Garvie (1992). Both of these samples are sandstone. In addition, all the samples contained a chlorite mineral with an unusually intense 003 reflection compared with the 001 and 002 peaks, from which it may be inferred that the mineral is a dioctahedral chlorite. Indeed, in three of the samples the 003 reflection was the most intense of any peak attributable to chlorite. One of the sandstone samples also contained a small amount of kaolin, presumably kaolinite (Fig. 5a). An ordered mixed-layer I-S is also abundant in all six samples, including both sandstone and shale. In air-dried patterns the presence of this phase is indicated mainly by a large peak at ~11–12 Å. Upon glycolation this peak 'splits' to give two peaks, one at 12–13 Å and the other ~9 Å. The XRD pattern also shows a small-angle peak at ~27 Å, which is not entirely resolved from the background in the glycolated traces. Following heat treatment there is a substantial increase in the intensity of the 10 Å peak, which may be assigned to the collapse of this mixed-layer I-S. The overall character of this phase, with respect to peak position intensities, and particularly the response to glycolation, indicates that it contains ~25% expandable (smectite) layers. Further confirmation of the dioctahedral nature of the chlorite, and that the chlorite-smectite present in the sandstones is tosudite-like, was provided both by the insolubility of these phases in 6 M HCl (Hayashi & Oinuma, 1964) and the position of the 060 reflection at ~1.50 Å.

Of the 12 samples collected from a variety of lithologies exposed along the A40 road between Monmouth and Ross-on-Wye (LORS 22 to LORS 33), seven clay fractions also showed a large-spacing peak similar to that described above for the samples from the Newport area. Complete analysis of peak positions in response to various treatments as well as testing with 6 M HCl once again confirmed the identification of a tosudite-like mineral in these samples. In addition, kaolinite occurs in nine out of the 12 samples, but is notably most abundant in those samples that also contain the tosudite-like mineral. Just like the Newport samples, an ordered mixed-layer I-S is also abundant in all the samples. Its presence is indicated mainly by a large broad peak at ~12 Å in the air-dried trace, which shifts to 13–14 Å upon glycolation, coupled with the appearance of distinct peaks at ~9.3 and 5.3 Å, and a large-spacing peak ⩾27 Å, not clearly resolved from the steeply sloping low-angle background (Fig. 5b). Discrete illite and chlorite are also ubiquitous in these samples, but in some samples the chlorite appears to be trioctahedral and in others dioctahedral.

The twelve samples of mudrock and fine-grained sandstone collected from Freshwater West, Pembrokeshire, contain a characteristic illite-chlorite assemblage. The illite is an aluminous dioctahedral variety and contains few, if any, smectite mixed layers since the 10 Å basal reflection is largely unaffected by glycol. Peak full widths at half height (FWHM) measured on all twelve samples average 0.40 ($\Delta^o 2\theta$) for the air-dried samples and 0.37 ($\Delta^o 2\theta$) for glycolated samples. One sample, from a clayey parting in sandstone, was almost monomineralic. The position of the non-basal peaks in a random powder pattern of this sample indicates that the $2M_1$ *trans*-vacant polytype is the dominant phase, although a high background in the region of the diagnostic prismatic peaks suggests that some material with more disordered stacking may also be present (Fig. 6a). With regard to the chlorite in these clay fractions, in at least four samples it appears to be a dioctahedral aluminous variety. This is evident from the intensity of the 003 reflection, which in these samples is the most intense of any chlorite peak, and is confirmed by the insolubility of the chlorite when tested with 6 M HCl and the position of the 060 at ~1.51 Å (Fig. 6b). Seven of the 11 samples analysed also contained a smectitic

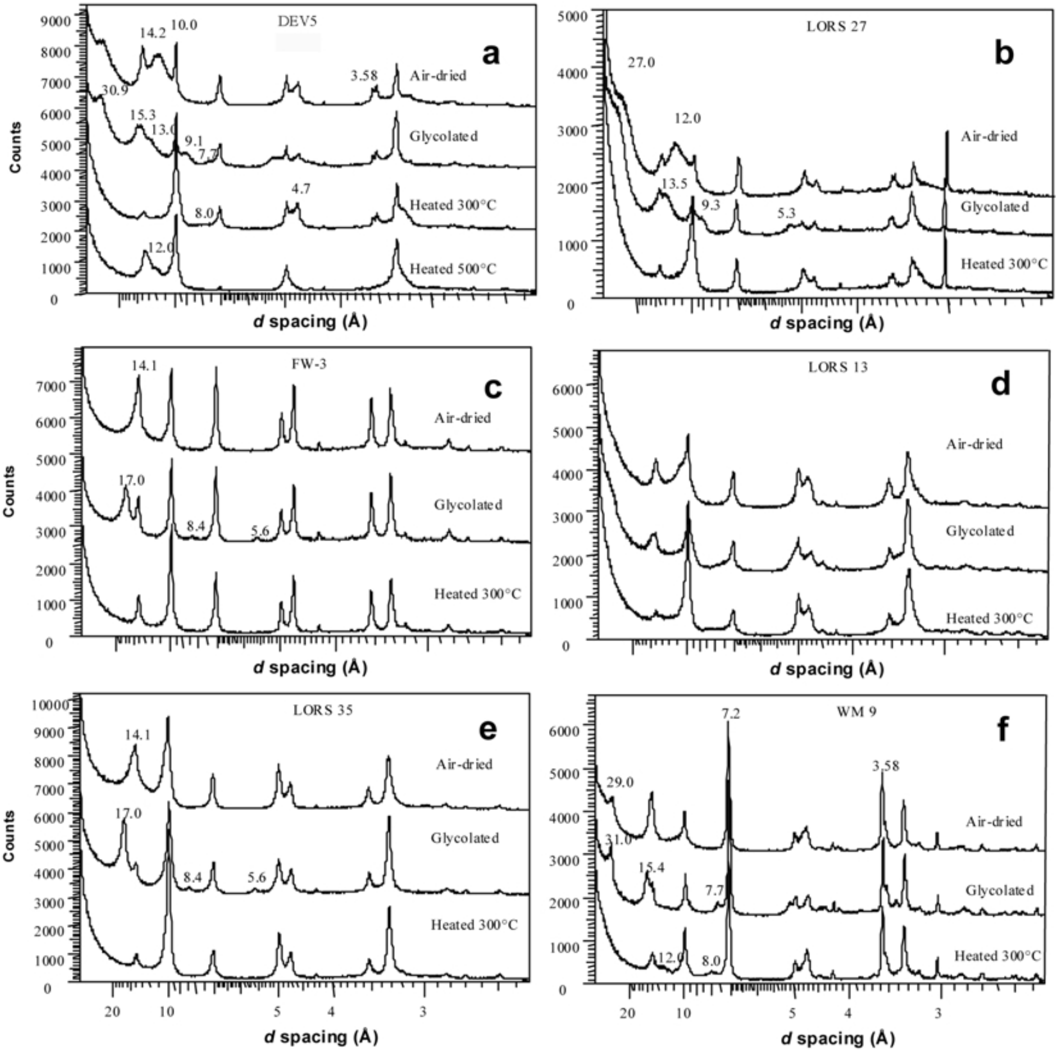

FIG. 5. XRD patterns of various samples collected for this review. Where shown, patterns for different treatments are offset vertically for clarity. (a) XRD patterns of tosudite-bearing sandstone (DEV5) from presumed Dittonian outcrop near Newport, South Wales (NGR ST312912). Tosudite gives notable peaks at 30.9, 15.3 and 7.7 Å in glycolated trace, and peaks at 12.0 and 8.0 Å in heated traces. After heating to 550ºC the 12 Å peak is accentuated relative to that at 8.0 Å. The peaks are unaffected by treatment with 6 M HCL (not shown). Note also the relatively high intensity of the peak at 4.7 Å following heating to 300ºC. Peaks at 13.0 and 9.0 Å also indicate the presence of abundant mixed-layer illite-smectite, and the peak at 3.58 Å indicates the presence of some kaolinite. (b) XRD pattern of sample (LORS 27) with abundant mixed-layer illite-smectite, from the Dittonian of Monmouthshire, south Wales. The ordered mixed-layer illite-smectite gives a prominent peak at ~12 Å in the air-dried trace, and 13.5, 9.3 and 5.3 Å in the glycolated trace. Note also the greatly enhanced 10.0 Å peak after heating to 300ºC due to collapse of the mixed-layer illite-smectite. Other minerals present in the sample include illite, chlorite (trioctahedral) and minor kaolinite. The sharp peak at ~3.03 Å is due to calcite. (c) XRD traces of a smectite-bearing sample from Freshwater West (FW-3). Smectite expands to 17 Å following glycolation with a rational series of higher orders, e.g. at 8.4 and 5.6 Å. This smectite is insoluble in 6 M HCL (not shown), identifying it as a dioctahedral smectite. The sample also contains 'well crystallized' illite and chlorite. (d) XRD patterns of sample LORS 13, showing abundant but low-expandability mixed-layer illite-smectite and indications of a tosudite-like phase. (e) XRD patterns of sample LORS 35 showing abundant dioctahedral smectite together with well crystallized illite and chlorite. Note the similarity of this sample to those from the Freshwater West locality some 60 km further west (Fig. 5c). (f) XRD patterns of a sample rich in kaolinite and tosudite from the West Midlands (WM 9). Tosudite gives intense peaks at 31.0, 15.4 and 7.7 Å in the glycolated trace.

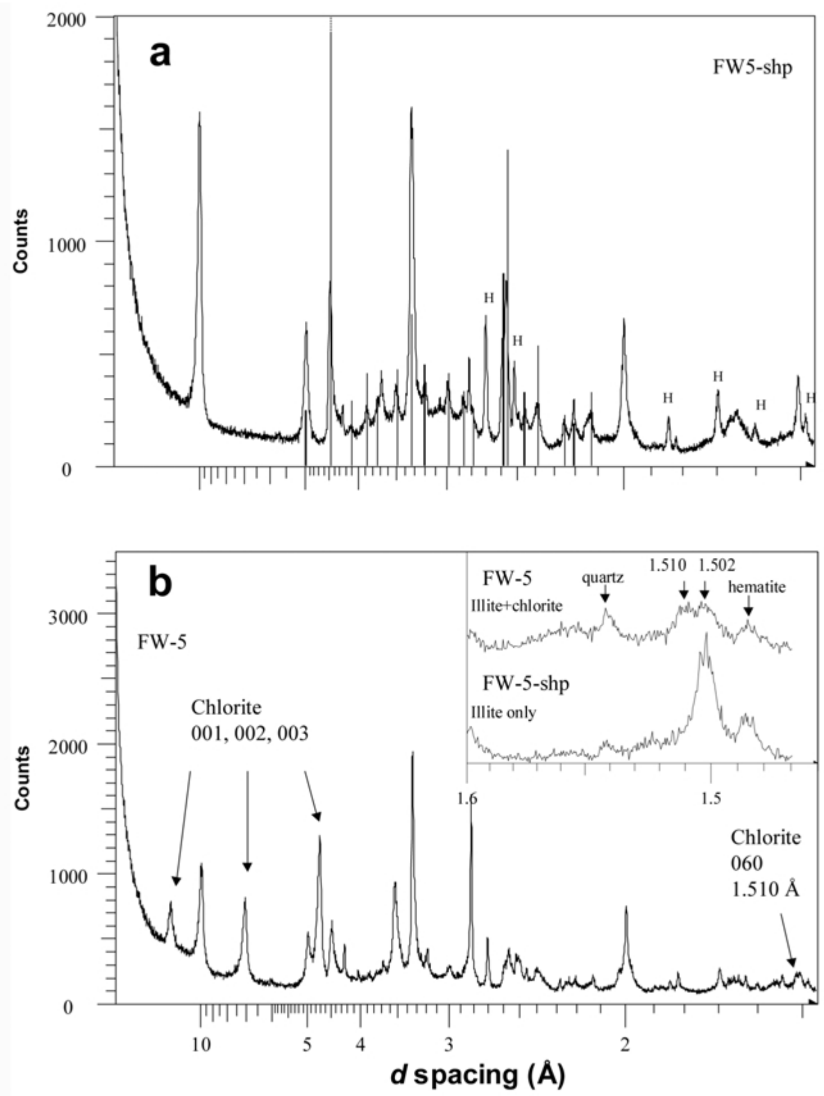

FIG. 6. (a) Random powder XRD pattern (<2 μm size fraction) of illite identified as a $2M_1$ *trans*-vacant polytype from the Dittonian of Pembrokeshire, Freshwater West, South Wales (sample FW-5-shp). Key peaks for polytype identification are shown by the stick pattern. The sample also contains abundant hematite (H). (b) Random powder XRD pattern (<2 μm size fraction) showing dioctahedral chlorite in sandstone from Freshwater West (FW-5). The dioctahedral nature is indicated by the intensity of chlorite 003 reflection and by the position of the 060 reflection at ~1.510 Å. The insert shows comparison of the 060 region of FW-5 with sample FW5-shp.

mineral, usually in minor amounts but sometimes as a moderately abundant phase. The mineral yields a well defined peak at ~17 Å after glycolation, and analysis of the peak positions of higher orders shows them to be rational in all cases. This indicates that the mineral is a pure smectite with no evidence of mixed-layering (Fig. 5c). This phase was not soluble when treated with 6 M HCl so that it may be concluded that it is a dioctahedral aluminous smectite. Finally, of the 12 Pembrokeshire samples examined, three contained kaolin, usually in minor amounts but in one sample (a buff, fine-grained quartzitic sandstone) it is abundant. The XRD patterns of the kaolin in this

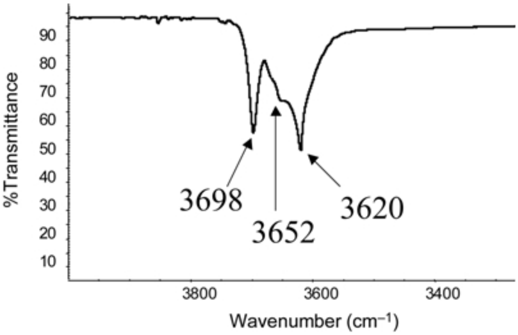

FIG. 7. FTIR spectra of the hydroxyl-stretching region of kaolinite in sample FW-9 from Freshwater West showing that the kaolinite is a disordered variety.

sample show rather broad peak widths at half peak height (>0.33 $\Delta°2\theta$) suggesting fine particle size. Furthermore, examination by FTIR spectroscopy indicates that the kaolin is poorly ordered kaolinite (Fig. 7). Examination of this sample by SEM shows a very tightly cemented texture (Fig. 8a) but at high magnification kaolinite could be identified in some parts of the matrix between the framework sandstone grains (Fig. 8b).

Three groups of samples were collected that could not be attributed stratigraphically with certainty. They are likely to be from either the upper part of the Dittonian or the lower part of the Breconian. The first group of samples (LORS 10–15) from the proximity of the boundary between the Ditton and Brecon Groups are sandstone and shale, collected at roadside outcrops on the A465 Heads of the Valleys road near Gilwern. These samples are characterized by a relatively simple illite and chlorite assemblage. However, the illite basal reflection at 10 Å is markedly asymmetrical, sometimes to such an extent as to define a separate peak. This asymmetry is completely removed by glycolation, leaving a sharp 10 Å reflection. The XRD diagram is similar, but not identical, to the calculated curve for an R3 ordered I-S with <10% smectite (Moore & Reynolds, 1997 p. 274). In all samples the 10 Å peak is sharply intensified after heat treatment. In general, the results indicate a mixture of R3 I-S and discrete illite. The chlorite in some samples appears trioctahedral (e.g. LORS 11) whereas a relatively intense 003 suggests there may be some admixture with a dioctahedral form in some of the others. In two samples (LORS 12 and 13) the 14 Å peak moves to a slightly larger-angle spacing after glycolation and to a slightly lower one after heating at 300° C. In these samples a very weak low-angle shoulder at ~30 Å can be seen on the diffraction pattern (Fig. 5d).

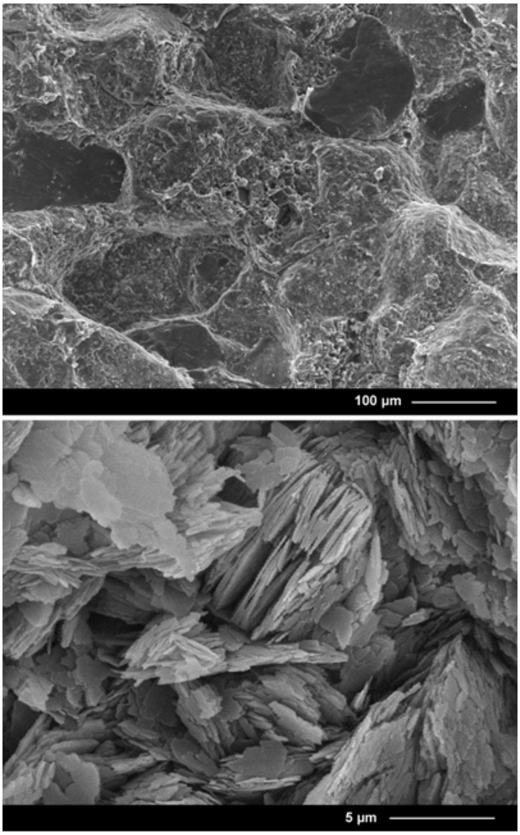

FIG. 8. SEM images of kaolinite-bearing sandstone (FW-9) from Freshwater West. The lower-magnification image shows the tightly cemented nature of the sample. The higher-magnification image shows kaolinite 'books' which can be found in parts of the sample.

Samples LORS 34–38, comprising three sandstones and two mudrocks, were collected from the base of the ORS escarpment along the A4069 road to Llangadoc. In these samples the clay mineralogy varies according to lithology. Sandstones contain an illite, chlorite and kaolinite assemblage with few interstratified smectite layers judging from the responses to ethylene glycol and heating. A similar assemblage also occurs in the mudrocks but, in addition, there is a smectitic mineral that shows a clearly defined reflection at ~17 Å after glycolation (Fig. 5e). High-order peak positions at

8.4, and 5.6 Å indicate that it is pure smectite and once again testing with 6 M HCl indicates that it is dioctahedral smectite, identical in these respects to the smectite found in the Ditton Group samples from Freshwater West (Fig. 5c). The XRD patterns of these samples (LORS 34−38) are also characterized by a very broad 7 Å reflection, especially evident in the sandstones. In part this may be due the presence of both kaolin and chlorite in some samples, but mainly it appears to be due to the small crystallite size of the kaolin. Identification of the kaolin mineral was confirmed by FTIR spectroscopy and the observation of characteristic OH-stretching bands in the 3700−3600 cm^{-1} region. The absence of evidence for intermediate bands indicates either very poorly crystalline kaolinite or possibly halloysite. However, the lack of any obvious response of the kaolin to solvation with ethylene glycol (Hillier & Ryan, 2002) is consistent with a poorly ordered kaolinite, rather than halloysite. Both sandstones from this group of samples also show a distinct but very small peak located at ~9.5 Å that is unstable when heated to 300ºC. An additional peak at 4.72 Å that also exhibits heat instability suggests the presence of a trace amount of the manganese mineral lithiophorite in the sandstones, presumably a modern weathering product, but this identification requires confirmation by other methods.

The final area from which a set of nine new presumed Dittonian samples were collected is along the A49 in Herefordshire and further north in the West Midlands. All of these samples contained kaolinite, often as an abundant phase. Additionally, seven out of the nine samples, all sandstones, contained abundant tosudite-like minerals, showing a characteristic large-spacing peak at ~32 Å after glycol treatment with a rational series of higher orders. Indeed, both tosudite and kaolinite (Fig. 9) are generally more abundant in these samples than in any others collected from the Wales-Welsh Borderland region (Fig. 5f) and, like the samples from the Monmouth/Ross on Wye area (LORS 22−33), tosudite is most abundant in those samples that contain the most kaolinite. Mixed-layer I-S, with ~30% expandable layers, is also present in all samples, but is relatively more abundant in the finer-grained rocks. Illite is ubiquitous, but notably of very much lower relative abundance compared to ORS samples from other parts of this region, especially those located in the most westerly localities.

Brecon Group. Nineteen samples of sandstone and mudrock were collected from an area encompassing the Taff Fawr (LORS 3−6 and MT 1−4), Taff Fechan (LORS 1−2), Usk (LORS 7−9) and Tawe valleys (LORS 16−21). All show essentially the same clay mineralogy, consisting of an illite and chlorite assemblage, usually with illite predominant. The illite is interstratified with a small amount of smectite (5−10%) as indicated by responses to glycol and heat treatment. Indeed detailed analysis of peak positions indicates that the illitic material in many of the Brecon Group samples is dominated by a highly illitic I-S of low expandability rather than illite *per se*. The evidence for this is that the whole 10 Å peak shifts following ethylene-glycol treatment, whilst heating produces a very marked increase in intensity (Fig. 10). HCl treatment confirms that illite in these rocks is a normal dioctahedral variety. In contrast, although the chlorite in some samples is clearly the more common trioctahedral type, in about half of the Brecon Group samples it is the more unusual dioctahedral type. This is illustrated by the XRD pattern of one sample, collected alongside the A470 road, in which the chlorite was unaffected by treatment with 6 M HCL and the 003 is the most intense of the basal chlorite peaks, both characteristics indicating its dioctahedral nature (Fig. 11a). Additionally, in some samples, the intensity distribution of the basal chlorite reflections suggests that the samples may contain a mixture of dioctahedral and trioctahedral types of chlorite. Kaolinite was not found in any samples of the Brecon Group.

Clay mineral assemblages of the Upper ORS

Six unpublished clay mineral analyses are available from the Grey Grits in the Taff Fechan and Taff Fawr valleys north of Merthyr Tydfil (Appendix A). The clay assemblages of all samples are dominated by illite plus trioctahedral chlorite. Kaolinite is absent. Illite is dioctahedral and contains 5−10% interstratified smectite, and in all six samples chlorite is a trioctahedral variety (Fig. 11b) as confirmed by its ready solubility, even in dilute (10%) HCl. Further east, however, two newly analysed samples from the Upper ORS of Monmouthshire (Kymin-1−2), both micaceous quartz pebble-bearing sandstones of the Upper ORS Quartz Conglomerate Group were found to contain illite, abundant kaolinite and mixed-layer

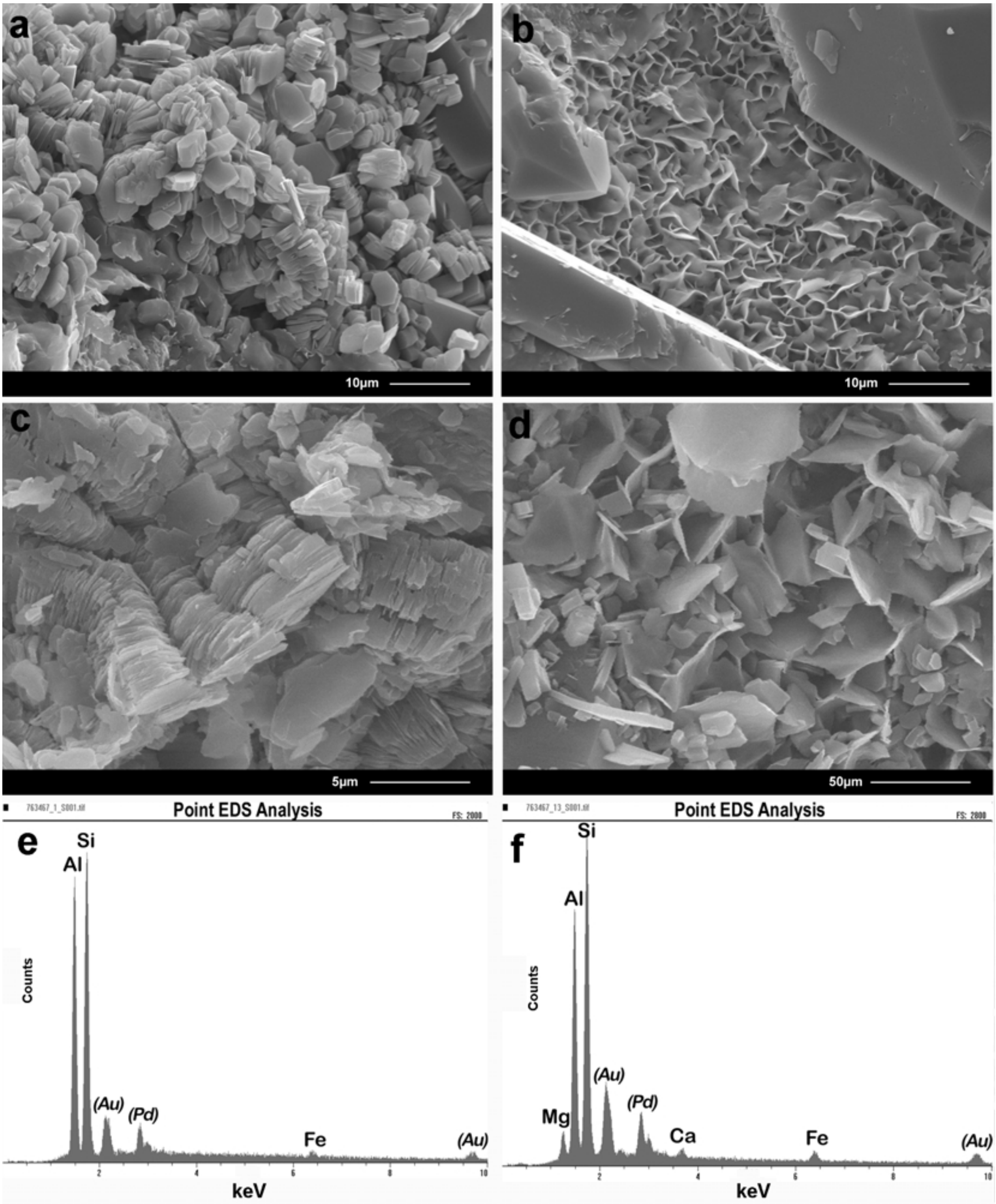

FIG. 9. SEM images and energy dispersive spectra (EDS) of kaolinite and tosudite from samples WM3 (a,b) and WM7 (c,d) from the West Midlands and Herefordshire. Tosudite is present in a honeycomb or box-work texture typical of many swelling clays. e = EDS spectra of kaolinite, f = EDS spectra of tosudite.

I-S, plus or minus minor chlorite. Mixed-layer I-S is also abundant in samples (WHB1–8) analysed from the Upper ORS at Portishead near Bristol (Fig. 11c). Although both chlorite and kaolinite may be present, neither is especially abundant. Maskall (1985) also reported abundant kaolinite in the Upper ORS of the area around the Forest of Dean.

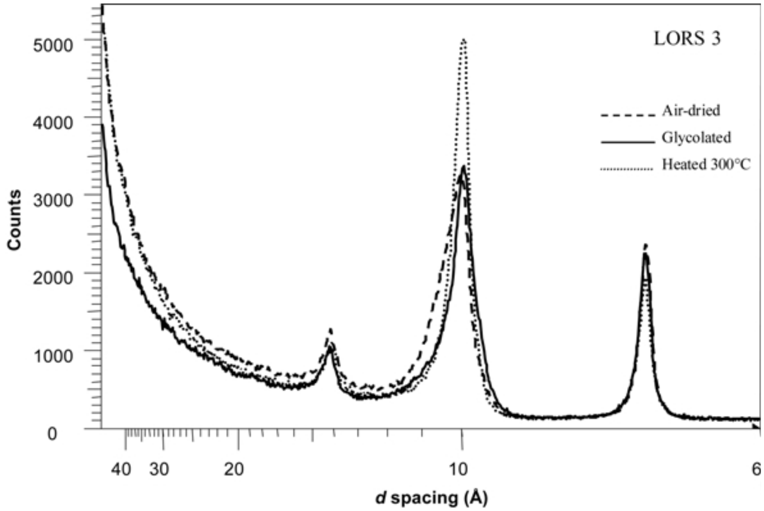

FIG. 10. XRD patterns of sample LORS 3; note substantial changes in the 10 Å peak profile between air-dried, glycolated and heated traces, indicating an abundance of low-expandability mixed-layer illite-smectite. Note that the patterns are offset for clarity.

Summary and origin of Wales and the Welsh Borderland clay mineral assemblages

The general findings for the clay mineralogy of the ORS of Wales and the Welsh Borderland may be summarized as follows. Samples from the Upper ORS in the west contain an assemblage of illite plus trioctahedral chlorite. This assemblage is also observed in parts of the Lower ORS, in both Breconian and Dittonian rocks, but in contrast to the Upper ORS the chlorite in the Lower ORS is often dioctahedral. Kaolinite was not observed in either Upper ORS or Lower ORS Breconian samples in the west, but it is present along with mixed-layer I-S in the most easterly outcrops of the Upper ORS such as in Monmouthshire and near Portishead. In the Dittonian, large-spacing interstratified minerals become especially prevalent, most notably in samples collected from the easternmost outcrops. These minerals include ordered mixed-layer I-S and tosudite. Garvie (1992) identified the presence of tosudite in the St Maughan's Group of the Dittonian near the Forest of Dean and the results of the new sampling campaign reported herein demonstrate its widespread occurrence across the eastern part of the region. Thus tosudite or a tosudite-like mineral can be found in the Lower ORS from Newport in the south through Herefordshire, and northwards into Shrophire and Worcestershire. Samples from the easternmost outcrops also contain abundant well ordered kaolinite. Kaolinite was also recorded further west in the Dittonian of West Wales, but is very poorly ordered. The appearance of discrete dioctahedral smectite in samples from the most westerly outcrops south of Landovery, and at Freshwater West is also a notable feature.

For the Downtonian strata, early results from the most easterly outcrops (Perrin, 1971) indicated the dominance of illite and smectite, the latter either as a discrete phase or interstratified with illite. The results of Parker *et al*. (1983) and Maskall (1985) for the Townsend Tuff generally confirm these observations but also demonstrate a progressive change westwards into an illite-chlorite assemblage, identical with that found in parts of the Breconian, Dittonian and Upper ORS strata in the more westerly parts of South Wales.

The factors that possibly influence the clay mineralogy of the ORS in Wales and the Welsh Borderland include: inheritance from sediment source areas, including the influence of volcanic activity; early diagenesis relating to conditions of deposition within sedimentary basins; later diagenesis where the sediments are affected by the percolation of waters of different chemical compositions; and late diagenesis/early metamorphism where the sediments are affected by increasing depth of burial or tectonic/hydrothermal activity. It is difficult to be certain which of these factors predominates in explaining the origin of the clay

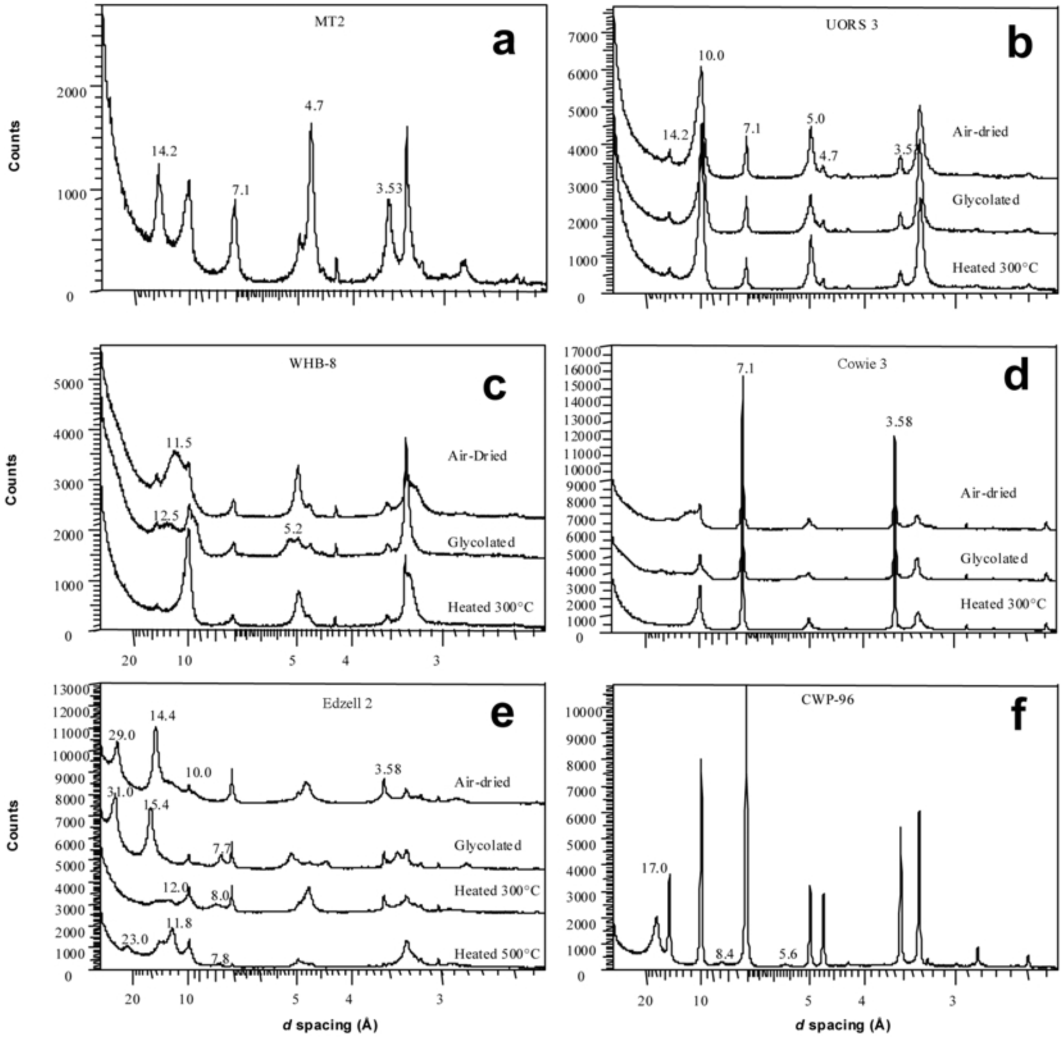

FIG. 11. XRD patterns of various samples collected for this review. Where shown, patterns for different treatments are offset vertically for clarity. (a) XRD pattern of sample MT2 following treatment with 6 M HCL. Note the intense chlorite 003 reflection at ~4.7 Å, almost twice as intense as any other chlorite peak. This, together with the insolubility of the chlorite in HCl indicates that the chlorite is dioctahedral. (b) XRD patterns of sample UORS 3, consisting of illitic clay and trioctahedral chlorite. (c) XRD patterns of sample WHB-8 from the Upper ORS of Portishead. Clay assemblage is dominated by ordered mixed-layer illite-smectite, together with minor illite and traces of kaolinite and chlorite. (d) XRD traces of kaolinite-rich sample (Cowie 3) from the Downtonian, Stonehaven Group. (e) XRD patterns of tosudite-rich sample (Edzell 2) from the Strathmore Group near Edzell. Sample also contains some illitic clay and a minor amount of kaolinite. (f) Glycolated trace of <2 μm fraction of a slate (CWP-96) from the Meadfoot Group. The clay assemblage is dominated by illite and chlorite but also contains a significant amount of a pure smectite with a peak at ~17 Å; no mixed-layering is indicated by the rationality of its peaks. Compare with the smectite observed in Fig. 5c,e.

minerals in the Welsh ORS and there is probably some degree of complex interaction between them all. Indeed, we authors have strong differences amongst ourselves in interpreting which processes have been most important. While one of us (Hillier) favours the importance of diagenesis, another (Wilson) prefers to place greater emphasis on provenance. In terms of the evidence itself there are also problems to consider. One difficulty is the inordinate thickness of the ORS succession and the lack of a clear stratigraphic control. Where such a control is possible, as with the study of the Townsend Tuff, it was concluded (Parker *et al.*, 1983; Maskall, 1985) that the clay mineralogy was controlled by maximum depth of burial, intensity of folding and proximity to basement. It is not entirely clear, however, that such an explanation is sustainable for the Welsh ORS succession as a whole with the information on its clay mineralogy that is now available. One obvious source of difficulty is that the Breconian and Upper ORS strata in the west show an apparently deep diagenetic zone clay mineral assemblage (illite-chlorite) as recognized by Parker *et al.* (1983), and yet are stratigraphically younger so presumably have not been buried as deeply as the Dittonian rocks which contain abundant mixed-layer clays. In addition, poorly ordered kaolinite and smectite occur in the ORS of the tectonized Pembrokeshire area. Furthermore, the Upper ORS of Wales passes conformably upwards into the Carboniferous Limestone, which commonly contains kaolinite, according to the data of Perrin (1971). In terms of an original detrital control, one possibility is to explain the illite-chlorite assemblage within the westerly outcrops of the Upper ORS and Breconian as a result of the influence of provenance from a northern continental source area consisting of a metamorphic terrain.

However, the problems of applying a diagenetic interpretation to the Welsh ORS succession as a whole may be more apparent than real. In this respect it is pertinent to consider variations in diagenetic grade in the overlying Carboniferous strata. Here grade, or organic maturity, is constrained by vitrinite reflectance and volatile matter data from coals (e.g. Parker *et al.*, 1983, their fig. 7; Bevins *et al.*, 1996), and demonstrate that equivalent diagenetic grades of samples of the same age may change considerably between

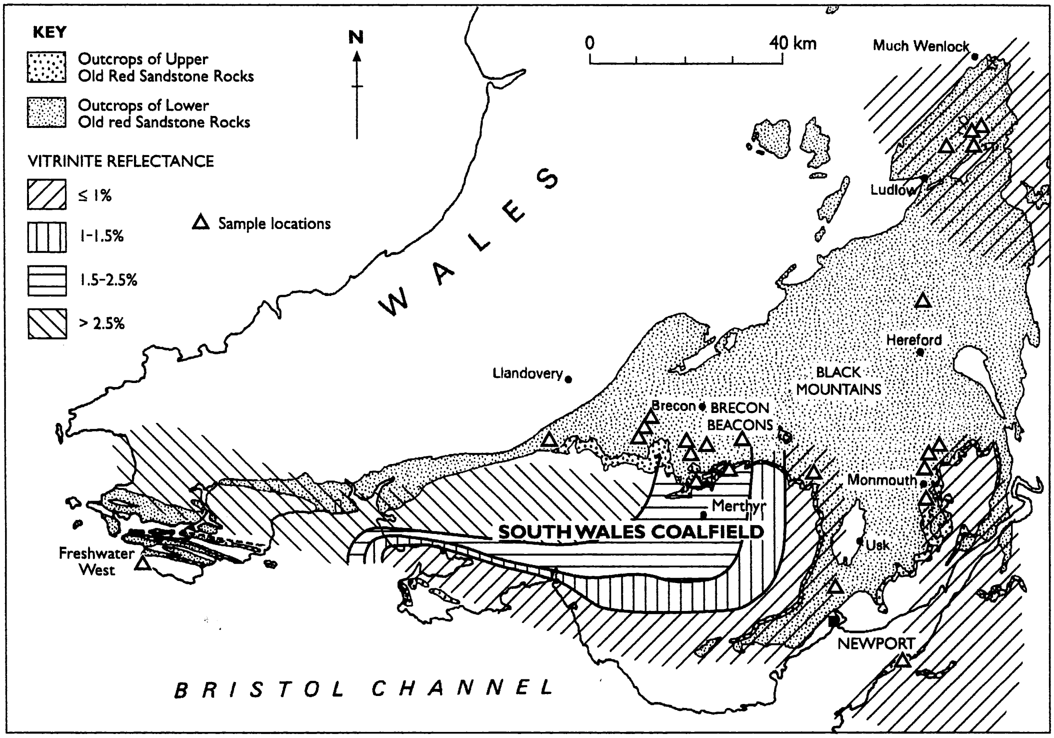

FIG. 12. Location of new samples (triangles) in the Welsh region collected for the present study. The figure also shows the pattern of increasing vitrinite reflectance in the overlying Carboniferous strata, which by inference may be extrapolated into the ORS.

localities that are only short distances apart. Thus for samples collected from a widely dispersed range of localities across the ORS outcrop (Fig. 12) it cannot be assumed that samples placed in stratigraphic order will be in the same order in terms of their relative diagenetic grade; indeed this is an unlikely assumption. In other words younger samples from one locality may have a higher diagenetic grade than older samples from another. With this in mind, it is clear that there is an overall trend in the composition of the clay mineral assemblages of the ORS, both Upper and Lower, in an east–west direction; a similar trend was documented by Parker *et al*. (1983) and Maskall (1985) for the Townsend Tuff. Such a trend could be simply interpreted in terms of increasing diagenetic grade from east to west (Fig. 12). Thus, ordered mixed-layer I-S shows a decrease in both expandability and abundance in a westerly direction, concomitant with an increase in discrete illite. Additionally, tosudite is common in the east and dioctahedral chlorite is common in the west. And finally kaolinite is most abundant in the east and less abundant in the west. Individually and collectively these three trends could be interpreted in terms of a general increase in diagenetic grade in a westerly direction, as is documented for the overlying Carboniferous (Fig. 12). Indeed, as far as the occurrence of kaolinite is concerned, SEM observations clearly indicate that the kaolinite in these rocks is of a diagenetic nature. The book-like and vermicular form of this mineral allow no other explanation (Fig. 9). To explain its greater abundance in the east, it could be surmised that diagenetic kaolinite formation has been promoted by a looser texture and more open and porous fabric of the Dittonian rocks, compared with those of Breconian and Upper ORS age in the west, thus enabling a freer circulation of sub-surface waters. Such an interpretation implies that kaolinite may never have been present in many of the more westerly samples. Equally, kaolinite may have been destroyed by a more advanced diagenesis in the west, and the same event affected the texture and porosity of the samples.

With regard to the origin of the tosudite, Garvie (1992) favoured a diagenetic as opposed to a hydrothermal origin. The occurrence of tosudite in other parts of the Lower ORS sequence, for example in Scotland (Wilson, 1971), and its common occurrence in other red beds, as summarized by Hillier (2003), does indeed favour a diagenetic origin in our opinion, but details of the exact process of tosudite formation remain unknown. In the ORS of Wales and the Welsh Borderland the distribution of tosudite in the east (Fig. 5f) and dioctahedral chlorite in the west (Fig. 11a) implies that dioctahedral chlorite could have formed from tosudite as a result of a greater degree of diagenetic alteration in the west. Kaolinite also may be linked to the formation of tosudite. If so it might imply the existence of a paragenetic transformation sequence from kaolinite to tosudite to sudoite (dioctahedral chlorite).

The occurrence of poorly ordered kaolinite and especially of pure dioctahedral smectite in the most westerly samples presents perhaps the biggest difficulty to applying a diagenetic interpretation to the sequence as a whole. These samples represent a part of the region where there is evidence from the ORS and from the overlying Carboniferous rocks that the diagenetic grade of the ORS should be the highest in the Wales-Welsh Borderland region, despite inconsistent correlations between organic maturity indicators and clay mineralogy (Gill *et al*., 1977; Robinson *et al*., 1980; Parker *et al*., 1983; Bloxam & Owen 1985; Bevins *et al*., 1996). Indeed the informal measurements of illite 'crystallinity' reported herein for samples from Freshwater West are clearly compatible with the low anchizone of low-grade metamorphism. In terms of a diagenetic interpretation, the occurrence of smectite is therefore anomalous and requires some alternative explanation. Apart from the occurrence of lithophorite in two samples from one locality, there is no obvious evidence of modern weathering, so that the occurrence of smectite and kaolinite cannot be easily explained away on this basis. One possible explanation that is compatible with the diagenetic interpretation as a whole, is that the smectite and the poorly ordered kaolinite represent retrograde alterations of a high grade diagenetic/low grade metamorphic illite-chlorite assemblage. This is a type of alteration increasingly documented in very low-grade metamorphic rocks, for example in the work of Nieto *et al*. (2005). This possibility should be given very serious consideration bearing in mind other evidence, especially features such as the development of cleavage in the ORS of Pembrokeshire (Parker *et al*., 1983). Otherwise it is very difficult to reconcile the observed assemblage, especially the presence of smectite, with the geological history the ORS of the West Wales region (Robinson *et al*., 1980; Bevins *et al*., 1996).

Furthermore, it may be of some significance that all of the areas where the pure smectite kaolinite association is observed are tectonized. For the Freshwater West samples, the Ritec Fault and associated faults traverse the area, whilst the group of samples collected further east along the A4069 road to Llangadock are located immediately adjacent to the Carreg-Cennen Church Stretton fault zone.

Another possibility, favoured by one of us (Wilson), is that the smectite, possibly the kaolinite, and certainly the dominant illite and chlorite assemblage of the most westerly regions are all original detrital clays. Such an interpretation requires that any diagenesis has not been of sufficient intensity to transform smectite to I-S or to destroy kaolinite. It also implies that at least equal emphasis should be placed on provenance rather than on diagenesis in the interpretation of the clay mineral assemblages of the region. Another of us (Hillier) acknowledges that some detrital clay mineral signatures may no doubt persist, but prefers to interpret the assemblages as overwhelmingly the product of a diagenetic alteration that increases in intensity from east to west.

NORTHERN ENGLAND AND SOUTHERN SCOTLAND

The ORS of this region consists of both the Lower and Upper divisions. Volcanic rocks form an important part of the succession, particularly around Cheviot where they are up to 1000 m thick. Further north at St Abbs, ~600 m of conglomerates, sandstones and red marls are associated with thick pyroclastic deposits and other volcanic rocks. The volcanic rocks of the Cheviot region are mostly andesitic and have been dated at ~396 Ma (Thirwall, 1988).

To the north, an extensive area of Upper ORS occurs, consisting of conglomerates, sandstones, marls and calcretes. The ages of these ORS deposits are Upper Devonian (Fammenian) and Carboniferous (Tournaisian, ?Visean). The Upper ORS passes conformably into rocks of Carboniferous age. There are no published clay mineral data for any samples of the ORS from Northern England. Wilson (1971) examined a number of Upper ORS samples from southern Scotland, bordering the Cheviot area, in which kaolinite and/or mixed-layer I-S are dominant. We can only speculate that similar assemblages might be encountered in the Upper ORS of northern England.

MIDLAND VALLEY OF SCOTLAND

Stratigraphy and sedimentology

The ORS of the Midland Valley of Scotland crops out in two main structural basins, the Strathmore basin to the northwest and the Lanark Basin in the southeast. The Strathmore basin is the larger and forms a large synclinal structure with an axis parallel to and bounded by the Highland Boundary Fault. The stratigraphy of the Lanark Basin is similar to that of the ORS outcrops of northern England and contains sediments largely derived from the Lower Palaeozoic terrain of the Southern Uplands, which at the time probably had an extensive cover of volcanic rocks. Most studies of the clay mineralogy have been concerned with rocks in the Strathmore Basin, with very few analyses from the ORS of the Lanark Basin.

The Lower ORS of the Strathmore basin is contained in a system of sub-basins and divided into the Stonehaven, Dunnottar, Crawton, Arbuthnott, Garvock and Strathmore Groups (Fig. 2). The oldest deposits, the Stonehaven Group, are of late Silurian age. They are succeeded by the Dunottar and Crawton Groups, consisting mostly of conglomerate with minor volcanic rocks. The Lintrathen ignimbrite and its correlatives form an important marker at the top of the Crawton Group and give a Silurian age of 411±6 Ma. The Arbuthnott Group is of early Devonian age (Pragian) and contains major accumulations of lava and pyroclastic rock including those in the Sidlaw and Pentland Hills. For the most part the volcanic rocks consist of highly altered andesite and basalt. The overlying Garvock Group contains an important calcrete near the top and the youngest Lower ORS Strathmore Group has been dated as Emsian. Sedimentological studies have shown that small alluvial fans bordered the proto-Midland Valley, whilst the central regions were dominated by a large fluvial system transporting sediment to the southwest. Most of the sediments are coarse, alluvial clastics although fine-grained lacustrine sediments are well developed in the Arbuthnott Group.

The Upper ORS of the Midland Valley is thickest in the east (up to 2000 m), and, as elsewhere, is conformable with the overlying Carboniferous. South of the Highland Boundary Fault, sandstones of Upper ORS age rest unconformably on Lower ORS strata in the vicinity of Arbroath, in Fife, and on the west coast near Ayrshire. There are also major occurrences of Upper ORS sandstones south of the Southern Upland Fault in the border country of Berwickshire and Roxburghshire.

Clay mineral assemblages in the Lower ORS

Stonehaven Group. The clay mineralogy of the sandstones and shales from the Stonehaven Group is known from Wilson (1971, Table 1, Nos 1–8) and from Marshall *et al*. (1994; three analyses from the Cowie Formation). The most distinctive feature of the clay mineralogy of the Stonehaven Group is the abundance of kaolinite in all lithologies, a finding recently confirmed (Fig. 11d) by analysis of newly collected samples (Appendix A; Cowie 1–7). However, kaolinite is not present in every sample (Marshall *et al*., 1994). Generally, samples from the Stonehaven Group also contain abundant illite. Moderate amounts of chlorite, mixed-layer I-S and minor mixed-layer chlorite-vermiculite were also recorded from the samples (Wilson, 1971). Chlorite-vermiculite was confined to sandstones but I-S was found in both sandstones and shales and was particularly abundant in one sample of shale. Wilson (1971) also recorded an unusual occurrence of a green clay mineral resembling glauconite in a sample of a greyish green to pale green sandstone.

Dunnottar and Arbuthnott Groups. A variety of features characterize the clay mineralogy of the succeeding Dunnottar and Arbuthnott groups examined by Wilson (1971, Table 1, Nos 9–14). In both, the common presence of dominant amounts of interstratified chlorite-vermiculite is distinctive, yielding a large-spacing peak at ~28 Å with a rational series of higher orders. The pattern was not affected by treatment with glycerol but heating at 600ºC induces a collapse to a 24 Å structure. A strong reflection at 1.534 Å indicated that the mineral is trioctahedral. All of the samples from these groups examined by Wilson (1971) were sandstones. Latterly, Marshall *et al*. (1994) reported on the analysis of a number of lacustrine flagstones and shales from the Dundee Formation of the Arbuthnott Group, which are also notable for their contents of mixed-layer chlorite-vermiculite.

Garvock Group. The samples from the interbedded clays and sandstones of the Garvock Group (Wilson (1971, Table 1, Nos 15–17) may contain abundant montmorillonite and other smectite minerals. Wilson (1971) characterized the montmorillonite by IR spectroscopy as a Cheto-type, in which there is little or no substitution of Al by Fe in the octahedral sheet.

Strathmore Group. Strata of the Strathmore Group are distinguished by the almost ubiquitous occurrence of a mixed-layer chlorite mineral, with a large spacing at 28 Å which expands to ~30 Å after glycerol treatment. Wilson (1971, Table 1, Nos 18–28) recorded this phase as the dominant mineral in nine of the 11 samples examined. The mineral is a dioctahedral chlorite-smectite (tosudite), as confirmed by a 060 spacing at 1.505 Å and by strong absorption at 3616 cm^{-1} in the OH-stretching region of the IR spectrum. The common presence of tosudite in the Strathmore Group was confirmed by analysis of a suite of newly collected samples from the vicinity of Edzell (Appendix A; Fig. 11e). Examination of these samples by SEM shows that the tosudite occurs most abundantly in the coarsest-grained samples where it is present in the 'honeycomb' pore-lining morphology so typical of many swelling clay minerals (Fig. 13).

Volcanic rocks. Wilson (1971) also made a series of clay mineral analyses of Lower ORS volcanic rocks from various localities in the Midland Valley and also from the Oban area. For those samples from the Midland Valley (Wilson, 1971, Table 1, Nos 29–37), interstratified trioctahedral chlorite-vermiculite, identical to that described in the volcanogenic sediments, was the dominant clay mineral recorded. From the region around Oban (Wilson, 1971, Table 1, Nos 38–43), the assemblages were either dominated by illite and chlorite

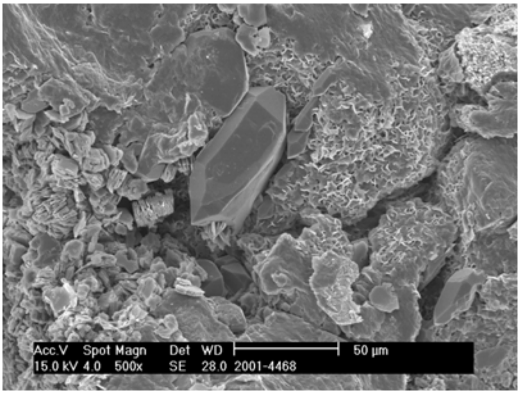

FIG. 13. SEM image of pore-lining tosudite showing the typical 'honeycomb' morphology and pore-filling kaolinite in coarse sandstone (Edzell 2) from Edzell, Scotland.

or by I-S. These local differences may be related to differences in the degree of diagenetic alteration (higher around Oban) or perhaps to variations in the bulk composition of the volcanic rocks.

Clay mineral assemblages of the Upper ORS

The clay mineralogy of these strata is dominated by a kaolinite and I-S assemblage (Wilson, 1971). Kaolinite is often well crystallized, as indicated by optical and electron microscope observations showing book-like forms and euhedral hexagonal particles, although XRD patterns rarely resolved the doublet at 4.18 and 4.13 Å, characteristic of highly crystalline kaolinite (Brindley, 1961). For this reason, Wilson (1971) concluded that the kaolinite in these rocks could be a mixture of well ordered and poorly ordered forms. With regard to the I-S in these rocks, it was found that expandabilities ranged from <5 to ~30% and that where there was a small I-S content the XRD pattern agreed well with a $1M_d$ mica polytype. Wilson (1971) further showed that two types of I-S could be distinguished in these rocks, based on differences in their DTA curves (Fig. 14) and on their morphology as seen under the transmission electron microscope (TEM) (Fig. 15). The first type was characterized by a DTA curve where the major dehydroxylation endotherm occurred at abnormally high temperatures (670–680ºC), and by a distinctive lath-like morphology showing elongation along the crystallographic *a* axis. The second type of I-S shows a DTA curve where dehydroxylation occurs at normal temperatures (530–550ºC) and the particles have an irregular platy morphology. Where the two types of I-S occur together, they show a double dehydroxylation endotherm on the DTA curve, and contrasting morphologies under the TEM. However, the two forms appeared to be indistinguishable by XRD of oriented specimens. Previously, Mackenzie (1957) had also pointed out the existence of illite with an 'abnormally' high dehydoxylation temperature in the Upper ORS of Roxburghshire and more widely in soils derived from the Upper ORS. Mackenzie (1957) correctly postulated that the differences might be related to which two of the three octahedral sites were occupied, since the three positions are not all equivalent with respect to the position of the hydroxyl groups in the oxygen-hydroxyl planes above and below the cations. These differences in DTA patterns have been fully explained by Drits *et al.* (1995). They showed that illites and smectites with *cis*-vacant 2:1 layers are characterized by dehydroxylation temperatures 150–200ºC higher than those with *trans*-vacant 2:1 layers and provided a complete explanation for these differences. Following the work of Drits *et al.* (1995), it is concluded that both *cis*-vacant and *trans*-vacant I-S occur in these strata, commonly in the same sample.

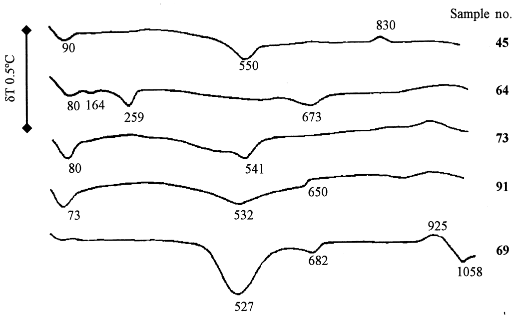

FIG. 14. DTA curves of ORS samples. No. 45: illite and chlorite from the Ousdale Mudstone. No.64: lath-shaped illite-smectite with goethite from pink feldspathic sandstone. No. 73: poorly shaped illite-smectite with kaolinite from pink pebbly sandstone. No. 91: poorly shaped and lath-shaped illite-smectite with kaolinite from pale red fine-grained sandstone. No. 69: kaolinite and lath-shaped illite-smectite from fine-grained shaley sandstone. Redrawn from Wilson (1971, his fig. 11).

Summary and origin of Midland Valley clay mineral assemblages

There are various questions concerning the origin of the clay minerals in the Lower ORS succession of the Midland Valley. These bear particularly upon the presence of kaolinite in the Stonehaven Group compared with the usual absence of this mineral in the rest of the Lower ORS succession; the origin of the interstratified minerals in various parts of the Dunnottar and Arbuthnot Groups, including regularly interstratified trioctahedral chlorite-vermiculite (corrensite); the origin of montmorillonite (or interstratified I-S) in the Garvock Group; and the origin of regularly interstratified dioctahedral chlorite-smectite (tosudite) in the Strathmore Group.

On the basis of a poorly defined platy morphology observed under the transmission electron microscope, Wilson (1971) concluded that the kaolinite in the Stonehaven Group was likely to be detrital in origin. New observations by SEM show

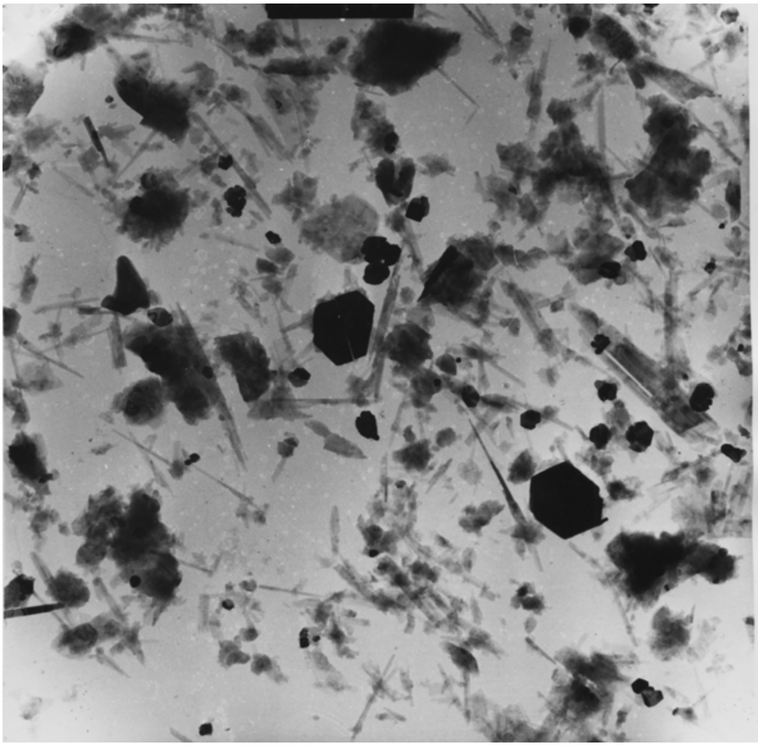

FIG. 15. TEM image of clay minerals in the Largs sandstone (Upper ORS) showing both platy and lath-like forms of illite. Hexagonal electron-dense particles are kaolinite.

that authigenic kaolinite is also abundant, at least in the sandstones (Fig. 16)

With regard to the corrensitic minerals in the Dunnottar and Arbuthnott Groups, Wilson (1971) suggested that this was directly related to the alteration of volcanic material since substantial quantities of the mineral are found both in volcaniclastic sandstones and in clay fractions separated from altered andesitic lavas associated with the sediments. It is possible that this mineral could also have been neoformed in the carbonate/evaporite facies developed in the lacustrine shales of the Arbuttnott Group (Marshall *et al.*, 1994). However, within the sandstones, there appears to be no necessity to postulate an alternative genetic mechanism when the relationship with volcanic material appears to be so clear-cut.

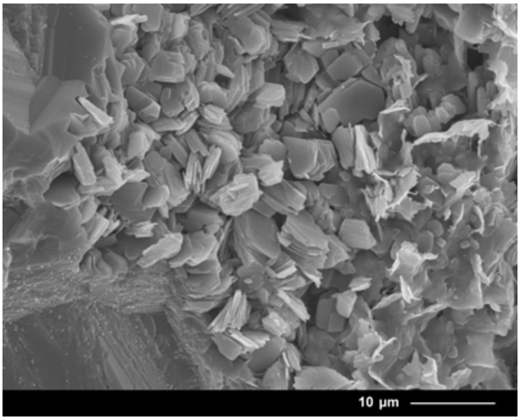

FIG. 16. SEM image of authigenic kaolinite in a sandstone from the Stonehaven Group (Cowie 3).

Wilson (1971) also suggested that I-S, as well as the montmorillonite found in the Garvock Formation, might also be related to inheritance and alteration of volcanic material. In support of a volcanic origin it is pertinent that the interstratified mineral is often found, usually in trace amounts, in the clay fractions separated from altered andesites associated with the Dunnottar and Arbuthnot Groups. However, in two samples it was the dominant clay mineral where it occurred in lath-like particles.

The origin of the tosudite in the Strathmore Group is problematic (Wilson, 1971). However, the identification of the same mineral in the Lower ORS in the St Maughan's Group near the Forest of Dean (Garvie, 1992), and more extensively in the Lower ORS of Wales and the Welsh Borderland, as documented above, lends a new perspective to the problem. Previously, tosudite has been widely reported from hydrothermally altered rocks (e.g. Sudo & Kodama, 1957; Hillier *et al*., 1996) but its widespread occurrence in ORS strata in Wales, England and Scotland make a localized hydrothermal fluid origin unlikely. Garvie (1992) favoured a diagenetic origin, as was previously suggested by Kulke (1969) for an occurrence in Triassic sandstones from Germany, and we concur that a diagenetic origin is most likely. Indeed, the variety of these examples seems to indicate that there is a clear association between dioctahedral chlorites and certain red beds (Hillier, 2003). It is also interesting to note that Wilson (1971) recorded minor amounts of chlorite-vermiculite in the clay mineral assemblages of the Stonehaven Group, samples that are otherwise notable for the presence of abundant kaolinite. Some of the kaolinite in the Stonehaven Group is clearly diagenetic, indicating an aluminous diagenetic system and this suggests that a dioctahedral mixed-layer clay (tosudite) is a more probable phase than a trioctahedral one (corrensite) in these rocks. This was confirmed by the analysis of the seven newly collected samples (Appendix A; Cowie 1–7). The wider implication of this observation is that the kaolinite-rich Stonehaven Group, containing evidence for incipient tosudite formation, may be of lower diagenetic grade than the younger Strathmore Group containing abundant tosudite. Indeed, this relative order of the two groups with respect to diagenetic grade is borne out by the independent work of Marshall *et al*. (1994) on vitrinite reflectance.

Regarding the Upper ORS of the Midland Valley, Wilson (1971) noted the similarity of the clay mineral assemblages of these rocks to those found in the sandstones of the Upper ORS of the Orcadian Basin, as well as sandstones from the Middle ORS around the Moray Firth. In both cases Wilson (1971) suggested that the assemblages of kaolinite and I-S that characterize these rocks were mixtures of detrital and authigenic clays.

ORCADIAN BASIN

Stratigraphy and sedimentology

North of the Grampian watershed, outcrops of ORS strata occur scattered around the margins of the Moray Firth, while those beneath drift cover in Caithness extend northwards to form Orkney and parts of Shetland. Collectively, these deposits formed in the Orcadian Basin. Although the ORS of the Orcadian Basin is for the most part of Middle Devonian age, strata ascribed to Lower ORS and the Upper ORS are also extensive. Much of the Lower ORS occurs as outliers that are marginal to the main ORS outcrop, and are developed as locally derived coarse conglomerate or breccia resting unconformably on the metamorphic basement. In many cases there is insufficient palaeontological evidence to date these deposits and many may well be marginal facies of younger ORS strata. The age of the oldest Lower ORS of the Orcadian basin is Emsian so that there is very little chronological overlap with the older Lower ORS of the Midland Valley.

The thickest and most extensive strata in the Orcadian basin belong to the Middle ORS, which in Caithness attains a thickness of 3–4 km. Most of the succession is composed of lacustrine 'flagstones', whereas to the south around the margins of the Moray Firth, and north in Shetland, these flagstones inter-finger with thick fluvial sandstones. The flagstones consist of repeated alternations of argillaceous limestones, pale sandstones, greenish white mudstones and black flags, arranged in rhythmic facies sequences on a scale of several metres. Towards the top of the Middle ORS successions, the lacustrinal lithofacies is everywhere replaced by dominantly fluvial sediments. In Shetland, pyroclastic deposits form an important part of the succession, and areas such as Walls were intruded and metamorphosed by late Devonian granitic plutons. Elsewhere volcanism was less important, although it is probable that the Grampian region was mantled by volcanic rocks associated with high-level plutons intruded largely during late Silurian to early Devonian times.

In the Orcadian Basin, the Upper ORS crops out mainly around the southern margins of the Moray Firth with a smaller area at Dunnet Head in Caithness and on the Island of Hoy in Orkney. It is mainly composed of sandstone of fluvial and aeolian origin and in general attains a thickness of

~1 km. In contrast to other regions, parts of the Upper ORS are conformable with the Middle ORS with which its affinities lie (Rogers *et al*., 1989), although there are also formations such as the Rosebrae Beds which have apparent faunal and lithological affinities with the 'Tournaisian Upper ORS' of other regions.

Clay mineral assemblages in the Orcadian Basin

The first investigation of the clay mineralogy of the Middle ORS mudrocks of the Orcadian Basin was made by Ferrero in Burrolet *et al.* (1969). Ferrero demonstrated that assemblages consisting of illite and chlorite (sometimes associated with vermiculite) dominated the Caithness succession but he also recognized kaolinite, an irregular mixed-layer illite-montmorillonite of an illitic composition, and minor occurrences of montmorillonite. His data were presented stratigraphically and interpreted principally in terms of 'degradative' and 'aggradative' transformations of detrital clay minerals in the lacustrine environment together with the influence of tectonism in the hinterland. Alternatively, he did suggest that 'mild metamorphism' of the succession might also account for the illite-chlorite assemblage, characteristic of such large tracts of the basin.

The dominance of the illite plus chlorite assemblage in Caithness was later confirmed by Wilson (1971), who noted that, in general, both minerals were highly crystalline and the common dioctahedral and trioctahedral types, respectively. Interstratified chlorite-smectite and infrequent minor montmorillonite and kaolinite, the latter co-dominant in some samples, were also recorded by Wilson (1971). Based on the identification of the illite as the high-temperature $2M_1$ polytype and the well crystallized nature of both the illite and chlorite, Wilson (1971) concluded that this assemblage was probably detrital, inherited from illitic and chloritic rocks in the source area. Wilson (1971) also studied samples from the belt of Middle ORS deposits that crop out around the margins of the Moray Firth and noted that the clay mineral assemblages of these rocks were more comparable to Upper ORS assemblages from elsewhere in Scotland because they consisted largely of I-S and kaolinite.

More recently, Hillier & Clayton (1989) and Hillier (1989, 1993) confirmed the results of these earlier studies and added more details concerning both the nature of the clay minerals present and their stratigraphic and geographic distribution. In particular, both the make up of the clay mineral assemblages and the characteristics of individual clay minerals, such as the expandability of I-S, illite 'crystallinity', and the ratio of $1M$ to $2M_1$ mica polytypes were determined and found to vary systematically with respect to the diagenetic and metamorphic grade. The majority of I-S minerals have expandibilities in the range <5−35% (Fig. 17). Hillier (1989) concluded that, according to the criteria of Środoń (1984), the micaceous material in many of the clay fractions from the Orcadian Basin mudrocks is, in fact, a mixture of discrete illite and I-S. Structural formulae calculated for the I-S minerals showed them to be aluminous and dioctahedral, with most of the layer charge derived from Al for Si substitution in the tetrahedral sheet (Table 1).

Chlorite in the Orcadian mudrocks is the IIb polytype, and electron microprobe analyses of the lowest diagenetic grade samples show that they are Mg-rich although, less commonly, authigenic Fe-rich chlorites are also encountered (Hillier, 1989, 1993). Corrensitic minerals often occur in association with the chlorites. Thus, chlorite may be interstratified to various degrees with smectite layers (Fig. 18). Sometimes, this is manifested only by slight changes in peak profile between air-dried and glycolated preparations, but in some samples a strong superlattice reflection occurred at ~28 Å, expanding to ~31 Å on glycolation, with a regular series of higher orders. This is indicative of a regularly interstratified chlorite-smectite with R1 ordering and is characteristic of the mineral corrensite. Hillier (1989) also identified a range of corrensitic minerals with variable proportions of smectite and chlorite layers ranging between corrensite and chlorite. These minerals were interpreted as mixed-layer chlorite-corrensite.

In the Shetland region of the Orcadian Basin, some clay mineral data from the Middle ORS were reported by Jeans (1995), who examined 168 samples and detailed various patterns of clay mineral distribution in relation to lithofacies. He noted the dominance of a mica-chlorite assemblage in the lacustrine sediments, the more micaceous nature of fluvial facies compared to the more chloritic lacustrine facies, and the presence of a purely micaceous assemblage in aeolian strata. Jeans (1995) also noted that the mica and chlorite were coarsely crystalline, suggestive of their authigenic development by the recrystallization of earlier clays. He also found that calcite was the

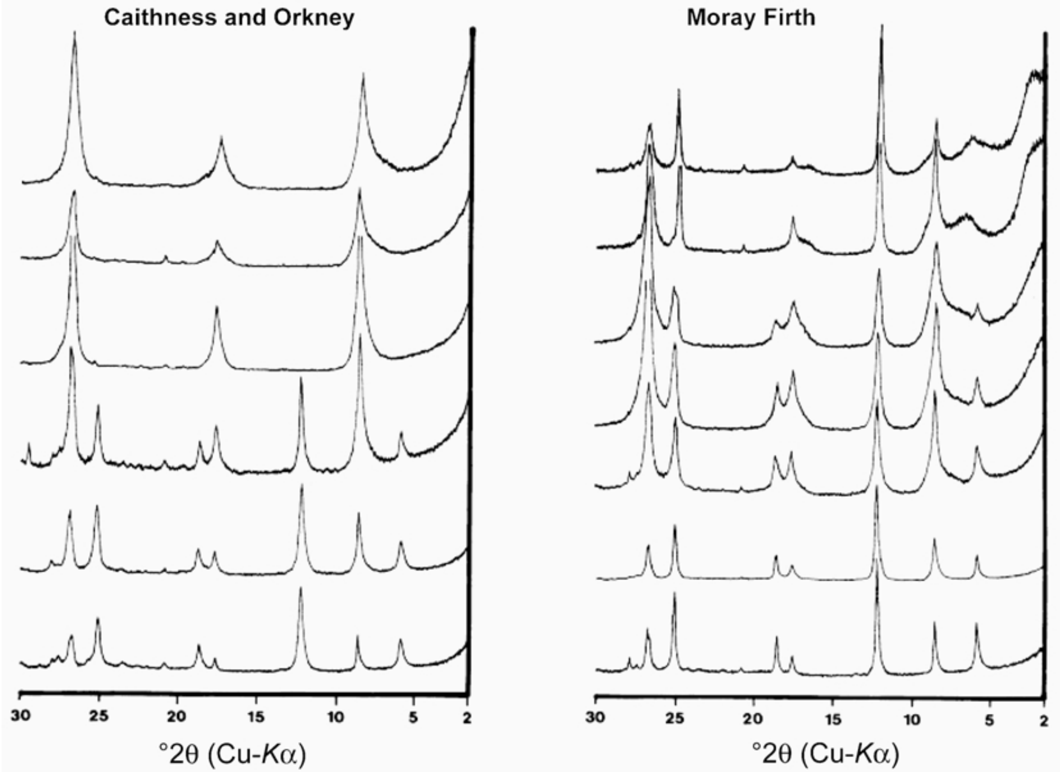

FIG. 17. XRD traces (glycolated <2 μm fractions) of interstratified illite-smectite and illitic clays from the Middle ORS Orcadian Basin arranged in order of decreasing expandability. In Caithness and Orkney illite-smectite expandability ranges from 10% to non-expandable. In the Moray Firth region, expandability ranges from 35% to non-expandable. All samples illustrated are mudrocks (after Hillier & Clayton, 1989).

dominant carbonate in these sediments with only minor amounts of dolomite present.

Summary and origin of clay mineral assemblages

As noted above, the first interpretations of the clay mineralogy of the Middle ORS mudrocks of Caithness and other areas (Burrolet *et al*., 1969; Wilson, 1971) tended to emphasize the role of detrital inputs from source areas, as well as changes related to the environment of deposition. However, the interpretations proposed by Hillier (1989, 1993), and Hillier & Clayton (1989) differ from those of the earlier studies placing more emphasis on the importance of diagenesis. Earlier studies assumed that strata had never been deeply buried, or heated to temperatures greater than those typical of moderate diagenesis. In fact, organic maturation data (Hillier & Marshall, 1992) show that large parts of the Middle ORS of the Orcadian Basin, including parts of Shetland, have been metamorphosed equivalent to low anchizonal grades. Other parts of the basin have been less affected so that there is, in fact, a wide range of diagenetic alteration with maximum palaeotemperatures estimated to range from ~100ºC to >350ºC.

Hillier & Clayton (1989) documented the regional variation in the expandability of I-S and of illite ‘crystallinity’ across the Orcadian Basin based on analysis of 360 shale samples. In the region of Caithness and Orkney, where I-S was encountered, it was of low expandability (10−15%). Hillier & Clayton (1989) showed that such samples were only found in the regions of lowest diagenetic grade in this area and that as diagenetic grade increased, there was a progressive and eventual complete loss of expandability. An increase in illite ‘crystallinity’, measured as the Kübler index (KI), was also shown to correlate with an increase in diagenetic grade (Fig. 19). Indeed, KI and vitrinite reflectance data indicate that some areas of Caithness are just within

TABLE 1. Structural formulae of illitic clays (0.2 μm size fraction) separated from Middle ORS mudrocks in the Orcadian Basin. For the original chemical analyses and further information see Hillier (1989).

Sample no.	SH170	SH471	SH514	SH941*	SH465	SH465**
Tetrahedral						
Si	6.56	6.81	6.73	6.75	6.71	6.73
Al	1.41	1.17	1.25	1.23	1.26	1.19
Ti	0.03	0.02	0.02	0.02	0.03	0.08
Total	8.00	8.00	8.00	8.00	8.00	8.00
Octahedral						
Al	2.94	3.11	3.07	3.07	3.19	2.91
Fe^{3+}	0.67	0.41	0.57	0.54	0.38	0.38
Mg	0.36	0.47	0.39	0.41	0.43	0.60
Mn	0.01	0.00	0.00	0.01	0.00	0.00
Total	3.98	3.99	4.03	4.03	4.00	3.89
Interlayer						
Ca	0.13	0.13	0.11	0.14	0.14	0.26
Na	0.12	0.06	0.05	0.05	0.04	0.10
K	1.44	1.34	1.28	1.22	1.36	1.53
Total	1.69	1.53	1.44	1.41	1.54	1.89
Layer charge						
Tetrahedral charge	1.41	1.16	1.25	1.23	1.26	1.19
Octahedral charge	0.42	0.50	0.30	0.32	0.41	0.94
Total	1.83	1.66	1.55	1.55	1.67	2.13
Interlayer charge	1.83	1.66	1.55	1.55	1.67	2.15

* 1.5% dolomite and 2.5% calcite subtracted from analysis
** <2 μm fraction

the epizonal in terms of the classification applied to low-grade metamorphic terrains (Merriman & Frey, 1999). Using a simple method similar to that of Maxwell & Hower (1967), Hillier (1989) also documented a progressive change in the proportion of mica polytypes. Micas in shales from areas of low diagenetic grade contained predominantly the $1M$ polytype, whereas micas from areas of high diagenetic or anchizonal grade were entirely of the higher-temperature $2M_1$ polytype (Fig. 20). The dominance of the $2M_1$ mica polytype was recognized by Wilson (1971) in the samples he examined from Caithness and was one of the main factors that led him to suggest a dominantly detrital origin for the illite-chlorite assemblage that characterizes much of the succession. However, the work of Hillier & Clayton (1989) and Hillier (1989) showed that the higher temperatures required for the formation of the $2M_1$ polytype were post-depositional. Hillier & Clayton (1989) also documented the distribution and characteristics of I-S from other parts of the Orcadian basin. In the outcrops surrounding the Moray Firth, I-S with expandability of 25−30% is encountered quite commonly (Fig. 21), and once again there is a trend for expandability to decrease with increasing grade, as measured independently by vitrinite reflectance (Fig. 17).

From a review of the evidence, Hillier & Clayton (1989) concluded that the I-S observed in mudrocks from the Orcadian basin was derived, by and large, from the diagenetic alteration of precursor smectite. This precursor smectite is no longer observed in any part of the basin because even the lowest diagenetic grades now observed are high enough, by analogy with modern sedimentary basins, to expect complete transformation of smectite to ordered mixed-layer I-S. Hillier & Clayton (1998) also showed that the precise correlation of the expandability of I-S with vitrinite reflectance data was different for the Caithness and Orkney region compared to the Moray Firth region. They argued such differences were possibly related to the different thermal histories of the two regions and differences in the kinetics of I-S diagenesis

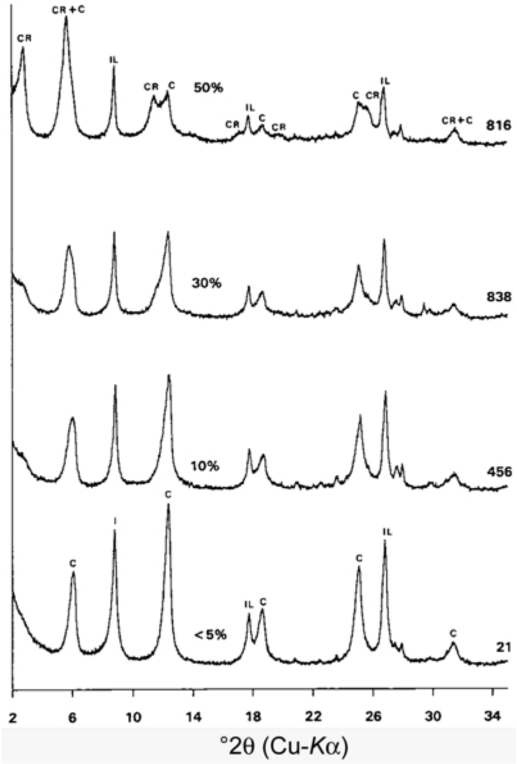

FIG. 18. XRD traces of corrensite and mixed-layer chlorite-corrensite from Middle ORS mudrocks from Orcadian Basin. Percentages indicate proportion of smectite layers (after Hillier, 1993).

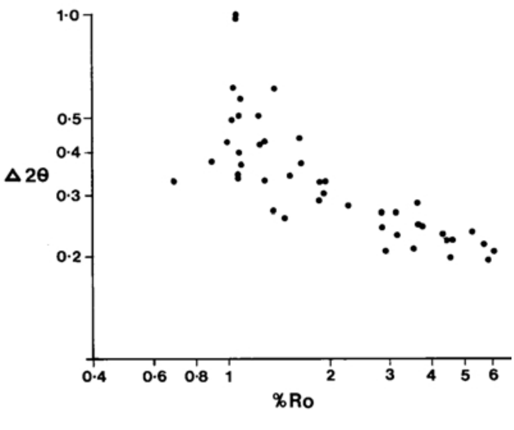

FIG. 19. Correlation of the Kübler Index of illite 'crystallinity' ($\Delta 2\theta$) with vitrinite reflectance (%Ro) in the Middle ORS of the Orcadian Basin (after Hillier & Clayton, 1989).

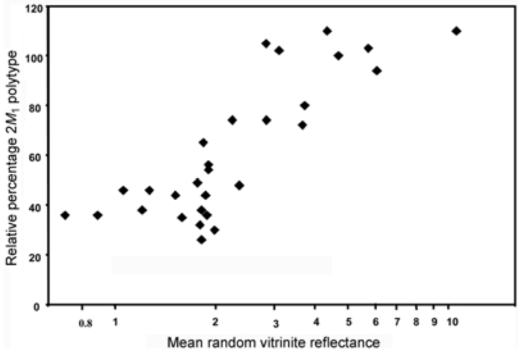

FIG. 20. Relative percentage of $2M_1$ mica polytype in the clay fraction of Orcadian Basin mudrocks and its correlation with vitrinite reflectance. The $2M_1$ polytype is the dominant polytype in those samples that have the highest vitrinite reflectance values.

compared to that of vitrinite reflectance. Such differences have also been documented for other sedimentary basins, e.g. Hillier *et al.* (1995).

The origin of the chlorite and mixed-layer chlorite-smectite in the Orcadian Basin shales was also studied in detail by Hillier (1989, 1993). Hillier (1993) showed that chlorite minerals were generally absent from areas with the lowest diagenetic grades. By examining the whole-rock mineralogy, Hillier (1993) was able to demonstrate that when chlorite was absent, dolomite was present, and *vice versa*. The relationship between the distribution of these phases with respect to diagenetic grade, together with the uniform geochemical composition of the suite of Orcadian mudrocks examined (e.g. the consistent MgO content regardless of mineralogy), indicates that most chlorite minerals in these rocks were formed by late diagenetic reactions between dioctahedral clay minerals and dolomite.

The illite-chlorite clay mineral assemblage documented by Jeans (1995) from southeast Shetland can also be interpreted as a low-grade metamorphic assemblage. Pertinent to such an interpretation is the fact that vitrinite reflectance data for southeast Shetland (Hillier & Marshall, 1992) average 5.4%, indicating epizonal conditions of low-grade metamorphism for this area (Merriman & Frey, 1999). It is also interesting to note Jeans' observation that calcite was the main carbonate in these sediments. As mentioned above, elsewhere in the Orcadian basin Hillier (1993) has shown that chlorite formed by a diagenetic reaction in which dolomite was a reactant and calcite a product. The overall clay and non-clay mineral assemblage in

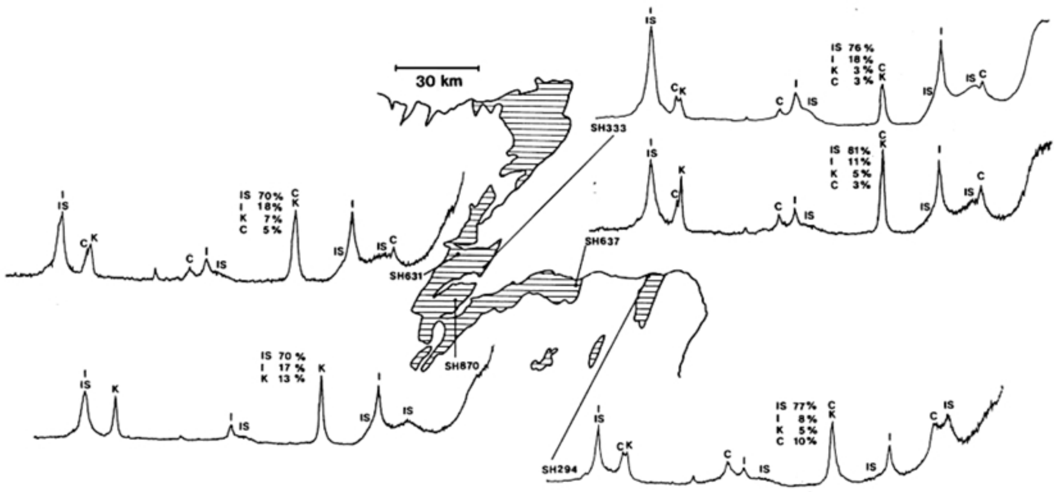

FIG. 21. Examples of the XRD patterns (glycolated) of clay fractions of Middle ORS mudrocks from localities around the Moray Firth, illustrating the abundance of mixed-layer illite-smectite (after Hillier, 1989).

southeast Shetland is thus compatible with chlorite formation in the lacustrine sedimentary rocks by this reaction during late diagenesis and low-grade metamorphism.

With regard to the origin of the clay minerals found in the Upper and Middle ORS sandstones in Scotland, Wilson (1971) interpreted the common I-S plus kaolinite assemblage in these rocks as a mixture of detrital clays and those resulting from diagenetic transformation. The basis for this interpretation was the common mixture of anhedral and euhedral clay crystals observed under the TEM. Strongly kaolinitic samples were often characterized by a mixture of indeterminate platy particles and crystals with a perfect hexagonal outline. Samples where the clay fractions were dominated by I-S tend to contain poorly shaped platy particles in addition to lath-like crystals elongated along the *a* axis. Wilson (1971) suggested that diagenetic I-S may have formed during anadiagenesis (Fairbridge, 1967) associated with deep burial, compaction, pore reduction and lithification. In contrast, kaolinite would be more likely to form in chemical conditions characteristic of a late epidiagenetic stage where uplift brought about the infiltration and downward migration of meteoric waters of low pH (Fairbridge, 1967).

Finally, it appears that the recent characterization of *cis*-vacant and *trans*-vacant I-S (Drits *et al.*, 1995) may be relevant to the origin of I-S in the ORS of Scotland. Studies of dehydroxylation temperatures, combined with other studies, show that *cis*-vacancy usually decreases with increasing illitization in diagenetic and hydrothermal sequences (Drits *et al.*, 1998; Lindgreen *et al.*, 2000). The DTA results illustrated by Wilson (1971) clearly indicate that the micaceous minerals in the Caithness Flagstones are *trans*-vacant types, whereas the I-S in the Upper and Middle ORS sandstones are *cis*-vacant types, *trans*-vacant types or a mixture of both. The conclusions of Hillier (1989) and Hillier & Clayton (1989), that I-S in the mudrocks of the Orcadian Basin represents the latter part of an illitization reaction through increasing temperature and pressure, were based on the assumption of a smectitic precursor which became progressively transformed. However, the presence of two populations of I-S particles in Middle ORS sandstones, with different morphologies and different *cis/trans* occupancies of the octahedral sheets, indicate that illitization, particularly in the sandstones, may have occurred in discrete stages or events. Unpublished work (Wilson) has also shown that the lath-like, *cis*-vacant illite can occur in ORS mudrocks. However, several studies summarized by Drits (2003) have shown that *cis*- and *trans*-vacant layers frequently occur in the same crystal. Furthermore, Drits *et al.* (1993) observed that *cis*-vacant illite was concentrated in the coarse size fraction and similarly Lee (1996) showed that 'hairy' Rotliegend illites are *trans*-vacant whereas platy ones concentrated in the coarser size fractions are *cis*-vacant. These trends are the opposite of those observed in the ORS. It can only be concluded, therefore, that the clay mineralogy of the Middle ORS of Scotland is ripe for re-examination, using the same techniques and approach as recently used by Drits *et al*. (1998) and Lindgreen *et al*. (2000), with additional emphasis on particle morphology.

OFFSHORE OLD RED SANDSTONE

Offshore, the ORS has been encountered in >150 boreholes (Glennie, 1998; Marshall & Hewett, 2003). In some instances it is recorded simply because the ORS was at one time defined as the economic basement required to be reached before drilling could be stopped. In some of these records little is known about the stratigraphy and sedimentology of the ORS. In fact, attempts have been made to use clay mineralogy as a stratigraphic tool because of the paucity of other means of correlating offshore ORS (Jeans, 1995). In other cases, the ORS forms important hydrocarbon reservoirs. These include the Argyll, Buchan, Embla, Stirling and part of the Auk field in the Northern North Sea, and the Clair Field situated to the west of Shetland. With the exception of the Clair Field, there is little information on the clay mineralogy of the offshore ORS, although Jeans (1995) records some information on ORS strata encountered in wells 13/17-1 and 13/19-1 in the outer Moray Firth, which he tentatively correlated with the Middle ORS succession in Caithness.

Clair Group

Stratigraphy and sedimentology. The Clair Group reservoir is up to 800 m thick and consists of a Devonian to Carboniferous sequence of subarkosic to litharenitic sandstones. An unconformity has been recognized between the Lower and Upper Clair groups which may possibly coincide with the Devonian-Carboniferous boundary (Allen & Mange-Rajetzky, 1992). The sandstones of the Lower Clair Group were deposited under fluvial and aeolian conditions, although there is evidence of a lacustrine system in the sandstones towards the top of the Group. The Upper Clair Group for the most part was deposited under fluvial conditions.

Clay mineralogy. Jeans (1995) reported on the clay mineralogy of three wells located in the Clair field, west of Shetland, and subsequently, Pay *et al*. (2000) detailed the clay mineralogy of the Devonian/Carboniferous sandstones in the Clair field. Pay *et al*. (2000) concluded that the Lower Clair Group contained a complex and abundant clay mineral assemblage that included corrensite, interstratified chlorite-smectite, Mg-chlorite, Fe-chlorite, illite and I-S. Kaolinite was absent from the major part of the Lower Clair Group sequence although it was recorded occasionally. This clay mineral assemblage contrasted with that found in the Upper Clair Group the clay fractions of which were dominated by smectite. For the Lower Clair Group, the corrensite mineral described by Pay *et al*. (2000) is characterized by a large-spacing reflection at 28–29 Å, which moves to 31 Å after glycolation. However, from electron microprobe analyses its cation chemistry is described as being similar to the dioctahedral corrensite described by Morrison & Parry (1986) from Permian red beds in the Lisbon Valley, Utah. Therefore, the mineral may be more appropriately described as tosudite, similar to that described from the Lower ORS by Garvie (1992) and by Wilson (1971). Earlier, Jeans (1995) had also recorded ‘corrensite’ in well 206/9-2 from the Clair field, but this could be tosudite since it occurs at the base of a sequence otherwise dominated by abundant kaolinite, clearly indicating that aluminous clays had been generated during diagenesis. For the most part, the tosudite appears to be associated with sandstones deposited in a fluvial and lacustrine environment. It may be noted that the clay mineral assemblages described for the Lower Clair Group are similar to those described by Wilson (1971) for the Lower ORS of Scotland south of the Highland Boundary Fault.

Origin of clay mineral assemblages. Pay *et al*. (2000) had no doubt that the clay mineral assemblages of the Clair Field sandstones were predominantly authigenic in origin and related to burial diagenesis. The evidence for this conclusion is based largely upon SEM observations which show that the clay minerals occur in pore-filling or pore-lining modes and in a variety of intricate morphologies. Thus kaolinite occurs in a vermiform morphology, illite and I-S occur as grain coatings and pore-bridging ribbons, and Fe-rich chlorites occur as clusters of pseudo-hexagonal particles, which line pores. Smectite, Mg-chlorites and interstratified chlorite-smectite, including corrensite (tosudite), display a pore-filling boxwork structure composed of individual irregular shapes. Pay *et al*.

(2000) envisaged that the trioctahedral chloritic minerals formed from detrital smectite, enriched in Mg and Fe by the dissolution of detrital ferromagnesian minerals, and possibly by saline waters derived from lacustrine sediments during deposition or early burial. It was noted that the corrensite (tosudite?) was associated with arkosic horizons, suggesting that Al may have been provided by the dissolution of detrital feldspars.

SOUTHWEST ENGLAND

Regional geology and metamorphism

Apart from early and late developments of marginal marine facies in some southern areas and extensive volcanism in the northern regions, terrestrial sedimentation dominated the ORS facies. This is in contrast to the marine Devonian basins that lay to the south and east in Somerset, Devon and Cornwall, southeast England, and the central and southern parts of the present North Sea. Together the various marine Devonian rocks from southwest England, some of which also include extensive volcanic rocks, span the whole of the Devonian period (Dineley, 1992). Furthermore, in contrast to the ORS, the Devonian rocks of southwest England are essentially all affected by some degree of low-grade metamorphism related to Variscan events, which also extend into the ORS of southwest Wales, terminating against the Variscan front (Fig. 1).

In southwest England, Devonian rocks form two major outcrops separated by the E–W Culm Basin containing Carboniferous rocks (Fig. 22). The Devonian rocks of the northern outcrop in north Devon and Somerset comprise the Exmoor Group; they are predominantly fluvio-deltaic strata from the top of the Lower Devonian (Emsian) to the top of the Middle Devonian, giving way to shallow marine strata in the Upper Devonian. Rocks forming the southern outcrop are predominantly marine and occupy much of Cornwall and south Devon. They include the Lower Devonian Dartmouth and Meadfoot groups, and the Middle to Upper Devonian Tamar Group. Older schists on the Start peninsula and the largely ophiolitic Lizard Complex form the southern margin of the Devonian

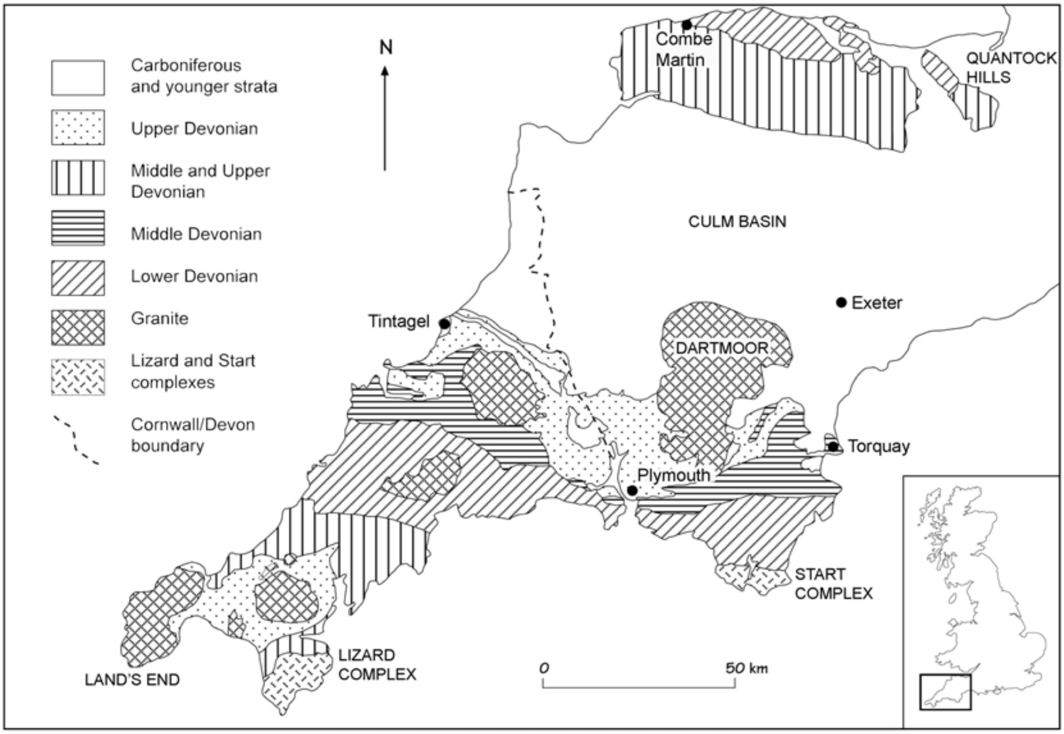

FIG. 22. Geological sketch map of the marine Devonian rocks of southwest England.

outcrop in south Devon and Cornwall. A series of granitic plutons was intruded into the southern outcrop of Devonian rocks in the late Carboniferous and early Permian (Holder & Leveridge, 1994).

The Devonian rocks of southwest England were deposited on the northern side of an evolving Rhenohercyian ocean basin that extended across northern Europe. Crustal extension began in the south of the region in the Early Devonian, and subsequently developed as a series of elongate rift basins that subsided and filled northwards. These basins were generated by rotation of basement blocks on listric faults, and commonly resulted in a half-graben basin-and-rise architecture. The basins are characteristically filled by thick, mudrock-dominated sequences, and the rises are formed of volcanic rocks and reef limestones (Leveridge *et al*., 2002).

As a result of Variscan tectonics during Devonian and early Carboniferous times, the Upper Palaeozoic strata of southwest England now form a fold-and-thrust belt of low-grade metamorphic rocks. Variscan deformation migrated from the south across the region, generating thrusts that advanced northwards closing and inverting passive margin basins (Holder & Leveridge, 1994). Two episodes of regional deformation are recognized. Closure of the more southerly Gramscatho Basin and inversion of the central Trevone Basin in the late Devonian to early Carboniferous is associated with the emplacement of a family of major thrust nappes. A second phase of deformation in the Upper Carboniferous resulted in out of sequence thrusting in the Trevone Basin, and inversion of the Culm Basin, a foreland basin lying to the north of the major nappes. Regional low-grade metamorphism ranges from late diagenetic through the anchizone to the epizone, in terms of metapelitic grades (Warr *et al*., 1991). Younger Upper Carboniferous rocks generally show lower grades (late diagenetic–lower anchizone) than the Lower Carbonifeous to Lower Devonian strata. Slaty cleavage development is spatially related to metapelitic grade, with penetrative fabrics tending to be associated with anchizonal to epizonal grades whereas late diagenetic to lower anchizonal rocks typically show a weak, non-penetrative cleavage fabric.

The regional pattern of metamorphism in some parts of southwest England shows a very general relationship between metapelitic grade and the stratigraphic succession, indicative of sedimentary burial (Warr *et al*., 1991, their figs 1, 2). There is some evidence that a burial pattern was acquired prior to folding and thrusting (e.g. Pamplin, 1990; Leveridge *et al*., 2002). Along the active southern margin, overthrusting of high-greenschist- and amphibolite-facies metapelites and metabasites of the Start and Lizard complexes represent inverted metamorphic sequences, and here tectonic burial has taken place.

Clay mineralogy

Over the past 25 years, the clay mineralogy of Devonian rocks has formed part of ~20 published and unpublished investigations into patterns of low-grade metamorphism in southwest England. However, while most of these studies have measured the Kübler Index of illite 'crystallinity' using separated <2 μm fractions, details of the clay fraction assemblages have not been provided in all cases (Warr *et al*., 1991, and references therein). Where these details are presented, a generalized pattern of changes in clay mineralogy has been related to increases in grade and changes in mudrock lithology (Merriman *et al*., 1996). Mudstones and shales in the late diagenetic zone commonly contain illite, with up to 10% smectite interlayers, and chlorite, with kaolinite and lepidocrocite as occasional minor constituents. Anchizonal slates are characterized by major amounts of $2M_1$ K-mica and chlorite, with occasionally lesser amounts of intermediate Na/K mica, paragonite, and minor albite, and the TiO_2 polymorphs anatase or rutile. Where present, discrete paragonite increases at the expense of Na/K mica and slaty cleavage becomes more intensely developed as grade increases through the lower to the upper anchizone. Epizonal slates consist of major amounts of $2M_1$ K-mica and chlorite, with lesser amounts of discrete paragonite, albite, and TiO_2 polymorphs.

Recorded occurrences of mixed-layer I-S minerals are restricted to late diagenetic mudstones and shales. For example, in the Plymouth area, Merriman *et al*. (1996) found I-S together with illite and chlorite in the Middle Devonian Saltash Formation and in the Upper Devonian Torpoint Formation. Warr (1995) recorded I-S in the Upper Devonian Lydford Slates, close to the western margin of the Dartmoor granite.

Although intermediate Na/K mica and paragonite have been recorded sporadically as minor constituents in anchizonal and epizonal slates, these minerals form 15−40% of clay fractions in the Middle to Upper Devonian Porthscatho Formation in south Cornwall (Merriman, unpublished BGS data). Associated clay minerals include major amounts of $2M_1$ K-mica and minor chlorite. The large Na clay content in the Porthscatho Formation, which forms the hanging wall of the Carrick Thrust (Leveridge & Holder, 1985), is in marked contrast with the absence or very small Na/K mica and paragonite contents in the Upper Devonian Mylor Slate Formation forming the footwall of the thrust.

The occurrence of pyrophyllite in Devonian rocks appears to be restricted to two areas. In the north of the region, Kelm (1986) reported a distinct pyrophyllite-bearing horizon that extended from Combe Martin to the Quantock Hills. On the north coast of Cornwall, pyrophyllite is found in Middle and Upper Devonian slates at anchizonal to epizonal grades in the Tintagel area (Primmer, 1985). Chloritoid microphyroblasts occur in the Tintagel High-Strain Zone, where they appear to post-date the development of the slaty cleavage (Warr *et al*., 1991).

Chlorite-mica stacks have been reported sporadically from Devonian slates in southwest England (Warr *et al*., 1991). They consist of chlorite intergrown with K- or Na-rich white mica and share the same crystallographic *a-b* stacking planes. Although the stacks were initially generated by late diagenetic burial (e.g. Merriman, 2005), those found in Devonian slates were deformed by kinking and flattening in the cleavage.

The widespread occurrence of kaolin group minerals in the Devonian from Cornwall and south Devon suggests that one or more retrogressive events have affected this region of southwest England. Despite high anchizonal and epizonal grades, Merriman (unpublished BGS data) recorded kaolinite in slates from the Lower Devonian Meadfoot Group, Middle to Upper Devonian Porthscatho Formation and Upper Devonian Mylor Slate Formation. One of us (Hillier, in press) has also observed pure smectite in the Meadfoot Group (Fig. 11f), similar to that observed in southwest Wales (Fig. 5c,e). The occurrence of smectite in otherwise low-grade metamorphic rocks is also suggestive of retrogressive diagenesis in the sense of Nieto *et al*. (2005). In some slates kaolinite is accompanied by lepidocrocite, suggesting that deep weathering may have caused retrogression. A kaolin

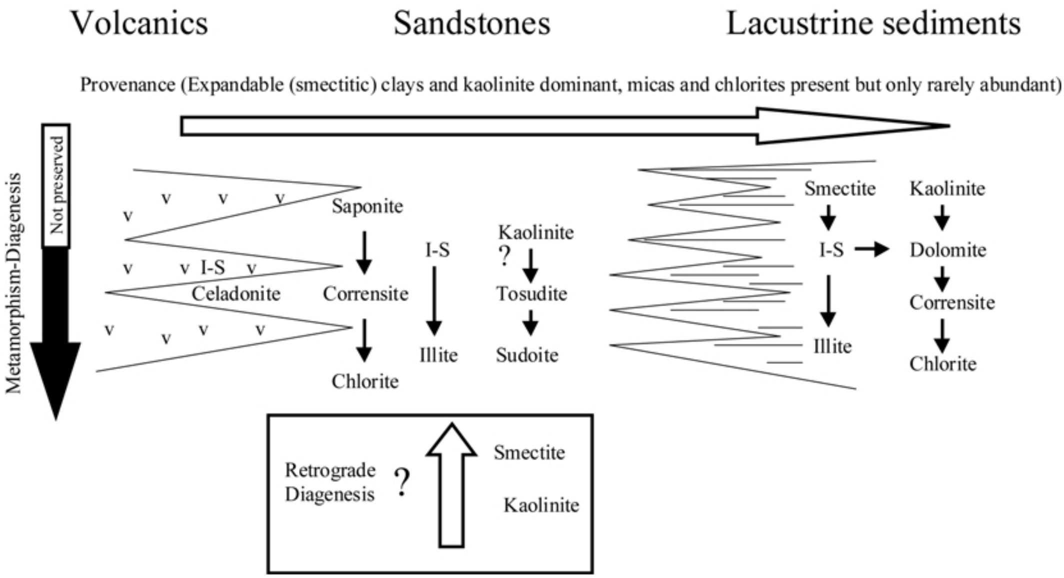

FIG. 23. General interpretative picture of the clay mineralogy of the ORS in terms of the three main facies associations, emphasizing the possible influence of diagenesis/low-grade metamorphism, with a lesser role for provenance and retrograde diagenesis. This interpretation implies a predominantly smectitic original clay mineral assemblage. Precursor clay minerals of earlier diagenetic stages are no longer observed as a result of the degree of diagenetic alteration having everywhere advanced beyond the stages indicated approximately by the arrow on the right-hand side of the figure.

group mineral, tentatively identified as dickite by Warr (1995), was found in slates from the Meadfoot Group. The kaolin mineral forms part of the slaty cleavage fabric close to a major fault (Start-Perranporth Line) separating schists of the Start Complex from Lower Devonian slates in south Devon, and its retrogressive origin is attributed to fluid movement along the fault zone.

CONCLUDING REMARKS

If anything conclusive can be said about the ORS and Devonian as a whole one can certainly say that its clay mineralogy is diverse. Some areas have been studied in more detail than others and there are still many areas where few or no data exist. Most of the clay minerals found in the ORS had already been identified by the time of the publication of Perrin's (1971) book. Later works have added details but interpretations have polarized between a detrital and a diagenetic origin. In the process of compiling this review we also find ourselves polarized as authors: on the one hand Hillier favours an overriding diagenetic interpretation of the clay minerals assemblages and on the other hand Wilson envisages a much more substantial influence of provenance. In some instances textural evidence shows clearly that the clay minerals can only have formed at some stage after deposition of the sediment. However, the origin of other clay mineral assemblages is not so clear and conclusions are based only upon more indirect inferential evidence, which is sometimes conflicting. In many instances, therefore, conclusions can only be tentative and further work and more systematic sampling is required if they are to become more definitive.

A generalized but by no means definitive interpretation that emphasizes the role of diagenesis and low-grade metamorphism in the broadest terms is summarized in Figure 23 for each of the three major ORS facies associations: namely, fine-grained lacustrine sediments, red beds of predominantly fluvial origin, and volcanic rocks and sandstones with an obvious volcanic provenance. In this interpretation the character of the clay assemblage is considered to be consistent with a major element of diagenetic control. This is judged by analogy with the patterns of clay mineral diagenesis observed in younger active sedimentary basins and by comparative means where the degree of diagenetic alteration of the ORS can be independently constrained. Such a major element of diagenetic control might not be surprising given the age and thickness of the ORS, notwithstanding later diagenetic and tectonic events over the ensuing 360 Ma of post-Devonian time. But we must emphasize that we do not agree entirely amongst ourselves that such an interpretation explains all our observations.

In accord with a diagenetic origin, assemblages of kaolinite and mixed-layer illite-smectite are abundant in the dominant sandstone facies and characteristic of areas of the lowest diagenetic grade, whereas assemblages of illite and chlorite characterize sandstones where there is evidence for a higher grade of diagenesis or low-grade metamorphism. For example, the pattern seen in both the Lower ORS and the Upper ORS travelling eastwards from the Welsh Borderland, through south Wales to west Wales can be interpreted in this way.

One of the new features this review has highlighted is the widespread occurrence of dioctahedral chlorite and dioctahedral chlorite-smectite (tosudite) especially in the Lower ORS. Offshore in the far north tosudite occurs in the Clair Field, to the west of Shetland. Further south it is abundant in the Dittonian rocks from the Midland Valley of Scotland, and in Wales and the Welsh Borderland tosudite is abundant in the eastern outcrop area whereas dioctahedral chlorite is abundant in the west. The distribution of these dioctahedral minerals in this latter region, along with the associated distribution of kaolinite, could be interpreted as a prograde diagenetic sequence of aluminous clay minerals whereby kaolinite is replaced by tosudite and subsequently tosudite is replaced by sudoite (dioctahedral chlorite) as a function of increasing temperature. This is clearly an aspect that requires further investigation, more especially since dioctahedral chlorites are common in many other red beds. This possible paragenetic sequence may therefore be of some general importance in the diagenesis of such rocks (Hillier, 2003).

Provenance, however, is undoubtedly a major factor controlling the occurrence of some clay minerals. For example, the corrensite found in certain sandstones of the Midland Valley of Scotland has a clear association with volcanism. Notably, corrensite has not been identified in sandstones outwith the Midland Valley. This is possibly a reflection of the very close association of volcanic rocks with sedimentation in this region compared to other regions. However, one could also argue that provenance and diagenesis must play something of a combined role here since many studies (e.g. Kübler, 1973; Hillier, 1993) have concluded that corrensite is a diagenetic mineral requiring a certain degree of diagenetic alteration to initiate its formation. Certainly, in many recent studies of the alteration of sequences of volcanic rocks, as summarized in Merriman and Frey (1999), a lowest-grade zone where saponite is the predominant clay mineral always supersedes the appearance of corrensite. In terms of the diagenetic interpretation advanced in Fig. 23, this would imply that the ORS and altered volcanic rocks of the Midland Valley do not preserve this lower-grade portion because they have been buried or heated to temperatures of sufficient intensity for the widespread formation of corrensite.

Another new feature identified in this review is the occurrence of disordered kaolinite and of pure dioctahedral smectite in the Lower ORS of west Wales. If one accepts that these are low-grade metamorphic rocks of anchizonal grade affected by Variscan events then the occurrence of smectite and kaolinite in these rocks is anomalous. To be consistent with the diagenetic interpretation as a whole, as advanced in Fig. 23, we have speculated that this may be an indication of retrograde diagenesis in the sense of Nieto *et al*. (2005). As yet textural studies have not been carried out to confirm this assertion, but the similarity to other examples of retrograde diagenesis, as documented by Nieto *et al*. (2005), is notable.

Again, there is much evidence to support an interpretation of the clay mineralogy of Middle ORS lacustrine sediments of the Orcadian Basin in terms of diagenetic/low-grade metamorphic alteration (Hillier, 1989, 1993), as summarized in Fig. 23. The expandability of the presently observed mixed-layer I-S is a function of diagenetic grade and this trend is interpreted as part of an illitization sequence. The implication is that the original detritus had a significant smectitic component that was converted by diagenetic processes to the illite-smectite observed in the shales today. In this interpretation, the earlier part of an illitization sequence with smectite as the main reactant, as shown in Fig. 23, is no longer preserved because post-Devonian burial and thermal history has been more than sufficient to advance illitization to the stages now observed. Since mixed-layer I-S accounts for ~30–40% by weight of the lowest diagenetic grade Orcadian Basin shales (Hillier, 1989; Table 3b) it is difficult to conceive of another reactant of sufficient volumetric importance from which it could have formed other than a more smectitic precursor clay. The picture, however, may be more complicated than this in detail, especially in the sandstones, where morphological and structurally different populations of I-S particles are commonplace. The Mg-rich chlorite that is widespread in the Orcadian basin lacustrine shales is also interpreted as a product of diagenesis (Hillier, 1993). Mg-rich chlorite formed by a late-stage diagenetic reaction amongst the detrital, dioctahedral clay mineral assemblage and dolomite that was formed early in the lacustrine sedimentary environment.

The concluding picture presented thus far, as summarized in Fig. 23, has emphasized diagenesis as possibly the major factor controlling the distribution of ORS clay mineral assemblages. It might also be argued, however, that provenance plays an equally important role. In this view the importance of an originally smectite-dominated detrital assemblage, as shown in Fig. 23, is questioned. Bearing in mind that in many areas the ORS was derived from low-grade metamorphosed Lower Palaeozoic sedimentary rocks, in addition to schists and granites eroded from the uplifted Caledonian mountain belts, it could be argued that these sources would provide a general background of unweathered fine-grained micaceous and chloritic material to the ORS sediment. That this may be the case is suggested by the observation of Maskall (1985) that the detrital sediments directly above the Townsend Tuff are characterized by an assemblage containing more illite and chlorite than the tuff itself. We have also observed that the youngest ORS of south Wales (Breconian and Upper ORS) contains clay mineral assemblages of an apparently higher diagenetic grade than stratigraphically older Dittonian and Downtonian rocks of the region. This could also be construed as evidence that conflicts with an overriding diagenetic interpretation, but the localities from which these observations are made are widely separated and consequently it is not certain that the apparently higher-grade assemblages directly overlie those consistent with lower grades. Additionally, the presence of smectite and kaolinite in the Dittonian sediments of Pembrokeshire, as well as the ORS of the Langadoc area further east, can be seen as inconsistent with a diagenetic interpretation. Although it can be argued that their presence might be explained by retrograde diagenesis, another explanation could be that the assemblage simply represents contributions of rocks and weathered materials from the source area. In this view, however, the occurrence of dioctahedral smectite is still something of an anomaly, since its survival from detrital origins implies virtually no diagenetic alteration of the rocks in this region at all.

In Scotland also there are features of the ORS that may conflict with a predominately diagenetic interpretation for the observed clay mineral assemblages. In particular, the assumption that diagenetic change proceeded from an initially smectitic sediment can be questioned. In this respect the arid to semi-arid palaeoclimate conditions prevailing, the relatively fresh nature of unstable primary minerals such as biotite (Wilson & Duthie, 1981) in ORS sediment, and the likelihood of rapid erosion of sediment consequent upon the uplift of igneous and metamorphic terrains could all be cited in support of a detrital assemblage in which largely unweathered illite and chlorite were predominant. Equally, proponents of a diagenetic model could counter that uplifted Caledonian terrains included significant thicknesses of volcanic rocks representing a likely source of much of the smectitic detritus required for this model. Nor can it be assumed that the presence of unstable minerals in sandstones implies that they should be accompanied and dominated by a largely unweathered illite-chlorite clay mineral assemblage, cf. the Alpine Molasse (Monnier, 1982). Central to this debate is the character and intensity of weathering during deposition of the ORS, about which we have no direct information. We know that the climate was arid to semi-arid most of the time, and that calcretes at various stages of development are a common feature of many ORS successions. There must also have been plenty of water around at other times since the vast majority of the sandstones are fluvial. Recently, Marriott & Wright (2004) have argued that palaeosols preserved in the ORS of west Wales are Vertisols. Such interpretations also require that the original sediment was highly smectitic, as Vertisols are unlikely to develop in clay dominated by illite and chlorite since they are not swelling clays. Clearly, the illite-chlorite-dominated *vs.* smectite-dominated debate for the original character of ORS detrital clay has much further to go.

In the largely marine Devonian rocks of Cornwall and Devon there is no doubt that low-grade metamorphism is the main control on the clay mineral assemblages observed. However, even here the occurrence of smectite and of kaolinite in otherwise illite-chlorite assemblages suggests that processes other than prograde metamorphism may also have been active.

Doubtless there are many more aspects of ORS and Devonian clay mineralogy that require much more detailed scrutiny, and it may be confidently predicted that clay mineralogy has much still to contribute to an understanding of the geological history of these rocks in the UK.

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APPENDIX A

Sample no.	Map Ref.	Stratigraphy	Locality	Lithology
LORS 1	SO 043163	Breconian	Taff Fechan valley	Sandstone
LORS 2	" "	" "	" "	Sandstone
LORS 3	SN 971208	" "	Taff Fawr valley	Shale
LORS 4	" "	" "	" "	Sandstone
LORS 5	SN 988178	" "	" "	Shale
LORS 6	" "	" "	" "	Sandstone
LORS 7	SO 159223	" "	Usk valley	Sandstone
LORS 8	" "	" "	" "	Sandstone
LORS 9	" "	" "	" "	Sandstone
LORS 10	SO 245144	Dittonian/Breconian?	Gilwern	Sandstone
LORS 11	" "	" "	" "	Sandstone
LORS 12	" "	" "	" "	Sandstone
LORS 13	" "	" "	" "	Shale
LORS 14	" "	" "	" "	Sandstone
LORS 15	" "	" "	" "	Sandstone
LORS 16	SN 926275	Breconian	Tawe valley	Shale
LORS 17	" "	" "	" "	Shale
LORS 18	SN 870195	" "	" "	Sandstone
LORS 19	" "	" "	" "	Shale
LORS 20	SN 852173	" "	" "	Sandstone
LORS 21	" "	" "	" "	Shale
LORS 22	SO 527155	Dittonian	A40	Sandstone
LORS 23	SO 531162	" "	" "	Sandstone
LORS 24	" "	" "	" "	Shale
LORS 25	SO 564188	" "	" "	Sandstone
LORS 26	" "	" "	" "	Shale
LORS 27	SO 565189	" "	" "	Sandstone
LORS 28	" "	" "	" "	Sandstone
LORS 29	" "	" "	" "	Sandstone
LORS 30	" "	" "	" "	Sandstone
LORS 31	" "	" "	" "	Sandstone
LORS 32	" "	" "	" "	Shale
LORS 33	" "	" "	" "	Sandstone
LORS 34	SN 732195	Dittonian/Breconian	A4069	Sandstone
LORS 35	" "	" "	" "	Shale
LORS 36	" "	" "	" "	Sandstone
LORS 37	" "	" "	" "	Shale
LORS 38	" "	" "	" "	Shale
UORS 1	SO 043163	UORS Grey Grits	Taff Fechan valley	Shale
UORS 2	SO 066128	" "	" "	Shale
UORS 3	" "	" "	" "	Shale
UORS 4	" "	" "	" "	Shale

APPENDIX A (*contd.*).

Sample No.	Map Ref.	Stratigraphy	Locality	Lithology
UORS 5	SO 017110	UORS Grey Grits	Taff Fawr valley	Sandstone
UORS 6	SO 016112	" "	" "	Sandstone
FW-1	SR 885993	Dittonian	Freshwater West	Sandstone
FW-2	" "	" "	" "	Shale
FW-3	" "	" "	" "	Sandstone
FW-4	" "	" "	" "	Sandstone
FW-5	" "	" "	" "	Sandstone
FW-5-shp	" "	" "	" "	Shale
FW-6	" "	" "	" "	Shale
FW-7	" "	" "	" "	Shale
FW-8	" "	" "	" "	Shale
FW-9	" "	" "	" "	Sandstone
FW-10	" "	" "	" "	Shale
FW-11	" "	" "	" "	Shale
WM 1	SO 579848	Dittonian	West Midlands	Sandstone
WM 2	SO 578861	" "	" "	Sandstone
WM 3	SO 579848	" "	" "	Sandstone
WM 4	SO 641857	" "	" "	Sandstone
WM 5	SO 566871	" "	" "	Sandstone
WM 6	SO 617849	" "	" "	Sandstone
WM 7 (1)	SO 508511	" "	Herefordshire	Sandstone
WM 8 (2)	SO 509509	" "	" "	Sandstone
WM 9 (3)	SO 508509	" "	" "	Sandstone
DEV1	ST 312912	Dittonian	Newport	Shale
DEV2	" "	" "	" "	Shale
DEV3	" "	" "	" "	Sandstone
DEV4	" "	" "	" "	Shale
DEV5	" "	" "	" "	Sandstone
DEV6	" "	" "	" "	Sandstone
MT1	SN 972212	Breconian	Taff Fawr valley	Sandstone
MT2	" "	" "	" "	Sandstone
MT3	" "	" "	" "	Sandstone
MT4	" "	" "	" "	Shale
Edzell 1	NO601707	Strathmore Group	Edzell	Sandstone
Edzell 2	" "	" "	" "	Sandstone
Edzell 3	" "	" "	" "	Sandstone
Edzell 4	" "	" "	" "	Shale
Edzell 5	" "	" "	" "	Sandstone
Cowie 1	NO887874	Stonehaven Group	Cowie Harbour	Shale
Cowie 2	" "	" "	" "	Sandstone
Cowie 3	NO884870	" "	" "	Sandstone
Cowie 4	NO883869	" "	" "	Shale
Cowie 5	NO881869	" "	" "	Sandstone
Cowie 6	" "	" "	" "	Sandstone
Cowie 7	" "	" "	" "	Sandstone
WHB-1	ST 464775	UORS-Shirehampton beds	Woodhill Bay	Shale
WHB-2	" "	" "	" "	Shale
WHB-3	" "	" "	" "	Sandstone
WHB-4	ST459769	UORS-Portishead beds	" "	Shale
WHB-5	" "	" "	" "	Sandstone
WHB-6	" "	" "	" "	Sandstone
WHB-7	" "	" "	" "	Shale
WHB-8	" "	" "	" "	Sandstone
Kymin-1	SO528124	UORS-Tintern Sandstone	Kymin, Monmouth	Sandstone
Kymin-2	" "	" "	" "	Sandstone