Carbon isotopic evidence for organic matter oxidation in soils of the Old Red Sandstone (Silurian to Devonian, South Wales, UK).

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Abstract

Petrographic and calcrete carbon isotope data from seasonally waterlogged Upper Silurian (Přídolí) to Lower Devonian (Pragian) palaeo-Vertisols of the Old Red Sandstone, South Wales, UK, are presented. The $\delta^{13}C$ values mostly range from -9 to -12‰ (VPDB), suggesting the soils were inhabited by abundant vegetation that when oxidised (perhaps with microbial assistance) resulted in CO_2-rich soils. Such soils would favour calcrete precipitation through equilibration of soil zone CO_2 with the relatively lower atmospheric pCO_2. However, reliably estimating palaeoatmospheric pCO_2 calculated from these carbon isotope data is a challenge.

Keywords: calcrete, carbon isotopes, Silurian, Devonian, soil carbonate, palaeosols

The physical appearances, sedimentary textures and depositional processes of soil carbonates have evolved through time, particularly through the Palaeozoic (Brasier 2011). One of the first major steps in terrestrial carbonate evolution was likely associated with the Palaeoproterozoic oxygenation of shallow marine and lacustrine environments (Brasier 2011), which led to widespread precipitation of calcium sulphates. Dissolution of highly soluble gypsum and anhydrite can lead to precipitation of less soluble calcite from terrestrial groundwaters (the ‘common ion effect’). The widespread incorporation of organic matter from early plants into soils has been hypothesised as the driver of a later major step in carbonate precipitation that likely took place in the Late Silurian or Early Devonian. This is because plant growth and organic matter incorporation raises soil zone pCO_2 via plant and microbial respiration or decay, which leads to enhanced production of carbonic acid. The latter can dissolve limestone bedrock (where present), and dissociate to form bicarbonate ions (HCO_3^-). On the other hand, if the accumulated soil zone carbon dioxide is able to escape (perhaps during dry seasons as the soils begin to crack), and pCO_2 is higher than atmospheric pCO_2, then outgassing of dissolved CO_2 can occur. This CO_2 loss drives an equilibrium reaction (reaction 1, below) to the right, leading to calcrete precipitation.

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + H_2O + CO_2 \quad (1)$$

Chemical weathering of silicate bedrock via interaction with carbonic acid is a major driver in perturbations of global atmospheric carbon dioxide levels (e.g. Berner & Kothavala 2001). The importance of respiring vascular plants with well-developed root systems (that locally lower soil zone pH) and symbiotic mycorrhizal fungi to this process has often been emphasised (e.g. Algeo *et al*. 2001; Berner *et al*. 2003).

Calcrete deposition also requires a source of calcium ions. This could be local chemical weathering of carbonate or volcanic bedrock, although in the Recent soils of New Mexico, USA, the calcium is demonstrably sourced from windblown dust (Capo and Chadwick, 1999). Increased levels of silicate weathering (leading to increased calcium availability) could also have encouraged post-Middle Devonian non-marine carbonate precipitation (Brasier, 2011).

At least from the Middle Devonian onwards, vascular plants with root systems have actively encouraged calcrete (sensu Wright and Tucker, 1991) precipitation through evapotranspiration, and directly controlled the geochemistry of the rhizosphere (see references in Brasier 2011). The effects of earlier (Silurian to Early Devonian), pre-vascular plant organic matter on calcrete precipitation and morphology, and on silicate mineral weathering, must also be considered. It has previously been suggested that the biological productivity of microbiota prior to vascular plants was similar to that of modern soils (Yapp & Poths 1994), and that microbially-produced CO_2 levels may have been high in the vadose zone prior to the Silurian (Keller & Wood 1993). Degassing of CO_2 from these soils could have produced calcite-supersaturated groundwaters before the later advent of vascular plants with roots actively engaged in the precipitation of calcrete.

Direct evidence of preserved organic matter in Late Silurian to Early Devonian terrestrial deposits is limited. The Anglo-Welsh Basin of South Wales and the Welsh Borderland (Fig. 1) has yielded an unrivalled record of early land plant history (e.g. Lang 1937; Edwards & Richardson 2004), in particular vascular plant remains such as *Cooksonia* (Edwards 1979). The majority of megafossil remains are allochthonous in nature, although downward-bifurcating drab haloes are common in palaeosols, and have been interpreted as surface water gleying around small-scale rooting structures that subsequently decayed (Allen1986; Allen & Williams,1982). Hillier *et al*. (2008) described shallow rooting structures from a wide range of terrestrial environments across the basin, and used circumstantial evidence to conclude that these structures could have been produced by the fungus *Prototaxites*. In addition to rooting structures, the Late Silurian to Early Devonian terrestrial deposits preserved a diverse ichnofauna that demonstrates a complex trophic structure (Morrissey *et al*. 2012). "Enigmatic" sedimentary structures such as millimetre-scale ripples and wrinkle structures provide evidence for widespread microbial presence around palaeosols and their spatially associated environments, constituting a plausible base to the trophic pyramid (Morrissey *et al*. 2012; Marriott *et al*. 2012).

Many Late Silurian to Early Devonian palaeosols from the Anglo-Welsh Basin contain abundant calcrete nodules (e.g. Allen 1974; Marriott & Wright 1993; Love & Williams 2000; Hillier *et al*. 2011*a*). The aim of this study was to test the possibility of a link between the palaeontological and sedimentary evidence for terrestrial biological activity, organic matter accumulation and the occurrence of these early calcrete nodules. Processes that could have caused the calcrete precipitation include evaporation, the common-ion effect, or loss of CO_2 from the soil to the relatively lower $p$$CO_2$ atmosphere (via reaction 1). Evidence for predominance of the latter process would suggest that Late Silurian to Early Devonian terrestrial organisms (either actively when alive or passively when dead) produced high $p$$CO_2$, carbonic acid rich soils prior to the evolution of deeper-rooted plants.

Calcrete carbon isotope geochemistry should portray the influence of soil zone organic matter on calcrete precipitation. Carbon isotope data from pre-Silurian calcretes are currently scarce, but values reported to date are all much closer to 0‰ VPDB than found in more recent examples. These ancient cases include the Cambrian La Flecha Formation calcretes of Argentina (-1 to -3‰; Keller *et al*., 1989; Buggisch *et al*., 2003), and Cambrian alluvial fan calcretes of the Guaritas Sequence of Brazil (-1.47 to -0.99‰; De Ros et al., 1994). Their relatively positive carbon isotope compositions likely reflect a very small or negligible contribution of biologically processed carbon to pre-Silurian soil zone CO_2. In contrast, Late Devonian to modern calcrete $\delta^{13}C$ values are mostly strongly negative (e.g. Ekart et al., 1999). Their signals are dominated by CO_2 respired by soil-inhabiting organisms, in addition to the CO_2 resulting from oxidation of dead soil zone organic matter (e.g. Cerling 1984; Driese & Mora 1993; Mora *et al*. 1996; Ekart *et al*. 1999). If organic matter oxidation in the Late Silurian and Early Devonian produced high soil zone pCO_2, facilitating and accelerating widespread calcrete precipitation via reaction 1, and potentially enhancing silicate bedrock weathering, this should be reflected in the calcrete $\delta^{13}C$ record.

Geological setting

Basin History

The Old Red Sandstone magnafacies outcrops across South Wales and the Welsh Borderland, U.K. (Fig. 1) and comprises predominantly terrestrial sequences that were deposited in the Anglo-Welsh Basin during the Late Silurian to Early Carboniferous. During this interval the basin lay on the southern margins of Laurussia within sub-tropical latitudes (c. 17º S; Channell *et al*. 1992; Friend *et al*. 2000). The Lower Old Red Sandstone Daugleddau Group (Fig. 2; Barclay *et al*. in press) is of Late Ludlow to Early Devonian (Emsian) age. Sequences of the lower part of the group (the Milford Haven Subgroup) were deposited mainly in dryland coastal plain and alluvial floodplain environments that developed in a semi-arid climate (Allen 1974; Barclay *et al*. 2005; Hillier & Williams 2006). Contemporaneous volcanic tuffs were likely sources of calcium for the calcretes and are interbedded throughout the succession (e.g. Marriott et al., 2009). The upper Přídolí Moor Cliffs Formation is a mudstone-dominated, heterolithic succession of moderately sinuous ephemeral river channel and floodplain deposits that were pedified to varying degrees as calcic palaeo-Vertisols, of which the C horizons are often defined by the presence of pedogenic calcrete (as further described below;Allen & Williams 1979; Marriott & Wright 1993; Marriott & Wright 2004). The formation also preserves low-gradient, high width-to-depth ratio ephemeral fluvial sandbodies (Love & Williams 2000; Williams & Hillier 2004). The top of the formation is marked by the Chapel Point Limestone Member (Fig. 2), a unit of well-developed stacked calcrete-containing palaeosols of significant aerial extent across the basin, which signifies a period of basin-wide sedimentary hiatus and pedogenesis close to the Silurian-Devonian boundary (Williams *et al*. 1982; Allen 1986; Wright & Marriott 1996).

A basin-wide change in palaeohydrology and geomorphology occurred across the Silurian-Devonian boundary, with the appearance of sandstone-dominated perennial fluvial channels of the lower Lochkovian Freshwater West Formation (Fig. 2). These may represent an overall wetter climate than that of the Late Silurian, possibly associated with a more intense monsoonal climate (Hillier *et al*. 2007; Morris *et al*. 2012). The presence of hydromorphic palaeosols indicates intervals of prolonged waterlogging (Hillier *et al*. 2007), the higher water table facilitating the preservation of plant micro- and macrofossils (Higgs 2004; Morris *et al*. 2011, 2012). During intervals of low precipitation and discharge, the basin essentially reverted to an ephemeral dryland mudstone-dominated system with well-developed calcic palaeo-Vertisols (Hillier *et al*. 2007). Most of the Late Silurian- Early Devonian deposits were derived from the north, with the exception of the late Lochkovian Ridgeway Conglomerate Formation, found south of the Ritec Fault in Pembrokeshire (Fig. 1), with deposits derived from the south. It represents an interval of transtensional related half-graben development in the basin, with increased topographic relief shedding ephemeral alluvial fan deposits into contemporaneous dryland alluvial valleys (Hillier & Williams 2007).

Pedogenic vs. groundwater calcretes

The term calcrete is defined as 'a near surface, terrestrial accumulation of predominately calcium carbonate, which occurs in a variety of forms from powdery to nodular to highly indurated' (Lampugh 1902; Goudie 1973; Wright & Tucker 1991). The term applies to carbonate accumulations in soils and palaeosols ('pedogenic calcretes'), and also to groundwater precipitates ('groundwater calcretes'; see Wright & Tucker 1991). Much calcrete in the Old Red Sandstone of the Anglo-Welsh Basin is pedogenic. Typical pedified red beds of the Old Red Sandstone are recognised by three soil horizons that occur as single vertical profiles or, more commonly, as a series of stacked profiles with complex depositional and pedogenic histories (Allen 1974, 1986; Marriott & Wright 1993, 2006). The upper (A) horizon is characterised by the presence of blue-grey vertically orientated vein-like features, ascribed by most authors to local reduction of iron ('drab haloes') around roots, but may also represent burrows or desiccation cracks. The middle (Bss) horizon is recognised by the presence of convex-up, wedge shaped peds with slickensided slip-planes. The lower (Ck) horizons possess various types of pedogenic carbonate, including sub-spherical nodules, elongate, columnar rods and crystallaria, ranging from stage I to V in development (*sensu* Machette 1985). Calcrete precipitation and growth in soils is displacive.

When compared to modern soil orders (US soil taxonomy) the A-Bss-Ck horizonation is most similar to that of Vertisols (Soil Survey Staff 1999), hence most palaeosols within the Anglo-Welsh Basin are interpreted as calcic palaeo-Vertisols (e.g. Allen 1986; Marriott & Wright 1993, 2004; Love & Williams 2000). Today the majority of Vertisols develop under conditions of limited moisture, but that are sufficient for plant growth (ustic regimes; Soil Survey Staff 1999). Many authors have interpreted the pedogenic features observed as evidence for a semi-arid palaeoclimate with distinct wet and dry seasons (Allen 1986; Marriott & Wright 1993, 1996, 2004). For example, shrinking and swelling of clays under such conditions leads to the formation of the slickensided slip-planes (Wilding & Tessier 1988), while pedogenic calcrete formation itself might require strong seasonality (e.g. Breecker *et al*. 2010). Seasonal wetting and drying of the soils promoted alternating periods of oxidation and reduction, and subsequent formation of redoximorphic indicators such as drab haloes around rooting traces, fractures and desiccation cracks (pseudogleying). In addition, and particularly common in the Conigar Pit Sandstone Member, is the development of red/purple and grey to grey/green colour mottling in sandstone bodies. The latter may be oval or outline depositional structures such as cross-lamination. They are interpreted as redoximorphic indicators of seasonal saturation as iron oxides were reduced (low chromas) or oxidised (high chromas) by a fluctuating water table (Hillier *et al*. 2007). Pedogenic calcretes are usually assumed to have obtained their carbon from a combination of atmospheric CO_2 and biological, respired CO_2 in the soil zone (e.g. Cerling 1984). Some re-working of carbon from older pedogenic calcrete is also to be expected in these systems.

Conversely, groundwater calcretes precipitate from mobile carbonate-rich groundwaters. These carbonates are commonly precipitated in layers within the capillary fringe zone, but they can be precipitated below the water table (Wright & Tucker 1991). They have been recognised in the Old Red Sandstone of the Anglo-Welsh Basin as sharp-based, layer-bound micritic calcretes with upper surfaces comprising vertical and cylindrical nodules (Hillier *et al*. 2011*b*). Groundwater calcretes may source their carbon from beyond the soil zone (e.g. underlying bedrock, or older pedogenic calcretes).

Localities and methodology

The majority of the calcretes sampled are from South-west Wales. Here there is good section exposure of recognisable, well-developed palaeosol profiles that have been extensively studied (e.g. Allen & Williams 1982; Williams *et al*. 1982; Marriott & Wright 1993, 2004; Love & Williams 2000; Williams & Hillier 2004; Hillier *et al*. 2007). Palaeosol profiles of the upper Přídolí Moor Cliffs Formation were examined, and carefully selected calcretes were sampled from Manorbier, Pembrokeshire (latitude 51.644212°, longitude -4.806869°) and Llansteffan, Carmarthenshire (latitude 51.752037°, longitude -4.634724°) (Fig. 1). Calcretes from the lower Lochkovian Freshwater West Formation were collected from palaeosols identified throughout the type section at Freshwater West, Pembrokeshire (latitude 51.652384°, longitude -5.057570°) and at representative shorter sections at Manorbier and Llansteffan. Samples from the late Lochkovian Ridgeway Conglomerate Formation were collected at Freshwater West.

Additional pedogenic calcrete nodules were sampled from central South Wales, from palaeosol profiles of the lower Lochkovian Freshwater West Formation (previously known in the region as the St. Maughans Formation, Barclay *et al*. 2005, in press; Fig. 2), Chapel Point Limestone Member, and Moor Cliffs Formation (previously known regionally as the Raglan Mudstone Formation). These were all identified in two cores from Tredomen Quarry (BGS registration numbers SO13SW/2 & SO13SW/3), near Brecon, Powys (Fig. 1; latitude 51.965185º, longitude -3.285985º; Morris *et al*. 2011, 2012).

All hand-specimens were examined with a binocular microscope and stained with Alizarin Red S and Potassium Ferricyanide to enable clear distinction between calcite and dolomite. Those deemed suitable for analysis and representative of each calcrete type were thin-sectioned. Half of each thin-section was then stained with Alizarin Red S and Potassium Ferricyanide prior to examination with a petrographic microscope. Detailed information on stable isotope measurement methods is provided in the supplementary information.

Results

Petrography, selection and sampling of calcretes

A summary of petrographic observations is given here, with more detailed descriptions in the supplementary information.

Moor Cliffs Formation palaeosols

At Manobier, the Moor Cliffs Formation is a thick sequence of predominantly brownish-red silty mudstones interbedded with subordinate conglomerates, tuffs and sandstone bodies (Williams *et al*. 1982; Marriott & Wright 1993, 2004; Love & Williams 2000). Marriott & Wright (1993) recognised 20 mudstone intervals that indicated varying degrees of pedification. Over half of the sequences they observed are complex, truncated cumulate profiles, with only 5 truncated simple profiles recognised. All three horizons typical of palaeo-Vertisols were recognised (A-Bss-Ck). The C horizons are rich in calcrete (Fig. 3), ranging in morphology from: 5 to 10 mm diameter discrete nodules; larger calcrete ‘rods’ of 10 to 40 mm diameter and up to 150 mm long; and coalescent calcrete rods and nodules (Marriott & Wright 1993), representing stages I – III in calcrete development (*sensu* Machette 1985). Although most of the calcrete rods are orientated vertically, some are aligned along wedge-shaped ped slip planes, where overprinting of the B horizon has occurred, indicative of (syn-sedimentary) reactivation of the slip planes. A representative sample from each calcrete type or development stage was taken (Table S1). Thin-section microscopy of one of the smaller nodules (Fig. 3a, 3b) reveals micrite surrounding clear, sparry calcite cement that infills irregular-shaped voids. A simple explanation of sparry calcite cementation (perhaps during burial) of burrows within siliciclastic host rock would not account for the relationship between the micrite and the spar. More likely is a two-stage process, starting with micritic calcite precipitation around an organic substrate (plants or other organisms, perhaps after their burial in the soil). Secondly the organic matter oxidized, leaving behind convolute voids, of up to 0.5 mm width and several millimetres in length, within the earlier-formed micrite. All stages of calcite precipitation could have happened syn-depositionally, associated with CO_2 degassing from the soil zone to the atmosphere. Samples of micritic oval pellets, 0.5 cm in diameter, probably of faecal origin (Allen & Williams 1981; Marriott *et al*. 2009) and calcitised horizontal burrow fills (perhaps *Beaconites barretti*; see Marriott *et al*. 2009), of up to 3 cm length and 0.5 cm width, were also taken (Table S1).

Calcretes from the top of the Moor Cliffs Formation were sampled from exposures at Llansteffan (Fig. 1), specifically from the Chapel Point Limestone Member (formerly the *Psammosteus* Limestone / Bishop’s Frome Limestone; see Fig. 3c and Barclay *et al*. in press). This pedogenic calcrete unit comprises aggraded well-developed (up to stage V) calcrete (C) horizons, totalling up to 20m thick (Marriott & Wright 1993; Jenkins 1998), suggesting a prolonged period of slow sedimentation and tectonic and climatic quiescence lasting many thousands of years (Allen 1974; Allen 1985; Wright & Marriott 1996; Jenkins 1998). In thin-section (Fig. 3d) these nodules exhibit typical calcrete fabrics like crystalline mosaics and circum-granular cracks that can be interpreted as primary in origin (Wright & Tucker, 1991). The mosaics and fracture-filling spar are therefore not seen as evidence for carbonate mobilisation during burial.

Freshwater West Formation palaeosols

The Conigar Pit Sandstone and Rat Island Mudstone Members of the Freshwater West Formation (Fig. 2) have been extensively described by Hillier *et al*. (2007) and Marriott & Wright (1993), respectively. The Conigar Pit Sandstone Member is the lower part of the formation and is characterised by interbedded heterolithics, sheet and multi-storey sandstones and mudstones. The mudstones represent 30% of the Conigar Pit Sandstone Member at Freshwater West, and were deposited either in shallow, ephemeral pools on the floodplain or as within-channel muddy braid bars (Hillier *et al*. 2007). Pedogenic processes have affected many of these muds (Fig. 4); the majority of the profiles recognised are cumulative. Blue-grey drab haloes, abundant within the A horizons, have been interpreted as the traces of roots, fungal hyphae or burrows (e.g. Fig. 4a, 4b; see also Hillier *et al*. 2007; Marriott & Wright 1993). Slickensided wedge-shaped peds in the B horizons (Hillier *et al*. 2007) and pedogenic calcretes are indicative of palaeo-Vertisols, although the slickensided peds are weakly-developed compared to those of the Moor Cliffs Formation. The majority of C horizons have stage I calcrete nodules, with some up to stage II-III (Hillier *et al*. 2007).

The Rat Island Mudstone Member is the upper part of the formation, containing pedified mudstones described by Marriott & Wright (1993) as weakly-developed calcic palaeo-Vertisols. They are more prevalent than those in the Conigar Pit Sandstone Member; the sandstone: mudstone ratio within the former being 1:3. The calcretes are mostly developed to stages I & II, with rare occurrences of stage III. The majority of profiles are cumulate, with only a small proportion truncated, and no evidence of reactivation (Marriott & Wright 1993).

Four forms of calcrete were collected from the Freshwater West Formation at Manorbier and Freshwater West (Fig. 1; Table S1). The first three are: large (commonly 5 cm diameter) pedogenic nodules (Fig. 4a); smaller, centimetre-sized, elongated calcrete nodules, sometimes oriented between peds (Fig. 4c); and small (up to 5mm diameter) transported calcrete clasts (for example Fig. 4d) in lenses of well-sorted intraformational conglomerates, likely deposited during flash-flooding events. Conglomerate lenses are several metres in length and up to 10 cm thick. They are set in homogenous red mudstone matrices exhibiting blocky ped textures. The fourth form of calcrete is calcite-filled cracks (Fig. 4e) at Freshwater West, interpreted as pedogenic crystallaria.

Thin-sections of nodules from the Conigar Pit Sandstone Member (Fig. 5; Table S1) display clay-rich calcitic peloids amalgamated into nodules, surrounded by central calcite spar-filled irregular and circumgranular cracks, set in matrices of haematitic clays and sub-angular quartz grains (e.g. Fig. 5a). Dark micritic margins to the largest cracks surround clear calcite similar to the relationship observed within the Moor Cliffs Formation nodules (Fig. 3). Here we similarly infer precipitation of micrite on an organic substrate, followed by oxidation of the organic matter and filling of the resulting void by spar. Circumgranular crack-filling spar is cut by stylolites (Fig. 5b, 5c), consistent with spar formation prior to deep burial. Within one vein in a single nodule (ATB 210810-7; Fig. 5d) were a very few crystals that did not stain with Alizarin Red that are either dolomite or siderite.

A thin-section of a nodule collected from a conglomerate in the Freshwater West Formation at Llansteffan reveals a spherulitic texure (Fig. 5e). A c. 100 micron thick, c. 5mm long laminar calcite crust surrounding a spherulitic clast comprises three couplets of light and dark laminae (Fig. 5f). It is tempting to speculate that this combination of spherulites and tufa-like laminar crust imply initial subaerial precipitation of the nodule in association with cyanobacteria (perhaps initially in a stream?). However, an entirely abiotic, phreatic origin for these textures is also plausible (e.g. Verrecchia *et al*. 1995; Wright *et al*. 1995).

Micritic areas of samples were targeted for stable isotope analysis. Thin-section ATB 220810-05 was selected for its relatively wide void-filling spar section (shown in Fig. 5a), and drilled using a computer-controlled micromill. Samples were obtained of the circumgranular crack-filling spar and its micritic lining, plus a micritic peloid. The few crystals of vein-filling dolomite or siderite and spatially-associated void-filling spar (Fig. 5d) were micromilled from a second thin-section (ATB 210810-7), but unfortunately samples obtained were not of sufficient size for analysis.

Tredomen Quarry core palaeosols

The Freshwater West and Moor Cliffs Formations also outcrop across central South Wales (Figs. 1 and 2; Allen & Dineley 1986). Both formations, including the Chapel Point Limestone Member, are recognised in two cores drilled at Tredomen Quarry (Fig. 1; Morris *et al*. 2012). The Freshwater West Formation comprises interbedded multi-channel sandstones, intraformational conglomerates, inclined and planar laminated heterolithics, and pedified mudstones. The majority of the latter are interpreted as calcic palaeo-Vertisols with A-Bss-Ck horizonation, mostly within truncated single profiles, but some are cumulate (Morris *et al*. 2012). The calcrete ranges from small (2-5mm in diameter), sparsely distributed sub-spherical micritic nodules (stage I), to larger (over 5mm in diameter) sub-spherical and elongate nodules (stage II). Two stage II-III (coalesced) calcrete horizons are interpreted as the Chapel Point Limestone Member. Underlying this are rocks of the

Moor Cliffs Formation, being predominately vertic and non-vertic calcic palaeosols, interbedded with inclined and planar-laminated heterolithics and minor sandstones with intraformational conglomeratic bases (Morris *et al*. 2012). The palaeosol profiles are commonly cumulate, often with no clear horizonation, although some truncated single profiles were observed. Pedogenic calcrete development ranges between stages I and II.

Five micritic nodules were chosen (three from the Freshwater West Formation, one from the Chapel Point Limestone Member and one from the Moor Cliffs Formation; Table S1) for stable isotope analysis. The selected examples showed no obvious signs of recrystallisation, fracture-filling cement or gley mottling (Fig. 6). Profiles showing such features were deliberately avoided as the initial intention was to attempt direct calculation of Siluro-Devonian palaeoatmospheric pCO_2 from calcrete $\delta^{13}C$ (Cerling 1984; 1991; 1992; see below) and $\delta^{13}C$ of fossil plants from the same locality. Gley mottling can indicate that the soil was waterlogged; rendering it unsuitable for use in the palaeosol pCO_2 model, and recrystallisation can allow re-setting of the carbonate $\delta^{13}C$ and $\delta^{18}O$ compositions (Quast *et al*. 2006).

In thin-section the nodules are petrographically similar and typical of calcretes, exhibiting sharp to slightly diffuse boundaries, and surrounded by circumgranular cracks. Several of the nodules are composite, comprised of spar-cemented coalesced micritic peloids. Floating sand grains are rare but are encountered, commonly exhibiting corroded margins. The observed textures are compatible with a primary calcrete origin.

Ridgeway Conglomerate Formation palaeosols

The Ridgeway Conglomerate Formation at Freshwater West (Fig. 1) comprises alluvial fan conglomerates interfingering with sheet sandstones, inclined and planar-laminated heterolithics and mudstones, interpreted as a low gradient fluvial system (Hillier & Williams 2007). Pedified mudstones are interpreted as calcic palaeo-Vertisols (Fig. 7a). They possess characteristic A horizons that are desiccation-cracked and calcretised, with drab-haloed root traces. These root traces may have originated from vascular plants, but fungal rooting structures have also been reported from this formation (Hillier *et al*. 2008). Some of the calcretes in this formation are of likely groundwater origin (Fig. 7b; Hillier *et al*. 2011*a*). These can be identified where they form thin continuous layers with sharp bases and tops.

Pedogenic calcretes are developed up to Stage III of Machette (1985), and rarely calcrete nodules are as large as 20 cm diameter. Some nodules are cross-cut by discontinuous and irregular sub-horizontal calcite-filled cracks that are interpreted as pedogenic crystallaria (Fig. 7a). Such calcite-filled fractures typically form sheets sub-parallel to bedding (Hillier & Williams 2007). In thin-section, the more common smaller nodules comprise millimetre-sized dark micritic (pedogenic) peloids coated in c. 100 micron-thick layers of (phreatic?) calcitic microspar (Fig. 7c) that also infills millimetre-sized cavities (Fig. 7d). This microspar is consistent with a 'secondary' phreatic cement-precipitating phase that followed initial precipitation of dark micritic carbonate within the soil. However, the precipitation of the spar could have occurred within swampy, waterlogged soils at times of high water table, making it arguably 'syn-depositional'. The largest nodules from the top of the Ridgeway Conglomerate Formation at Freshwater West (ATB 220810-13; Table S1) are spherulitic, composed of curved columnar calcite crystals that grew out from a reduction spot in the nodule centre (Fig. 7e). The curving of the crystals can be ascribed to spherulitic crystal growth.

Results of stable isotope geochemistry

Bulk micritic samples of the nodules were micro-drilled for stable isotope analyses. Carbon and oxygen isotope data from this study (all VPDB) are tabulated in full in the supplementary information and presented here in a cross-plot (Fig. 8), and on a plot of collated Palaeozoic calcrete carbon isotope data (Fig. 9). A summary of the results is given in Table 1. Overall, calcrete carbon isotope values range from ca. -12‰ (Conigar Pit Sandstone Member at Manorbier) to -6.9‰ (from near the top of the Ridgeway Conglomerate Formation at Freshwater West). Oxygen isotopes were mostly lower than -9‰, ranging from ca. -14‰ (from near the top of the Ridgeway Conglomerate Formation at Freshwater West) to -5.8‰ (from crystallaria in the Conigar Pit Sandstone Member at Freshwater West). A micro-milled thin-section of Conigar Pit Sandstone Member calcrete (Fig. 5a) yielded uniform $\delta^{13}C$ values for central void-filling spar (-10.0‰), microsparry crystallaria around the void-filling spar (-10.1‰), and micritic nodule calcite (-10.1‰). The $\delta^{18}O$ values of these samples showed some variation, with the latest-stage void-filling spar yielding a value of -8.1‰, the surrounding microsparry crystallaria -13.6‰, and the micritic nodule -13.8‰.

Two samples of coalified remains from rhyniophytoids from Tredomen Quarry (Morris *et al*. 2011) gave $\delta^{13}C$ of -24.2‰ and -25.0‰. Two samples of charcoalified *Prototaxites* gave $\delta^{13}C$ of -24.6‰ and -25.5‰. One sample of coalified *Prototaxites* gave $\delta^{13}C$ of -26.9‰ VPDB. These are all consistent with a primary origin from photosynthesising organisms using the C_3 photosystem pathway. It is possible that the isotopic values from *Prototaxites* reflect its heterotrophic consumption of C_3 photosynthesising organisms, rather than indicating *Prototaxites* was an autotrophic organism itself (e.g. Boyce *et al*. 2007).

Discussion

Diagenesis and geochemical alteration of the oxygen isotopes

Thin-sections of the pedogenic nodules reveal micritic peloids with circumgranular cracks that are interpreted as original soil textures (e.g. Fig. 5a; Table S1). Several of the features observed are consistent with precipitation of the micritic and microsparitic fabrics in waterlogged soils, including gleying and the circum-granular cracks themselves. Coarse, clear calcite spar and very minor vein-filling dolomite or siderite (the latter seen only in one late-stage spar-filling fracture) could conceivably reflect cementation of void spaces during burial. This 'late stage' calcite spar is found in burrows that were clearly syn-sedimentary voids (perhaps after organic matter oxidation) and circum-granular cracks that could have progressively opened as the water-logged soils dried out. Oxygen isotope values of c. -9 to -14‰ values seem incompatible with precipitation from meteoric waters in the interpreted sub-equatorial setting of these rocks in the Late Silurian and Early Devonian (Channell *et al*. 1992). They would, however, be consistent with re-setting of carbonate $\delta^{18}O$ by high temperature fluids during burial. One might speculate that the late-stage spar of the Conigar Pit Sandstone Member exhibits less negative $\delta^{18}O$ and $\delta^{13}C$ values than the relatively older micritic nodules and void-lining microsparitic crystallaria (Fig 5a and Fig. 8) because the spar was less susceptible to oxygen isotopic alteration than the micrite. Based on examination of Oligocene terrestrial carbonates of the Himalayas, however, Bera et al. (2010) considered that oxygen isotope compositions were best preserved in samples with over 70% micrite. They suggested that this was because the lowest water:rock ratios would normally be found in the most micritic samples. In the Conigar Pit Sandstone Member it seems possible the micrite was more permeable to oxygen isotope altering fluids than the spar.

Post-depositional alteration of carbon isotopes?

Carbonate carbon isotopes are less likely to be re-set than carbonate oxygen isotopes during burial because of a strong buffering effect from pre-existing carbonate carbon (e.g. Banner & Hanson 1990). The lack of $\delta^{13}C$ variation encountered between the three micromilled Conigar Pit Sandstone Member fabrics (early micrite, early microspar, and late spar) can be interpreted as early-formed calcrete carbon dominating the $\delta^{13}C$ signal of late-stage fluids, or alternatively complete late-stage overprinting of an earlier (higher) $\delta^{13}C$ signal.

Rocks of the Anglo-Welsh Basin have experienced low grade metamorphism at temperatures of c.175 to 350°C (up to lower greenschist facies; Bevins and Robinson, 1988). One consequence of low-temperature metamorphism of carbonates in the presence of silicates can be production and loss of CO_2 ('decarbonation') such that carbon and oxygen stable isotopes may be affected. The carbon dioxide produced by such reactions is usually enriched in ^{13}C and ^{18}O in comparison to the calcite (Shieh and Taylor, 1969), meaning the calcite is likely to become relatively depleted in ^{13}C and ^{18}O. In addition, metasomatic fluids passing through the carbonate rock provide an opportunity for isotopic exchange to occur, particularly for oxygen. Rocks with a significant silicate component are liable to have experienced shifts in their oxygen and carbon stable isotopic compositions as a result of metamorphism, and these calcretes clearly fall in that category. However, large shifts in $\delta^{13}C$ and $\delta^{18}O$ (ca. 5 to 10 *per mil* decreases) by decarbonation only occur if substantial proportions of the carbon and oxygen are converted to CO_2 and lost from the rock (Valley, 1986). Large effects are usually found in cases of contact metamorphism that also include a component of equilibration of isotopically light igneous CO_2 with sedimentary carbonate CO_2 (see Valley, 1986). In the Old Red Sandstone strata examined, the lack of minerals that are common products of decarbonation reactions (e.g. wollastonite and tremolite) and lack of evidence for substantial recrystallisation of the calcretes, argues against significant metamorphic effects on their carbon and oxygen isotope values.

A negative shift in calcrete $\delta^{13}C$ could result from post-depositional isotopic exchange with a significant external source of organic carbon. However there is no clear evidence of carbon migration (such as veining) from underlying Ordovician organic-rich shales into the Old Red Sandstone sections investigated. The carbon isotopic compositions of marine carbonates of the Coralliferous Formation (which lies stratigraphically between the Ordovician shales and the lower Old Red Sandstone units described here) were measured to determine whether they have been affected by migration of organic carbon from Ordovician shales. These limestones gave bulk compositions in the region of ca. -2‰ VPDB (our unpublished data), suggesting there has not been a significant upward migration of low $\delta^{13}C$ carbon into the Coralliferous Formation (and, by inference, the overlying Old Red Sandstone units). It is concluded that the most likely source of isotopically light carbon that could have affected the carbon isotopic compositions of these nodules during deep burial is organic matter from within the ancient soils themselves.

The strongest evidence against significant post-depositional re-setting of these calcrete carbon isotopic signals comes from their unaltered petrographic appearances, which are hard to reconcile with geochemical processes that would demand substantial recrystallization sufficient to affect the carbon signals. Field and petrographic evidence (including, for example, nodules reworked in conglomerates) suggests most of the calcite precipitation occurred prior to burial, and the geochemical data do not require input of carbon from any source other than organic matter originally present in the (likely seasonally waterlogged) soils.

Explanations for low calcrete $\delta^{13}C$ values

Assuming that the carbon isotopic compositions of these calcretes are mostly unaltered then consideration must be given to why these values are more negative than those of North American calcretes of similar age (see Fig. 9). One explanation might be that calcrete precipitation took place under different conditions. Mora *et al*. (1991) and Driese *et al*. (1992) suggested that the precipitation of the North American Bloomsburg Formation calcretes took place at shallow soil depths (a few centimetres), given small Silurian plant rooting systems (e.g. Algeo *et al*. 1995). In the Bloomsburg Formation palaeosols, this would have favoured a strong, relatively ^{13}C rich atmospheric CO_2 contribution to the calcrete $\delta^{13}C$ (e.g. Mora *et al*. 1996), resulting in isotopic values of > -7‰ (Driese *et al*. 1992). Perhaps the contribution of atmospheric CO_2 to the Old Red Sandstone calcretes was relatively lower than found in the North American examples. This could be the case if the Old Red Sandstone soils originally contained greater volumes of respiring organisms and oxidizing organic matter. Determining the relative contributions of organic matter from these two settings is challenging because the majority of the plant material has not been preserved. No plant fossils were described in association with the Bloomsburg paleosols (Driese et al., 1992). However, in general the plant fossil record from the Bloomsburg Formation is meager, the most significant report from Ludlovian strata being non-vascular thalloid fragments that are part of the *Nematothallus* complex (Strother, 1988). In comparison the plant assemblages from the latest Silurian to earliest Devonian Anglo-Welsh Basin are more abundant and diverse, with evidence of vascular plants (Edwards and Richardson, 2004). It is notable that Lower Cretaceous calcretes of the Wealden Beds, UK, that were also deposited in partially waterlogged to marshy soils, have very comparable $\delta^{13}C$ values (-9 to -12.5‰; Robinson et al., 2002). There, Robinson et al. (2012) suggested the ingress of atmospheric CO_2 to the soils was low to negligible. In these scenarios of soils inhabited by abundant plants the Old Red Sandstone calcrete carbon isotope signals would be dominated by isotopically light carbon from the organic matter.

Further possibilities might include the effects of soil zone microbiota. First, in anoxic environments anaerobic methanogenesis can provide a source of dissolved carbon that has extremely low $\delta^{13}C$ values (commonly ca. -75‰; Irwin et al., 1977; Whiticar, 1999):

$$2CH_2O \rightarrow CH_4 + CO_2. \qquad (2)$$

Due to production of CO_2, an accompanying lowering of soil water pH is expected, unless methanogenesis is coupled to significant Fe(III) reduction (Andrews et al., 1991):

$$13CH_2O + 2Fe_2O_3 + 3H_2O \rightarrow 6CH_4 + 7HCO_3^- + 4Fe^{2+} + OH^- \qquad (3)$$

However such methanogenesis usually occurs in environments lacking acetate (Whiticar, 1999). These places are mostly proximate to areas that are sulphate-rich, where sulphate reducing bacteria can out compete methanogens for the acetate (Whiticar, 1999). Sulphate minerals (or their pseudomorphs) and sulphides are distinctly lacking in the examined sections, so the above mechanisms can probably be discounted.

Where acetate (CH_3COO^-) is present (i.e. where bacterial sulphate reduction is not prevalent), methanogenesis can occur through acetate fermentation:

$$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2 \qquad (4)$$

Subsequent oxidation of the methane by iron reduction could supply very low $\delta^{13}C$ dissolved carbon (Andrews et al., 1991):

$$CH_4 + 2Fe_2O_3 \rightarrow HCO_3^- + 4Fe^{2+} + 3OH^- \qquad (5)$$

There is clear evidence of iron reduction in the studied sections such as gley mottling, and even reduction spots in some nodule centres. Such features could also have been produced by anaerobic microbial oxidation of organic matter, using Fe^{3+} as the oxidant (Andrews et al., 1991):

$$3H_2O + 2Fe_2O_3 + CH_2O \rightarrow HCO_3^- + 4Fe^{2+} + 7OH^- \qquad (6)$$

The $\delta^{13}C$ of the bicarbonate produced via organic matter oxidation would reflect the $\delta^{13}C$ of the organic matter (measured here as -25‰). Direct oxidation of the organic matter (i.e., aerobic respiration by soil zone organisms including plant roots, fungi and invertebrates), or of biogenic methane, could obviously also occur in oxic conditions (e.g. Irwin et al., 1977):

$CH_2O + O_2 \rightarrow CO_2 + H_2O$ (7)

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (8)

Here some carbonic acid is produced that could be used in the chemical weathering of pre-existing carbonate rock, or more likely in this case of calcium silicate grains from interbedded volcanic ash horizons (e.g. Berner, 1992; reaction 9):

$2CO_2 + 3H_2O + CaAl_2Si_2O_8 \rightarrow Ca^{2+} + 2HCO_3^{-} + Al_2Si_2O_5(OH)_4$ (9)

Through supply of calcium ions, reaction 9 could help to drive calcite precipitation (via reaction 1). A likely product of this chemical weathering is kaolinite, which has been found in Lower Old Red Sandstone rocks of Wales (Hillier et al., 2006). Some of this kaolinite has been interpreted as potentially having survived diagenesis (Hillier et al., 2006), while illite, the likely product of kaolinite diagenesis, is common in the clays of Freshwater West (Hillier et al., 2006).

A key feature of all of the above processes is that they require the presence of organic matter, or at least of organic carbon compounds derived from breakdown of such material, within the ancient soils. Reactions 4, 5 and 6 all take place in anoxic conditions (including waterlogged soils) and have the advantage of directly explaining features associated with iron reduction. Yet the calcretes examined are non-ferroan to only slightly ferroan, staining dominantly pink to rarely purple with Alizarin Red S and potassium ferricyanide. This suggests they dominantly formed under oxic conditions, with low $\delta^{13}C$ carbon liberated via oxidation of organic matter following reactions 7 and 8. Calcrete formation under oxic conditions is clearly also compatible with the red colouration of these clay-rich Old Red Sandstone rocks.

The strong and consistent signal from C_3 photosynthesis seen in the $\delta^{13}C$ of the calcretes measured, together with the $\delta^{13}C$ of organic matter, the lack of sulphides or sulphates, and the great abundance of carbonate nodules, is taken as evidence for significant organic matter oxidation in (and later de-gassing of CO_2 from) these ancient soils. The palaeoclimate must have been strongly seasonal. During the wet season, plant-associated respiration in the soils was high. When soils were waterlogged anaerobic microbial oxidation of organic matter (plus some methanogenesis) may have occurred. These processes will have generated carbonic acid, which in turn liberates calcium ions. Most calcrete precipitation likely took place during the dry season, as evapotranspiration increased concentrations of calcium ions in increasingly oxic soil waters, and CO_2 de-gassed to the atmosphere. Because carbonic acid-rich soils enhance chemical weathering of silicate bedrock, implicated in drawdown of atmospheric CO_2 levels (e.g. Berner 1998), this finding is of relevance to modelling Silurian to Devonian atmospheric pCO_2 (e.g. Lenton *et al*. 2012).

Calculation of palaeoatmospheric CO_2

In the right circumstances palaeoatmospheric CO_2 concentrations can be directly estimated from pedogenic calcrete $\delta^{13}C$ (e.g. Cerling 1984, 1991, 1992; Driese *et al*. 1992; Andrews *et al*. 1995; Ekart *et al*. 1999; Royer *et al*. 2001; Breecker *et al*. 2010; Bera *et al*. 2010). This is because a high (palaeo-)atmospheric CO_2 contribution to soil zone gases can result in ^{13}C-rich calcretes, while high contributions from respired CO_2 (including oxidation of isotopically light vegetation) drive $\delta^{13}C$ of pedogenic calcrete to lower values. The equation for estimating palaeoatmospheric pCO_2 from calcrete $\delta^{13}C$ (after Cerling 1984; 1991; Ekart *et al*. 1999) is:

$$C_{air} = S(z) * (\delta^{13}C_s - 1.0044\ \delta^{13}C_\phi - 4.4 / \delta^{13}C_{air} - \delta^{13}C_s) \quad (3)$$

where C_{air} is the calculated CO_2 concentration of the palaeoatmosphere; S(z) is the CO_2 contribution from soil respiration as a function of depth (z); $\delta^{13}C_s$ is the $\delta^{13}C$ of soil CO_2 (calculated from calcrete $\delta^{13}C$ using the temperature dependent fractionation factor of Romanek *et al*. 1992); $\delta^{13}C\phi$ is the $\delta^{13}C$ of soil respired CO_2 (measured from contemporaneous organic carbon); and $\delta^{13}C_{air}$ is the $\delta^{13}C$ of palaeoatmospheric CO_2 (here calculated from $\delta^{13}C_{org}$ of -25‰, assuming consistent fractionation by photosynthesis, to be -5.75‰, using Schaller et al., 2011). On the basis of calcrete $\delta^{13}C$ values around -5‰ from the Silurian Bloomsburg Formation of North America, Mora *et al*. (1991) and Driese *et al*. (1992) concluded that Silurian to Early Devonian atmospheric pCO_2 was very high: above 3000 ppmV.

In the case of the Siluro-Devonian soil carbonates described here, it is not clear that they are a suitable source for deducing palaeoatmospheric pCO_2. Firstly, it is recommended that calcrete samples are taken from at least 50cm depth below the palaeosurface (Royer et al., 2001). This is because in modern soils of the south western USA, soil carbonate $\delta^{13}C$ has been shown to be variable above this depth due to mixing of soil respired CO_2

and atmospheric CO_2 (Cerling, 1984; Ekart et al., 1999). In common with most palaeosols, it is not easy to tell whether many of the nodules described here originally formed at 50cm depth or less. This is in part because of syn-depositional movement via the self-mulching process (argillopedoturbation), as well as truncation of the A horizons (Marriott & Wright 2006). Secondly, there is considerable uncertainty over the correct value to use for S(z). An exceptionally high value of 20 000 ppmV (Royer *et al*. 2001) might be appropriate if the soils were waterlogged when most of the carbonate precipitated. In their study of Lower Cretaceous calcretes formed in seasonally waterlogged soils, Robinson et al. (2002) chose to apply an S(z) value of 10 000 ppmV. However this S(z) value was too low to allow palaeoatmospheric pCO_2 calculation from calcretes inferred to have formed in the wettest, marshy palaeoenvironments. Third, using a value for $\delta^{13}C\phi$ obtained from measurement of contemporaneous organic carbon (-25‰) ignores the possibility here of a methanogenic contribution to soil respired CO_2. Using a lower value for $\delta^{13}C\phi$, allowing for some methanogenesis □□□□□□□□□□□□□□would raise the calculated palaeoatmospheric pCO_2.

If unaltered, our carbon isotope data would only be broadly compatible with the high Late Silurian atmospheric pCO_2 that Mora *et al*. (1991) and Driese *et al*. (1992) suggest if a very high value for S(z) applies, or if $\delta^{13}C\phi$ was lower than -25‰. For example, using our measured organic carbon $\delta^{13}C$ value of -25‰ with a micritic calcrete $\delta^{13}C$ value of -10.1‰ (Conigar Pit Sandstone Member micromilled sample) at 25 °C with an S(z) value of 20 000 ppmV yields a calculated palaeoatmospheric pCO_2 of c. 2500 ppmV. However, Breecker et al., 2010, noted that most modern calcrete precipitation in semi-arid environments occurs during dry seasons, when values of S(z) are significantly lower (c. 2500 ppmV). Using an S(z) value of 2500 ppmV, with all other parameters as above, yields a calculated palaeoatmospheric pCO_2 of just 300 ppmV. Further constraints on the correct value to use for S(z) here, and on $\delta^{13}C\phi$, are therefore required before reliable estimates of palaeoatmospheric pCO_2 can be made from these palaeosol carbonates.

Conclusions

The Moor Cliffs Formation, Freshwater West Formation and Ridgeway Conglomerate Formation all have calcrete $\delta^{13}C$ values within the range of -7 to -12‰, with an average of -10.1‰ (VPDB). The most likely source of isotopically light carbon that could have exchanged with the carbonate carbon during burial is intraformational organic matter. The carbon isotopes suggest these widespread and abundant pedogenic calcrete nodules formed principally by de-gassing of CO_2 from seasonally water-logged, organic-carbon rich soils, to the atmosphere. If these assumptions are correct then calculations of Late Silurian atmospheric pCO_2

from our calcrete carbon isotope data could only yield results broadly consistent with those obtained from North American soils of similar age (Mora *et al*. 1991; Driese *et al*. 1992) if an exceptionally high value of 20 000 ppmV is used for S(z) in these calculations, or if our estimated value of -25‰ for $\delta^{13}C\phi$ is too low. Relative lack of constraint on these parameters highlights a need for further research on ancient microbial processes in fossil soils.

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Figure Captions

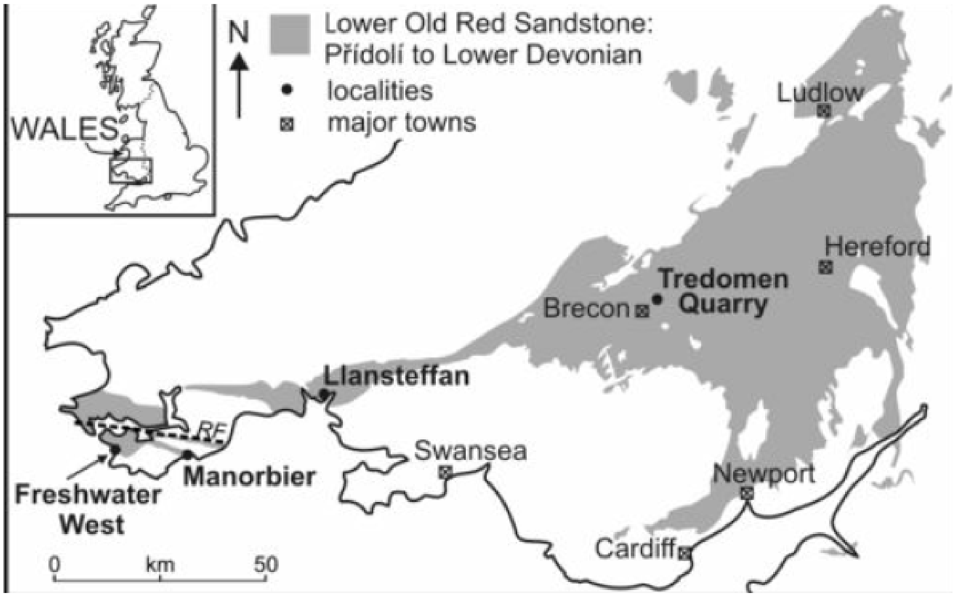

Fig. 1. Map showing the extent of the Lower Old Red Sandstone in South Wales and locations studied (Freshwater West; Manorbier; Llansteffan; and Tredomen Quarry) RF = Ritec Fault. Inset map shows the location of South Wales in the UK. Scale bar is 50 km.

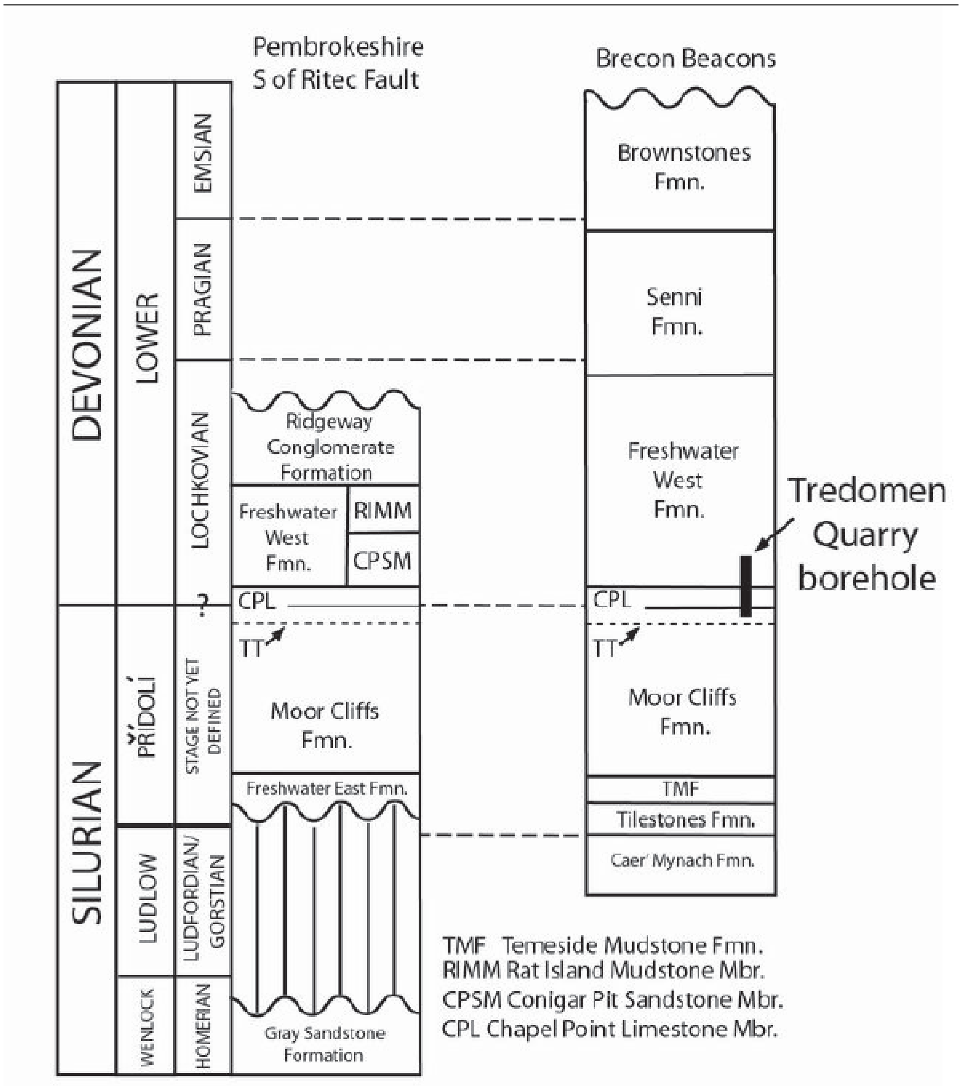

Fig. 2. Stratigraphic columns illustrating the studied formations of Lower Old Red Sandstone in Pembrokeshire and Brecon Beacons; the Moor Cliffs Formation including the Chapel Point Limestone Member (CPL) that outcrops above the Townsend Tuff (TT); the Conigar Pit Sandstone (CPSM) and Rat Island Mudstone (RIMM) Members of the Freshwater West Formation; and the Ridgeway Conglomerate Formation. The stratigraphic position of the core taken at Tredomen Quarry is also marked.

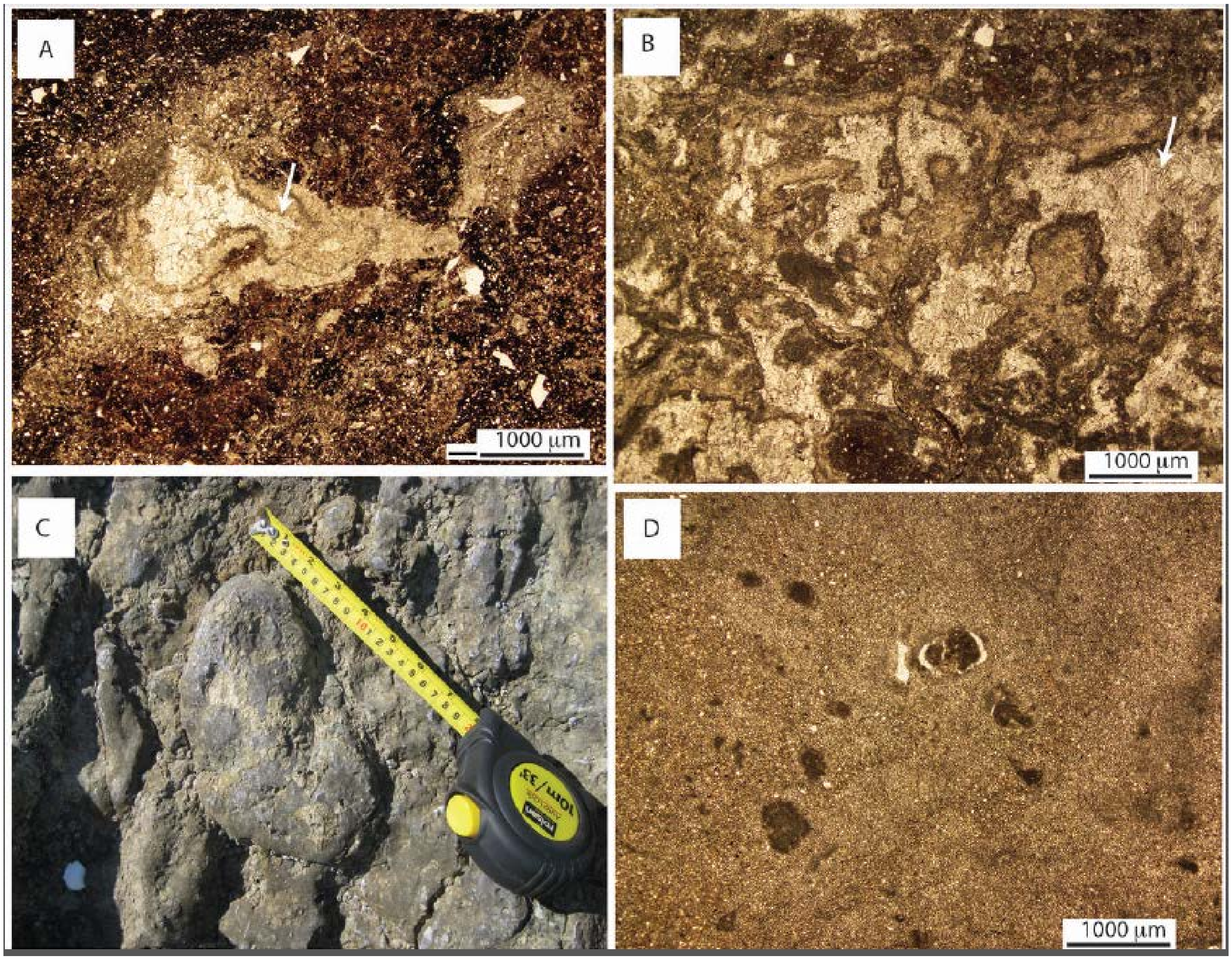

Fig. 3. Calcretes of the Moor Cliffs Formation. A) and B): Plane polarised light images of thin-section of ATB MC 5 (an elongate, 15mm long and 3mm wide nodule from Manorbier), showing irregularly-shaped patches of micrite that likely precipitated on an organic (perhaps plant root) substrate that was later (syn-depositionally) oxidised, leaving a void that was infilled by clear calcite spar (arrowed). Note that the vertical lines seen in the spar near the arrow are twin planes in the calcite spar, and not evaporite pseudomorphs. C): A large, elongate (20 cm long, 10 cm wide), rounded nodule in the Chapel Point Limestone Member at Llansteffan. D): A plane polarised light image of thin-section ATB 190810-01 (a 10 cm diameter nodule from the Chapel Point Limestone Member at Llansteffan), showing the crystalline microspar mosaic and mm-sized grains coated with clotted micritic fabrics. Scale bars in A, B and D are all 1000 µm. Scale of the tape measure in C is in cm (below) and inches (top).

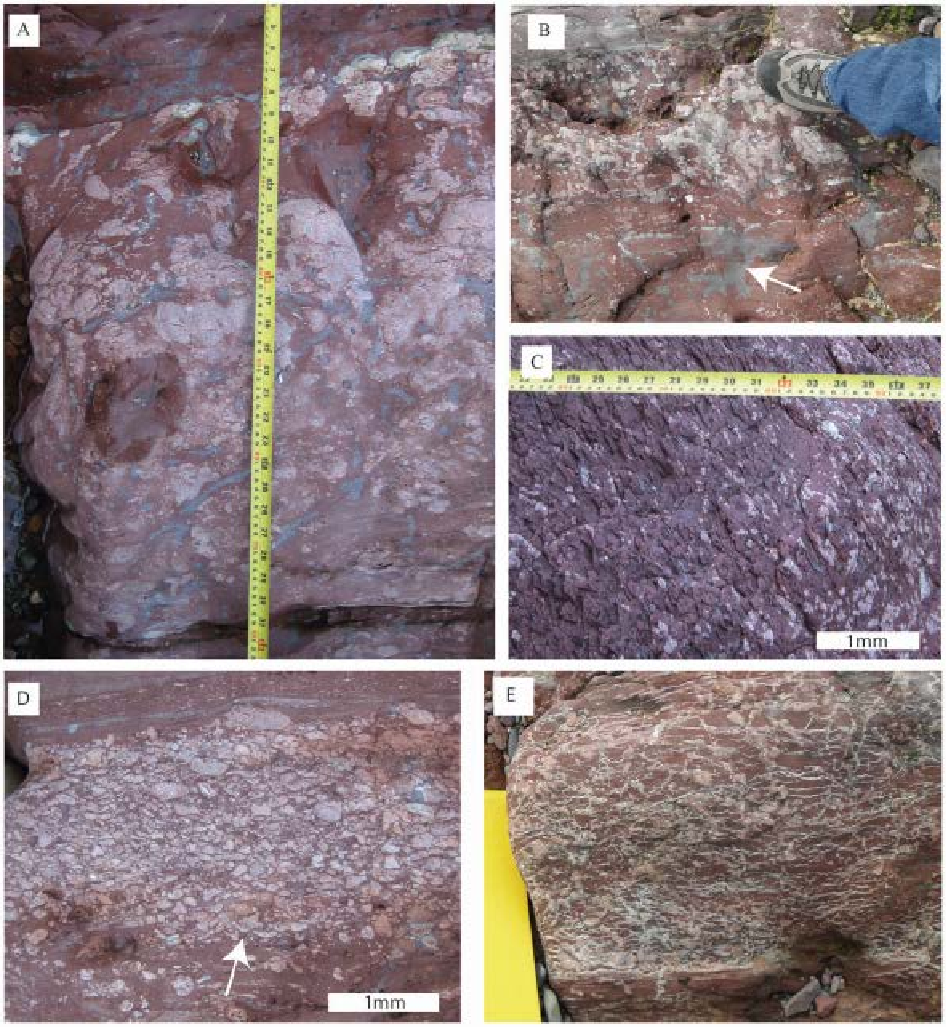

Fig. 4. Outcrop images of the Freshwater West Formation. A) Large pedogenic nodules in a palaeo-Vertisol of the Conigar Pit Sandstone Member at Manorbier (top of palaeosol is towards top of image). Scale on tape measure is in inches (right side) and centimetres (left side). B) Palaeo-Vertisol with pedogenic calcrete nodules and downward branching 'drab haloes' (arrowed) at Freshwater West. Note the palaeo-Vertisol has a gradational base and truncated top. The boot is approximately 12 cm wide. C) Smaller nodules oriented parallel to pedogenic slickensides in a Conigar Pit Sandstone Member palaeo-Vertisol at Manorbier (top of palaeosol is to the right). D) Transported calcrete nodule clasts in a Conigar Pit Sandstone Member conglomerate at Manorbier (arrow points to the base of the bed). E) Calcite-filled fractures interpreted as pedogenic crystallaria in a palaeo-Vertisol at Freshwater West. The field of view is approximately 20cm from top to bottom.

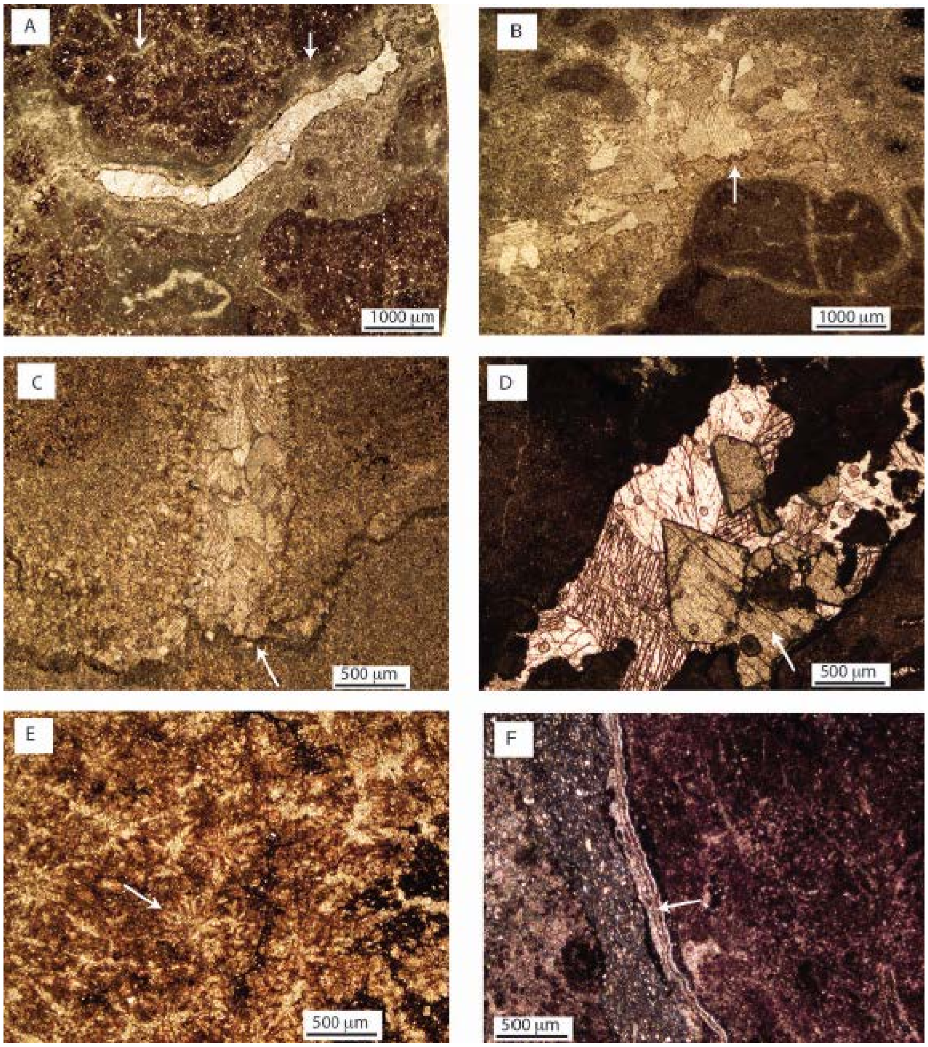

Fig. 5. Freshwater West Formation calcretes in thin-section. A) Thin-section of ATB 220810-05, a calcrete nodule from the Conigar Pit Sandstone Member at Freshwater West. Clay-rich calcitic peloids amalgamated into nodules, surrounded by central calcite spar-filled irregular and circumgranular cracks (left arrow), set in matrices of haematitic clays and sub-angular quartz grains. The margins of the largest cracks are commonly lined with a layer of dark micrite (right arrow). B) Thin-section of ATB 210810-11 (calcrete conglomerate clast cut by crystallaria, from Conigar Pit Sandstone Member at Manorbier) showing stylolites (arrowed) cutting across the circumgranular crack-filling spar. C) Thin-section of nodule ATB 220810-09 (Rat Island Mudstone Member at Freshwater West) showing a uniform crystalline appearance. The matrix is cut by stylolites (arrowed) and millimeter-scale 'veinlets' of sparry calcite. D) Thin-section of nodule ATB210810-7 showing dolomite or siderite rhombs (arrowed) in a fissure. E) Thin-section of nodule ATB 190810-7 from a conglomerate in the Freshwater West Formation at Llansteffan, revealing spherulitic calcitic microspar. A spherulite is arrowed. F) Laminar calcite crust of c. 100 microns thickness and c. 5mm length (arrowed)

around the outside of the spherulitic clast shown in D. Scale bars in A and B are 1000 µm. Scale bars in C to F are 500 µm.

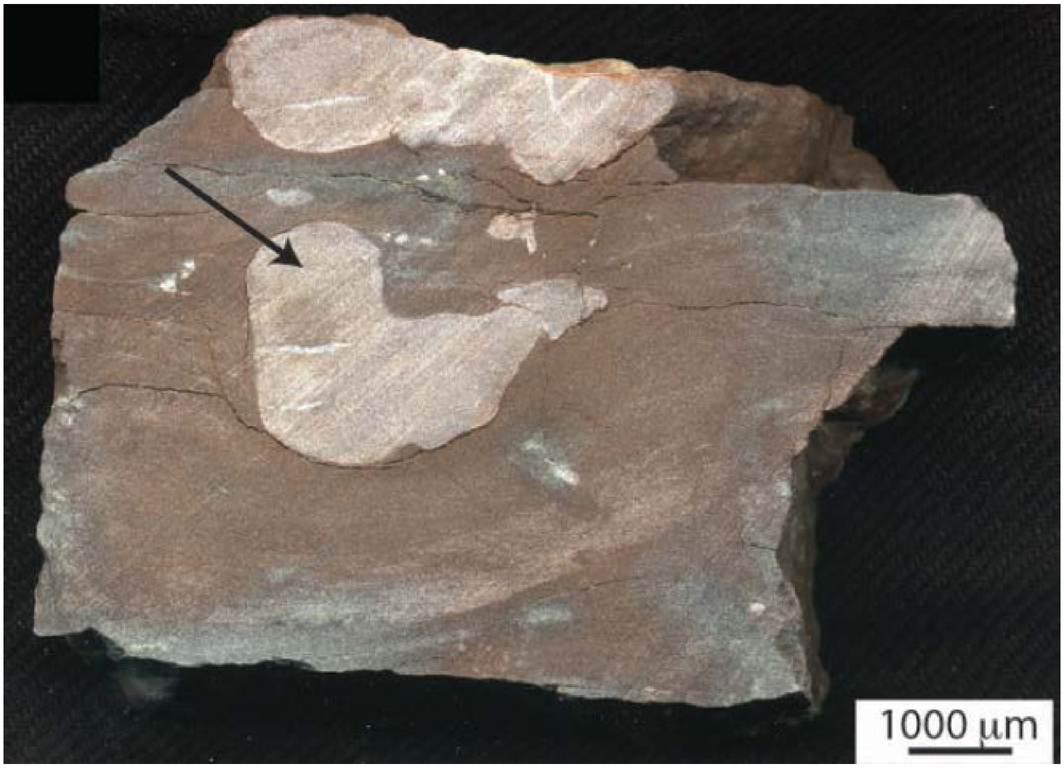

Fig. 6. Calcrete nodule from Tredomen Quarry Core SO13SW/3 (BGS). A cut hand-specimen of nodule 1 is shown (arrowed; scale bar is 1000 µm).

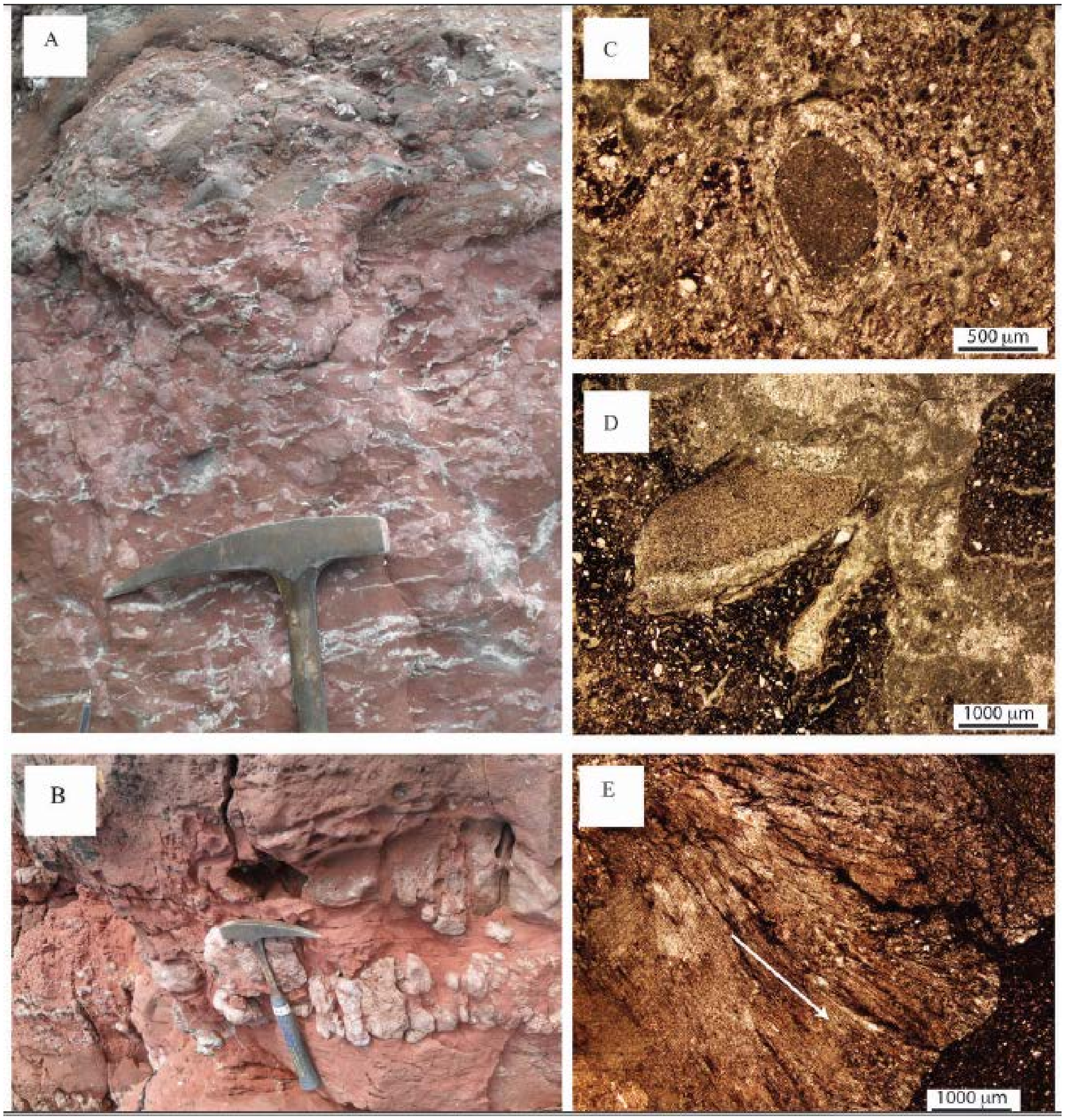

Fig. 7. Calcretes of the Ridgeway Conglomerate Formation at Freshwater West. A) Calcrete nodules and crystallaria in a palaeo-Vertisol that is interbedded with alluvial fan conglomerates. B) Large, 10cm long and layer-bound (groundwater calcrete?) nodules near the top of the Ridgeway Conglomerate Formation at Freshwater West. C) A thin-section of nodule ATB 220810-11 revealing millimetre-sized dark micritic peloids coated in c. 100 micron-thick layers of calcitic microspar. D) Patches of clear spar that infilled millimeter-sized irregular cavities (burrows?) or cracks in thin-section ATB 220810-11. E) Image of thin-section ATB 220810-13, from a very large c. 20 cm diameter nodule, part composed of curved columnar calcite crystals These grew out from a reduction spot in the centre of the nodule (not visible in this image) into the surrounding clay-rich matrix (arrow shows the direction of crystal growth). Hammer head for scale in A and B is 17 cm wide; Scale bar in C is 500 µm, and 1000 µm in D and E.

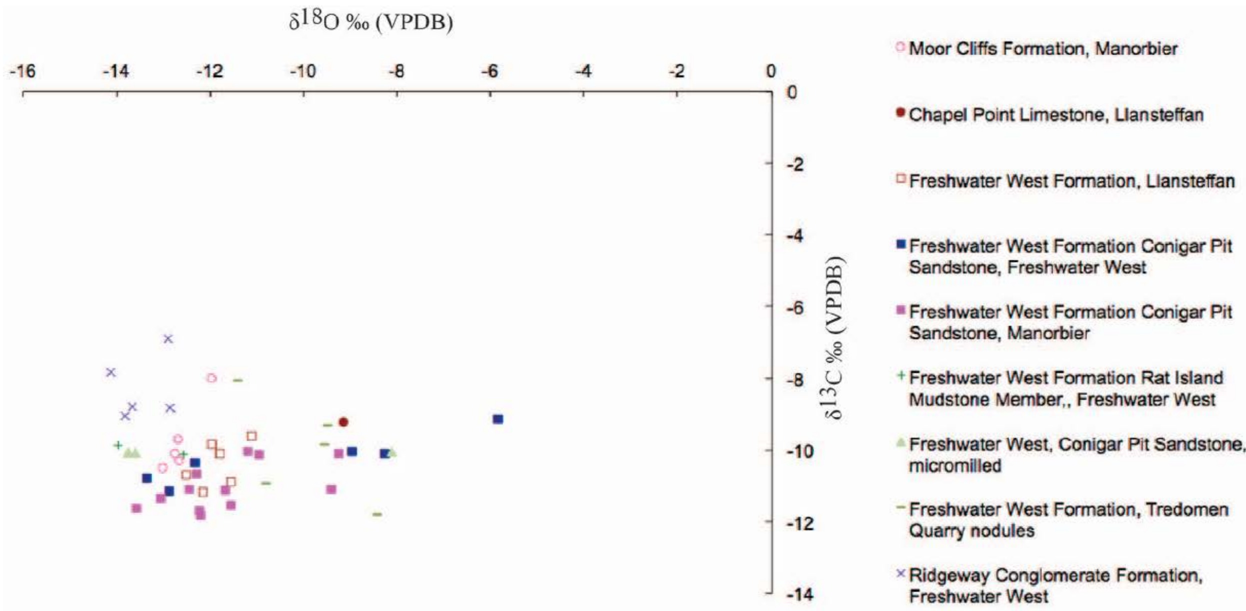

Fig. 8. Cross-plot of carbon and oxygen isotopes for all calcrete samples measured. Overall calcrete $\delta^{13}C$ values range from ca. -12‰ to -6.9‰, and $\delta^{18}O$ ranges from ca. -14‰ to -5.8‰.

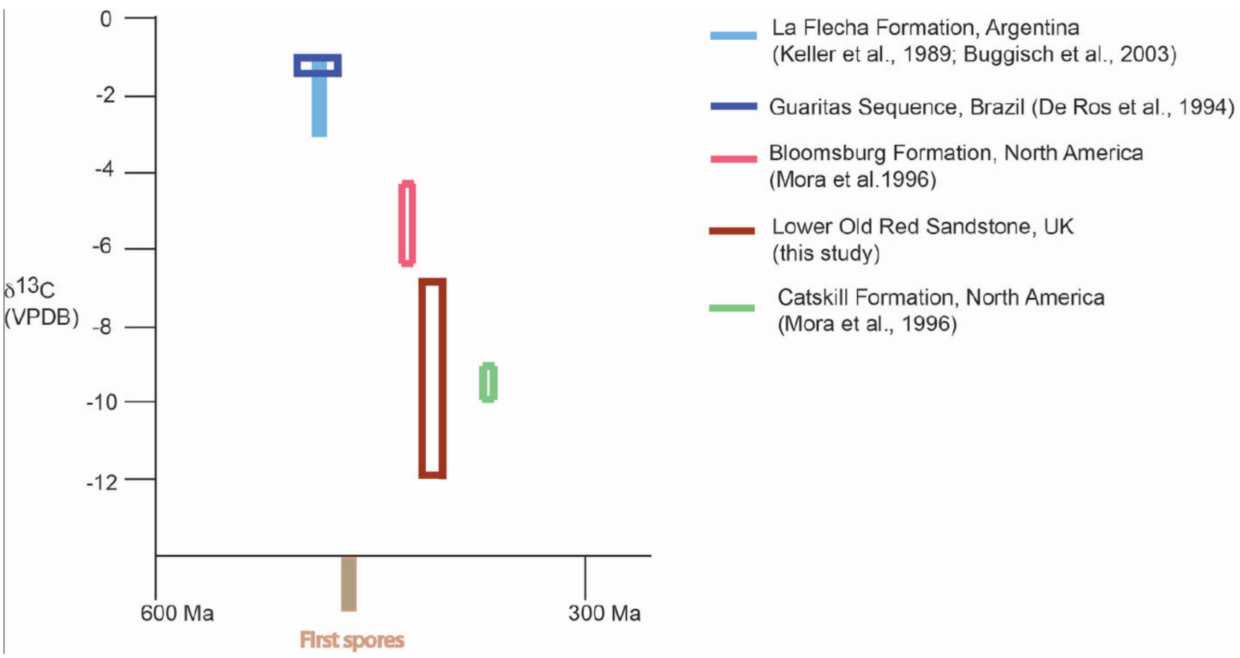

Fig. 9. Carbon isotopic compositions of selected Cambrian to Carboniferous calcretes. Very few data have been published on late Cambrian to Silurian calcrete carbon isotopes (shown here). A representative selection of data from Devonian and Carboniferous calcretes is given in this figure. This plot shows a transition from calcretes with carbon isotopic compositions close to 0 per mil in the Late Cambrian, to calcretes with low $\delta^{13}C$ (VPDB) compositions by the Late Silurian. This likely reflects different and evolving causes of

carbonate precipitation in terrestrial environments (e.g. ‘common-ion effect’ versus organic matter oxidation and CO_2 degassing).