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Palaeogeographical and eodiagenetic settings of host-replacing phreatic calcrete intervals developed in mud deposits of the Famennian Kinnesswood Formation in the Pennyseorach Subbasin of south-west Scotland

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ABSTRACT

In the Pennyseorach Subbasin of south-west Scotland, the Famennian Kinnesswood Formation of the Inverclyde Group includes several, *ca* 1 to 3 m thick erosional remnants of host-replacing phreatic calcrete hardpans developed in mud deposits. The latter are most unusual hosts for such calcretes due to their relative impermeability, which would normally prevent them from sufficiently accommodating the circulation of an aquifer. In previously documented phreatic calcretes, mud deposits clearly acted as aquicludes that sharply constrained calcrete development. In the Kinnesswood Formation at Pennyseorach, tall desiccation fissures allowed groundwater to circulate in thick, semi-consolidated mud deposits. Because of the inferred development of an adjacent evaporitic basin, the mixing of fresh and evaporitic groundwaters raised the pH enough for the replacement of phyllosilicates by calcite to occur along the fissure walls, forming 'fissure calcretes'. The latter gradually expanded and eventually coalesced into mature, 'columnar host-replacing phreatic calcrete hardpans' in which 90 to 100% of the muddy host material was replaced by calcrete. At Pennyseorach, host-replacing phreatic calcrete hardpan formation not only affected the transition zone between the Doughend Sandstone and Foul Port Members of the Kinnesswood Formation (the Dunagoil Calcrete interval), as in other localities of south-west Scotland, but also affected the uppermost part of the formation, which is marked by several erosion surfaces downcutting into columnar host-replacing phreatic calcrete hardpan intervals in association with the episodic rise and fall of base-level. These newly recorded host-replacing phreatic calcrete hardpan intervals from the upper part of the Kinnesswood Formation have a tightly constrained stable isotopic signature that is distinct from that of both the Dunagoil Calcrete and the successive host-replacing phreatic calcrete hardpans of the Visean Clyde Sandstone Formation within the same group, underlining their potential as stratigraphic markers and palaeoenvironmental indicators.

Keywords Columnar host-replacing phreatic calcrete hardpans, Famennian, fissure calcretes, Kinnesswood Formation, south-west Scotland, stable isotopes.

INTRODUCTION

The Famennian to mid-Visean Inverclyde Group of south-west Scotland includes several intervals in which the host sediment was thoroughly replaced by phreatic calcrete along the entire thickness of the palaeo-aquifer (Jutras *et al.*, 2011; Young & Caldwell, 2011a; Jutras, 2017, 2022; Young & Caldwell, 2019). Other occurrences of this rare type of calcrete have only been documented in mid-Visean successions of eastern Canada (Jutras *et al.*, 1999, 2001; Jutras & Prichonnet, 2002) and in Cenozoic successions of Western and Central Australia (Mann & Horwitz, 1979; Arakel & McConchie, 1982; Jacobson *et al.*, 1988; Arakel *et al.*, 1989), where they have been interpreted as the products of calcium-bearing fresh groundwater mixing with high-pH groundwater at the margin of evaporitic basins in hyper-arid environments.

The host material of all previously documented intervals of such calcretes is coarse and porous sediment or regolith in which groundwater can flow unrestrained. These host-replacing phreatic calcrete hardpans (HRPCHs) are typically massive, laminar or brecciated, and are often defined by a sharp base, directly above basement rocks or sediments with low permeability (Jutras *et al.*, 1999, 2001; Jutras & Prichonnet, 2002; Jutras, 2017). The focus of this paper is on successive HRPCH intervals developed in mud deposits of the Famennian Kinnesswood Formation (basal unit of the Inverclyde Group) in the Pennyseorach area of south-east Kintyre, south-west Scotland. This is the first report of such thoroughly developed calcretes in fine, low-porosity material that typically acts as an aquiclude during phreatic calcrete development (e.g. Jutras *et al.*, 2016; Jutras, 2017, 2022). The palaeoenvironmental and diagenetic settings of this newly identified succession of HRPCH intervals are herein described and compared with those of other HRPCH occurrences in the late Famennian to mid-Visean Inverclyde Group of south-west Scotland (Jutras *et al.*, 2011; Jutras, 2017, 2022), including incompletely developed occurrences on the Isle of Arran (Tandon & Friend, 1989).

EVOLVING NOMENCLATURE

Host-replacing phreatic calcrete hardpans

Several terms have been used to refer to thick intervals of calcrete that developed below the water table in hyper-arid settings and that not only invaded their host sediment, but thoroughly replaced it, leaving a multi-metric interval of nearly pure lime (>90% calcite). Such thick bodies of relatively pure calcrete were first referred to as 'valley calcretes' (Butt *et al.*, 1977), although they are not limited to valley settings, or 'groundwater calcretes' (Mann & Horwitz, 1979; Arakel & McConchie, 1982; Jacobson *et al.*, 1988; Arakel *et al.*, 1989; Wright & Tucker, 1991; Jutras *et al.*, 1999, 2001; Jutras & Prichonnet, 2002), although all other types of calcrete also form by precipitation from groundwater, either above or below the water table. The term 'phreatic calcrete hardpan' has been suggested (Jutras *et al.*, 2007b), but because the latter term could possibly also refer to thin lenses of host-displacing phreatic calcrete, the more specific term 'host-replacing' phreatic calcrete was recently proposed, with the term 'hardpan' added for thick, tabular bodies of >90% pure calcrete (Jutras, 2017, 2022). As discussed by Wright & Tucker (1991), such calcretes are generally over 3 m thick and up to 12 m thick (e.g. Jutras *et al.*, 1999, 2001), but many documented HRPCHs are erosional remnants below disconformities (Jutras *et al.*, 1999, 2001, 2007a, 2007b, 2011; Jutras & Prichonnet, 2002, 2005; Jutras, 2022). Although these erosional remnants can be less than 3 m thick in some cases, the original calcrete is assumed to have been several metres thick.

Host-replacing phreatic calcrete hardpans should not be confused with pore-filling phreatic calcrete or dolocrete cement (e.g. Tandon & Narayan, 1981; Sassi *et al.*, 1984; Maizels, 1987; Khalaf, 1990; El-Sayed *et al.*, 1991; Kaemmerer & Revel, 1991; Spötl & Wright, 1992; Colson & Cojan, 1996; Nash & Smith, 1998, 2003; Nash & McLaren, 2003). They should also not be confused with nodules or thin (1 to 30 cm) lenses of invasive phreatic calcrete developed by mineral displacement (e.g. Tandon & Friend, 1989; Lang *et al.*, 1990; Purvis & Wright, 1991; Tandon & Gibling, 1997; Khadkikar *et al.*, 1998, 2000; Jutras *et al.*, 2001, 2016; Hillier *et al.*, 2011; Jutras, 2022). These other types of phreatic calcretes or dolocretes are more common occurrences in which the original host material is largely preserved, and in which unusually high groundwater pH conditions are not implied.

Fissure calcretes and columnar host-replacing phreatic calcrete hardpans

The terms 'rod cornstone' (Tandon & Friend, 1989) and 'columnar calcrete' (e.g. Zhou *et al.*, 1994; Lauriol & Clark, 1999; Zucca *et al.*, 2018) have been used to describe calcretes with a vertical structure. However, such calcretes typically do not occur as rods or columns, but as vertical sheets along fissures. Lauriol & Clark (1999) introduced the term 'fissure calcrete', which better describes their structure, and which is used in this paper. When calcrete occupies >90% of the fissured interval, the term 'columnar HRPCH' is used herein, because the structure is at that stage reminiscent of columnar basalt.

GEOLOGICAL SETTING

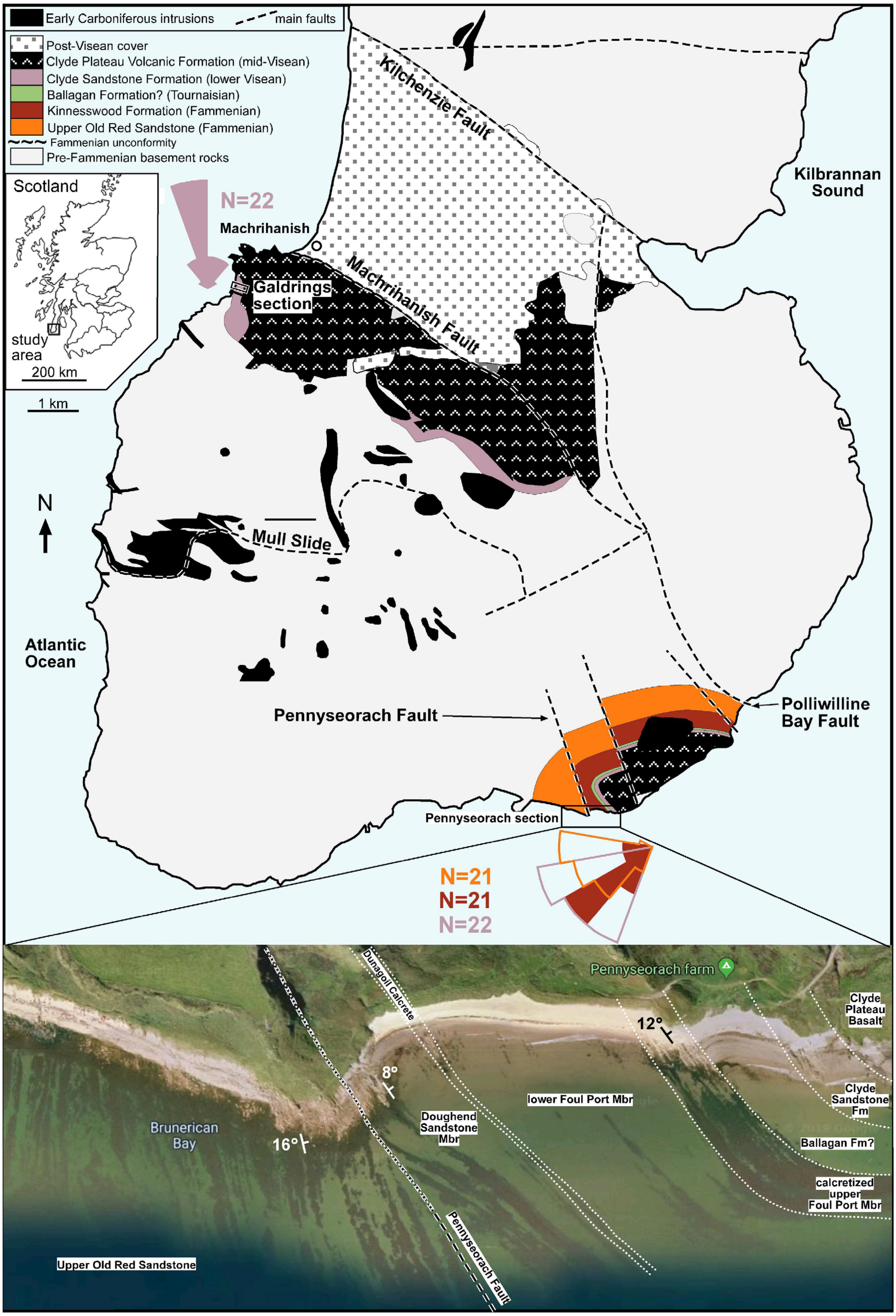
A low-angle unconformity separates the early Famennian Stratheden Group (Upper Old Red Sandstone: UORS) from the late Famennian to mid-Visean Inverclyde Group in south-west Scotland (Fig. 2), but consistent facies distribution and palaeocurrent vectors suggest a similar basin architecture and tectonic setting for both units in the Bute Shoulder and Cumbraes Trough, north-east of the study area (Jutras, 2022). However, a more significant unconformity separates the Famennian UORS from the Ludlow to early Emsian Lower Old Red Sandstone (LORS), which is part of the pre-Famennian basement, and which regionally comprises the Arbuthnott and Garvock groups (British Geological Survey, 1996) (Fig. 2).

In the Pennyseorach area of south-east Kintyre, a relatively thick succession of the UORS and Kinnesswood Formation was identified below the Clyde Sandstone Formation (Young & Caldwell, 2019). However, *ca* 15 km to the north-west in the Galdrings section near Machrihanish (Fig. 1), a very thin exposure gap separates the Clyde Sandstone Formation from basement rocks, suggesting that the UORS and Kinnesswood Formation do not occur in that area (Jutras, 2017; Young & Caldwell, 2019). Despite the two contrasting successions, Young & Caldwell (2019) included both sections within their South Kintyre Basin.

Where it is most complete, in the Cumbraes Trough of Great Cumbrae (north-east of the study area), the Famennian Kinnesswood Formation (*sensu* Marshall *et al.*, 2019) is subdivided as the basal Doughend Sandstone Member and the overlying Foul Port Member (Monro, 1999; Young & Caldwell, 2011b) (Fig. 2). The Doughend Sandstone Member is characterized by pinkish-red sandstone, conglomerate and minor mudrock that are rich in pedogenic calcite and calcrete nodules, including nodular hardpans (Jutras, 2022). The lower part of the Foul Port Member is dominated by brick-red mudrock with large, abundant and interconnecting 'pseudo-synclines' that have been interpreted as the result of the intermittent deposition and dissolution of evaporites in a playa setting (Jutras, 2022). One thin occurrence of peritidal limestone near the base of this member (the Doughend Limestone marker of Paterson & Hall, 1986) suggests that the evaporites may have formed in the context of sea incursions followed by restriction (Jutras, 2022). The upper part of the Foul Port Member (*sensu* Caldwell & Young, 2013; West Bay Cornstone Member of Paterson & Hall, 1986) in the Cumbraes Trough is coarser, more calcrete-rich, and does not include pseudo-synclines (Jutras, 2022). On the adjacent Bute Shoulder, the Foul Port Member is absent above the Doughend Sandstone Member, the top of which is instead the host of a HRPCH that is interpreted to be contemporaneous with the intermittent deposition of evaporites in the lower part of the Foul Port Member within the Cumbraes Trough (Jutras, 2022).

At all localities on the Isle of Arran, the Doughend Sandstone Member and the lower part of the Foul Port Member are absent, and the UORS–Kinnesswood Formation contact is instead occupied by a HRPCH hosted by the upper part of the UORS, which is disconformably overlain by calcrete-rich red sandstone, mudrock and conglomerate that are typical of the upper part of the Foul Port Member (Jutras *et al.*, 2011) (Fig. 2). The Isle of Arran includes three contrasting successions of the UORS and Inverclyde Group, which appear to have been deposited in separate basins. However, documented HRPCHs on Arran and Bute all occur at approximately the same interval, directly above the Doughend Sandstone Member, when present, and disconformably below the upper Foul Port Member (the 'Arran Cornstone Formation' of Tandon & Friend, 1989) (Jutras *et al.*, 2011; Jutras, 2022) (Fig. 2). Because of their relevance as stratigraphic markers, these penecontemporaneous HRPCHs were formalized as the Dunagoil Calcrete (type-locality in south-west Bute), a lithodemic sub-unit of the Kinnesswood Formation (Jutras, 2022) (Fig. 2).

In the Cumbraes and Northeast Arran troughs, as well as on the Bute Shoulder, the Kinnesswood Formation is overlain by grey and red beds of the Ballagan Formation, which includes intervals of marginal marine, grey mudrock (Young & Caldwell, 2011a, 2012; Millward *et al.*, 2018) (Fig. 2). At these localities, the Tournaisian Ballagan Formation is overlain by the early to mid-Visean Clyde Sandstone Formation, which mainly comprises thick intervals of grey or reddish-grey sandstone and thin



Early Carboniferous intrusions
main faults
Post-Visean cover
Clyde Plateau Volcanic Formation (mid-Visean)
Clyde Sandstone Formation (lower Visean)
Ballagan Formation? (Tournaisian)
Kinnesswood Formation (Fammenian)
Upper Old Red Sandstone (Fammenian)
Fammenian unconformity
Pre-Fammenian basement rocks
Scotland
study area
200 km
1 km
N
N=22
Machrihanish
Galdrings section
Kilchenzie Fault
Machrihanish Fault
Kilbrannan Sound
Mull Slide
Atlantic Ocean
Pennyseorach Fault
Polliwilline Bay Fault
Pennyseorach section
N=21
N=21
N=22
Pennyseorach farm
Dunagoil Calcrete
12°
8°
16°
Clyde Plateau Basalt
lower Foul Port Mbr
Doughend Sandstone Mbr
Brunerican Bay
Clyde Sandstone Fm
Ballagan Fm?
calcretized upper Foul Port Mbr
Upper Old Red Sandstone
Pennyseorach Fault

Fig. 1. Simplified geology of the study area (modified from British Geological Survey, 1996, and Young & Caldwell, 2019) with rose diagrams (colour coded by unit) compiling palaeocurrent data derived from the geometry of sandstone and conglomerate channels in the Pennyseorach (data from this study) and Machrihanish (data from Jutras, 2017) subbasins. The upper inset shows the locality of the study area in Scotland, and the lower inset shows the Pennyseorach section of south-east Kintyre viewed from a Google Earth© satellite image.

intervals of purple or red mudrock. The Clyde Sandstone Formation is either separated from the overlying *ca* 335 Ma Clyde Plateau Volcanic Formation (*sensu* Monaghan & Parrish, 2006) by a weathering profile or by the thin Laggan Cottage or Birgidale formations (Young & Caldwell, 2011a, 2012, 2019) (Fig. 2). Thick additional occurrences of HRPCH have been documented from three intervals of the Clyde Sandstone Formation in the Machrihanish area (Galdrings section; Fig. 1) of the Kintyre Peninsula (Jutras, 2017; Young & Caldwell, 2019).

METHODS

Field observations and stratigraphic measurements

The bulk of this study relied on field observations and stratigraphic measurements to understand the sedimentological and eodiagenetic evolution of the calcrete-bearing Pennyseorach section.

Stable isotopic analyses

A total of 14 samples of 95 to 100% pure calcrete from the Kinnesswood Formation in the Pennyseorach section were analysed for their stable carbon and oxygen isotopic contents ($\delta^{13}C$ VPDB and $\delta^{18}O$ VPDB – Vienna Pee Dee Belemnite) (Table S1). Part of the uppermost calcretized succession was affected by profuse calcite veining, presumably in relation to the emplacement of thick lava flows less than 50 m higher in the succession, but all samples were retrieved from areas not affected by veining. The samples were powdered and analysed by dual-inlet mass spectrometry at the GEOTOP laboratory of Université du Québec à Montréal (Canada) using a GV Instruments Multicarb preparation system connected to an Isoprime Dual Inlet mass spectrometer (Isoprime Limited, Stockport, UK) (Table S1).

Palaeocurrent measurements

To help reconstruct the palaeogeography at the time of HRPCH formation, palaeocurrent vectors were obtained from the geometry of sandstone and conglomerate channel structures (Table S2), the sides of which converge downflow (Potter & Pettijohn, 2012). These structures develop from downcutting during times of high flow velocity and therefore provide the best type of palaeoflow indicators for basin reconstructions (see discussion in Jutras *et al.*, 2015).

RESULTS

General stratigraphy of the Pennyseorach section

In south Kintyre, the UORS and Inverclyde Group are best exposed in the coastal area south of Pennyseorach Farm (Fig. 1) (Young & Caldwell, 2019). In this section, the UORS is mainly composed of quartzose red conglomerate, sandstone and mudrock that are mostly devoid of calcrete (Fig. 3).

A fault separates the UORS from the heavily calcretized Doughend Sandstone Member of the Kinnesswood Formation, which is otherwise characterized by a similar succession as the former, albeit less coarse, less quartzitic and less well-sorted. This sub-unit comprises a *ca* 17 m succession of pinkish sandstone, pebbly sandstone, polymictic conglomerate and mudrock with abundant calcrete nodules, including a *ca* 4.5 m nodular calcrete hardpan near the base (Fig. 3). Just as in the Bute Shoulder (Jutras, 2022), the Doughend Sandstone Member at Pennyseorach is sharply overlain by a HRPCH, which evolves from laminar at the base to massive in the middle, and to a perpendicular-to-bedding columnar structure at the top, resulting in a total thickness of *ca* 3 m (Fig. 3). The calcrete is nearly pure calcite, but a few remaining quartz grains suggest a sandy host for the laminar base. The HRPCH is in turn

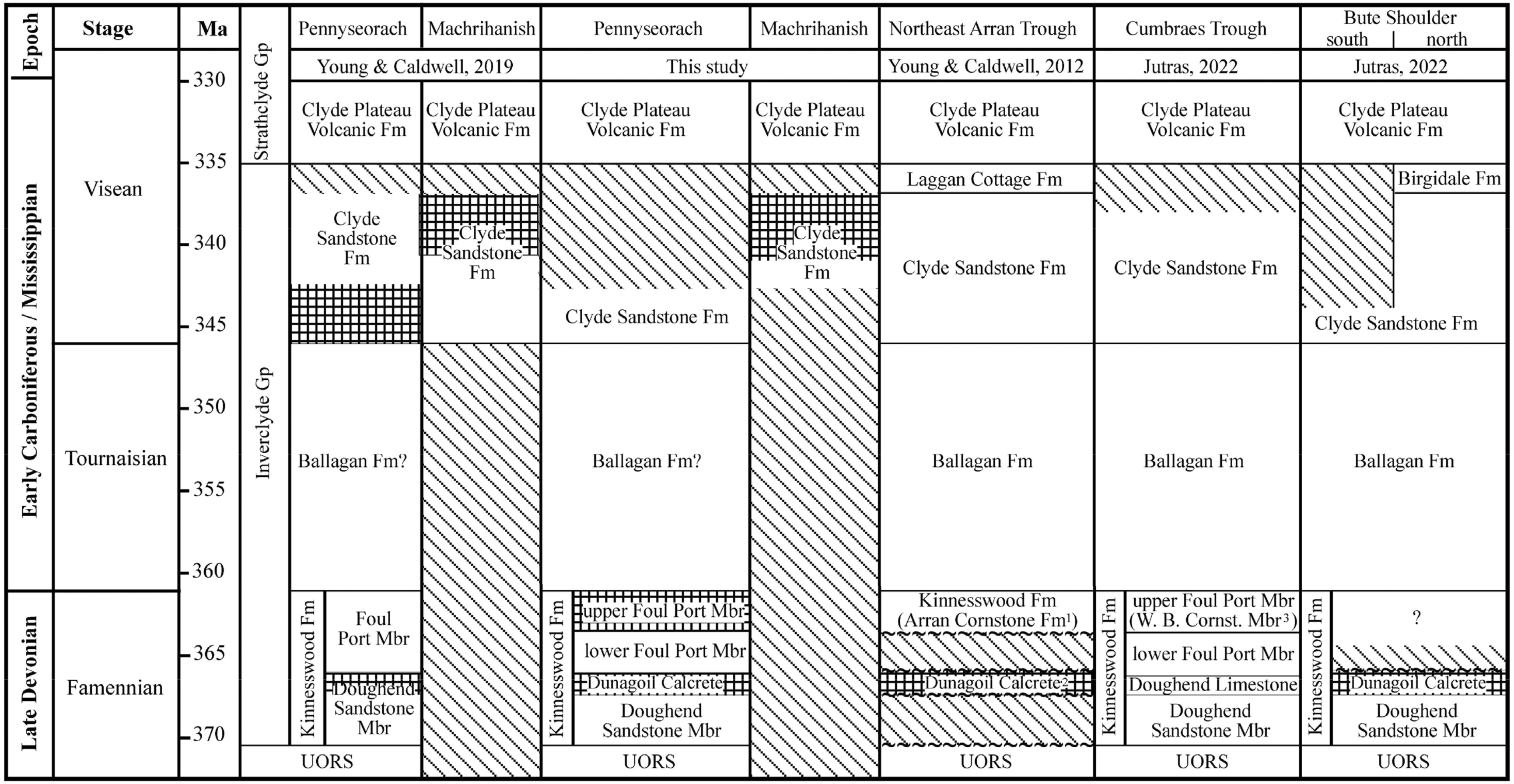


Fig. 2. Stratigraphic table comparing the stratigraphic interpretations of Young & Caldwell (2019) versus this study in the Pennyseorach and Machrihanish subbasins of south Kintyre, as well as versus the most recent stratigraphic interpretations of contemporaneous basin successions in other parts of south-west Scotland. UORS: Upper Old Red Sandstone: (1) based on Tandon & Friend (1989); (2) unnamed calcrete in Young & Caldwell (2012); (3) W. B. Cornst. Mbr: West Bay Cornstone Member, based on Paterson & Hall (1986). Dashed pattern: hiatus; square pattern: heavily calcretized interval.

sharply overlain by a poorly-exposed succession of red mudrock corresponding to the Foul Port Member (Fig. 3). These stratigraphic relationships suggest that the intervening HRPCH correlates with the Dunagoil Calcrete sub-unit of the Kinnesswood Formation (*sensu* Jutras, 2022).

A *ca* 20 m stratigraphic gap separates the uppermost exposure of brick-red mudrock from a *ca* 12 m thick succession of red mudrock and narrow channel-fills of red sandstone and polymictic pebble conglomerate (herein assigned to the upper part of the Foul Port Member), *ca* 80% of which is thoroughly replaced by calcrete (Fig. 3). Clast composition in the conglomerates is dominated by quartz and meta-mudrock pebbles typical of the Neoproterozoic to Cambrian Dalradian Supergroup basement rocks, which occupy most of the Kintyre Peninsula (Strachan *et al.*, 2002). The conglomerates also include some red sandstone clasts that may be derived from the LORS, which also forms part of the pre-Famennian basement in southern Kintyre (British Geological Survey, 1996).

A *ca* 21 m stratigraphic gap separates the highly calcretized red beds of the upper Foul Port Member from a non-calcretized succession dominated by larger channels of grey and reddish-grey sandstone and quartzose conglomerates that are typical of the Clyde Sandstone Formation. In this view, the intervening gap would at least in part correspond to the Ballagan Formation interval and possibly includes unexposed beds of this structurally weak unit. As in many other localities of south-west Scotland, the uppermost Clyde Sandstone Formation is deeply weathered below the Clyde Plateau Volcanic Formation (Fig. 3).

Complex host-replacing phreatic calcrete facies and contact relationships in the upper Foul Port Member

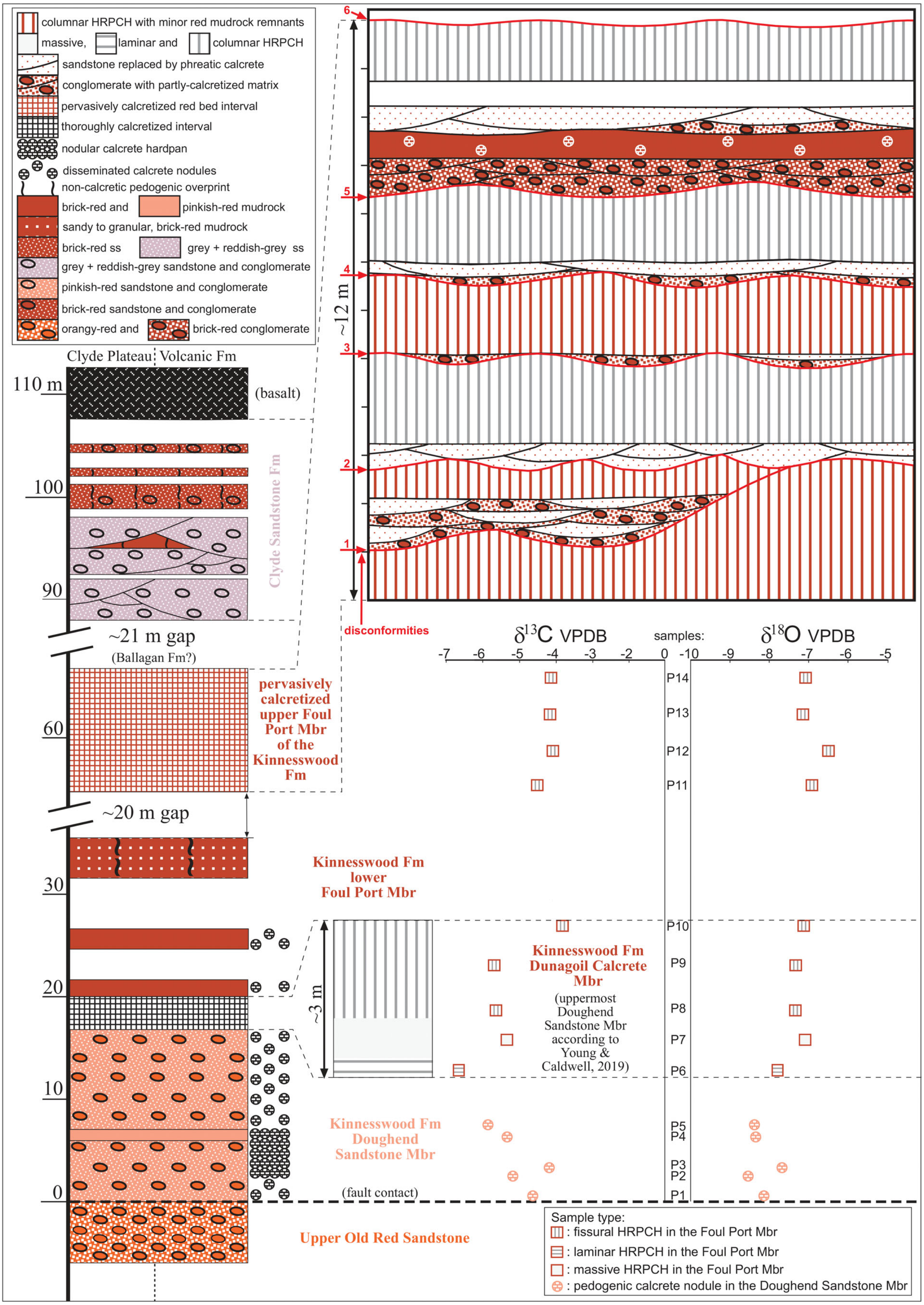
The *ca* 12 m thick exposure of the upper Foul Port Member at Pennyseorach includes several erosional remnants of stratigraphic intervals in which calcrete has replaced most of its host sediment over a significant thickness (up to *ca* 3 m), thus meeting the criteria for HRPCHs (Wright & Tucker, 1991; Jutras, 2022). The succession includes six intervals of columnar HRPCH along with several occurrences of massive HRPCH developed in sandstone channels (Figs 3 and 4A). All of these calcretes are composed of 90 to 100% calcite, and some of them are partly tainted by iron oxides. In three columnar HRPCH intervals, *ca* 1 to 10% of the volume is occupied by perpendicular-to-bedding sheets of red mudrock remnants (Fig. 4B). The three other columnar calcrete intervals are thoroughly replaced by calcrete, but because they lack the massive and cross-channelized structure of HRPCHs developed in coarser intervals, the host sediment is assumed to have been red mudrock as well. Although perpendicular-to-bedding in terms of general structure, some of these calcretes show parallel-to-bedding laminar structures within the columns (Fig. 4B).

Each columnar HRPCH is separated from intervening cross-channelized deposits by an erosion surface (minor disconformities marked on Figs 3 and 5A), with one occurrence pinching-out on a large residual knob of the most basal exposure of columnar HRPCH (Fig. 3). In the intervals of partly calcretized cross-channelized deposits, sandstone channel-fills are thoroughly replaced by massive phreatic calcrete, whereas the pebble conglomerate channel-fills were only affected by partial calcretization of their granular matrix (Fig. 3). Each of these partly calcretized intervals of cross-channelized deposits is concordantly overlain by a thick interval of columnar HRPCH (Fig. 3).

The base of the uppermost interval of clastic deposits is occupied by non-calcretized conglomerate channel-fills disconformably overlying a columnar HRPCH and conformably overlain by a succession of red mudrock with calcrete nodules. The latter is in turn overlain by an almost thoroughly calcretized succession of sandstone and conglomerate channel-fills separated by a small gap from the uppermost columnar HRPCH (Fig. 3).

Stable isotopic data

The stable isotopic composition of calcretes in the Kinnesswood Formation at Pennyseorach is consistent with that of upper Palaeozoic meteoric carbonates (*sensu* Veizer *et al.*, 1999), with $\delta^{13}C$ values ranging between −3.76 and −6.64, and $\delta^{18}O$ values ranging between −6.51 and −8.55 (Table S1). A slight tendency towards heavier values of both $\delta^{13}C$ and $\delta^{18}O$ is observed up-section (Fig. 3). When plotted on a $\delta^{13}C$ versus $\delta^{18}O$ diagram, HRPCH samples from the upper Foul Port Member at Pennyseorach do not overlap with other HRPCHs from the Inverclyde Group in south-west Scotland, nor with Cenozoic HRPCHs from Western and Central Australia (Fig. 5; Table S1).



columnar HRPCH with minor red mudrock remnants
massive, laminar and columnar HRPCH
sandstone replaced by phreatic calcrete
conglomerate with partly-calcretized matrix
pervasively calcretized red bed interval
thoroughly calcretized interval
nodular calcrete hardpan
disseminated calcrete nodules
non-calcretic pedogenic overprint
brick-red and pinkish-red mudrock
sandy to granular, brick-red mudrock
brick-red ss grey + reddish-grey ss
grey + reddish-grey sandstone and conglomerate
pinkish-red sandstone and conglomerate
brick-red sandstone and conglomerate
orangy-red and brick-red conglomerate
Clyde Plateau Volcanic Fm
110 m
(basalt)
100
Clyde Sandstone Fm
90
~21 m gap
(Ballagan Fm?)
60
pervasively calcretized upper Foul Port Mbr of the Kinnesswood Fm
~20 m gap
30
Kinnesswood Fm lower Foul Port Mbr
20
10
0
~12 m
~3 m
1
2
3
4
5
6
disconformities
δ13C VPDB
samples:
δ18O VPDB
-7 -6 -5 -4 -3 -2 0 -10 -9 -8 -7 -6 -5
P14
P13
P12
P11
P10
P9
P8
P7
P6
P5
P4
P3
P2
P1
Kinnesswood Fm Dunagoil Calcrete Mbr
(uppermost Doughend Sandstone Mbr according to Young & Caldwell, 2019)
Kinnesswood Fm Doughend Sandstone Mbr
(fault contact)
Upper Old Red Sandstone
Sample type:
: fissural HRPCH in the Foul Port Mbr
: laminar HRPCH in the Foul Port Mbr
: massive HRPCH in the Foul Port Mbr
: pedogenic calcrete nodule in the Doughend Sandstone Mbr

Fig. 3. Summary of the Pennyseorach section (a more detailed section was provided by Young & Caldwell (2019), with slightly different stratigraphic correlations). Insets: detailed descriptions of the Dunagoil Calcrete interval (top of the Doughend Sandstone Member according to Young & Caldwell, 2019) and of the host-replacing phreatic calcrete hardpan (HRPCH)-bearing upper Foul Port Member interval (lower part of the Clyde Sandstone Formation according to Young & Caldwell, 2019).

Palaeocurrents

Based on palaeocurrent vectors derived from channel geometry, the UORS in the Pennyseorach area was sourced from the ENE, whereas the Inverclyde Group was sourced from the north-east (Fig. 1). A similarly small deviation of palaeocurrent vectors between the UORS and the Inverclyde Group was observed in the Bute Shoulder and Cumbraes Trough (Jutras, 2022). In contrast, Young & Caldwell (2019) collected easterly palaeocurrent vectors from the orientation of cross-laminae in sandstones of the Kinnesswood Formation in the Pennyseorach section, which are not here considered to be indicative of the palaeo-position of the main source area. The combination of meta-mudrock and minor red sandstone clasts in polymictic conglomerates of the upper Foul Port Member is consistent with the pre-Famennian geology of the inferred source area to the north-east (British Geological Survey, 1996).

DISCUSSION

Hydrological conditions for the formation of thick, host-replacing phreatic calcrete hardpans

Based on the well-documented gradational transition from host-replacing phreatic calcrete to evaporitic gypsite at the margin of several Cenozoic evaporitic basins in Western and Central Australia, Arakel & McConchie (1982) proposed that such calcretes form where a fresh groundwater discharge mixes with evaporitic groundwater. In support of this, experimental studies have shown a steep increase in the solubility: (i) of alumina above a pH of *ca* 8; (ii) of amorphous silica above a pH of *ca* 9; and (iii) of crystalline quartz above a pH of *ca* 9.8; whereas calcite becomes less soluble than all three above a pH of 9 (Blatt *et al.*, 1980). Hence, silicate and clay minerals can be replaced by calcite above a pH of 9, and especially so above a pH of 9.8. For this reason, swept-in silicate and clay minerals are known to dissolve in evaporitic basins (Sonnenfeld, 2003), which can show pH values well above 9.8 in the modern world (for a list of examples, see table 3 in Sorokin, 2017) and as high as 11.05 in Kenya's Lake Magadi (Eugster, 1970). Although palaeo-groundwater pH at the margin of ancient evaporitic basins is difficult to determine, a pH greater than 10.5 was inferred at the margin of a Visean evaporitic basin in eastern Canada based on the concentration of Mg-phases within associated palaeokarst infills (Jutras, 2016).

It is therefore inferred that the well-developed HRPCH occurrences in the Kinnesswood Formation at Pennyseorach developed at the margin of a recurrent Famennian evaporitic basin. In this setting, a calcium-bearing freshwater aquifer that flowed towards the evaporitic basin experienced a significant rise in pH as it mixed with evaporitic groundwater, which would have led to the thorough replacement of silicate and clay minerals by calcite along the entire thickness of the aquifer.

Stable isotopes

Evolution towards slightly heavier stable isotopic values up-section at Pennyseorach (Fig. 3) may reflect a certain degree of aridification with time, because degassing and evaporation preferentially remove ^{12}C and ^{16}O, and as precipitation and vegetation conversely concentrate them (e.g. Stiller *et al.*, 1985; Cerling, 1991; Rossinsky Jr & Swart, 1993; Andrews *et al.*, 1998; Hsieh *et al.*, 1998; Pentecost, 2005). In this case, aridification might be underestimated given the fact that the pedogenic calcretes at the base of the succession would have formed closer to the surface than the phreatic calcretes located higher in the succession, which would have favoured degassing and evaporation processes.

The lack of overlap in $\delta^{13}C$ versus $\delta^{18}O$ ranges between HRPCHs of the upper Foul Port Member at Pennyseorach and other HRPCH occurrences in the Inverclyde Group (Fig. 5) is consistent with the conclusion that they formed at a different interval than those of the Dunagoil Calcrete or, contrary to the conclusions of Young & Caldwell (2019), the Clyde Sandstone Formation. A lack of

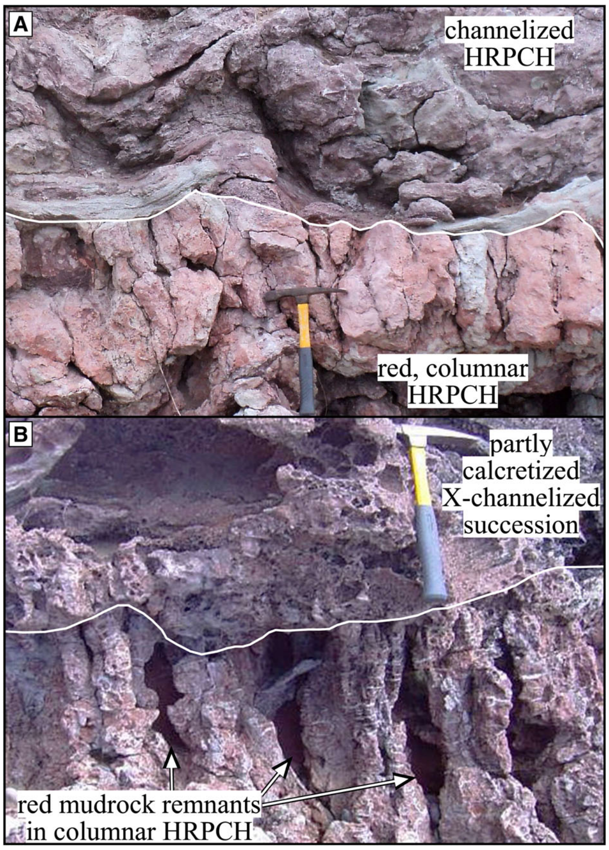


Fig. 4. (A) Erosional contact between a columnar host-replacing phreatic calcrete hardpan (HRPCH) and an overlying succession of cross-channelized red conglomerate and massive HRPCH that shows evidence of being originally composed of sand. (B) Thin vertical sheets of red mudstone remnants exposed in part of a columnar HRPCH. Hammer handle is 28 cm in length.

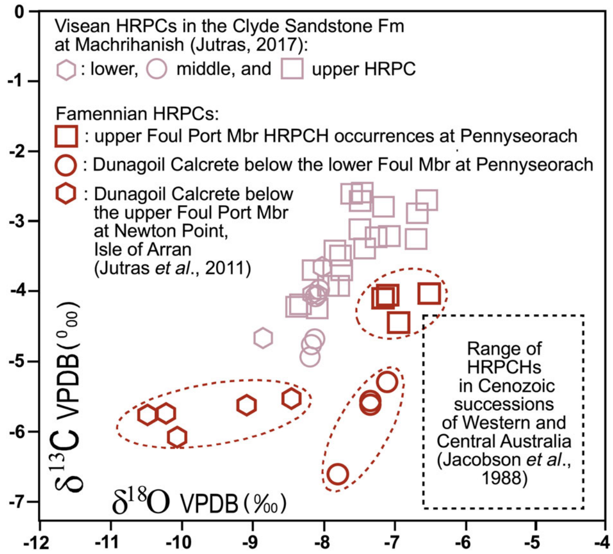


Fig. 5. $\delta^{13}C$ VPDB versus $\delta^{18}O$ VPDB values in host-replacing phreatic calcrete hardpans (HRPCHs) of the Famennian upper Foul Port Member at Pennyseorach and in the slightly older Dunagoil Calcrete within the same section (data from this study), as well as at Newton Point (Hutton's Unconformity) on the Isle of Arran (data from Jutras *et al.*, 2011). The diagram also includes data from three HRPCHs in the Visean Clyde Sandstone Formation in the Galdrings section of Machrihanish (data from Jutras, 2017). In all cases, samples from the uppermost 10 cm of the HRPCHs were excluded due to possible overprints above the water table.

overlap is also observed between penecontemporaneous Dunagoil Calcrete occurrences at Pennyseorach and Newton Point (north-west Arran) due to contrasting $\delta^{18}O$ values (Fig. 5). However, it should be noted that the HRPCH at Newton Point formed in basement regolith of the source area, (Jutras *et al.*, 2011), whereas all other calcretes plotted in Fig. 5 formed within sedimentary basin successions. Just as heavier $\delta^{18}O$ values tend to develop near the top of a HRPCH due to higher evaporation rates (e.g. Jutras *et al.*, 1999), a similar trend can be expected basinward as the aquifer reaches closer to the surface. In contrast, the sedimentary basin typically hosts more vegetation, which would prevent $\delta^{13}C$ values from increasing as much as $\delta^{18}O$ values. Because they all formed in a similar setting, contrasting $\delta^{13}C$ and/or $\delta^{18}O$ values in HRPCHs assigned to the Dunagoil Calcrete, upper Foul Port Member and Clyde Sandstone Formation in the South Kintyre Basin are here considered to be stratigraphically more significant, reflecting differences in climate and/or plant species assemblages (*sensu* Alonso-Zarza & Wright, 2010, and references therein).

General tectonostratigraphic setting

Palaeocurrent, provenance and sedimentary facies data suggest that the UORS and Inverclyde Group at Pennyseorach were altogether sourced from a north-west/south-east trending scarp developed along the nearby Polliwilline Bay Fault (Figs 1 and 6A to E). In the context of a nearly north–south shortening direction inferred for the Devonian to Early Carboniferous tectonics of Scotland (Coward, 1993), sedimentation in the area of Pennyseorach may have been associated with a slightly restraining bend along the Polliwilline Bay Fault, which would have mainly experienced dextral movement (Fig. 6A to E). As in the Bute

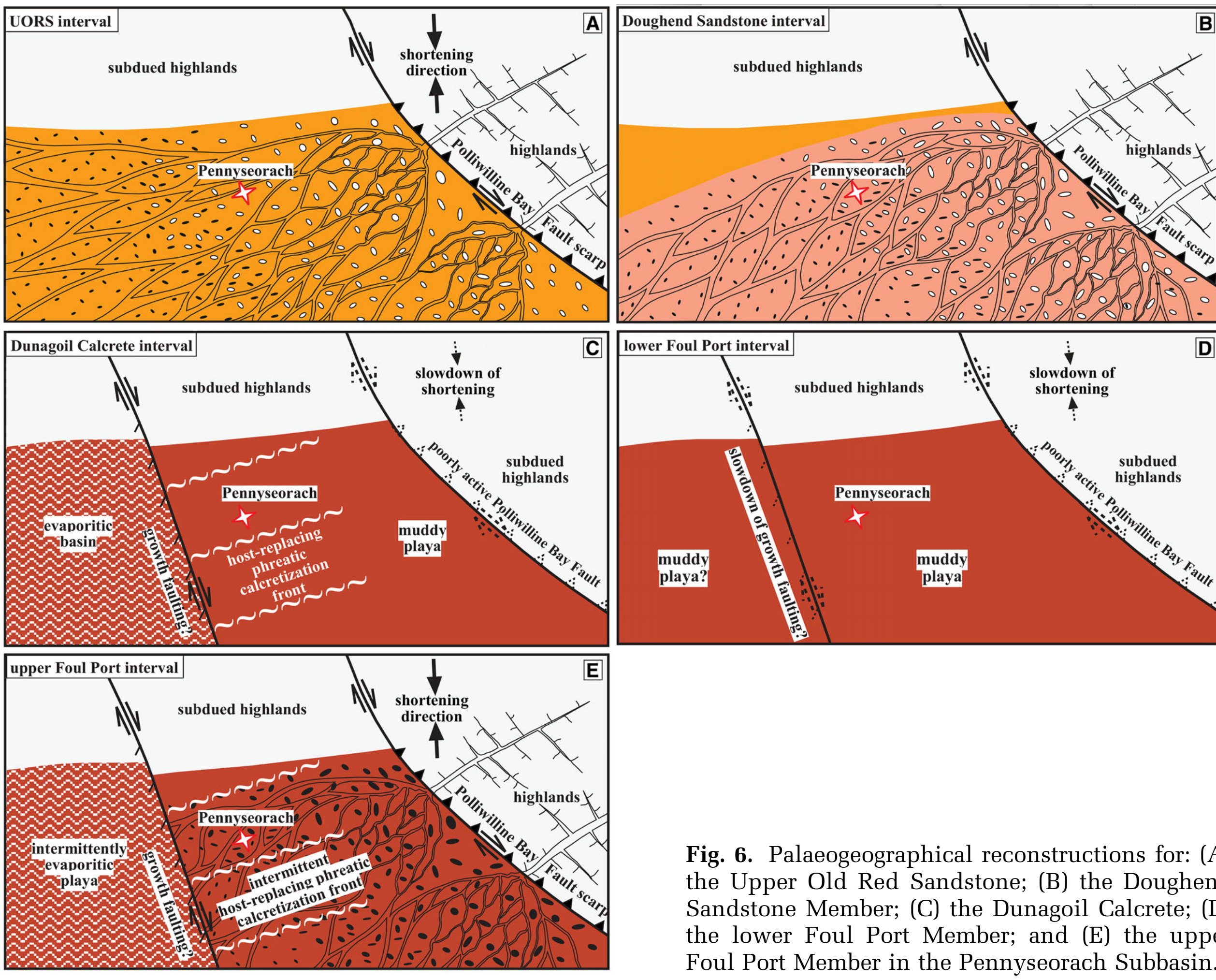


Fig. 6. Palaeogeographical reconstructions for: (A) the Upper Old Red Sandstone; (B) the Doughend Sandstone Member; (C) the Dunagoil Calcrete; (D) the lower Foul Port Member; and (E) the upper Foul Port Member in the Pennyseorach Subbasin.

Shoulder and Cumbraes Basin (Jutras, 2022), a slight deviation of palaeocurrents from the UORS to the Inverclyde Group (Fig. 1) might reflect minor tectonic readjustments, but no significant differences in basin architecture.

The palaeocurrent vectors at Pennyseorach are nearly opposite to those recorded in the Galdrings section of Machrihanish (Fig. 1), suggesting that the two successions are part of two separate subbasins of the south Kintyre Basin (*sensu* Young & Caldwell, 2019), herein referred to as the Pennyseorach and Machrihanish subbasins. Moreover, the Clyde Sandstone Formation is thicker at the Galdrings section and is marked by three thick intervals of HRPCH that are absent at Pennyseorach. Furthermore, as noted earlier, the Galdrings section starts with the Clyde Sandstone Formation and does not include any beds of the UORS and Kinnesswood Formation. It is therefore possible that the Machrihanish Subbasin only became active after the Pennyseorach Subbasin became inactive as a depocentre (Fig. 2), although both subbasins were eventually overlapped by the Clyde Plateau Volcanic Formation.

Palaeogeographical and eodiagenetic settings of Famennian units in the Pennyseorach Subbasin

The Upper Old Red Sandstone and Doughend Sandstone Member of the Kinnesswood Formation

A tropical arid setting is inferred for both the UORS and the overlying Doughend Sandstone Member of the Kinnesswood Formation due to their thorough oxidation and lack of organic remains. However, the presence of abundant calcretes in the latter suggests significantly lower sedimentation rates (*sensu* Leeder, 1975; Wright & Marriott, 1996; Alonso-Zarza & Wright, 2010) than in the former, which is mostly devoid of calcrete. Both units are dominated by cross-channelized conglomerate and sandstone deposits, suggesting a gravelly to sandy-braidplain environment (Fig. 6A and B).

The Dunagoil Calcrete

As noted earlier, it is inferred that the Dunagoil Calcrete at Pennyseorach developed in the vicinity of an evaporitic basin. Based on palaeocurrent data and basin reconstruction, this evaporitic basin would have developed to the south-west of the calcrete, away from the source area delineated by the north-west/south-east trending Polliwilline Bay Fault (Fig. 6C).

The Dunagoil Calcrete on Bute occurs at a basin margin on the footwall of a growth fault (Jutras, 2022), and its occurrences at Newton Point and Corrie on the Isle of Arran developed in regolith of older rocks (Jutras *et al.*, 2011), also at basin margins and presumably adjacent to a fault-bound basinal trough (the Northeast Arran Trough according to Young & Caldwell, 2012). At Pennyseorach, growth faulting may also have been necessary to accommodate sea incursions in a restricted setting, eventually generating a marked lateral transition from fresh intra-basinal groundwater to high-pH evaporitic groundwater (Fig. 6C). The NNW–SSE trending fault that separates the UORS from the Kinnesswood Formation at Pennyseorach (satellite image in Fig. 1) is possibly inherited from such a growth fault, as it shares a similar trend with the growth fault that separates the contemporaneous Bute Shoulder and Cumbraes Trough (Jutras, 2022).

The Dunagoil Calcrete at Pennyseorach does not include windows of preserved host material apart from some floating sand grains (<1% of the calcrete volume) in the laminar to massive basal *ca* 1.2 m (Fig. 3). Based on this and a thin gradational contact with the underlying unit, it is inferred that the host sediment at the base of the HRPCH corresponds to the top of the Doughend Sandstone Member. However, the vertical structure of the upper *ca* 1.8 m of HRPCH (Fig. 3) suggests that the latter may hide the contact between Doughend-type sand deposits and lower Foul Port-type mud deposits, because perpendicular-to-bedding calcrete structures are more likely to occur along desiccation fissures developed in smectite-rich deposits (e.g. Tandon & Friend, 1989). If this interpretation is correct, Dunagoil Calcrete development at Pennyseorach occurred subsequent to deposition of the Doughend Sandstone Member and synchronous to part of the lower Foul Port Member, which are similar stratigraphic relationships to those observed on Bute (Jutras, 2022). Further evidence for the development of HRPCH in fissured mud deposits is discussed below in the subsection on the calcretized upper Foul Port Member.

The lower Foul Port Member

In contrast with the Cumbraes Trough succession, the lower Foul Port Member at Pennyseorach is not as affected by pervasive pseudosynclinal structures that have been interpreted as the result of a cyclic deposition and dissolution of evaporites (Jutras, 2022). Hence, based on limited outcrop exposures, it is inferred that the lower Foul Port Member at Pennyseorach was deposited in a mainly non-evaporitic playa (Fig. 6D) and that an adjacent evaporitic basin was only present during deposition of the base of this muddy sub-unit (Fig. 6C).

The upper Foul Port Member

Cross-channelized conglomerates and sandstones in the upper Foul Port Member record the return to a gravelly to sandy-braidplain environment at Pennyseorach, which suggests that this unit corresponds to a time of tectonic rejuvenation along the Polliwilline Bay Fault scarp (Fig. 6E). New sea incursions in a restricted setting must have occurred near Pennyseorach during this time interval to account for the formation of successive HRPCHs (Fig. 6E). Each of these incursions must have been followed by significant base-level lowering to account for the removal of overlying sediment and the dissection of each columnar HRPCH (Figs 3, 4A and 7), which would have originally formed a few metres below the surface (*sensu* Mann & Horwitz, 1979).

Phreatic calcretization of sandstone channel-fills in the upper Foul Port Member

In the upper Foul Port Member at Pennyseorach, it is noteworthy that sandy channel-fills are almost completely replaced by massive phreatic calcrete, whereas gravelly channel-fills are mostly hosting pore-filling calcrete and only show minor replacement of the granular matrix by calcrete. At an inferred groundwater pH greater than 9.8, the siliciclastic material that characterizes both types of fills should altogether be highly soluble (Blatt *et al.*, 1980). Hence, this distinction between sandy and gravelly channel-fills must be related to greater surface area per volume in sand-size than gravel-size clasts, which would accelerate replacement by providing more contact surfaces for mineral/water interaction.

Formation of thick intervals of columnar host-replacing phreatic calcrete in mud deposits of the upper Foul Port Member

As noted earlier, stratigraphic relationships suggest that the host sediment of columnar HRPCHs in the upper part of the Pennyseorach section correlates with the upper Foul Port Member succession in the Northeast Arran Trough (*sensu* Young & Caldwell, 2012; Arran Cornstone Formation, *sensu* Tandon & Friend, 1989). This correlation is important because the equivalent succession on Arran provides clues regarding the embryonic stages of such calcretes, which were studied in detail by Tandon & Friend (1989), but which are not observable in the more thoroughly calcretized section at Pennyseorach. Because of the obstruction to groundwater flow that HRPCHs present, the latter typically go through frequent alternations between dissolution and precipitation, resulting in very complex internal structures and the eradication of features associated with early development stages (Jutras *et al.*, 1999, 2007b). As mentioned by Tandon & Friend (1989), the upper Foul Port Member succession in the Northeast Arran Trough is marked by pervasive desiccation fissures in its smectite-rich intervals, which are mostly mudrock, but which also include some fine lithic wacke. Many of these fissured intervals on Arran host closely spaced fissure calcretes ('rod cornstones' of Tandon & Friend, 1989; Fig. 8). Based on evidence of mineral replacement in floating grains of quartz within the calcretes and on the lack of evidence for significant structural displacement, the latter authors concluded that the clay matrix was most likely replaced by calcrete as well, rather than mechanically displaced.

The observations on Arran (for example, Fig. 8) and in a few areas of incomplete HRPCH formation in the equivalent succession at Pennyseorach (Fig. 4B) suggest that the columnar HRPCHs first developed as separate vertical sheets of calcrete within desiccation fissures that were providing pathways for groundwater circulation in the phreatic zone (Fig. 7C and D). Gradual replacement of the muddy host between fissures by phreatic calcrete eventually led to fully coalesced columns of calcrete with, in some cases, less than 1% of the host material left (Fig. 7E). The non-coalescing fissure calcretes ('rod cornstones') on Arran are interpreted as the result of the same process occurring over a less prolonged period of time, possibly due to higher sedimentation rates at that locality.

General model for the formation of successive host-replacing phreatic calcrete hardpan intervals in the upper Foul Port Member at Pennyseorach

In summary, the sedimentology, eodiagenetic history and intra-formational stratigraphic relationships of the upper Foul Port Member at Pennyseorach are interpreted as follows:

- Erosion surfaces intermittently developed during times of low base-level (Fig. 7A).
- The deposition of coarse, cross-channelized clastic successions would have occurred during times of high basin subsidence rates, source area rejuvenation and rising base-level (Fig. 7B), which would have allowed seawater to eventually invade an inferred adjacent intra-basinal trough (Fig. 6E).
- Deposition of the muddy intervals would have occurred during times of high base-level and subdued topography in the source area through occasional sheet floods (Fig. 7C). Each sheetflood would have been followed by prolonged sub-aerial exposure under an arid climate to account for the development of a tight network of tall desiccation fissures, the thorough oxidation of the associated deposits, and the presence of abundant pedogenic calcrete nodules in one preserved interval near the top of the exposed succession (Fig. 3). The up to >3 m tall desiccation fissures would have provided pathways for the flow of phreatic groundwater within otherwise impermeable, semi-consolidated muds (Fig. 7C).
- A subsequent period of low sedimentation rates and restricted marine conditions under a hyper-arid climate would have caused the development of high pH groundwater in marginal parts of the basin, leading to the thorough replacement of sandy material by massive phreatic calcrete and to the development of fissure calcretes in mud deposits higher in the phreatic zone (Fig. 7D). The fissure calcretes gradually evolved and coalesced into a mature, columnar HRPCH (Fig. 7E).
- Subsequent base-level lowering generated intra-basinal erosion down to the columnar HRPCH (Fig. 7F), leaving another irregular erosion surface that will subsequently be buried during the next rise in base-level.

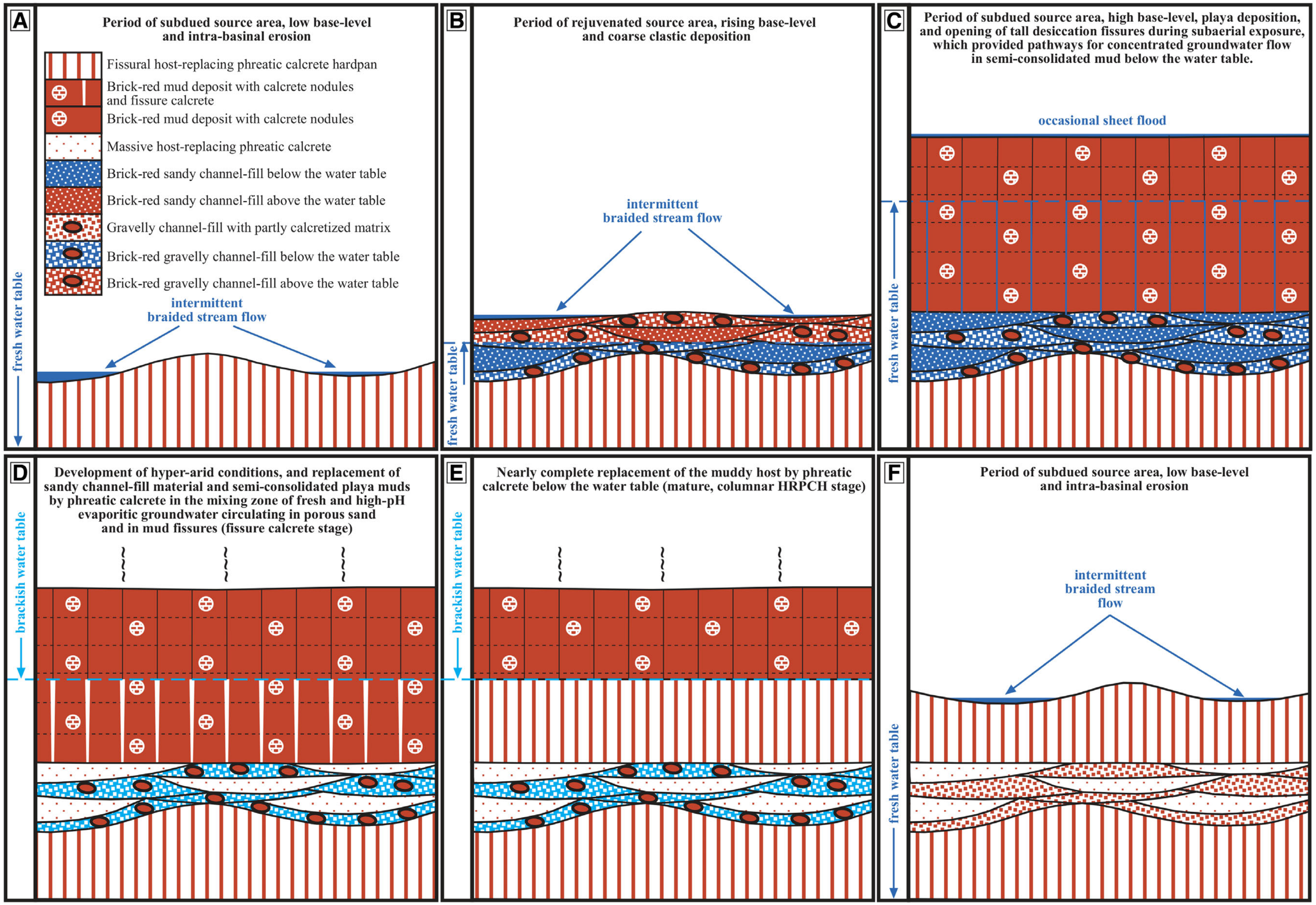


Fig. 7. Proposed model for the clastic sedimentology and calcrete petrology of the upper Foul Port Member at Pennyseorach from one erosional surface to the next.

Fig. 8. Closely spaced fissure calcretes ('rod cornstones' of Tandon & Friend, 1989) in the upper Foul Port Member ('Arran Cornstone Formation' of Tandon & Friend, 1989) of the Kinnesswood Formation in the Northeast Arran Trough (*sensu* Young & Caldwell, 2012). Hammer handle is 28 cm in length.

With minor nuances, this succession of events repeated itself several times in the remnant *ca* 12 m thick succession, with each cycle starting with the deposition of coarse, cross-channelized deposits and ending with the downcutting of a columnar HRPCH (Fig. 3).

CONCLUSIONS

Although rare in the geological record, thick host-replacing phreatic calcrete hardpans (HRPCHs) are common occurrences within the Inverclyde Group of south-west Scotland, being recorded: (i) below the upper Foul Port Member of the Kinnesswood Formation on Arran (Jutras *et al.*, 2011), Bute (Jutras, 2022) and at Pennyseorach (the Dunagoil Calcrete interval); (ii) within several intervals of the upper Foul Port Member at Pennyseorach (main subject of this paper); and (iii) within three intervals in the upper part of the Clyde Formation at Machrihanish (Jutras, 2017). If the conclusion that they necessitate the nearby presence of a high pH evaporitic basin in order to form is correct (e.g. Arakel & McConchie, 1982; Jutras *et al.*, 2007b), this implies that such basins were intermittently present during most of the Famennian and the Visean in the small, fragmented basins of south-west Scotland, accommodated by growth-fault-bound subbasins such as the Cumbraes Trough (*sensu* Young & Caldwell, 2012; Jutras, 2022).

Whereas previous studies on HRPCHs indicated that they formed in porous material above aquicludes, the Pennyseorach Subbasin of south-west Scotland includes several cases in which such calcretes managed to develop within non-porous, muddy material because tall desiccation fissures provided pathways for concentrated groundwater circulation (Fig. 7C to E). A large amount of time must be necessary for the process of phreatic calcrete to gradually replace the material of the fissure walls, prograde within the muddy host, and eventually coalesce to form a mature columnar HRPCH. Hence, the development of such thick, columnar HRPCHs in mud deposits must require very low sedimentation rates.

Based on their heavier carbon isotopic contents, the succession of massive and columnar HRPCHs in the upper half of the Pennyseorach section developed in more arid conditions than the slightly older Dunagoil Calcrete in the same section (Fig. 5). There is also a lack of overlap in the stable isotopic ranges of several HRPCH occurrences from different basins and time periods (Fig. 5) despite inferred similarities in their general palaeogeographical and palaeoenvironmental settings. Hence, the contrasting stable isotopic ranges must record some minor differences in terms of climate, hydrological setting and/or vegetation cover.

The tight clustering of stable isotopic values that is observed in HRPCHs from specific times and places (Fig. 5) can make them useful as stratigraphic markers. As discussed in Jutras (2017), the well-constrained isotopic values of HRPCHs are likely helped by the relative homogenization of groundwater chemistry that can take place in the saturated zone, thus allowing subtle palaeoenvironmental nuances to be recorded as contrasting isotopic signatures. Furthermore, if paired with the study of palynomorphs, the stable isotopic composition of HRPCHs has the potential to provide useful information on secular changes in arid continental environments related to rainwater chemistry and the evolution of land vegetation.

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DATA AVAILABILITY STATEMENT

Numerical data from this study are available as supplementary files.

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Supporting Information

Additional information may be found in the online version of this article:

Table S1. Stable carbon and oxygen isotopic contents ($\delta^{13}C$ VPDB and $\delta^{18}O$ VPDB) in various types of calcretes within the Pennyseorach section (data from this study) as well as in host-replacing phreatic calcrete hardpans from the Inverclyde Group at other localities of south-west Scotland (data from Jutras *et al.*, 2011, and Jutras, 2017).

Table S2. Palaeocurrent vectors (in degrees) derived from the geometry of channel structures in the Upper Old Red Sandstone and Inverclyde Group at Pennyseorach (P; data from this study) and at Machrihanish (M; data from Jutras, 2017).