The onset of the Permo-Carboniferous glaciation: reconciling global stratigraphic evidence with biogenic apatite $\delta^{18}$O records in the late Viséan.

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Abstract. The $\delta^{18}$O values of phosphatic microfossils recovered from NW Ireland are used to determine the timing and magnitude of cooling associated with the onset of the Carboniferous glaciation. Microfossil fish $\delta^{18}$Oapatite demonstrates a $+2.4\%$ (V-SMOW) shift, which, once corrected for $\delta^{18}$Oseawater changes due to evolving ice-volumes, equates to an approximate 4.5 °C reduction in equatorial sea-surface-temperature (SST) between the basal Asbian and the mid-Brigantian (late Viséan). Both conodont and microfossil fish $\delta^{18}$Oapatite indicate stabilisation of an “Ice-House” climate.
during the Brigantian and into the Serpukhovian. Substantial upper Viséan cooling identified herein is in good agreement with global glacioeustatic records.

Supplementary material: Further information on the palaeogeography, lithostratigraphy and palaeoenvironments of the sections examined as well as the sample composition and analytical methodology of oxygen isotope analyses is available at www.geolsoc.org.uk/SUP00000.
The Permo-Carboniferous glaciation (late Palaeozoic ice age [LPIA]) is recognised as one of the most significant in Earth’s history and has also been identified as an important analogue for modern climate (Montañez, et al. 2007). Despite this, considerable disagreement remains, particularly concerning the timing of the main phase of glaciation. Earlier studies proposed a relatively simplistic protracted glaciation throughout much of the Carboniferous and Permian (e.g. Veevers & Powell 1987). More recently, discrete glacial and temperate episodes have been recognised superimposed on larger-scale climate trends (e.g. Fielding, et al. 2008).

Glaciogenic deposits and erosional surfaces provide, essentially, the only direct evidence for past glaciations. However, significant difficulties are associated with their use in this respect, since they are often undateable, extensively reworked or even completely eroded during subsequent glacial advances (Frank, et al. 2008). For this reason, distal proxies have become popular for reconstructing ancient “Ice-house” phases. By definition though, proxies only provide a substitute record and all of the controlling factors of the 'system' must be well-understood before palaeoclimatic interpretations are attempted.

The proliferation in the use of stable isotopes, particularly those of oxygen, to construct high-resolution records of palaeoenvironmental shifts has demonstrated the potential for well-understood proxy systems. The bulk of published work has focussed on utilising carbonates as isotopic media; however, as ancient carbonates are susceptible to diagenetic alteration, screening of older samples is vital. Although methods have been developed to assist in selecting only well-preserved carbonate samples for analysis (e.g. Mii, et al. 2001), the potential for carbonate alteration has led to an expansion in the use of biogenic phosphate as an alternative isotopic reservoir. The relative high-fidelity of the isotopic signal preserved by biogenic phosphate has been demonstrated through a number of histological and geochemical studies (e.g. Trotter, et al. 2007, Joachimski, et al. 2009). Isotopic analyses of Palaeozoic phosphates are predominantly undertaken on the bioapatite of ichthyolith (fish microfossil) and
conodont elements. The latter represent the only mineralised parts of an extinct group of small, pelagic or nektobenthic, primitive, jawless marine vertebrates (Aldridge, et al. 1993). Importantly, conodont elements have an outer layer of hyaline tissue, which, like ichthyolith enameloid, is densely crystalline and ideal for preserving primary $\delta^{18}O$ signatures.

During the Early Carboniferous, Ireland was located just south of the palaeoequator and marine sediments accumulated across a series of shallow platforms and basins during a transgressive phase spanning the suspected onset of the LPIA. Conodonts and ichthyoliths recovered from five related, late Viséan to Serpukhovian, thermally mature (conodont colour alteration index [CAI] of c. 3.5), sedimentary sequences, were isotopically analysed. The predominantly shallow marine succession examined in NW Ireland represents a unique opportunity to examine the onset of the LPIA due to (i) the relatively expanded temporal record preserved, (ii) commonly occurring ichthyolith and conodont elements and (iii) good biostratigraphical control.

**Results.** The results of oxygen isotope analyses on conodont (n = 12) and ichthyolith (n = 36) apatite samples are presented in Fig. 1. $\delta^{18}O_{\text{ichthyolith}}$ values show an increasing trend from the basal Asbian to the Brigantian, ranging from 15.1 to 19.1‰ (V-SMOW). Conodont and ichthyolith $\delta^{18}O$ values are relatively stable throughout the Brigantian with conodonts demonstrating a slight decrease from the mid-Brigantian into the Serpukhovian (21.1‰ to 20.2‰ V-SMOW). $\delta^{18}O_{\text{ichthyolith}}$ values were found to be relatively consistently depleted in $^{18}O$ by an average of 2.0‰ ±0.6‰ ($1\sigma$, n = 5) in comparison to conodonts recovered from either the same sample or laterally equivalent stratigraphic levels (Fig. 1). Where multiple samples were analysed from the same level, no statistically significant, consistent $\delta^{18}O$ differences were observed which indicate palaeoecological effects.
Discrepancy between conodont and ichthyolith $\delta^{18}$O. A “vital-effect” is discounted as an explanation for the offset between the two phosphatic media analysed since no evidence exists for the fundamental physiological difference between fish and conodonts which would be required to explain the essentially stable discrepancy across the range of taxa analysed. Additionally, an offset of a greater magnitude has been identified between similar fish and conodont taxa in coeval but thermally more mature strata elsewhere in Ireland (Barham 2010).

Neither can palaeoecology explain the 2‰ difference between conodonts and ichthyoliths, since significant overlap is expected in the habitats of the conodonts and fish analysed. The average $\delta^{18}$O offset would hypothetically translate either into a habitat palaeotemperature difference of 8 to 9 °C (Pucéat, et al. 2010) or a significant difference in salinity. It is difficult to conceive such large, consistent, primary $\delta^{18}$O_seawater differences either vertically within the tropical water column or laterally across the predominantly shallow platform studied.

Alternatively, it has been suggested that conodont elements, due to their dense apatite structure (like enamel), more accurately preserve primary environmental signals, whilst the more intrinsically porous Palaeozoic ichthyoliths are prone to isotopic depletion via interaction with relatively $^{18}$O-depleted diagenetic fluids (Barham 2010, Žigaite, et al. 2010). However, the mechanism of a relatively stable diagenetic O-exchange induced isotopic offset is difficult to conceive and inorganic O-exchange with the PO$_4^{3-}$ group occurs very slowly (Blake, et al. 1997). The deposition of $^{18}$O-depleted apatite within the primary pore spaces of ichthyoliths could also account for the observed isotopic offset, although no significant or consistent microscopic evidence for this was observed. $\delta^{18}$O_ichthyolith values were interpreted to be less faithful than those of conodonts due to the more plausible palaeotemperatures derived from $\delta^{18}$O_conodont values. Using the equation of Pucéat et al. (2010), temperatures calculated on $\delta^{18}$O_ichthyolith in part exceeded 50 °C, whilst $\delta^{18}$O_conodont values translate into more viable palaeotemperatures of 30 to 35 °C, considering the palaeogeographic setting of Ireland and
uncertainties in estimating the absolute oxygen isotopic composition of Mississippian seawater (Pucéat, et al. 2010). In addition, $\delta^{18}O_{\text{conodont}}$ values are correlatable: average late Viséan $\delta^{18}O_{\text{conodont}}$ values of 20.7‰ from NW Ireland are compatible with coeval average values of 21‰ reported by Buggisch et al. (2008) from northern Spain. Furthermore, conodont elements consistently appeared lustrous whilst ichthyoliths, in contrast, commonly displayed coarsened, partially recrystallised basal tissue indicating a different preservation of both phosphatic microfossils.

Although $\delta^{18}O_{\text{ichthyolith}}$ values appear to have been affected by diagenesis, the offset from (primary) $\delta^{18}O_{\text{conodont}}$ values is relatively uniform, which is consistent with the comparative work of Barham (2010) and Žigaite et al. (2010). We tentatively suggest that in order to compensate for this diagenetic effect, $\delta^{18}O_{\text{ichthyolith}}$ values may be corrected through comparison with temporally and spatially coeval conodonts. $\delta^{18}O_{\text{ichthyolith}}$ values in this study may therefore be translated by the average offset of +2.0‰ to best estimate their original values and reconstruct a corrected-ichthyolith-conodont $\delta^{18}O$ dataset.

Despite probable diagenetic overprinting of ichthyolith oxygen isotope values, the positive trend in the Asbian may be interpreted as primary and representative of palaeoclimatic conditions since: (i) the steady increase in $\delta^{18}O_{\text{ichthyolith}}$ is statistically unlikely if the data represent a “random walk”, (ii) thermal gradients are insufficient to explain the magnitude of the observed positive trend. Hypothetically, the $\delta^{18}O$ increase through the Asbian could be the sole result of complete overprinting at a relatively low temperature (40 to 50 °C) and a plausible thermal gradient of c. 30 °C/km. However, complete overprinting of $\delta^{18}O_{\text{ichthyolith}}$ values is improbable at these relatively low temperatures without enzyme mediation (Blake, et al. 1997). It might also be expected that complete overprinting would result in lower $\delta^{18}O$ values reflecting the peak temperatures experienced during diagenesis (c. 200°C according to regional CAI values). Furthermore, partial thermal gradient overprinting would require a hypothetical gradient much steeper than that developed in the region (Corcoran & Clayton 2001). Finally, $\delta^{18}O_{\text{ichthyolith}}$ values remain stable through Brigantian strata despite similar thermal gradients,
(iii) $\delta^{18}$O$_{\text{ichthyolith}}$ values from coeval but geographically separate strata are compatible, and (iv) as discussed below, the isotopic evolution identified is palaeoenvironmentally plausible.

**Palaeotemperature and palaeoclimate interpretations.** Regardless of whether absolute $\delta^{18}$O$_{\text{ichthyolith}}$ values can be corrected for an offset, the overall increasing $\delta^{18}$O trend can be interpreted independently in terms of palaeoenvironmental change since the trend retains a primary signal. The positive oxygen isotope shift should, therefore, represent changes in $\delta^{18}$O$_{\text{seawater}}$ associated with the evolution of the depositional environment and the expansion of continental ice-masses, as well as cooling of SST. Changes in local salinity may have affected $\delta^{18}$O$_{\text{seawater}}$ (the interval of highest $\delta^{18}$O$_{\text{apatite}}$ values broadly coincides with the most restricted conditions). However, the majority of the positive $\delta^{18}$O trend is correlated with platform carbonates with no substantial salinity changes being evident from the sedimentology or faunal composition. Furthermore, $\delta^{18}$O$_{\text{apatite}}$ values are relatively stable from the Brigantian onwards despite a large range of lithologies (and environments) being sampled in an often rapidly fluctuating sequence and average $\delta^{18}$O$_{\text{conodont}}$ values from the most restricted depositional interval analysed, are essentially identical to those reported from Spain.

Determining the magnitude of SST cooling requires knowledge of the change in $\delta^{18}$O$_{\text{seawater}}$ as a consequence of the growth of isotopically light ice-masses (Fig. 2). It is proposed that the climate of the early- to mid-Viséan may have been transitional to icehouse (Shi & Waterhouse 2010), i.e. broadly akin to the present ($\delta^{18}$O$_{\text{seawater}} = 0\%$ V-SMOW) or less glaciated ($\delta^{18}$O$_{\text{seawater}} = -0.5\%$ V-SMOW). By Serpukhovian times, ice-sheets are interpreted to have been comparable in extent to the Last Glacial Maximum (LGM; González-Bonorino & Eyles 1995), with $\delta^{18}$O$_{\text{seawater}}$ as high as 1.2\% (Fairbanks 1989). Since this dataset does not continue far into the Serpukhovian, a $\delta^{18}$O$_{\text{seawater}}$ value of 1\% (V-SMOW) is assumed for the peak glacial conditions identified here. This implies that the formation of ice sheets in Gondwana may have accounted for c. 1.5\% of the total 2.5\% increase documented in
\( \delta^{18}O_{\text{apatite}} \). The remaining change of 1‰ is interpreted to reflect approximately 4 to 5 °C cooling, comparable to tropical SST change during the LGM (Beck, et al. 1997). It is arguable that this estimate represents a cooling minimum since the marine lithologies sampled may not capture glacial maxima. This may also explain why no obvious ice-sheet coupled isotopic fluctuation is recorded.

**Comparison of results to other studies.** Fig. 3 compares the results of this work with a number of significant studies on the LPIA. The Viséan-Serpukhovian boundary has been identified as marking the start of significant climate deterioration using sedimentological data (Fig. 1 of Fielding, et al. 2008) and oxygen isotope data (Mii, et al. 2001, Buggisch, et al. 2008). However, late Viséan cooling has recently been suggested based on \( \delta^{18}O \) values of brachiopod shells from Spain (Armendáriz, et al. 2008). More significantly, sedimentary cyclicity and eustatic fluctuations with Milankovitch periodicities have been reported from Asbian and Brigantian strata: (i) in the northwest Irish sections examined (Schwarzacher 1989, Barham 2010), (ii) elsewhere in Ireland and Britain (Wright & Vanstone 2001), (iii) in equivalent Canadian sequences (Giles 2009), (iv) in the stratigraphically significant Arrow Canyon Section in Nevada, America (Bishop, et al. 2009), and (v) elsewhere globally (Rygel, et al. 2008 and references therein). The compatibility of this collective body of work strongly indicates an initiation of cooling before the Viséan-Serpukhovian transition (Fig. 3).

The reasons for the disagreement between supposedly globally representative oxygen isotope records are not entirely clear at present. Despite the usefulness illustrated by isolated studies of low-magnesium brachiopod calcite, the dataset compiled by Frank et al. (2008) demonstrates (i) the significant spread of \( \delta^{18}O_{\text{carbonate}} \) data relative to \( \delta^{18}O_{\text{apatite}} \), and (ii) the incoherence of the trendline, which bears little or no correlation with any other indicators of the LPIA, produced by combining the results of studies from different palaeogeographic areas.
The palaeogeographic spread of samples is a particularly pertinent consideration since the majority of oxygen isotope studies are based on sequences deposited in epeiric seas which, due to their somewhat restricted nature are more susceptible to local palaeoenvironmental-induced heterogeneities in $\delta^{18}$O$_{\text{seawater}}$ (Brand, et al. 2009). It may be inaccurate to compare the absolute values of coeval oxygen isotope analyses from different continental seas since they likely had different $\delta^{18}$O$_{\text{seawater}}$ properties. The sedimentary strata examined in this study were all deposited from the same regional watermass and where stratigraphic overlap exists, $\delta^{18}$O$_{\text{apatite}}$ values are found to be very consistent (Fig. 1). In any case, only the $\delta^{18}$O trend in this study is given particular credence.

Discrepancies between studies utilising different fossil hardparts may be explained by currently unrecognised physiological effects or differential diagenetic susceptibilities. More generally, inadequate or different bio- and lithostratigraphic constraints and incomplete stratigraphic resolution of the extremely dynamic climate system may explain conflicting results. In the case of the comprehensive $\delta^{18}$O$_{\text{apatite}}$ dataset of Buggisch et al. (2008), an inability to correlate late Viséan to early Serpukhovian isotopic curves may be explained by (i) the variable diagenetic conditions experienced by the Cantabrian Sections (CAI 1.5 to 7), and/or (ii) difficulties associated with precisely plotting data from several condensed Cantabrian Sections. This paper is based on over 2.5 times as much data, within a stratigraphy which is approximately 20 times more expanded, than that of Buggisch et al. (2008), making for a more resolved picture of climate dynamics during this interval. However, the discrepancies between the various studies clearly indicate the need for more research during this critical climatic interval.

**Implications for the onset of the LPIA.** The correlation between increasing $\delta^{18}$O$_{\text{apatite}}$ values and the global litho- and sequence-stratigraphic records of glacioeustatic fluctuations represents the first integration of proxies supporting a late Viséan onset for a significant phase of the LPIA. It is proposed
that rapid climate deterioration began at the base of the Asbian and by Brigantian times the magnitude of glaciation was comparable to the LGM. An “Ice-House” climate state was maintained from mid-Brigantian times and, although limited to a single datum, no rapid degradation of climate apparently occurred at the Viséan-Serpukhovian boundary.
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References


Fig. 1. δ\(^{18}\)O data of conodont and ichthyolith apatite. Columns from the left illustrate western European Stages, British Substages and conodont biozones respectively. Question marks at the Asbian-Brigantian boundary represent a current disagreement in the local biostratigraphy (Sevastopulo & Wyse Jackson 2009, and references therein).

Fig. 2. Illustration of how SST interpretations may vary depending on assumptions of initial (Init.) and temporal evolution (Δ) of the isotopic composition of seawater. Note that the absolute temperature scale is based on the (likely) erroneous assumption that δ\(^{18}\)O\(_{\text{seawater}}\) has not changed through time. The trendlines plotted were produced by combining the conodont and ichthyolith datasets after a +2‰ translation of δ\(^{18}\)O\(_{\text{ichthyolith}}\) values.

Fig. 3. Comparison of climate proxies used to reconstruct the onset of the LPIA. Background shading indicates periods suggested to be glaciated by that particular study. Black arrows mark the proposed onset of significant cooling at the base of the Asbian. All data are plotted relative to the timescale of Davydov et al. (2004).
(a) Init. $\delta^{18}O=-0.5\%$  
$\Delta\delta^{18}O=1.5\%$  
$\Delta T=-4.5^\circ C$

(b) Init. $\delta^{18}O=0\%$  
$\Delta\delta^{18}O=1.2\%$  
$\Delta T=-5.8^\circ C$

(c) Init. $\delta^{18}O=-1.2\%$  
$\Delta\delta^{18}O=2.4\%$  
$\Delta T=-0.7^\circ C$

(d) Init. $\delta^{18}O=0\%$  
$\Delta\delta^{18}O=0\%$  
$\Delta T=-10.8^\circ C$