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Research paper

Diagenetic alteration of the structure and $\delta^{18}O$ signature of Palaeozoic fish and conodont apatite: Potential use for corrected isotope signatures in palaeoenvironmental interpretation

M. Barham [a,*], M.M. Joachimski [b], J. Murray [a], D.M. Williams [a]

[a] Earth and Ocean Sciences, School of Natural Sciences, National University of Ireland, Galway, University Road, Galway, Ireland
[b] GeoZentrum Nordbayern, University of Erlangen-Nürnberg, Schlossgarten 5, D-91054 Erlangen, Germany

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ABSTRACT

The oxygen isotopic compositions of Carboniferous conodonts and fish microfossils (ichthyoliths), from identical samples, were analysed in tandem in order to test whether these phosphatic media can be reliably used for palaeoclimatic reconstruction. The structure of conodonts and of most ichthyoliths analysed are somewhat analogous to the enamel and dentine/bone tissue, respectively, of modern mammals. Therefore, the diagenetic susceptibilities of the taxa analysed may provide important clues to other palaeoclimatic studies utilising a variety of biogenic apatite.

Thermal maturation indices and scanning electron microscopy were used to characterise the preservation of biogenic apatite. Despite a high conodont colour alteration index (CAI) of ~5.5, conodont elements appear to have been only mildly affected by diagenetic alteration. In contrast, ichthyoliths were commonly recrystallised and exhibited diagenetic apatitic overgrowths containing amorphous pyrolytic carbon, interpreted as indicating that at least some overgrowth material derived from the original biogenic apatite.

Diagenetic alteration has resulted in ichthyolith $\delta^{18}O$ values being systematically lower by, on average, 2.9‰ ($1\sigma = \pm 0.3$) relative to conodont apatite. Conodont samples yielded regionally correlatable isotope values, which can be interpreted in terms of more palaeoenvironmentally sensible palaeotemperatures relative to ichthyolith values. Densely crystalline, enamel-like conodont elements are interpreted as the more robust phosphatic medium to preserve original isotopic compositions. The strong correlation ($r = 0.8$) of the $\delta^{18}O$ values of the more structurally pristine conodont and commonly recrystallised ichthyolith apatite, indicates that (i) despite diagenetic lowering of absolute isotope values, original palaeoenvironmental records may be preserved *and* (ii) diagenetic overprinting may result in a stable offset, and therefore be correctable, locally.

1. Introduction

The analysis of oxygen isotopes bound within both biogenic and abiogenic compounds has been a vital tool in palaeoclimatic research since the pioneering work of Epstein et al. (1951, 1953). Marine biomineralising organisms produce hard parts by sequestering elements from their ambient aquatic habitats. Ideally, these compounds should provide a compositional 'snap-shot' of the enclosing water mass, with skeletal oxygen isotope ratios reflecting the temperature and $\delta^{18}O$ of the fluid from which the hardparts precipitated. Most importantly, for reconstructions of palaeoenvironmental variables (such as temperature), the hardparts investigated should have formed in isotopic equilibrium with surrounding waters and the original isotope ratios should not have been subsequently altered.

Biogenic carbonate is the most commonly utilised mineral phase in oxygen isotope studies, predominantly due to its relative abundance and refined analytical methodology. Despite the potential of biogenic phosphate having been recognised many decades ago (e.g. Longinelli, 1965, 1966; Longinelli and Nuti, 1968, 1973a, 1973b; Kolodny et al., 1983; Luz et al., 1984), its use in palaeoclimatic research has remained relatively limited. Advances in analytical procedures (e.g. O'Neil et al., 1994; Trotter et al., 2008; Joachimski et al., 2009) and a number of studies recognising the prospect of precise, unaltered measurements (e.g. Trotter and Eggins, 2006; Trotter et al., 2007; Joachimski et al., 2009) have led to a recent expansion in the use of biogenic apatite for palaeoclimate work. Apatite has particularly found favour in Palaeozoic studies due to difficulties associated with identifying and avoiding diagenetically altered coeval carbonates (Rush and Chafetz, 1990; Wenzel et al., 2000; Joachimski et al., 2004; Bassett et al., 2007).

Previous Palaeozoic isotope studies on biogenic apatite have predominantly utilised conodont apatite, with an elemental composition given as $Ca_5Na_{0.14}(PO_4)_{3.01}(CO_3)_{0.16}F_{0.73}(H_2O)_{0.85}$ by Pietzner et al.

* Corresponding author. Tel.: +353 91495157; fax: +353 91494533.
E-mail addresses: milobarham@yahoo.co.uk (M. Barham), joachimski@geol.uni-erlangen.de (M.M. Joachimski), john.murray@nuigalway.ie (J. Murray), michael.williams@nuigalway.ie (D.M. Williams).

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(1968), rather than the apatite of fish microfossils (ichthyoliths). Conodont elements represent the only mineralised tissues of this extinct jawless early vertebrate group (Sansom et al., 1992, 1994; Aldridge et al., 1993). Conodont elements were arranged in a complex array (collectively termed the "apparatus") within an oral cavity. Internal lamination patterns, coupled with observations of element repair, suggest that elements were at least occasionally enveloped in secretory soft-tissue (Hass, 1941). However, functional analyses and abundant evidence of wear patterning have proven that elements functioned to directly manipulate food items and were exposed during feeding (Purnell and von Bitter, 1992; Purnell, 1993, 1994, 1995). The evidence of prolonged wear and repair indicates that elements were retained rather than replaced and so should reflect an approximate average of the water chemistry the creature was exposed to throughout its life. It should be noted that a slight bias should exist towards the waters inhabited in later life by the particular conodont animal under consideration (though no substantial evidence exists for differing habitats during the creatures lifespan) since the outer layers accreted at this stage are volumetrically more substantial. Results from previous oxygen isotope studies of conodonts (Joachimski et al., 2009), the occurrence of conodonts in dysoxic or anoxic organic-rich shales and the details of trunk and eye musculature (Gabbot et al., 1995), all imply that conodonts were nektobenthic or pelagic. Conodonts should therefore have occupied at least partially overlapping habitats with coeval pelagic fish and the bioapatite of both taxa should have primarily been representative of the temperature and chemistry of ancient seawater. Any significant discrepancy in $\delta^{18}O$ values between conodont and ichthyolith materials could thus pose questions for the general use of biogenic apatite as a palaeoenvironmental proxy.

Despite both comprising apatite, conodont and ichthyolith elements express differing histology (Turner et al., 2010); although the tissues are argued to be sufficiently analogous to support a vertebrate affinity for conodonts (e.g. Dzik, 1986; Sansom et al., 1992, 1994). Conodont elements are covered in enamel-like hyaline tissue (lamellar and densely crystalline), which serves as a barrier to protect the more porous internal "white matter". In contrast, the chondrichthyan and actinopterygian fish remains analysed here have an incomplete and thin (or absent) protective enamel-like (enameloid/vitrodentine or ganoin) veneer covering porous, canal-traversed dentine-like tissue. Therefore, ichthyoliths represent a more "open system" to any percolating fluids and are more susceptible to alteration as a result. Conodont apatite has previously been argued to be resistant to any alteration of the primary isotope signature up to a CAI of 5 (Pucéat et al., 2007; Joachimski et al., 2009), except where enzyme mediated microbiological activity (Blake et al., 1997; Zazzo et al., 2004) or high temperature fluids were involved (Pucéat et al., 2004).

Although conodont elements and ichthyoliths commonly co-occur in disaggregated Palaeozoic rock residues, it is also not unusual for either taxon to be absent for whatever palaeoenvironmental or palaeoecological reasons. Given the importance of stratigraphic resolution and flexibility of sample selection for palaeoenvironmental reconstructions, studies should (ideally) not be restricted to only one phosphatic medium. An over-reliance on conodont apatite limits the lithologies and potential palaeoenvironments which can be analysed. Conodonts were exclusively marine, whereas fish had managed to colonise freshwater habitats by Devonian times at the latest (Smith et al., 2002). Until now, conodont and ichthyolith apatite isotope data were commonly treated as interchangeable (e.g. Joachimski and Buggisch, 2002). However, recent work by Žigaite et al. (2010) has demonstrated a significant ~2‰ isotopic discrepancy between the two taxa (with ichthyoliths yielding lower values). This present study was initiated to assess the mutual compatibility of both (apatitic) oxygen isotope sources and to test whether they can be utilised for palaeoenvironmental analysis with any degree of confidence (particularly after thermal maturation), by examining in detail the structure and isotope signal of the two taxa concurrently.

2. Materials and methods

2.1. Sample acquisition, microfossil extraction and screening

A short (~2 m long) stratigraphic section spanning the Viséan–Serpukhovian (Mississippian, Carboniferous) boundary near the village of Kilnamona in County Clare, Ireland [52.869°N 9.073°W] was examined in detail, with 11 individual horizons sampled for microfossils. The section comprises relatively condensed crinoidal limestones and shales of the Slievenaglasha, Magowna and Clare Shale Formations, deposited north of the Shannon Basin on the periphery of the Burren Platform. CAI values of 5.5, in accordance with other regional maturation indices (Clayton et al., 1989; Goodhue and Clayton, 1999), indicate the sediments have been subjected to a relatively high peak burial temperature.

Limestone samples were processed following a slightly modified version of that described in Armstrong and Brasier (2005). Rock samples (2 kg) were broken into 3–5 cm sized fragments and dissolved in ~6%, buffered formic acid solutions for 24–48 h, after which they were sieved and larger residual rock fragments were returned to a new acid solution. Organic-rich calcareous shales were disaggregated using a combination of alternating desiccation and immersion in hot water as well as dilute oxidant and formic acid treatment. Phosphatic microfossils were recovered from sieved insoluble residues from nine of the 11 sampled horizons, six of these yielded sufficient quantities for mono-generic and even mono-specific isotope analyses.

Conodonts and ichthyoliths were carefully examined under a standard binocular microscope, with the best preserved (most lustrous, with the least visible evidence of recrystallisation) elements being selected for isotope analysis, although some obviously degraded elements were also tested for comparison (Table 1). Only P_1-elements were selected for isotopic investigation, none of which preserved basal bodies, which have been identified as sources of diagenetically altered apatite (Wenzel et al., 2000). Oxygen isotope analyses were performed on the conodont genera *Gnathodus* and *Lochriea*, which were part of an open-water biofacies (Somerville and Somerville, 1998). The actinopterygian scales and palaeoniscid teeth studied belonged to fish lacking any documented palaeohabitat preference; however, the chondrichthyan cladodont and *Thrinacodus* taxa analysed, are reported to have been surface-water dwellers or preferred open shelf environments, respectively (Ginter, 2009).

In order to document microstructural details, a range of conodont and ichthyolith elements, comparable to those selected for isotopic analysis, were examined using a Hitachi scanning electron microscope (SEM) in the Department of Anatomy, NUI, Galway. Additionally, surface textures were investigated in more detail using a LabRAM HR Laser Raman spectrometer in the Martin Ryan Institute of NUI, Galway (beam width 2 μm, wavelength 532 μm).

2.2. Precipitation of silver phosphate and oxygen isotope analysis

Since oxygen is bound within conodont and ichthyolith apatite in three different sites (CO_3^{2-}, H_2O and PO_4^{3-}), it is important that only oxygen within the chemically stable phosphate group is targeted in order to avoid spurious, readily diagenetically influenced results. The phosphate groups within ~1 mg conodont and ichthyolith fractions were chemically converted through a series of steps to Ag_3PO_4, using a slightly modified version of the method developed by O'Neil et al. (1994), as described in Joachimski et al. (2009).

Oxygen isotope analyses were performed on CO gas produced from the purified Ag_3PO_4 samples using a high Temperature Conversion Elemental Analyser (TC-EA) coupled online to a ThermoFinnigan Delta Plus isotope ratio mass spectrometer. All oxygen isotope analyses were carried out in the Stable Isotope Laboratory at the University of Erlangen-Nürnberg, Germany.