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Assessing the fidelity of fossil marine microvertebrate oxygen isotope signatures and their potential palaeo-ecological and -climatic utility

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The biogenic apatite that constitutes conodont elements (feeding structures of extinct marine chordates) has become a preferred analytical target for Palaeozoic O-isotope studies investigating sea hydrology, surface temperature and palaeoenvironmental change. Despite their growing application in geochemical based palaeoenvironmental reconstructions, the paucity or absence of conodont fossils in certain facies necessitates greater flexibility in selection of geologically robust O-bearing analytical compounds. Microvertebrate teeth and scales offer a potential bioapatite substitute for conodonts from the mid Palaeozoic. Microvertebrate bioapatite is particularly advantageous given the groups fossil record extending from the Palaeozoic to the modern day and laboratory demonstration of apatite precipitation in isotopic equilibrium with the aquatic environment in extant species. Furthermore, microvertebrates have occupied fresh to fully marine environments since the mid-Palaeozoic, thus widening the scope in which bioapatite-based O-isotope studies can be undertaken, given conodont restriction to marine environments. However, significant tissue heterogeneity within vertebrates and differential susceptibility of these tissues to diagenetic alteration have been raised as significant barriers for their reliability in O-isotope studies.

Physically and thermally pristine microvertebrate and co-occurring conodont fossils from the Devonian and Carboniferous of the Lennard Shelf, Canning Basin, Western Australia, were analysed using bulk (gas isotope ratio mass spectrometry - GIRMS) and in-situ (secondary ion mass spectrometry - SIMS) methodologies, with the latter technique allowing investigation of specific tissues within vertebrate elements. The $\delta^{18}O_{conodont}$ results obtained are comparable to temporally and palaeolatitudinally equivalent areas in Western Europe and provide a baseline standard for comparison against $\delta^{18}O_{microvertebrate}$ values. Despite an absence of obvious diagenetic influences, bulk analysis of microvertebrate bioapatite (teeth and scales) yielded $\delta^{18}O$ values depleted by 2-4‰ relative to co-occurring conodonts. SIMS analysis of hypermineralised tissues in both scales and teeth produced $\delta^{18}O$ values comparable with those of associated conodonts, and reflective of realistic palaeo- sea-surface-temperatures. The susceptibility of porous fossil tissues to microbial activity, fluid interaction and introduction of mineral precipitates post-formation is demonstrated in microvertebrate dentine, which showed significant heterogeneity and consistent depletion of ^{18}O despite the samples being thermally pristine. The hypermineralised tissues present in both teeth and scales appear resistant to many diagenetic processes and indicate potential for palaeoclimatic reconstructions and palaeoecological investigations where they can be specifically targeted. The development of robust palaeoclimatic records over ~450 Ma will provide vital context to the evolution of Earths biosphere and clearer understanding of likely future responses under a changing climate.