1 Assessing the fidelity of marine vertebrate microfossil $\delta^{18}\text{O}$ signatures and their
2 potential for palaeo-ecological and -climatic reconstructions

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4 Brett Roelofs ^{a,*}, Milo Barham ^{a,b}, John Cliff ^c, Michael Joachimski ^d, Laure Martin ^e
5 and Kate Trinajstić ^{b,f}

6

7 ^aDepartment of Applied Geology, Curtin University, GPO Box U1987, Perth, WA
8 6845, Australia

9 ^bThe Institute for Geoscience Research (TIGeR), Department of Applied Geology,
10 Curtin University, GPO Box U1987, Perth, Australia

11 ^cEnvironmental Molecular Science Laboratory (EMSL), Pacific Northwest National
12 Laboratory, P.O. Box 999 Richland, WA 99352, USA.

13 ^dGeoZentrum Nordbayern, University of Erlangen-Nuremberg, Schlossgarten 5,
14 91054 Erlangen, Germany

15 ^eCentre for Microscopy, Characterisation and Analysis (CMCA), The University of
16 Western Australia, Perth, WA 6009, Australia

17 ^fDepartment of Environment and Agriculture, Curtin University, GPO Box U1987,
18 Perth, WA 6845, Australia

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26 ABSTRACT

27 Conodont biogenic apatite has become a preferred analytical target for oxygen
28 isotope studies investigating ocean temperature and palaeoclimate changes in the
29 Palaeozoic. Despite the growing application in geochemically-based
30 palaeoenvironmental reconstructions, the paucity or absence of conodont fossils in
31 certain facies necessitates greater flexibility in selection of robust oxygen-bearing
32 compounds for analysis. Vertebrate microfossils (teeth, dermal denticles, spines)
33 offer a potential substitute for conodonts from the middle Palaeozoic. Vertebrate
34 bioapatite is particularly advantageous given a fossil record extending to the present
35 with representatives across freshwater to fully marine environments, thus widening
36 the scope of oxygen isotope studies on bioapatite. However, significant tissue
37 heterogeneity within vertebrates and differential susceptibility of these tissues to
38 diagenetic alteration have been raised as potential problems affecting the reliability
39 of the oxygen isotope ratios as palaeoclimatic proxies. Well-preserved vertebrate
40 microfossils and co-occurring conodont fossils from the Upper Devonian and Lower
41 Carboniferous of the Lennard Shelf, Canning Basin, Western Australia, were
42 analysed using bulk (gas isotope ratio mass spectrometry, GIRMS) and in-situ
43 (secondary ion mass spectrometry, SIMS) methodologies, with the latter technique
44 allowing investigation of specific tissues within vertebrate elements. The $\delta^{18}\text{O}_{\text{conodont}}$
45 results may be interpreted in terms of palaeolatitudinally and environmentally
46 sensible palaeo-salinity and -temperature and provide a baseline standard for
47 comparison against vertebrate microfossil $\delta^{18}\text{O}$ values. Despite an absence of
48 obvious diagenetic modification, GIRMS of vertebrate denticles yielded $\delta^{18}\text{O}$ values
49 depleted in ^{18}O by 2-4 ‰ relative to co-occurring conodonts. SIMS analysis of
50 dentine tissues exhibited significant heterogeneity, while hypermineralised tissues in

51 both scales and teeth produced $\delta^{18}\text{O}$ values comparable with those of associated
52 conodonts. The susceptibility of permeable phosphatic fossil tissues to microbial
53 activity, fluid interaction and introduction of mineral precipitates post-formation is
54 demonstrated in the dentine of vertebrate microfossils, which showed significant
55 heterogeneity and consistent depletion in ^{18}O relative to conodonts. The
56 hypermineralised tissues present in both teeth and scales appear resistant to many
57 diagenetic processes and indicate potential for palaeoclimatic reconstructions and
58 palaeoecological investigations.

59

60 Keywords: SIMS; GIRMS; apatite; temperature; histology; oxygen-isotopes

61

62 **1. Introduction**

63 The Palaeozoic marine oxygen isotope record is punctuated by a series of
64 excursions and perturbations reflecting climatic events that are often associated with
65 significant biological reorganisations (e.g. Brand, 1989; Gruszczyński et al., 1989;
66 Caplan and Bustin, 1999; Veizer et al., 1999; Jeppsson et al., 2002; Joachimski and
67 Buggisch, 2002; Kaiser et al., 2006; Trotter, 2008; Schobben et al., 2015).
68 Fluctuations in the oxygen isotope record have been elicited from analysis of marine
69 organisms with the ability to precipitate mineralised tissues in isotopic equilibrium
70 with the ambient water. The shells of Palaeozoic low-Mg calcite brachiopod taxa
71 have been commonly used (Popp et al., 1986; Veizer et al., 1986, 1997; Brand, 1989,
72 2004; Carpenter et al., 1991; Hays and Grossman, 1991; Wadleigh et al., 1992;
73 Azmy et al., 1996; Mii et al., 1997, 1999; Van Geldern et al., 2006; Korte et al.,
74 2008) due to their relative abundance, ease of sampling and the relative resistance of
75 low-Mg calcite, compared to aragonite or high-Mg calcite, to post-mortem

76 modification. Recent work however has shown that even low-Mg calcite is highly
77 susceptible to diagenesis over time (Cummins et al., 2014). This issue is
78 compounded by imperfect screening methods for the identification of recrystallised
79 calcite, which may cause resetting of oxygen isotope values (e.g. Wenzel et al.,
80 2000). In addition, O-isotope heterogeneity has been identified in a number of
81 brachiopod shells, indicating fractionation is occurring during the formation of these
82 hard tissues (e.g. Auclair et al., 2003; Yamamoto et al., 2011; Rollion-Bard et al.,
83 2016). The typically sessile ecology of brachiopods also means that each analysis
84 must be independently considered in the context of the specific temperature and
85 chemistry of the water depth it inhabited. Consequently, this limits the comparison
86 of oxygen isotope signatures to brachiopod taxa occupying similar ecological niches
87 (Popp et al., 1986; James et al., 1997).

88 Bioapatite offers a more physically and chemically resistant oxygen-bearing
89 alternative to brachiopod calcite due to a greater mineral hardness and stability of the
90 P-O bond in PO_4^{3-} (e.g., Grimes et al., 2003; Joachimski et al., 2004). The
91 mineralised feeding elements of conodonts (Lindström, 1974; Dzik, 1991;
92 Goudemand et al., 2011) comprise a relatively homogenous chemical composition
93 $(\text{Ca}_5\text{Na}_{0.13}(\text{PO}_4)_{3.01}(\text{CO}_3)_{0.16}\text{F}_{0.73}(\text{H}_2\text{O})_{0.85})$ (Pietzner et al., 1986) and have become
94 increasingly used in oxygen isotope studies. Despite a non-ubiquitous internal
95 structure among all taxa (Donoghue, 1998; Trotter et al., 2007), the mineralised
96 element crowns typically comprise a translucent finely crystallised hyaline tissue and
97 an inner albid tissue (Lindström, 1964; Pietzner et al., 1968; Barnes et al. 1973;
98 Donoghue, 1998; Trotter et al., 2007; Jones et al., 2012). Analysis of their
99 hypermineralised tissues indicates conodont elements offer greater uniformity in
100 $\delta^{18}\text{O}$ values in comparison to those obtained from brachiopod calcite (e.g. Wallace

101 and Elrick, 2014). Consistent oxygen isotope signatures have been observed between
102 conodont genera belonging to different biofacies in the Late Devonian (Joachimski
103 et al., 2009) and Carboniferous (Joachimski and Lambert, 2015), supporting a shared
104 near sea-surface marine habitat and free swimming lifestyle, as suggested from their
105 biology (e.g. Gabbott et al., 1995). This observation may be dependent on location,
106 time period and genera analysed, as recent work on Ordovician (Quinton and
107 Macleod, 2014), Permian (Joachimski et al., 2012) and Triassic (Trotter et al., 2015)
108 conodonts has shown discernible differences in $\delta^{18}\text{O}$ values between some genera.
109 Despite some taxon-specific discrepancies in $\delta^{18}\text{O}$, correlatable oxygen isotope ratios
110 have proven useful in wider geographical comparisons (e.g. Joachimski et al., 2009).

111 The biostratigraphic utility and widespread distribution and abundance of
112 conodont elements in many marine deposits has facilitated the development of a
113 temporally resolved isotope record spanning many significant faunal reorganisations
114 associated with climatic perturbations from the Ordovician (Trotter et al., 2008) to
115 the Triassic (Joachimski et al., 2009; Rigo et al., 2012; Sun et al., 2012; Trotter et al.,
116 2015). However, conodont fossils are not ubiquitous in all facies, limiting their
117 potential as a sea surface temperature proxy in many regions. Even where present, a
118 paucity of conodont elements can preclude preferred single genera sample analysis
119 and fine resolution sampling due to minimum sample mass requirements in standard
120 analytical methodologies. As a consequence of these limitations, other common,
121 diagenetically resistant oxygen-bearing compounds must be identified to expand
122 accurate palaeoenvironmental interpretations across different temporal intervals and
123 depositional settings.

124 We studied a range of vertebrate microfossil elements using GIRMS to
125 determine the stability of biogenic phosphate over geological timescales, as well as

126 the degree to which ecology and diagenesis influence oxygen isotope ratios in
127 different vertebrate microfossil remains. Secondary ion mass spectrometry (SIMS)
128 analysis was applied to test whether all vertebrate microfossil tissues are equally
129 prone or resistant to alteration of their O-isotopic ratios. In order to establish the
130 validity of vertebrate microfossil $\delta^{18}\text{O}$ signatures and their potential use as
131 palaeoclimatic indicators, the oxygen isotope ratios of vertebrate microfossils were
132 compared with those of co-occurring conodonts. Both GIRMS and SIMS analyses
133 were undertaken on Frasnian (Upper Devonian) conodont samples as well as
134 multiple Famennian (Upper Devonian) and Tournaisian (Lower Carboniferous)
135 conodont and vertebrate remains to i) document any potential discrepancies between
136 the two methods and; to ii) identify potential causes of disruption of primary oxygen
137 isotope signatures in different vertebrate tissues.

138

139 **2. Background**

140 *2.1. Vertebrate microfossil histology*

141 Marine vertebrate microfossils (typically less than 5 mm in size) most
142 commonly comprise teeth, scales and fin spines. The hard tissues of vertebrates are
143 highly heterogeneous, consisting of three broad types; bone, dentine and enamel.
144 These tissues are differentiated by the levels of mineralisation and organic matter
145 content. Bone comprises a 50-70 % mineralised component with 20-40 % organic
146 matter and 5-10 % water (Clarke, 2005). Dentine is approximately 70 % mineralised
147 with 20-24 % protein and 6-10 % water, whereas enamel is highly mineralized (96
148 %) with only 1 % protein and approximately 3 % water, which is present on or
149 between the hydroxyapatite crystals (Stack, 1955; Pasteris et al., 2008; Goldberg et
150 al., 2012; Hand and Frank, 2014). The O-hosting sites within biogenic apatite also

151 differ significantly between vertebrate hard tissues (Pasteris et al., 2008). Bone and
152 dentine comprise 6 and 5 wt % CO_3^{2-} respectively, with only ~3.5 wt % present in
153 enamel (LeGeros and LeGeros, 1983; Cerling and Sharp, 1996). This low CO_3^{2-}
154 concentration compared to dentine and bone, in addition to a high degree of
155 mineralisation (>80 wt %, Li, 2013), makes the hypermineralised tissues (enamel,
156 enameloid, ganoine and acrodin) present in vertebrate teeth and scales more resistant
157 to physical and chemical alteration. Detailed information on tooth and scale
158 histology of analysed taxa is provided in the supplementary material (A1-VH).

159

160 *2.2. Application of vertebrate tissues in Palaeozoic oxygen isotope studies*

161 Oxygen isotopes of vertebrate bioapatite tissues have been previously used to
162 determine palaeoenvironmental conditions in the Palaeozoic (Kolodny and Luz,
163 1991; Barham, 2012a; Fischer et al., 2013) and Mesozoic (Kolodny and Raab, 1988;
164 Kolodny and Luz, 1991; Lécuyer et al., 1993; Pucéat et al., 2003; Billon-Bruyat et
165 al., 2005; Fischer et al., 2012). Applying gas isotope ratio mass spectrometry
166 (GIRMS) to Palaeozoic vertebrate fossils, however, has produced inconsistent results
167 when whole fossils are used. Analysis of Upper Devonian actinopterygian teeth
168 (Joachimski and Buggisch, 2002) initially suggested that original oxygen isotope
169 ratios were preserved in the tooth apatite. Other works however, have revealed that
170 Palaeozoic vertebrate teeth and dermal denticles are typically depleted in ^{18}O
171 (relative to conodont elements) between 2.4 and 2.9 ‰ (Barham et al., 2012a;
172 Žigaite et al., 2010). This has led to the suggestion that vertebrate microfossil
173 elements are susceptible to diagenetic affects and thus may not preserve original
174 isotopic signatures (Barham et al., 2012a). However, given that secondary alteration

175 may be tissue-specific or screened and subsequently avoided, the potential still exists
176 for the geochemistry of these fossils to serve as a palaeoclimatic archive.

177

178 **3. Materials and methods**

179 *3.1. Sample collection, processing and imaging*

180 Upper Devonian vertebrate microfossils are common in the distal slope facies
181 of the Virgin Hills Formation (late Frasnian - middle Famennian; Fig. 1; Playford et
182 al., 2009; Trinajstić and George, 2009; Trinajstić et al., 2014; Roelofs et al., 2015)
183 and in the conodont-poor facies of the Fairfield Group (Upper Devonian-Lower
184 Carboniferous) (Roelofs et al., 2016; Thomas, 1957, 1959). Twenty kilogram
185 samples were collected from single beds at Horse Spring (18°11'41" S, 126°01'69"
186 E) (sample prefix VHS), Oscar Hill (18°04'07" S, 125°26'41" E) (sample prefixes
187 OH, Si) and Laurel Downs (18°01'37" S, 125°18'43" E) (sample prefixes 1984,
188 CCA, MT and MTM) (Fig. 1) and processed using a buffered 10 % acetic acid
189 solution (following the methodology of Jeppsson et al., 1999). The rock samples
190 were disaggregated as whole rocks with rinsing occurring every 24-48 h, depending
191 on the degree of disaggregation. This process was repeated, with fresh 10 % buffered
192 acetic acid, until the rocks had been sufficiently broken down to allow for the
193 removal of isolated fossils. Residues were rinsed and sieved (0.125 mm sieve) to
194 further separate microfossils before picking the >0.125 mm fraction under a Nikon
195 stereomicroscope. Detailed examination of microfossils was performed using a
196 Hitachi TM-3030 desktop Scanning Electron Microscope (SEM) at Curtin
197 University with accelerating voltages ranging from 5-15 kV and variable pressures.
198 Eight larger holocephalan teeth (>10 mm mesio-distally) were recovered directly
199 from the disaggregated rock residues. A single tooth (MTM1-H9) was exposed from

200 the rock sample along its labial face and extracted prior to processing. Additional
201 imaging of analysed specimens was performed using a Leica stereomicroscope
202 camera at the Western Australian Museum.

203 Horse Spring samples yielded 200 conodont elements corresponding to
204 Conodont Zone (CZ) 11 (Frasnian; Klapper, 1989). Conodont yields from Oscar Hill
205 samples taken for this study yielded mainly undiagnostic elements with a single long
206 ranging Famennian conodont *Spathognathodus acidentatus* recovered. Previous
207 sampling by Nicoll and Druce (1979) indicated a latest Famennian age (*praesulcata*
208 Conodont Zone) for outcrop at Oscar Hill. Tournaisian rock samples (Table 2) were
209 collected from a bioclastic limestone bed of the Laurel Formation (sample number
210 1984-04), exposed approximately 35 km northwest of the town of Fitzroy Crossing
211 (Fig. 1). A Tournaisian age is supported by the presence of the conodont taxa
212 *Clydagnathus cavusformis* and *Bispathodus aculeatus*, and is consistent with
213 previous age determinations (Druce and Radke, 1979; Nicoll and Druce, 1979). A
214 refinement of early Tournaisian for the sampled area is indicated by the overlap of
215 shark species *Thrinacodus ferox*, *Protacrodus aequalis* and *Protacrodus* sp. 1
216 (Roelofs et al., 2016).

217

218 3.2. Analytical methodology

219 The GIRMS method has conventionally been used to accurately determine
220 the $\delta^{18}\text{O}$ values of pooled apatite fossils through the analysis of chemically purified
221 Ag_3PO_4 . To obtain ~1 mg of fossil material required for replicate analyses, samples
222 comprising multiple vertebrate microfossil elements, or single elements comprising
223 multiple tissue types, are often required. The incorporation of different fossil tissues
224 within analyses reduces data confidence as tissue geochemistry is differently affected

225 by biological processes including organism physiology (e.g. Thorrold et al. 1997),
226 post-mortem microbial activity (Blake et al., 1997, 1998; Zazzo et al., 2003) as well
227 as physico-chemical influences such as diagenesis (e.g. Iacumin et al., 1996).

228 The use of laser ablation techniques on biogenic phosphate has demonstrated
229 the potential to measure and quantify variation in $\delta^{18}\text{O}$ from in-situ tissues (Cerling
230 and Sharp, 1996). Such in-situ techniques minimise potential contamination and
231 alteration of samples during preparation and reduce the required sample size (Brady,
232 2004). Trotter et al. (2008) later established the use of secondary ion mass
233 spectrometry (SIMS) on biogenic phosphate to elicit reliable $\delta^{18}\text{O}$ values from both
234 fossil and modern tissue. This success of this work has been replicated with a
235 particular focus on conodonts, in reconstructing Palaeozoic paleoclimates and
236 paleoceanographies (Rigo et al., 2012; Wheeley et al., 2012; Trotter et al., 2015;
237 Chen et al., 2016). Whether this technique can be applied to Palaeozoic vertebrates
238 and the preservation of $\delta^{18}\text{O}$ in highly heterogeneous fossil tissues has not been
239 thoroughly explored. Application of this technique to modern shark teeth (Trotter et
240 al., 2008; Žigaite and Whitehouse, 2014) has shown preservation of original oxygen
241 isotope signatures in hypermineralised tissues as well as heterogeneity and depletion
242 of ^{18}O within the more permeable dentine (Žigaite and Whitehouse, 2014).

243 Following the approach of Trotter et al. (2008), aliquots of a single large
244 fragment of Durango apatite crystal were used as an oxygen isotope standard for
245 comparison between GIRMS and SIMS methods and published data. It should be
246 noted that recent work by Sun et al. (2016) has highlighted a 4.4 ‰ inter-crystal $\delta^{18}\text{O}$
247 variation between Durango apatite crystals as well as intra-crystal variation that
248 ranged from 0.7-1.8 ‰. To minimise the potential effects of crystal heterogeneity,
249 ion probe spots were concentrated on small areas within small fragments of a single

250 crystal. Additionally, as this work focuses on intra-fossil variation as well as
251 comparing fossils on the same mount, potential variation between crystal fragments
252 does not significantly alter the conclusions of this work.

253

254 *3.2.1. GIRMS oxygen isotope analyses*

255 Stable oxygen isotope ratios were determined on conodont and vertebrate
256 microfossil material at the Stable Isotope Laboratory of the University of Erlangen-
257 Nürnberg, Germany, following a modified version of the procedure developed by
258 O'Neil et al. (1994) and described in Joachimski et al. (2009). Conodont, vertebrate
259 microfossil and Durango apatite samples (0.7-2.0 mg) were chemically converted to
260 trisilverphosphate (Ag_3PO_4) and the oxygen isotope ratios of ~0.2 mg sample
261 aliquots were analysed as CO produced in a high temperature conversion elemental
262 analyser (TC-EA) attached on-line to a ThermoFisher Delta V Plus mass
263 spectrometer. Oxygen isotope compositions are reported in δ notation in ‰ relative
264 to Vienna Standard Mean Ocean Water (VSMOW) (Table 1). The analyses were
265 calibrated by performing a two-point calibration (Paul et al., 2007) using NBS 120c
266 (+21.7 ‰) and a commercial Ag_3PO_4 (+9.9 ‰). All standards were calibrated to
267 TU1 (+21.11 ‰) and TU2 (+5.45 ‰; Vennemann et al., 2002). A laboratory
268 standard, as well as NBS 120c were used as control standards and processed together
269 with the samples. Replicate analyses of the international standard NBS 120c and
270 internal laboratory standards were performed between every four unknowns, as well
271 as at the start and end of each measuring day to monitor accuracy and
272 reproducibility. Reproducibility was typically ± 0.2 ‰ (1σ). NBS 120c was measured
273 as $+21.7 \pm 0.1$ ‰ (1σ , $n = 12$) VSMOW (within uncertainty reported by Laporte et
274 al., 2009). Most samples were measured in triplicate, with limited Ag_3PO_4 from

275 samples OH4-C and 1984-C only allowing duplicate and single analyses,
276 respectively.

277 3.2.2. SIMS oxygen isotope analyses

278 Conodont and vertebrate microfossils, with fragments of a Durango apatite
279 crystal were mounted on double sided tape attached to standard glass plates. Large
280 holocephalan teeth were cut labio-lingually using a Dremel rotary tool and ground
281 flat with 1200 grit sandpaper prior to mounting on the tape along the smooth surface.
282 Struers EpoFix epoxy resin was used to form standard one-inch round mounts and
283 then polished to expose the desired tissues using successively finer polishing cloths
284 to a 1 μm finish. The mounts were then carefully cleaned with detergent, distilled
285 water and isopropanol in an ultrasonic bath and coated with gold (30 nm in
286 thickness) prior to SIMS analyses.

287 Oxygen isotope ratios were determined using a Cameca IMS 1280 multi-
288 collector ion microprobe located at the Centre for Microscopy, Characterisation and
289 Analysis (CMCA), University of Western Australia (UWA) in March and November
290 2014. Analyses were performed with a ca. 2.5 nA Cs^+ beam with a total impact
291 energy of 20 keV rastered on a ca. 20 x 20 μm area on the sample surface.
292 Instrument parameters included a magnification of 130 $\times$ between the sample and
293 field aperture (FA), 400 μm contrast aperture (CA), 4000 μm FA, 110 μm entrance
294 slit, 400 μm exit slits, and a 40 eV band pass for the energy slit with a 5 eV gap
295 toward the high energy side. Secondary O^- ions were accelerated to 10 keV and
296 analysed with a mass resolving power of approximately 2200 using dual Faraday
297 Cup detectors. A normal-incidence electron gun was used to provide charge
298 compensation and NMR regulation was employed for magnetic field control.

299 Ten seconds of pre-sputtering was followed by automatic centering of the
 300 secondary beam in the FA and CA. Each analysis consisted of 20 four-second cycles,
 301 which gave an average internal precision of ± 0.2 ‰ (1σ). Analytical sessions were
 302 monitored for drift and precision using a bracketing standard (Durango apatite; $+9.9$
 303 ± 0.3 ‰, (1σ , $n = 9$); characterised via GIRMS of three samples analysed in triplicate
 304 from the same crystal) for every six sample analyses. Instrumental mass fractionation
 305 (IMF) was corrected using Durango apatite following the procedure described in
 306 Kita et al. (2009). The spot-to-spot reproducibility (external precision) was typically
 307 ± 0.3 - 0.4 ‰ (1σ) on Durango apatite during all of the analytical sessions, except two
 308 sessions at ± 0.2 ‰ (sample HT2) and ± 0.5 ‰ (sample MVM2). Uncertainty on each
 309 spot was calculated by propagating the errors on instrumental mass fractionation
 310 determination and internal error on each sample data point. The resulting uncertainty
 311 was typically between ± 0.3 and ± 0.6 ‰ (1σ). Raw $^{18}\text{O}/^{16}\text{O}$ ratios and corrected $\delta^{18}\text{O}$
 312 (reported relative to VSMOW) are presented in Table 2.

313

314 **4. Results**

315 *4.1. Fossil preservation*

316 Visual inspection (both macro- and microscopic) confirmed conodont
 317 elements were well-preserved, showing no evidence of coarsening crystallites,
 318 pitting, overgrowths or other visible signs of diagenetic modification (Fig. 2; Nöth,
 319 1998). Vertebrate microfossil elements are similarly apparently well-preserved with
 320 smooth lustrous surfaces present on the cusps of teeth and dermal denticle crowns. In
 321 cross section, the dentine of all teeth was light grey to white in colour with the
 322 exception of sample MTM1-H9, which showed a dark grey discolouration around
 323 one margin that correlates to the previously exposed labial surface of the tooth.

324 Reddish coloured staining is present within the basal tissue in sample MTM1-H1,
325 along with calcite cement in some of the pore canals that extend from the cusp
326 surface to the basal tissue.

327

328 4.2. *GIRMS $\delta^{18}\text{O}$ analysis of vertebrate microfossil elements*

329 The $\delta^{18}\text{O}$ values of Famennian vertebrate microfossils ranged from +16.2-
330 17.1 ‰ (VSMOW) (Table 1) with a mean of +16.7 ‰. The $\delta^{18}\text{O}$ values obtained
331 from the Tournaisian vertebrate microfossil samples are more variable than
332 Famennian values, ranging from +15.7 to 19.1 ‰. The largest disparity in $\delta^{18}\text{O}$ was
333 measured in the outer cusp tissue of Tournaisian holocephalan teeth (+16.0 to 19.1
334 ‰, mean of +17.8 ‰; Fig. 3). Similar $\delta^{18}\text{O}$ values were obtained from ctenacanthid
335 (+16.0 ‰) and protacrodont (+17.1 ‰) scales from the Famennian. Inter-taxa
336 variation of <1.2 ‰ was found for Tournaisian acanthodian (+17.0 ‰), lungfish
337 (+16.5 ‰), ctenacanthiform (+16.9 ‰), protacrodont (+16.1 and +17.2 ‰) and
338 palaeoniscoid scales (+19.0 ‰) (Table 1). Significant intra-specific disparity in $\delta^{18}\text{O}$
339 values within Tournaisian vertebrate scales was seen between protacrodont scales
340 recording values of +16.1 and +17.2 ‰. The lowest $\delta^{18}\text{O}$ values were recorded in
341 Tournaisian palaeoniscoids, with values of +15.7 (radial bone) and +15.9 ‰ (tooth)
342 (Fig. 3). However, $\delta^{18}\text{O}$ values of associated palatal teeth were consistently higher at
343 +18.0 ‰ (sample 1984-B) and +18.1 ‰ (sample 1984-H).

344

345 4.3. *SIMS $\delta^{18}\text{O}$ analyses*

346 In-situ oxygen isotope analyses were performed on three late Famennian and
347 two early Tournaisian conodont elements (Table 2). Conodont $\delta^{18}\text{O}$ values from
348 averaged spot analyses on three late Famennian S-elements range from +18.7 to 20.8

349 ‰ (Table 2), with an average value of $+19.6 \pm 0.5$ ‰. Two to five individual spots
 350 were analysed on the blades of the S-elements with a deviation between spots on
 351 each element ranging from 0 to $+1.0$ ‰ (Table 2). Two P₁ elements (*sensu* Purnell et
 352 al., 2000) of the early Tournaisian conodont *Clydagnathus cavusformis* produced
 353 average $\delta^{18}\text{O}$ values of $+19.9$ ‰ (± 0.4 ‰, $n = 4$) and $+20.9$ ‰ (± 0.9 ‰, $n = 5$).

354 Clusters of three to five spots (within an area of $<1 \text{ mm}^2$), were focused on
 355 enameloid, dentine and basal tissues of four holocephalan teeth (Fig. 4).
 356 Occasionally, one or more analytical spots missed the tissue targeted and average
 357 values were determined from remaining spot analyses. Average $\delta^{18}\text{O}$ values of spots
 358 ($n = 5$) targeting enameloid tissues in tooth MTM1-H1 produced values for spot
 359 clusters of $+9.2 \pm 0.9$ and $+18.0 \pm 0.2$ ‰ (Fig. 5A). The same enameloid tissue in
 360 sample MTM1-H9 was analysed, with individual clusters comprising two to three
 361 spots from four areas of the tooth (Fig. 5B) producing average $\delta^{18}\text{O}$ values between
 362 $+21.4 \pm 0.7$ and $+21.8 \pm 0.1$ ‰. Dentine was analysed in all four holocephalan teeth
 363 with an average $\delta^{18}\text{O}$ value of $+17.9 \pm 1.4$ ‰ (1σ , $n = 35$). No consistent differences
 364 in $\delta^{18}\text{O}$ are present between upper dentine, close to the occlusal surface of the tooth,
 365 and lower dentine tissues, located toward the basal body (Fig. 5). The enamel of
 366 three protacrodont teeth was tested using clusters of three to four spots and exhibited
 367 average $\delta^{18}\text{O}$ values of $+17.9 \pm 0.4$ ‰ ($n = 3$), $+18.9 \pm 0.2$ ‰ ($n = 3$) and $+19.2 \pm 0.3$
 368 ‰ ($n = 3$) (Figs. 4, 6b). The dentine tissues in one tooth (1984-Dh1) showed a
 369 progressive depletion in ^{18}O from near the cusp apex ($+16.2 \pm 0.2$ ‰) to less
 370 mineralised dentine in the basal tissues ($+13.8 \pm 0.5$ ‰) (Fig. 4). A similar decrease
 371 in $\delta^{18}\text{O}$ is seen over 10 individual spots in an *Ageleodus* shark tooth (AG1, Fig. 6C),
 372 which presented a general trend in $\delta^{18}\text{O}$ from $+17.3$ ‰ in the cusp dentine, to $+8.3$
 373 ‰ in the basal tissue. Three sets of analyses were performed on the dentine tissue of

374 three cladodont cusps, which showed average $\delta^{18}\text{O}$ values between $+7.5 \pm 2.1$ ($n = 4$)
375 and $+11.5 \pm 2.7$ ($n = 4$) ‰ (Table 2).

376 Two sets of $\delta^{18}\text{O}$ values were recorded from different areas on a Famennian
377 shark spine, a series of three spots near the margin of the spine (average $+16.5 \pm 0.3$
378 ‰, $n = 4$) and three spots located centrally ($+18.5 \pm 0.4$ ‰, $n = 3$). An average $\delta^{18}\text{O}$
379 value of $+20.3$ ‰ was recorded for scale crown surface tissues across different taxa
380 from the Tournaisian samples. A difference of up to 2.1 ‰ was observed between
381 spots on individual tissues. Dentine tissues from a Famennian protacrodont scale
382 ($+12.8 \pm 1.0$ ‰, $n = 2$), Tournaisian lungfish ($+8.8 \pm 1.9$ ‰, $n = 3$ and $+14.9 \pm 1.3$ ‰,
383 $n = 5$) and an acanthodian scale ($+16.7 \pm 1.3$ ‰) recorded $\delta^{18}\text{O}$ values consistently
384 lower than the tissues close to the crown surfaces of the scales.

385

386 **5. Discussion**

387 *5.1. Comparison of GIRMS and SIMS $\delta^{18}\text{O}$ analyses*

388 Traditional GIRMS targets the PO_4^{3-} group and eliminates analysis of any
389 less stable oxygen compounds (carbonate, organics, water) (Firsching, 1961; Wright
390 and Hoering, 1989; Crowson et al., 1991; O’Neil et al., 1994). The use of whole
391 vertebrate microfossils, in order to obtain minimum sample masses (~ 0.3 - 1 mg)
392 required for this method, can be problematic. Potential differences in the O-isotopic
393 signal of fossilised phosphate tissues may be masked when vertebrate bioapatite is
394 homogenised. The highly permeable and porous nature of fossil dentine, which is the
395 bulk component of fossil teeth and dermal denticles, is highly susceptible to physical
396 and chemical alteration (Kohn and Cerling, 2002; Koch et al., 2007). This
397 susceptibility results, in part, from significant porosity and permeability increasing
398 potential isotopic exchange between bioapatite and circulating fluids associated with

399 diagenesis, as well as the potential for microbe mediated phosphate precipitation and
400 alteration (Kolodny et al., 1983; Kastner et al., 1990; Blake et al., 1997, 1998; Zazzo
401 et al., 2003).

402 The use of SIMS, as an alternative method for obtaining targeted $\delta^{18}\text{O}$ data
403 from fossil bioapatite, is advantageous where fossil yields are below the mass
404 required by GIRMS methods and when samples comprise different tissues (Wenzel
405 et al., 2000; Trotter et al., 2008; 2015). However, SIMS indiscriminately analyses
406 any oxygen-bearing compounds, including PO_4^{3-} , CO_3^{2-} and OH^- present within
407 bioapatite (Passey and Cerling, 2006; Aubert et al., 2012). The presence of the CO_3^{2-}
408 anion in bioapatite (either primary or as a secondary cement) can be particularly
409 problematic as it is more susceptible to diagenetic alteration than PO_4^{3-} , with the C-O
410 bond comparably weaker than the P-O bond (e.g. Iacumin et al., 1996).

411 Recent work by Wheeley et al. (2012) suggested $\delta^{18}\text{O}_{\text{conodont}}$ values obtained
412 from SIMS were comparable with those of GIRMS for Silurian conodonts. However,
413 it must be noted, offsets of ~ 1 ‰ between SIMS and GIRMS methods were
414 observed in some Silurian conodont genera (Wheeley et al., 2012). Subsequent work
415 by Trotter et al. (2015) showed an average offset of 0.6 ± 0.2 ‰ between the two
416 methodologies, similar to earlier work of 0.7 ‰ (Trotter et al., 2008). Published data
417 are currently considered insufficient to fully assess the presence and/or reasons for
418 any discrepancies; however, it appears small but measurable offsets exist. Here
419 fragments from a single crystal of Durango apatite were utilised to calibrate SIMS
420 analyses. GIRMS analysis gave an average $\delta^{18}\text{O}$ value of $+9.9$ ‰ (± 0.3 ‰, 1σ) from
421 triplicate analysis of three individual fragments of the same crystal, within error of
422 the published value of $+9.8$ ‰ reported by Rigo et al. (2012). GIRMS analysis of the
423 conodont genera *Ancyrodella* ($+19.0 \pm 0.2$ ‰) indicated a <0.2 ‰ difference when

424 compared to the $\delta^{18}\text{O}$ values obtained from SIMS of both *Ancyrodella* (+19.2 ‰±0.3
425 ‰) and *Palmatolepis* (+19.1 ‰) P₁ conodont elements from the same sample. The
426 $\delta^{18}\text{O}_{\text{conodont}}$ values resolved from the two methods indicate valid comparisons can be
427 made between SIMS and GIRMS analyses within error.

428

429 5.2. Canning Basin $\delta^{18}\text{O}_{\text{conodont}}$ values in a global context

430 The presence of open marine conditions in the Canning Basin, in the Late
431 Devonian and Early Carboniferous, is important if $\delta^{18}\text{O}_{\text{conodont}}$ values are to be used
432 as a globally representative baseline to assess the validity and palaeoenvironmental
433 relevance of $\delta^{18}\text{O}$ values from vertebrate microfossils. The significant faunal
434 cosmopolitanism found in ammonoid (Becker, 2000), conodont (Nicoll and Druce,
435 1979; Klapper, 2006) and vertebrate microfossil taxa (Turner, 1982; Trinajstić and
436 George, 2009; Hairapetian et al., 2015; Roelofs et al., 2015, 2016; Trinajstić et al.,
437 2015) in the Late Devonian and Early Carboniferous suggests that pathways existed
438 for significant faunal exchange. Furthermore, the recovery, from the Lennard Shelf,
439 of globally correlative carbon isotope signatures associated with the Kellwasser
440 Event (Stephens and Sumner, 2003; Playton et al., 2013; George et al., 2014; Hillbun
441 et al., 2015), and presence of a significant regression (Talent et al., 1993) and
442 negative $\delta^{13}\text{C}$ excursion (Andrew et al., 1994) related to the Hangenberg Event, are
443 all suggestive of a local marine system coupled to global oceanic conditions. Despite
444 these indicators of an open marine system, the $\delta^{18}\text{O}_{\text{conodont}}$ values from Frasnian
445 conodont Zone 11 (*jamieae* CZ) in the Canning Basin (+19.1-19.5 ‰) are
446 approximately 1-1.5 ‰ higher than the $\delta^{18}\text{O}_{\text{conodont}}$ values (normalised to NBS 120c
447 = +21.7 ‰) from latitudinally equivalent sites reported in Joachimski et al. (2004,
448 2009). The difference between the Canning Basin CZ 11 values and other sites may

449 be due to local variations in temperature and salinity and demonstrate the importance
 450 of natural global variations in water composition, particularly when constructing
 451 composite isotope curves. In contrast to the Frasnian sample, a paucity of conodont
 452 elements from the Famennian and Tournaisian makes it difficult for well constrained
 453 ages and, therefore, direct comparison of Canning Basin $\delta^{18}\text{O}_{\text{conodont}}$ with coeval
 454 global values. The Oscar Hill locality, from which the Famennian samples were
 455 taken, suggested deposition occurred during the latest Famennian based on conodont
 456 elements (*praesulcata* CZ, Nicoll and Druce, 1979). An average $\delta^{18}\text{O}_{\text{conodont}}$ value of
 457 +19.6 ‰ is comparable to values from other latitudinally similar sites from the
 458 *praesulcata* CZ from the Cantabrian Mountains, Spain (~+19.4 ‰) and Montagne
 459 Noire, France (~+17.6-19.5 ‰) (Buggisch et al., 2008; values were corrected by -0.7
 460 ‰ to account for a difference in the reported $\delta^{18}\text{O}$ of standard NBS 120c). An early
 461 Tournaisian age for the Carboniferous sample was inferred from conodont and
 462 vertebrate microfossil remains. The average $\delta^{18}\text{O}$ value for *C. cavusformis* P₁-
 463 elements tested was +20.4 ± 0.9 ‰. This is similar to the $\delta^{18}\text{O}_{\text{conodonts}}$ from the
 464 *sulcata* CZ interval (~+19.7-20.5 ‰, values were corrected by -0.7 ‰ to account for
 465 a difference in $\delta^{18}\text{O}$ of standard NBS 120c) in the Cantabrian Mountains, Spain
 466 (Buggisch et al., 2008). The results indicate that conodonts from the Frasnian to the
 467 Tournaisian in the Canning Basin are preserving isotopic signatures similar to
 468 conodonts from other pan tropical sites.

469

470 5.3. $\delta^{18}\text{O}$ variation in vertebrate microfossil tissues

471 The enameloid and dentine of four holocephalan teeth, all attributed to the
 472 same species, showed significant differences in $\delta^{18}\text{O}$ values as a result of histology,
 473 and therefore, mineral composition and susceptibility to diagenesis. The dense

474 enameloid tissue present in holocephalan teeth is similar in hardness to that of
 475 enamel (Ishiyama et al., 2012) and comprises the outer layer of the crown as well as
 476 pore linings penetrating the crown (Fig. 5). The $\delta^{18}\text{O}$ values obtained (via SIMS)
 477 adjacent to pore canals produced more consistent results (mean value of $+21.5 \pm 0.2$
 478 ‰ for pore enameloid) than the outer mineralised layer of the crown, where $\delta^{18}\text{O}$
 479 averages of spot clusters varied between $+5.9 \pm 2.2$ and $+19.5 \pm 0.2$ ‰. The
 480 enameloid tissue found along the outer surface of tooth MTM1-H1 (Fig. 5A) shows
 481 slight (spot no. 21-25) to considerably depletion (spot no. 1-5) of ^{18}O compared to
 482 co-occurring conodont $\delta^{18}\text{O}$ values. As this is not seen on the non-exposed side of
 483 the tooth MTM1-H9 from the same sample, it may represent alteration of the outer
 484 tissues prior to burial. There is also the potential for these values to be analytical
 485 artefacts due to topography induced through the differential polishing of the tooth
 486 and resin, or may result from diagenetic alteration, as the more discoloured areas in
 487 the tooth commonly show lower $\delta^{18}\text{O}$ values (Fig. 5B). Recent work has indicated
 488 that apparently well-preserved (i.e. lustrous) hypermineralised fossil tissues (e.g.
 489 Žigaitė et al., 2015) may not necessarily be indicative of pristine geochemistry. The
 490 presence of variable ‘staining’ in the teeth may reflect diagenetic mineralisation or
 491 alteration and may explain the significantly lower $\delta^{18}\text{O}$ values in peripheral
 492 hypermineralised tissues.

493 In general, the pore enameloid (Fig. 5B spot no. 4, 11-13, 17-18) of the
 494 holocephalan teeth analysed appears to more reliably preserve the original oxygen
 495 isotope ratios in comparison to the outer enameloid tissues (Fig. 5B spot no. 1-3, 5-7,
 496 14-16), which are more readily exposed to post-mortem (or post-shedding), as well
 497 as burial, processes. The dentine tissue analysed from four holocephalan (Table 2)
 498 did not show any consistency in $\delta^{18}\text{O}$ values between individual teeth (Table 2). In

499 addition the most significant degree of $\delta^{18}\text{O}$ variation came from a single tooth
 500 (MTM1-H1). Here three areas within the tooth (MTM1-H1) were analysed. The first
 501 cluster of spots (Fig. 5a spot no. 6-10; $+15.8 \pm 0.8 \text{ ‰}$) located in the cusp dentine; the
 502 second spot cluster (Fig. 5a spot no. 11-15; $+19.5 \pm 0.2 \text{ ‰}$) present in an area of
 503 osteodentine; and a third spot cluster in the basal tissue (Fig. 5a spot no. 16-20;
 504 $+17.6 \pm 0.1 \text{ ‰}$). Of these, the spot cluster at the basal area of HTM-H1 produced an
 505 average $\delta^{18}\text{O}$ value ($+19.5 \pm 0.2 \text{ ‰}$ $n = 5$) comparable to average $\delta^{18}\text{O}_{\text{conodont}}$ from the
 506 same sample $+20.3 \pm 0.8 \text{ ‰}$. The high $\delta^{18}\text{O}$ value may indicate that parts of the basal
 507 tissue, even though primarily consisting of permeable dentine, may be capable of
 508 preserving the original isotopic signatures under appropriate conditions.

509 The general structure of acrodin present in the tooth tip of many
 510 palaeonisciform fish is similar to the woven structure of enamel in elasmobranchs
 511 (Ripa et al., 1972; Ørvig, 1978a; Reif, 1985; Sasagawa et al., 2012) and thereby
 512 prospective in terms of resistance to diagenetic modification or disruption of isotopic
 513 signatures. The $\delta^{18}\text{O}$ values obtained from four spot analyses of the acrodin tip of a
 514 tooth (Mt-4 PN) support this histological robustness with a $\delta^{18}\text{O}$ value ($+20.7 \pm 0.2$
 515 ‰ $n = 4$) and a standard deviation ($1\sigma = \pm 0.5 \text{ ‰}$) comparable with associated
 516 conodonts (Fig. 6A, Table 2). The $\delta^{18}\text{O}$ value for the palaeoniscoid tooth dentine is
 517 depleted in ^{18}O ($+15.9 \pm 0.9 \text{ ‰}$) and similar to values from dentine in associated
 518 vertebrate microfossil taxa.

519 SIMS analyses were conducted on a range of scales belonging to
 520 acanthodians, chondrichthyan and palaeoniscoids. Scales attributed to each of these
 521 groups hosted $\delta^{18}\text{O}$ values within 1 ‰ of coeval conodont values (Fig. 4), which
 522 indicate that some scale tissues are preserving primary isotopic signatures. However,
 523 identifying the tissues that host these signatures is difficult as the spot size from the

524 SIMS beam is larger than some of the targeted tissues. This causes a degree of
 525 ambiguity in the $\delta^{18}\text{O}$ results due to the unquantifiable influence of surrounding
 526 tissues. The presence of ganoine, a tissue homologous with enamel (Qu et al., 2013),
 527 in some palaeoniscoid fish may explain the relatively high average $\delta^{18}\text{O}$ value of
 528 $+19.5 \pm 1.3 \text{ ‰}$. Reconciling the average $\delta^{18}\text{O}$ value of $+20.9 \pm 1.6 \text{ ‰}$ for the
 529 acanthodian scale (1984-04 Ac, Fig. 4) analysed is difficult, as scales of this taxa
 530 typically lack hypermineralised tissues and instead comprise an acellular bone base
 531 and a dentine layer covering the crown (Sire et al., 2009). Hypermineralised tissues
 532 such as ganoine have been reported in Palaeozoic acanthodians (e.g. Richter and
 533 Smith, 1995), which highlights the need for individual scales to be analysed rather
 534 than relying on the generalised histology of particular taxa. Overall, the results
 535 obtained from scales indicate that multiple taxa have the potential to be used to elicit
 536 apparently original isotopic data and interpret ancient environmental conditions.

537

538 *5.4. Comparison of GIRMS and SIMS $\delta^{18}\text{O}$ analyses of vertebrate microfossils*

539 As dentine tissues constitute the bulk of the vertebrate microfossils tested
 540 here, it is expected that results from GIRMS would be comparable to SIMS analyses
 541 of dentine from the same sample if the greater part of the signal detected by SIMS
 542 was from phosphate. This hypothesis is not fully supported by co-analysed fossils
 543 here (Fig. 7). Only two of the six analysed fossils produced average dentine $\delta^{18}\text{O}$
 544 SIMS values within $<1 \text{ ‰}$ of the GIRMS values. This is likely due to an insufficient
 545 number of spots, which were unable to encompass the full range of O-isotope
 546 variation within a single fossil. SIMS analysis of the lungfish scale (MT4-LPSi, Fig.
 547 7) highlights the significant variation even within a small cluster of spots ($\pm 1.9 \text{ ‰}$ n
 548 $= 3$, $\pm 1.3 \text{ ‰}$ $n = 5$). The potential for the alteration of PO_4 (since GIRMS analyses

549 are lower than coeval conodonts inhabiting the same water mass, see Section 5.5)
550 and contributions from other altered O-bearing compounds suggests SIMS and
551 GIRMS may not be comparable for heterogeneous tissues. Specific analysis of
552 hypermineralised tissues using both GIRMS and SIMS is required to determine if the
553 variation in hypermineralised tissue is low enough to produce comparable results
554 between the methods.

555

556 *5.5. Diagenetic influences*

557 Whole vertebrate microfossils analysed using GIRMS are commonly
558 depleted in ^{18}O when compared to coeval conodont elements (Žigaitė et al., 2010;
559 Barham et al., 2012a, b; Fischer et al., 2013). Since it has been demonstrated that
560 modern fish precipitate bioapatite in isotopic equilibrium with ambient water
561 (Kolodny et al., 1983; Vennemann et al., 2001; Puceat et al., 2010), and the
562 palaeoecology of many of the taxa are thought to overlap with those of coeval
563 conodonts, the lower $\delta^{18}\text{O}$ values are interpreted to have occurred as a consequence
564 of diagenetic changes in the less mineralised tissues. The 2.4 and 2.5 ‰ average
565 offsets found for Famennian and Tournaisian specimens examined herein (Fig. 3),
566 respectively, are close to those reported between Silurian conodonts and fish scales
567 (2.5 ‰; Žigaitė et al., 2010). The low colour alteration index (CAI) of the Silurian
568 conodonts (<1.5; Žigaitė et al., 2010) indicate thermally immature sediments, similar
569 to what is found in the Canning Basin, and may explain the similarity of the
570 discrepancy in $\delta^{18}\text{O}$ values. Moreover, Barham et al. (2012a) reported a more
571 significant depletion in ^{18}O from Mississippian, Viséan ichthyoliths from Ireland that
572 were associated with conodonts with CAI of >5, and indicated that the lower $\delta^{18}\text{O}$
573 values were influenced, but not necessarily controlled, by increasing diagenesis and

574 thermal alteration. It is difficult to extrapolate the results of thermal alteration from
575 conodonts to vertebrate microfossils given the significant taxonomic differences
576 between these groups. However, significant degrees of homology have been
577 identified between the hypermineralised tissues of vertebrates and conodont hyaline
578 tissue (Donoghue, 1998; Donoghue et al., 2000; Nemliher and Kallaste, 2012).
579 Therefore, it is not unreasonable to expect the preserved phosphate in both conodont
580 and vertebrate hard tissues would be affected in a similar fashion to thermal
581 maturation processes. Given the similar magnitude of conodont-vertebrate
582 microfossil $\delta^{18}\text{O}$ offset in thermally mature (CAI ~ 5.5 in Barham et al., 2012a
583 reported $\delta^{18}\text{O}$ offset of 2.9 ‰) and immature regions (CAI < 1.5 ; offset of 2.5 ‰
584 from Žigaitė et al., 2010; 2.4 and 2.5 ‰ offsets found herein), it can be assumed that
585 there is no linear correlation between thermal maturation and depletion of $\delta^{18}\text{O}$ in
586 vertebrate microfossil tissues.

587 The lower $\delta^{18}\text{O}$ values of vertebrate microfossils may be influenced by the
588 susceptibility of their fossil tissues to chemical processes (Ayliffe et al., 1994; Wang
589 and Cerling, 1994; Koch et al., 1997; Kohn et al., 1999; Sharp et al., 2000; Kohn and
590 Cerling, 2002; France and Owsley, 2015). Given the composition and
591 porosity/permeability of their dentine tissues, recrystallization of existing minerals
592 (Kolodny and Luz, 1991; Kolodny et al., 1996) as well as precipitation of secondary
593 O-bearing minerals (Martill, 1988; Blake et al., 1997; Kohn et al., 1999; Trueman
594 and Palmer, 2003), both with theoretically different O-isotope compositions, are
595 more significant considerations for vertebrate microfossils during early diagenesis
596 (Koch et al., 1997; Sharp et al., 2000; Zazzo et al., 2004). The extent to which these
597 aforementioned causes of alteration affect O-isotope ratios will be largely
598 determined by original structure and composition of the analysed tissues (e.g. Kohn

599 and Cerling, 2002). Oxygen in apatite is present in the PO₄, CO₃ and OH groups
600 (Driessens and Verbeeck, 1990). The phosphate component provides the most stable
601 O-bond with no isotopic exchange observed in low temperature inorganic systems
602 (Kolodny et al., 1983; Shemesh et al., 1988). The oxygen in carbonate however is
603 susceptible to diagenetically induced fractionation (Luz et al., 1984; Nelson et al.,
604 1986; Kolodny and Luz, 1991; Barrick and Showers, 1994, 1995; Wang and Cerling,
605 1994; Fricke et al. 1998; Kohn et al., 1999). Occurring at around 2-6 wt % in bone
606 and dentine (LeGeros and LeGeros, 1984; Driessens and Verbeeck, 1990),
607 diagenetic affects may influence the final $\delta^{18}\text{O}$ values measured by SIMS. The
608 effects of OH⁻ fractionation and substitution by other compounds such as CO³ (Kohn
609 et al., 1999) however, will not likely cause significant variation in the final $\delta^{18}\text{O}$
610 values as the wt % in dentine and bone is low (<1.6 wt %, Cerling and Sharp, 1996).

611 SIMS $\delta^{18}\text{O}$ analysis of modern shark teeth (Žigaitė and Whitehouse, 2014)
612 identified average $\delta^{18}\text{O}$ variation of 1.2 ‰ within the dentine tissue. Mean variation
613 between the parallel bundled enameloid (+21.2-23.1 ‰) and dentine tissue (+20.6-
614 21.8 ‰) was also recorded. Žigaitė and Whitehouse (2014) noted the use of H₂O₂ in
615 the pre-treatment cleaning process may have contributed to variation in the $\delta^{18}\text{O}$
616 values. However, it was concluded that organic matter, which is typically ^{18}O
617 depleted, was the likely cause of this variation. The fossil shark and holocephali
618 teeth tested here also showed significant discrepancies between tissues, as well as
619 depletion in ^{18}O (Figs. 4, 5b, 6). However, such variation in the fossil specimens
620 analysed here, cannot be attributed to original organic material as this would have
621 degraded to the point where it would be undetectable, although decay products could
622 have influenced the isotope ratios. Interestingly, analysis of teeth taken from freshly
623 caught sharks (Vennemann et al., 2001) recorded comparable values between the

624 dentine and enamel tissues using GIRMS. The isolation of PO_4 eliminates the
625 influence of ^{18}O depleted organic matter, which may have resulted in $\delta^{18}\text{O}$ variation
626 between the dentine and enamel. Work by Zazzo et al. (2003), has demonstrated
627 fractionation of phosphate within bone can occur within a few days post-mortem
628 under oxic conditions, with the presence of microbial enzyme activity significantly
629 increasing the rate of oxygen isotope exchange. In contrast, enamel was found to be
630 significantly resistant to changes in the original oxygen isotope ratios (Zazzo et al.,
631 2003). The susceptibility for isotopic alteration under microbially-mediated
632 conditions for tissues with originally higher organic matter content, could explain the
633 lower oxygen isotope values of the dentine of the shed teeth analysed by Žigaitė and
634 Whitehouse (2014). Microbial “catalysts” have been previously used to explain the
635 alteration of PO_4 $\delta^{18}\text{O}$ in bioapatite (Kolodny et al., 1983; Kastner et al., 1990). The
636 Upper Devonian and Lower Carboniferous vertebrate microfossil elements analysed
637 here were obtained from limestones formed in well oxygenated shallow water
638 marine settings (Druce and Radke, 1979). Given the lack of thermal maturity or any
639 evidence for fluid alteration of the sequences studied, microbially-induced alteration
640 within incompletely mineralised tissues in vertebrate microfossils ex-vivo and/or
641 during early diagenesis (eogenesis) must be considered a plausible mechanism for
642 lower $\delta^{18}\text{O}$ -values.

643 Evidence for recent weathering processes affecting $\delta^{18}\text{O}$ -values is present in
644 one of the holocephalan teeth (MTM1-H9, Fig. 5B), which had a portion of the
645 occluso-labial face of the crown protruding from a rock. It is difficult to constrain the
646 length of time the tooth was exposed, however it is likely that it was affected by a
647 range of weathering processes including frequent scrub fires and interaction with
648 meteoric fluids. The effect of exposure was evident with the outer enameloid layer of

649 the tooth producing values progressively depleted in ^{18}O toward the exposed surface.
650 The low $\delta^{18}\text{O}$ values between +5.2-5.9 ‰ (Fig. 5B spot no. 1-3) at the exposed face
651 correspond to significant degradation of the enameloid and dentine. However, the
652 affected area was small and the dentine within the tooth ($+19.5 \pm 0.7$ ‰) was found
653 to be comparable to the outer enameloid surface on the non-exposed face (+21.4 ‰,
654 Fig. 6b). This suggests relative localisation of alteration and overall robustness of the
655 tissue to short-term abiotic processes.

656

657 *5.6. Palaeoecological influences*

658 Understanding the biology of ancient sharks and fish as well as the
659 environments they inhabited is important to contextualise variation present in tissues,
660 particularly hypermineralised tissues, where primary isotope values are thought to be
661 original. Glaciation, resulting in the preferential locking of ^{16}O in terrestrial ice-
662 sheets, was present during the late Famennian and early Tournaisian (Kaiser et al.,
663 2006). Evidence suggests these glacial conditions were not as extensive as the
664 modern climate state (Isaacson et al., 2008), hence a $\delta^{18}\text{O}_{\text{seawater}}$ offset of -0.5 ‰
665 (VSMOW) is inferred to account for greater ^{16}O concentrations in the oceans than in
666 the present-day. Assuming these glacial conditions and subsequent offset to
667 $\delta^{18}\text{O}_{\text{seawater}}$, average $\delta^{18}\text{O}$ values (+17.8, +18.9 and +19.2 ‰) from protacrodont tooth
668 enamel (uncorrected for diagenetic alteration due to their hypermineralised
669 condition) indicate palaeotemperatures of between 34 and 42° C (calculated using
670 the equation of Lécuyer et al., 2013). Such sea-surface temperatures are considerably
671 higher than those calculated from coeval conodont (25 and 29° C using the equation
672 of Lécuyer et al., 2013).

673 Enrichment of ^{16}O as a result of bioapatite precipitation from a water mass
674 influenced by meteoric fluids in both the Protacrodont (Fig. 5b) teeth cannot be
675 easily dismissed. However, this would imply migratory habits for the taxa, as the
676 fauna and facies of the Laurel Formation indicate an exclusively marine setting
677 (Druce and Radke, 1979). Similar to the habits of extant shark species such as
678 *Carcharhinus leucas* (bull shark) (Copeia, 1971) and *Glyphis gangeticus* (Ganges
679 shark) (Compagno, 1997), Palaeozoic shark taxa are known to have inhabited
680 freshwater environments on both a permanent (e.g. Xenacanth, Ginter et al., 2010;
681 members of the *Ageleodus* genus, Downs and Daeschler, 2001) and temporary basis
682 (e.g. *Lissodus*, Fischer et al., 2013). Strontium isotope analysis has been previously
683 employed on chondrichthyan taxa (Scharer et al., 2012; Fischer et al., 2013; 2014;
684 Raoult et al., 2016) in order to quantify the salinity variable. It may be necessary to
685 include this form of analysis in order to isolate the palaeotemperature signal of
686 vertebrate microfossil O-isotope data when incorporating fossil taxa known to
687 inhabit different environments.

688 Significant ecological differences within fully marine extant shark genera are
689 reflected in the O-isotope ratios of the mineralised tissues (Vennemann et al., 2001).
690 The potential migration of ancient sharks across latitudes or water depths must also
691 be taken into account when interpreting O-isotope data from nektonic fossil taxa.
692 Significant migratory behaviour is observed in extant taxa such as *Odontaspis ferox*
693 (Fergusson et al., 2008), which has been found at depths of 850 m as well as very
694 shallow coastal waters. In addition, members of the species *Carcharodon carcharias*
695 (great white shark) have been frequently observed migrating long distances, in some
696 cases over 20,000 km in less than a year (Bonfil et al., 2005). Migratory issues of
697 extinct species may be compounded in groups such as the Ctenicanthiforms where

698 tooth development is slower than that observed in modern sharks (Williams, 2001;
699 Botella et al., 2009). Analysis of species with fast tooth replacement rates may
700 mitigate some migratory factors as teeth are more likely to preserve local conditions.
701 Tooth formation can be as quick as 9-12 days within some extant selachians (Moss,
702 1967); however, determining similar tooth replacement in Palaeozoic species is
703 currently difficult to ascertain.

704

705 **6. Conclusions**

706 The hypermineralised bioapatite present in vertebrate teeth and scales
707 provides a proxy capable of reconstructing marine oxygen isotope records from the
708 middle Palaeozoic to the modern day. The densely crystalline tissues that form
709 enamel, enameloid and acrodin show the greatest potential of preserving original
710 oxygen isotope signatures. Results presented herein from a broad range of taxa
711 (scales of acanthodians as well as the scales and teeth of chondrichthyans and
712 actinopterygians) indicate eliciting palaeoenvironmental data from other vertebrate
713 groups is likely.

714 The utilisation of SIMS, which permits tissue specific analysis, suggests
715 dentine tissue is more susceptible to alteration due to a higher porosity and
716 permeability inherited from an originally high organic component. The low CAI of
717 conodont fossils analysed here suggests thermal maturation is not the dominant
718 factor in the lower $\delta^{18}\text{O}$ values obtained from vertebrate microfossils. Instead, this
719 work suggests ex-vivo microbial activity may be a more likely factor in the alteration
720 of the original oxygen isotope ratios.

721 Going forward, it is clear that a range of Palaeozoic vertebrate groups offer
722 an alternative tool for reconstructing palaeoenvironmental conditions (watermass

723 palaeotemperature and palaeohydrological condition). In addition, the presence of
724 potentially original isotopic signatures provides a basis for applications in
725 chemostratigraphy where conodonts are rare or absent. SIMS analysis of targeted
726 hypermineralised vertebrate microfossil tissues can resolve original O-isotope values,
727 and therefore can be used in a similar fashion to, and correlated with, $\delta^{18}\text{O}_{\text{conodont}}$.
728 However, minimising potential $\delta^{18}\text{O}$ variation as a consequence of species dependant
729 factors such as migratory habits remains critical. Ideally analyses should include
730 multiple species and comparisons to co-occurring or coeval conodonts from other
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732

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756

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1262

1263 **Fig. 1.** Regional geology map and sampled sites from the Lennard Shelf, Canning
1264 Basin, Western Australia (modified from Playford et al., 2009).

1265

1266 **Fig. 2.** Frasnian *Palmatolepis* P-elements. (A) Back-scattered electron microscope
1267 image in aboral view with x4 magnified inset (i) highlighting the well-preserved
1268 ornamentation. (B) Stereo microscope image of a polished *Palmatolepis* sp. element
1269 showing the well-preserved internal microstructures and low Colour Alteration Index
1270 (CAI).

1271

1272 **Fig. 3.** Gas Isotope Ratio Mass Spectrometry (GIRMS) analyses of vertebrate
1273 microfossil elements from the late Famennian (i) and early Tournaisian (ii). Data
1274 points give average value of replicate analyses, vertical bars represent 1 std.dev.
1275 Coeval conodont values obtained from SIMS (late Famennian = $+19.6 \pm 0.5$ ‰ and;
1276 early Tournaisian = $+20.3 \pm 0.8$ ‰) were generally higher than vertebrate microfossil
1277 values analysed by GIRMS.

1278

1279 **Fig. 4.** Secondary Ion Mass Spectrometry (SIMS) $\delta^{18}\text{O}$ analyses of vertebrate
1280 microfossil elements from the late Famennian (i) and early Tournaisian (ii). Data
1281 points are the averages of spot clusters with 1 std.dev. given by the vertical error
1282 bars. Average vertebrate microfossil $\delta^{18}\text{O}$ values are plotted as difference relative to
1283 the $\delta^{18}\text{O}$ of co-occurring conodonts to focus on the tissue-specific differences

1284 regardless of geological age. Conodont $\delta^{18}\text{O}$ values were obtained from secondary
 1285 ion mass spectrometry (SIMS) ($\delta^{18}\text{O}_{\text{conodont}}$ values for the late Famennian = +19.6
 1286 ± 0.5 ‰ and; early Tournaisian = +20.3 ± 0.8 ‰). Grey area represents 1 std.dev. of
 1287 average co-occurring $\delta^{18}\text{O}_{\text{conodont}}$ obtained by SIMS.

1288

1289 **Fig. 5.** $\delta^{18}\text{O}$ of tissue types from two early Tournaisian Holocephalan teeth compared
 1290 to average $\delta^{18}\text{O}$ of coeval conodonts (+20.3 ± 0.8 ‰). (A) Tooth (MTM1-H1)
 1291 showing analysis of enameloid and dentine tissues; (A) Analysis of a tooth (MTM1-
 1292 H9) showing variation in $\delta^{18}\text{O}$ values associated with exposure of the labial surface
 1293 (indicated by dashed line). Coloured boxes correspond to spot clusters depicted in
 1294 the graphs A, B. Grey area represents 1 std.dev. (± 0.8 ‰) of the average $\delta^{18}\text{O}$ of
 1295 associated conodonts analysed by SIMS. For (B) spot numbers 1-3, 5-7 and 14-16
 1296 represent surface enameloid with pore enamel represented by spot numbers 4, 11-13
 1297 and 17-18.

1298

1299 **Fig. 6.** Systematic $\delta^{18}\text{O}$ variation in early Tournaisian vertebrate microfossil tissues
 1300 analysed via SIMS. Location of ion-probe spots indicated on stereo-microscope
 1301 images of polished analytical surface. (A) Palaeoniscoid fish tooth (MT-4 PN) with
 1302 acrocin cap and dentine tissue analysed; (B) Analysis of enameloid and dentine
 1303 tissues from Protacrodont tooth (1984-04 Dh2), referred to as *Dalmehodus* cf.
 1304 *turnerae* (Roelofs et al., 2016); (c) Tooth of the chondrichthyan *Ageleodus* (1984-04
 1305 AG1) showing a transect of spot analyses from the cusp apex to the base. All values
 1306 plotted relative to a co-occurring conodont $\delta^{18}\text{O}$ value of +20.3 ± 0.8 ‰. Grey areas
 1307 in graphs represent 1 std. dev. (± 0.8 ‰) of $\delta^{18}\text{O}$ analyses of co-occurring conodonts.

1308

1309 **Fig. 7.** Comparison of GIRMS and tissue specific targeting via SIMS analysis on
 1310 individual fossil elements from the (i) Famennian (average conodont $\delta^{18}\text{O}$ value of
 1311 $+19.6 \pm 0.5$ ‰ from three elements) and (ii) Tournaisian (average conodont $\delta^{18}\text{O}$
 1312 value of $+20.3 \pm 0.8$ ‰ from two elements). Grey area in the graph represents 1
 1313 std.dev. of $\delta^{18}\text{O}$ analyses of co-occurring conodonts.

1314

1315 **Table 1**

1316 Late Famennian and early Tournaisian vertebrate microfossils and standards
 1317 analysed using gas isotope ratio mass spectrometry (GIRMS).

1318

1319 ^a Number of replicate analysis

1320 ^b Frasnian

1321 ^c Famennian

1322 ^d Tournaisian

1323

1324 **Table 2**

1325 $\delta^{18}\text{O}$ values of Durango apatite and late Famennian to early Tournaisian vertebrate
 1326 microfossils analysed using SIMS.

1327 ^a Number of replicate analysis

1328 ^b Frasnian

1329 ^c Famennian

1330 ^d Tournaisian

1331 ^e Enameloid

1332 ^f i and ii notation indicate different individual fossils

Figure 1

Fig. 1. Regional geology map and sampled sites from the Lennard Shelf, Canning Basin, Western Australia (modified from Playford et al., 2009).

Figure 2

Fig. 2. Frasnian *Palmatolepis* P-elements. **(A)** Back-scattered electron microscope image in aboral view with x4 magnified inset (i) highlighting the well-preserved ornamentation. **(B)** Stereo microscope image of a polished *Palmatolepis* sp. element showing the well-preserved internal microstructures and low Colour Alteration Index (CAI).

Figure 3

Fig. 3. Gas Isotope Ratio Mass Spectrometry (GIRMS) analyses of vertebrate microfossil elements from the late Famennian (i) and early Tournaisian (ii). Data points give average value of replicate analyses, vertical bars represent 1 std.dev. Coeval conodont values obtained from SIMS (late Famennian = $+19.6 \pm 0.5$ ‰ and; early Tournaisian = $+20.3 \pm 0.8$ ‰) were generally higher than vertebrate microfossil values analysed by GIRMS.

Figure 4

Fig. 4. Secondary Ion Mass Spectrometry (SIMS) $\delta^{18}\text{O}$ analyses of vertebrate microfossil elements from the late Famennian (i) and early Tournaisian (ii). Data points are the averages of spot clusters with 1 std.dev. given by the vertical error bars. Average vertebrate microfossil $\delta^{18}\text{O}$ values are plotted as difference relative to the $\delta^{18}\text{O}$ of co-occurring conodonts to focus on the tissue-specific differences regardless of geological age. Conodont $\delta^{18}\text{O}$ values were obtained from secondary ion mass spectrometry (SIMS) ($\delta^{18}\text{O}_{\text{conodont}}$ values for the late Famennian = $+19.6 \pm 0.5 \text{ ‰}$ and; early Tournaisian = $+20.3 \pm 0.8 \text{ ‰}$). Grey area represents 1 std.dev. of average co-occurring $\delta^{18}\text{O}_{\text{conodont}}$ obtained by SIMS.

Figure 5

Fig. 5. $\delta^{18}\text{O}$ of tissue types from two early Tournaisian Holocephalan teeth compared to average $\delta^{18}\text{O}$ of coeval conodonts ($+20.3 \pm 0.8 \text{ ‰}$). (A) Tooth (MTM1-H1) showing analysis of enameloid and dentine tissues; (A) Analysis of a tooth (MTM1-H9) showing variation in $\delta^{18}\text{O}$ values associated with exposure of the labial surface (indicated by dashed line). Coloured boxes correspond to spot clusters depicted in the graphs A, B. Grey area represents 1 std.dev. ($\pm 0.8 \text{ ‰}$) of the average $\delta^{18}\text{O}$ of associated conodonts analysed by SIMS. For (B) spot numbers 1-3, 5-7 and 14-16 represent surface enameloid with pore enamel represented by spot numbers 4, 11-13 and 17-18.

Figure 6

Fig. 6. Systematic $\delta^{18}\text{O}$ variation in early Tournaisian vertebrate microfossil tissues analysed via SIMS. Location of ion-probe spots indicated on stereo-microscope images of polished analytical surface. (A) Palaeoniscoid fish tooth (MT-4 PN) with acrodin cap and dentine tissue analysed; (B) Analysis of enameloid and dentine tissues from Protacrodont tooth (1984-04 Dh2), referred to as *Dalmehodus* cf. *turnerae* (Roelofs et al., 2016); (c) Tooth of the chondrichthyan *Ageleodus* (1984-04 AG1) showing a transect of spot analyses from the cusp apex to the base. All values plotted relative to a co-occurring conodont $\delta^{18}\text{O}$ value of $+20.3 \pm 0.8$ ‰. Grey areas in graphs represent 1 std. dev. (± 0.8 ‰) of $\delta^{18}\text{O}$ analyses of co-occurring conodonts.

Figure 7

Fig. 7. Comparison of GIRMS and tissue specific targeting via SIMS analysis on individual vertebrate microfossil elements from the (i) Famennian (average conodont $\delta^{18}\text{O}$ value of $+19.6 \pm 0.5 \text{ ‰}$ from three elements) and (ii) Tournaisian (average conodont $\delta^{18}\text{O}$ value of $+20.3 \pm 0.8 \text{ ‰}$ from two elements). Grey area in the graph represents 1 std.dev. of $\delta^{18}\text{O}$ analyses of co-occurring conodonts.

Table 1

Late Famennian and early Tournaisian **vertebrate microfossils** and standards analysed using gas isotope ratio mass spectrometry (GIRMS).

Location	Sample no.	Formation (Fm.)	Age	Sample	Taxa	Sample size (mg)	n ^a	$\delta^{18}\text{O}$ (‰)	1 σ
Horse Spring	VHS-312	Virgin Hills Fm.	Fr ^b	<i>Ancyrodella</i>	Conodont	0.88	3	19.0	0.2
Oscar Hill	OH-4 A	Gumhole Fm.	Fn ^c	Palatal teeth	Palaeoniscoid	0.99	3	17.0	0.1
Oscar Hill	OH-4 B	Gumhole Fm.	Fn ^c	Scale	Protacrodont	2.04	3	17.1	0.2
Oscar Hill	OH-4 C	Gumhole Fm.	Fn ^c	Scale	Ctenacanthid	0.60	2	16.0	0.6
Oscar Hill	OH-4 D	Gumhole Fm.	Fn ^c	Tooth cusp	<i>Helodus</i>	0.89	3	17.2	0.3
Oscar Hill	OH4-SS1	Gumhole Fm.	Fn ^c	Spine	Shark	-	3	16.3	0.1
Laurel Downs	1984-04 A	Laurel Fm.	Tn ^d	Scale	Ctenacanthid	1.25	3	16.9	0.1
Laurel Downs	1984-04 B	Laurel Fm.	Tn ^d	Palatal teeth	Palaeoniscoid	0.82	3	18.0	0.2
Laurel Downs	1984-04 C	Laurel Fm.	Tn ^d	Radial bone	Palaeoniscoid	0.70	1	15.9	0.1
Laurel Downs	1984-04 D	Laurel Fm.	Tn ^d	Teeth	Palaeoniscoid	0.85	3	15.7	0.5
Laurel Downs	1984-04 E	Laurel Fm.	Tn ^d	Scale	Palaeoniscoid	1.51	3	17.3	0.6
Laurel Downs	1984-04 F	Laurel Fm.	Tn ^d	Tooth cusp	Holocephalan	1.63	3	17.3	0.2
Laurel Downs	1984-04 M	Laurel Fm.	Tn ^d	Tooth cusp	Holocephalan	0.87	3	17.7	0.1
Laurel Downs	1984-04 G	Laurel Fm.	Tn ^d	Scales	Acanthodian	0.77	3	17	0.4
Laurel Downs	1984-04 H	Laurel Fm.	Tn ^d	Palatal teeth	Palaeoniscoid	1.42	3	18.1	0.4
Laurel Downs	1984-04 J	Laurel Fm.	Tn ^d	Scale	Lungfish	1.44	3	16.5	0.2
Laurel Downs	1984-04 K	Laurel Fm.	Tn ^d	Scale	Protacrodont	1.13	3	16.1	0.3
Laurel Downs	1984-04 L	Laurel Fm.	Tn ^d	Scale	Protacrodont	0.96	3	17.3	0.5
Laurel Downs	MTM1-H1	Laurel Fm.	Tn ^d	Tooth cusp	Holocephalan	-	3	19.1	0.1
Laurel Downs	MTM1-H4	Laurel Fm.	Tn ^d	Tooth cusp	Holocephalan	-	3	16	0.2
Laurel Downs	MTM1-H5	Laurel Fm.	Tn ^d	Tooth cusp	Holocephalan	-	3	18.8	0.2
Laurel Downs	MTM1-H8	Laurel Fm.	Tn ^d	Tooth cusp	Holocephalan	-	3	18.8	0.1
Laurel Downs	MTM1-H9	Laurel Fm.	Tn ^d	Tooth cusp	Holocephalan	-	3	17.4	0.3
Laurel Downs	MT4-LPS	Laurel Fm.	Tn ^d	Scale	Lungfish	-	3	15.1	0.0

^a Number of replicate analysis

^b Frasnian

^c Famennian

^d Tournaisian

Table 1

Late Famennian and early Tournaisian vertebrate microfossils and standards analysed using gas isotope ratio mass spectrometry (GIRMS).

^a Number of replicate analysis

^b Frasnian

^c Famennian

^d Tournaisian

Table 2

$\delta^{18}\text{O}$ values of Durango apatite and late Famennian to early Tournaisian microfossils analysed using SIMS.

Location	Sample no.	Formation (Fm.)	Age	Sample	Taxa	Tissue	n ^a	$\delta^{18}\text{O}$ (‰)	1 σ
Horse Spring	VHS-312a	Virgin Hills Fm.	Fr ^b	P-element	<i>Palmatolepis</i>	Hyaline	4	19.1	0.3
Horse Spring	VHS-312b	Virgin Hills Fm.	Fr ^b	P-element	<i>Ancyrodella</i>	Hyaline	4	19.2	0.3
Oscar Hill	OH4-CS2	Gumhole Fm.	Fn ^c	S-element	Conodont	Hyaline	5	19.9	0.5
Oscar Hill	Si-OH4i ^f	Gumhole Fm.	Fn ^c	S-element	Conodont	Hyaline	2	20.1	1
Oscar Hill	Si-OH4ii ^f	Gumhole Fm.	Fn ^c	S-element	Conodont	Hyaline	2	18.8	0
Oscar Hill	OH4-SS1	Gumhole Fm.	Fn ^c	Shark spine	Unknown	Dentine	4	16.5	0.4
Oscar Hill	OH4-SS1	Gumhole Fm.	Fn ^c	Shark Spine	Unknown	Dentine	3	18.5	0.3
Oscar Hill	OH4-Pri	Gumhole Fm.	Fn ^c	Scale	Protacrodont	Unknown	2	17.9	0.1
Oscar Hill	OH4-Prii	Gumhole Fm.	Fn ^c	Scale	Protacrodont	Unknown	2	12.8	1
Laurel Downs	CCA1	Laurel Fm.	Tn ^d	P-element	<i>Clydagnathus</i>	Hyaline	5	20.9	.9
Laurel Downs	CCA2	Laurel Fm.	Tn ^d	P-element	<i>Clydagnathus</i>	Hyaline	4	19.9	0.4
Laurel Downs	1984-04 Ac	Laurel Fm.	Tn ^d	Scale	Acanthodian	Unknown	2	20.6	1.6
Laurel Downs	1984-04 Ac	Laurel Fm.	Tn ^d	Scale	Acanthodian	Dentine	1	16.7	n/a
Laurel Downs	1984-04 Pr	Laurel Fm.	Tn ^d	Scale	Protacrodont	Unknown	3	20.1	0.3
Laurel Downs	1984-04 Ct	Laurel Fm.	Tn ^d	Scale	Ctenacanthid	Unknown	2	20.6	2.1
Laurel Downs	1984-04 Pcd	Laurel Fm.	Tn ^d	Scale	Palaeoniscoid	Unknown	2	19.5	1.3
Laurel Downs	MT4-LPSi ^f	Laurel Fm.	Tn ^d	Scale	Lungfish	Unknown	3	8.8	1.9
Laurel Downs	MT4-LPSi ^f	Laurel Fm.	Tn ^d	Scale	Lungfish	Unknown	5	14.9	1.3
Laurel Downs	MT4 Ptp	Laurel Fm.	Tn ^d	Palatal teeth	Palaeoniscoid	Cusp	4	15.7	0.5
Laurel Downs	MT4 Ptp	Laurel Fm.	Tn ^d	Palatal teeth	Palaeoniscoid	Dentine	4	14.9	1.1
Laurel Downs	Mt-4 PN	Laurel Fm.	Tn ^d	Tooth	Palaeoniscoid	Acrodin	4	20.7	0.5
Laurel Downs	Mt-4 PN	Laurel Fm.	Tn ^d	Tooth	Palaeoniscoid	Dentine	3	15.9	0.9
Laurel Downs	1984-04 AG1	Laurel Fm.	Tn ^d	Tooth	<i>Ageleodus</i> sp.	Dentine	3	17.2	0.1
Laurel Downs	1984-04 AG1	Laurel Fm.	Tn ^d	Tooth	<i>Ageleodus</i> sp.	Dentine	5	13.1	1.1
Laurel Downs	1984-04 AG1	Laurel Fm.	Tn ^d	Tooth	<i>Ageleodus</i> sp.	Dentine	2	10.1	2.5
Laurel Downs	1984-04 Dh1	Laurel Fm.	Tn ^d	Tooth	Protacrodont	Enameloid	3	17.9	0.4
Laurel Downs	1984-04 Dh1	Laurel Fm.	Tn ^d	Tooth	Protacrodont	Dentine	3	16.2	0.2
Laurel Downs	1984-04 Dh1	Laurel Fm.	Tn ^d	Tooth	Protacrodont	Dentine	3	13.8	0.5
Laurel Downs	1984-04 Dh2	Laurel Fm.	Tn ^d	Tooth	Protacrodont	Enameloid	4	19.2	0.2
Laurel Downs	1984-04 Dh2	Laurel Fm.	Tn ^d	Tooth	Protacrodont	Dentine	4	16.4	0.7
Laurel Downs	1984-04 Dh3	Laurel Fm.	Tn ^d	Tooth	Protacrodont	Enameloid	3	18.9	0.3
Laurel Downs	1984-04 Sti ^f	Laurel Fm.	Tn ^d	Tooth	Cladodont	Dentine	4	7.5	2.1
Laurel Downs	1984-04 Sti ^f	Laurel Fm.	Tn ^d	Tooth	Cladodont	Dentine	4	11.5	0.8
Laurel Downs	1984-04 Stii ^f	Laurel Fm.	Tn ^d	Tooth	Cladodont	Dentine	4	16.1	2.7
Laurel Downs	MTM1-H1	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Surface en ^d	5	18.1	0.5
Laurel Downs	MTM1-H1	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Surface en ^d	5	9.2	0.9
Laurel Downs	MTM1-H1	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Dentine	5	19.5	0.2
Laurel Downs	MTM1-H1	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Dentine	5	15.6	0.8
Laurel Downs	MTM1-H1	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Dentine	5	17.6	0.1
Laurel Downs	MTM1-H4	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Dentine	4	18.7	0.1
Laurel Downs	MTM1-H4	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Dentine	4	19.2	0.4
Laurel Downs	MTM1-H5	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Dentine	4	17.3	0.2
Laurel Downs	MTM1-H5	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Dentine	4	17.3	0.3

Laurel Downs	MTM1-H9	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Surface en ^e	3	5.9	2.2
Laurel Downs	MTM1-H9	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Pore en ^e	3	21.4	0.3
Laurel Downs	MTM1-H9	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Surface en ^e	3	17.8	0.4
Laurel Downs	MTM1-H9	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Pore en ^e	2	21.8	0.1
Laurel Downs	MTM1-H9	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Pore en ^e	1	21.4	n/a
Laurel Downs	MTM1-H9	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Surface en ^e	3	19.5	0.7
Laurel Downs	MTM1-H9	Laurel Fm.	Tn ^d	Tooth	Holocephalan	Dentine	3	17.2	0.4

^a Number of replicate analysis

^b Frasnian

^c Famennian

^d Tournaisian

^e Enameloid

^f i and ii notation indicate different individual fossils

Table 2

$\delta^{18}\text{O}$ values of Durango apatite and late Famennian to early Tournaisian vertebrate microfossils analysed using SIMS.

^a Number of replicate analysis

^b Frasnian

^c Famennian

^d Tournaisian

^e Enameloid

^f i and ii notation indicate different individual fossils