



The 18O/16O ratio in vertebrate biogenic apatite as a proxy to Palaeozoic seawater temperatures

Živilė Žigaitė (1), Alberto Pérez-Huerta (2), Michael M. Joachimski (3), and Oliver Lehnert (3)

(1) Department of Evolution and Development, Uppsala University, Norbyvägen 18A, SE-75236 Uppsala, Sweden (Zivile.Zigaite@gmail.com), (2) Department of Geological Sciences, University of Alabama, 201 7TH Avenue, Tuscaloosa, AL 35487, USA, (3) Geozentrum Nordbayern, University of Erlangen-Nürnberg, Schlossgarten 5, D-91054 Erlangen, Germany

Stable oxygen isotope ratios in vertebrate microfossils, conodonts as well as early fish dermal scales, have been used as proxies to palaeoseawater temperatures, and Palaeozoic climate. The compact tissues of conodont elements and fish scales, such as albite (Trotter et al. 2006, 2007) or enamel (Žigaitė et al. 2010) are supposed to have a high potential in preserving the primary oxygen isotope signal, which may correspond to the ambient palaeoseawater. However, application of analytical methods has not always been taken into consideration, particularly obtaining the 18O/16O values by a wet chemistry phosphatic remnant separation from bioapatite (Joachimski et al. 2002, 2004, 2006, 2009; Žigaitė et al. 2010) versus an ion microprobe bulk tissue-selective microsampling (e.g. Wheeley et al. 2010), which are not comparable. Recently, a new phosphate-water paleothermometer equation (Pucéat et al. 2010) based on advanced analytical techniques has yielded an offset of about +2‰, producing the paleotemperatures for the Early Palaeozoic up to 8°C higher than previously considered (e.g. Trotter et al. 2008). Multiple reasons, ranging from diagenetic alteration of isotopic signal to circular change of palaeoseawater isotopic composition, may cause the final variations of isotopic signal. The acid preparation of fossil biominerals and other chemical processing play an important role affecting the 18O/16O ratio as well. Results of our study reveal that the enrichment in heavy 18O isotopes in the Early Palaeozoic fish bioapatite may be directly correlated with a poor preservation of fossil biominerals. Additionally, the $\delta^{18}\text{O}$ ratios appear to be strongly species-dependent, which may refer either to specific susceptibility to diagenesis, or to specific palaeobiological isotope assimilation in vertebrate biominerals.

- Joachimski, M. M., Buggisch, W. 2002. Conodont apatite $\delta^{18}\text{O}$ signatures indicate climatic cooling as a trigger of the Late Devonian mass extinction. *Geological Society of America, Geology*, 30, 8, 711-714, 2 figs.
- Joachimski, M. M., van Geldern, R., Breisig, S., Buggisch, W., Day, J. 2004. Oxygen isotope evolution of biogenic calcite and apatite during the Middle and Late Devonian. *International Journal of Earth Sciences (Geologische Rundschau)*, 93, 542-553.
- Joachimski, M.M., Breisig, S., Buggisch, W., Talent, J.A., Mawson, R., Gereke, M., Morrow, J.M., Day, J., Weddige, K. 2009. Devonian climate and reef evolution: insights from oxygen isotopes in apatite. *Earth and Planetary Science Letters*, 284, 599-609.
- Pucéat, E., Joachimski, M.M., Bouilloux, A., Monna, F., Bonin, A., Motreuil, S., Morinière, P., Hénard, S., Mourin, J., Dera, G., Quesne, D. 2010. Revised phosphate-water fractionation equation reassessing palaeotemperatures derived from biogenic apatite. *Earth and Planetary Science Letters*, doi:10.1016/j.epsl.2010.07.034.
- Trotter, J.A., Eggins, S.M. 2006. Chemical systematics of conodont apatite determined by laser ablation ICPMS. *Chemical Geology*, 233, 196-216.
- Trotter, J.A., Fitz Gerald, J.D., Kokkonen, H., Barnes, C.R. 2007. New insights into the ultrastructure, permeability, and integrity of conodont apatite determined by transmission electron microscopy. *Lethaia*, 40, 97-110.
- Trotter, J.A., Williams, I.S., Barnes, Ch. R., Lécuyer, Ch., Nicoll, R. S. 2008. Did Cooling Oceans Trigger Ordovician Biodiversification? Evidence from Conodont Thermometry. *Science*, 321: 550-554.
- Wheeley, J. R., Smith, P. M., Boomer, I. 2010. Assessing the utility of Ion Microprobe analyses of conodonts for ancient ocean palaeothermometry. *Deciphering Paleozoic Paleoenvironmental Changes Using Stable and Radiogenic Isotope Proxies; Geological Society of America Annual Meeting*, Paper No: 216-9.
- Žigaitė, Ž., Joachimski, M.M., Lehnert, O., Brazauskas, A. 2010. $\delta^{18}\text{O}$ composition of conodont apatite indicates climatic cooling during the middle Pridoli. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 294: 242-247.