

Accepted Manuscript

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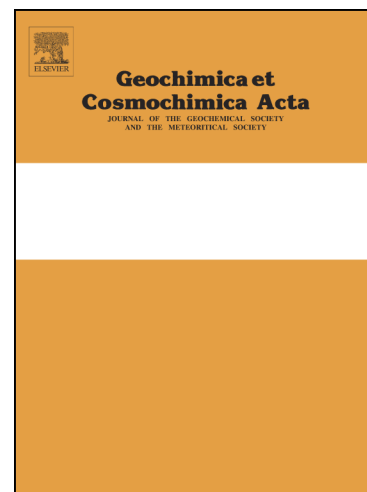
PII: S0016-7037(17)30728-7
DOI: <https://doi.org/10.1016/j.gca.2017.11.015>
Reference: GCA 10554

To appear in: *Geochimica et Cosmochimica Acta*

Received Date: 8 February 2017
Accepted Date: 10 November 2017

Please cite this article as: Bergmann, K.D., Finnegan, S., Creel, R., Eiler, J.M., Hughes, N.C., Popov, L.E., Fischer, W.W., A paired apatite and calcite clumped isotope thermometry approach to estimating Cambro-Ordovician seawater temperatures and isotopic composition, *Geochimica et Cosmochimica Acta* (2017), doi: <https://doi.org/10.1016/j.gca.2017.11.015>

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A paired apatite and calcite clumped isotope thermometry approach to estimating Cambro-Ordovician seawater temperatures and isotopic composition

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The secular increase in $\delta^{18}\text{O}$ values of both calcitic and phosphatic marine fossils through early Phanerozoic time suggests either that 1) early Paleozoic surface temperatures were high, in excess of 40°C (tropical MAT), 2) the $\delta^{18}\text{O}$ value of seawater has increased by 7–8‰ VSMOW through Paleozoic time, or 3) diagenesis has altered secular trends in early Paleozoic samples. Carbonate clumped isotope analysis, in combination with petrographic and elemental analysis, can deconvolve fluid composition from temperature effects and therefore determine which of these hypotheses best explain the secular $\delta^{18}\text{O}$ increase. Clumped isotope measurements of a suite of calcitic and phosphatic marine fossils from late Cambrian- to Middle-late Ordovician-aged strata—the first paired fossil study of its kind—document tropical sea surface temperatures near modern temperatures (26–38°C) and seawater oxygen isotope ratios similar to today’s ratios.

1. Introduction

Carbonate and phosphatic rocks retain our most complete evidence of climatic conditions in Earth’s deep past. Determining how temperature and seawater oxygen isotope ($\delta^{18}\text{O}$) fluctuations influenced carbonate and phosphatic $\delta^{18}\text{O}$ records over geologic time, therefore, is crucial for understanding the coupled evolutions of Earth’s climate and biota. This is particularly true in early Paleozoic time, when climate transitions are hypothesized to have played a major role in the radiation of many animal lineages (e.g. Rasmussen et al., 2016; Trotter et al., 2008).

Efforts to extrapolate from these $\delta^{18}\text{O}$ records broader inferences about climate and biotic evolution have been hampered, however, by the difficulty of making meaningful comparisons among data derived from disparate sources. For example, $\delta^{18}\text{O}$ measurements of conodont apatite by secondary ion mass spectrometry (SIMS) were used to propose high Early Ordovician sea surface temperatures >40°C that declined to modern-like surface temperatures (<25°C) by late Middle Ordovician time; this cooling was postulated to have spurred the radiation of diverse skeletonized calcitic taxa in the Middle Ordovician (Rasmussen et al., 2016; Trotter et al., 2008). In contrast, $\delta^{18}\text{O}$ records of Paleozoic brachiopods have been used to argue that early Paleozoic calcitic skeletons grew at extremely low temperatures (e.g. 2°C) (Giles, 2012), and that the bulk isotopic composition of seawater increased 7‰ from early Paleozoic values to present levels (Jaffrés et al., 2007; Kasting et al., 2006; Prokoph et al., 2008; Veizer et al., 1999, 1997; Veizer

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