

Clumped isotope calibration using modern brachiopods: Implications for reconstructions of temperature and the oxygen isotopic composition of seawater

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Reconstructions using the isotopic compositions (⁸⁷Sr/⁸⁶Sr, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$) of fossil brachiopods have provided fundamental insights into the evolution of the Earth's seawater over the course of the Phanerozoic (e.g. Veizer *et al.* [1]). However, the interpretation of oxygen isotopic reconstructions is complicated by the fact that the $\delta^{18}\text{O}$ of carbonate is a function of both temperature and the oxygen isotopic composition of the water ($\delta^{18}\text{O}_{\text{sw}}$) in which the carbonate grew. The carbonate clumped isotope (Δ_{47}) paleothermometer, which is based on the temperature-dependent ordering of ¹³C and ¹⁸O atoms into bonds with each other in the carbonate mineral lattice, provides a means to isolate the temperature and $\delta^{18}\text{O}_{\text{sw}}$ signals because Δ_{47} is independent of the isotopic composition of the water in which the carbonate grew [2].

Our clumped isotope calibration is based on 7 specimens of modern brachiopods spanning a temperature range of 1-29°C. Sample locations and depths were carefully selected in order to minimize the effects of seasonal temperature variability. Three replicate analyses were performed for each sample. Our results indicate that brachiopod carbonate shows a relationship of Δ_{47} to temperature that is similar to the previously published inorganic calcite relationship [2]. However, the new brachiopod calibration does yield different temperatures at the extremes of the calibration temperature range, and may be more consistent with the inorganic calcite relationship of Zaarur *et al.* [3].

In addition, the results of our ongoing investigation into the isotopic heterogeneities within single brachiopod shells (primary versus secondary calcite layers) will be presented and discussed.

[1] Veizer *et al.* (1999) *Chem. Geol.* **161**, 59-88. [2] Ghosh *et al.* (2006) *Geochim. Cosmochim. Acta* **70**, 1439-1456. [3] Zaarur *et al.* unpublished data.

WHAT DETRITAL ZIRCONS TELL US ABOUT GROWTH OF THE CONTINENTAL CRUST

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Zircons provide the only evidence for Earth having a crust older than 4.0 Ga but how extensive was that crust? If it was not extensive when did the continental crust start to form, what was its rate of growth, was growth continuous or episodic and what was time interval between formation of primitive continental crust and remelting of that primitive crust to form stable, cratonic crust? To answer these questions we have analyzed 1500 detrital zircons from the World's major rivers for Lu-Hf, U-Th-Pb and O isotopes. The Lu-Hf system gives a model age for the time at which continental crust that melted to form the granitic magma from which the zircon crystallized separated from the mantle, the U-Th-Pb system dates the crustal melting event and O isotopes can be used to determine whether the crustal source region included a significant sedimentary component. Continents that have been covered include Europe, Russia, North America, Africa and Australia. If we confine our discussion to 500 zircons with mantle-like O isotopic values (between 4.25 and 6.25) to eliminate zircons that crystallized from a hybrid source (e.g. zircons from S-type granites) the maximum model age observed is 4150 Ma and there is little evidence of growth of the continental crust starting before 4.0 Ga. This conclusion is in agreement with Nd model ages for Earth's oldest sediments, and with observation that there is no known preserved continental crust older than that age. However six of the eight model ages that exceed 4.0 Ga have been extrapolated over two billion years from their U/Pb age and uncertainty in the Lu/Hf ratio used in the calculations make the reliability of these ages questionable. We conclude that there is no unambiguous evidence in our data for growth of the continental crust prior to 4.0 Ga and that significant growth of the continental crust was delayed until 3.5 Ga. Distinct peaks can be recognized in the Hf model age histogram at 400-1100 Ma, 1600-2500 Ma and 3000-3500 Ma but we caution against interpreting this as proof of episodic growth because the peaks differ between continents and because we have yet to analyze zircons from South America, SE Asia and Antarctica for Hf and O isotopes. The U-Pb ages show five distinct peaks that correspond to the five known supercontinent-forming events suggesting that continent-continent collisions are periods of enhanced crustal melting. The time difference between the formation of primitive continental crust, as recorded by the Hf model ages, and remelting of that crust to form cratonic crust, as recorded by the U-Pb age, varies between 0 and 3.8 Gyr and averages 780 Myr.]