Empirical calibration of the clumped isotope paleothermometer using calcites of various origins

Ulrike Wacker [a,*], Jens Fiebig [a,b], Julian Tödter [c], Bernd R. Schöne [d], André Bahr [a], Oliver Friedrich [a,b,1], Thomas Tütken [e], Eberhard Gischler [a,b], Michael M. Joachimski [f]

[a] *Institute of Geosciences, Goethe-University, Altenhöferallee 1, 60438 Frankfurt am Main, Germany*
[b] *Biodiversity and Climate Research Center, Senckenberganlage 25, 60325 Frankfurt am Main, Germany*
[c] *Institute for Atmospheric and Environmental Sciences, Altenhöferallee 1, 60438 Frankfurt am Main, Germany*
[d] *Department of Applied and Analytical Paleontology (INCREMENTS), Institute of Geosciences, University of Mainz, Johann-Joachim-Becherweg 21, 55128 Mainz, Germany*
[e] *Steinmann-Institut für Geologie, Mineralogie und Paläontologie, Poppelsdorfer Schloss, University of Bonn, 53115 Bonn, Germany*
[f] *GeoZentrum Nordbayern, University of Erlangen-Nürnberg, Schloßgarten 5, 91054 Erlangen, Germany*

Abstract

We present the first universal calibration of the clumped isotope thermometer for calcites of various mineralizing types. These are an eggshell of an ostrich, a tropical bivalve, a brachiopod shell, cold seep carbonate, and three foraminifera samples that grew between 9 and 38 °C. $CaCO_3$ was digested at 90 °C using a common acid bath. Considering a difference in phosphoric acid fractionation factors between reaction at 25 and 90 °C of 0.069‰ (Guo et al., 2009), the function between growth temperature T and the excess of ^{13}C–^{18}O bonds in the evolved CO_2 is expressed by a linear regression between $1/T^2$ and absolute Δ_{47} ($R^2 = 0.9915$):

$$\Delta_{47} = 0.0327(\pm 0.0026) \times 10^6/T^2 + 0.3030(\pm 0.0308) \text{ (with } \Delta_{47} \text{ in ‰ and } T \text{ in K).}$$

Both the slope and intercept of our regression line deviate significantly from the first experimental calibration based on synthetic calcites digested at 25 °C (Ghosh et al., 2006a) and from several other studies having confirmed this pioneering calibration (i.e., Came et al., 2007; Tripati et al., 2010; Thiagarajan et al., 2011; Grauel et al., 2012; Saenger et al., 2012; Zaarur et al., 2013). However, our relationship between temperature and absolute Δ_{47} values is indistinguishable from that determined by Henkes et al. (2013) if the same difference in phosphoric acid fractionation factors between 25 and 90 °C is applied to both datasets. Our study and that of Henkes et al. (2013) have in common that data were primarily projected onto the absolute scale proposed by Dennis et al. (2011) – a reference frame that allows comparison of clumped isotope data measured in different laboratories. Furthermore, at any T, our regression line lies within 0.006‰ of the theoretical calcite calibration of Guo et al. (2009). The observation that both empirical calibrations are indistinguishable from each other implies that clumped isotope data can be directly compared between laboratories and referenced to a unique temperature calibration if (1) the phosphoric acid digestion temperature is set to 90 °C, and (2) raw data are primarily projected to the absolute scale.
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* Corresponding author. Tel.: +49 69 79840175; fax: +49 69 79840185.
 E-mail address: u.wacker@em.uni-frankfurt.de (U. Wacker).
[1] Present address: Institute of Earth Sciences, Im Neuenheimer Feld 234-236, 69120 Heidelberg, Germany.