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Clumped isotope signatures in modern brachiopod carbonate

Rosemarie E. Came [a,*], Uwe Brand [b], Hagit P. Affek [c]

[a] Department of Earth Sciences, The University of New Hampshire, Durham, NH 03824, USA
[b] Department of Earth Sciences, Brock University, St. Catharines, Ontario L2S 3A1, Canada
[c] Department of Geology and Geophysics, Yale University, New Haven, CT 06520, USA

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ABSTRACT

We present a temperature to Δ_{47} relationship for naturally occurring modern brachiopods, which was established using a suite of thirteen brachiopod specimens from twelve sampling localities that span a mean annual seawater temperature range of −0.8 to 29.0 °C. Sample locations and depths were selected to maximize the range of temperatures covered by the calibration while minimizing the seasonal temperature variability impacting the samples. Linear least-squares regression analysis yields the following relationship expressed using the Ghosh et al. (2006) reference frame:

$$\Delta_{47} = (0.0478 \pm 0.0099) \cdot 10^6/T^2 + (0.1164 \pm 0.1203) \quad \left(n = 13; R^2 = 0.91; 95\%\mathrm{CI}\right).$$

This equation lies within the 95% confidence interval of the original relationship determined using synthetic calcite (Ghosh et al., 2006), but is in better agreement with the newly revised calibration of Zaarur et al. (2013). However, despite this broad agreement, our equation has a shallower slope than the equations for synthetic calcites, and yields temperatures at the warm end of the calibration temperature range ($\Delta_{47} = 0.640$‰) that are as much as 3.1 °C offset from those predicted using the equation of Zaarur et al. (2013). On the other hand, our new equation has a steeper slope than the Henkes et al. (2013) equation for modern brachiopods and mollusks. This finding is consistent with the hypothesis that differences in the protocols employed by laboratories that use different temperatures of phosphoric acid digestion cause the observed discrepancies between the Δ_{47} values reported by various laboratories.

1. Introduction

The carbonate $\delta^{18}O$ paleotemperature proxy, which utilizes the thermodynamically controlled fractionation of oxygen isotopes between seawater and marine carbonate (Urey, 1947; McCrea, 1950; Epstein et al., 1951), has led to significant advances in the fields of paleoceanography and paleoclimatology. For example, the reconstruction of Pleistocene glacial–interglacial cycles using the $\delta^{18}O$ of marine carbonate fossils (Emiliani, 1955; Hays et al., 1976) was instrumental in the eventual acceptance of the astronomical theory of the ice ages originally hypothesized by Milankovitch (1941) and Croll (1864). More recently, the $\delta^{18}O$ of ancient carbonate fossils has been used to quantify the magnitude of temperature change during large and rapid global warming episodes such as the Paleocene–Eocene Thermal Maximum (e.g., Zachos et al., 2008) and the end Permian (e.g., Brand et al., 2012), and has led to the discovery of long-term variations in the Earth's climate over the last 550 Ma (e.g., Veizer et al., 2000). However, despite these successes, the application of the $\delta^{18}O$ proxy has been limited due to the fact that the $\delta^{18}O$ of carbonate ($\delta^{18}O_C$) is not simply a function of calcification temperature; but rather, it is a function of both calcification temperature and the oxygen isotopic composition of the water in which the carbonate formed ($\delta^{18}O_W$). Therefore, the application of $\delta^{18}O$ as a paleoclimate tool requires an assumption about the $\delta^{18}O$ of seawater, yet $\delta^{18}O_W$ can be impacted on short timescales by evaporation/precipitation, on glacial–interglacial timescales by Raleigh distillation and the formation of ice sheets, and perhaps on longer timescales by poorly constrained secular changes in the $\delta^{18}O$ of the ocean.

The difficulty associated with the $\delta^{18}O_W$ assumption has led to the development of alternative paleotemperature proxies, such as coral Sr/Ca (Beck et al., 1992; Gaetani and Cohen, 2006), foraminiferal Mg/Ca (Nürnberg et al., 1996), the unsaturation index of C_{37} alkenones (Prahl and Wakeham, 1987), and TEX_{86} (Schouten et al., 2002). These proxies have been applied with great success (e.g., Lear et al., 2000; Linsley et al., 2000; Sachs et al., 2001; Came et al., 2007a; Mutterlose et al., 2010). However, as with all proxies, each of these has limitations. Organic proxies, such as TEX_{86} and the unsaturation index of C_{37} alkenones, pose a difficulty because temperature estimates are not obtained using the same phase as the $\delta^{18}O_C$ measurement, thereby introducing significant error in the calculated $\delta^{18}O_W$. Coral Sr/Ca can only

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* Corresponding author. Tel.: +1 603 862 1720.
E-mail address: Rosemarie.Came@unh.edu (R.E. Came).

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be applied to questions involving tropical sea surface temperatures. The application of the foraminiferal Mg/Ca proxy requires the Mg and Ca concentrations of the ocean to be the same as today (limiting the timescale), and the proxy is further influenced by both carbonate ion concentration (Rosenthal et al., 2006) and salinity (Arbuszewski et al., 2010). Moreover, the temperature sensitivity of Mg/Ca is poor in carbonates that grow in cold surface waters or in the deep ocean (Elderfield and Ganssen, 2000; Rosenthal et al., 2006; Marchitto et al., 2007; Curry and Marchitto, 2008), making this proxy less effective for reconstructions involving cold temperatures.

The recently developed carbonate "clumped isotopes" (Δ_{47}) paleotemperature proxy has the potential to circumvent these difficulties. The Δ_{47} proxy takes advantage of the thermodynamically controlled ordering of ^{13}C and ^{18}O in the carbonate mineral lattice (Ghosh et al., 2006; Schauble et al., 2006; Eiler, 2007). This ordering or "clumping" occurs independently of the isotopic composition of the water in which the carbonate formed and therefore does not require an assumption about the $\delta^{18}O$ of seawater (Ghosh et al., 2006). Furthermore, the $\delta^{18}O_C$ and the Δ_{47} temperature estimate are obtained simultaneously – in the same phase – allowing a calculation of $\delta^{18}O_W$ using a single sample. Finally, the initial Δ_{47} of a carbonate may be retained on timescales of hundreds of millions of years (Dennis and Schrag, 2010), assuming that the carbonate sample has not been "reset" by burial alteration and has not undergone dissolution and re-precipitation of authigenic calcite.

The first published equation describing the relationship between temperature and the Δ_{47} of CO_2 extracted from carbonate materials was determined by the group at Caltech using seven analyses of synthetic calcites that were grown in the laboratory at known temperatures (Ghosh et al., 2006). Following the publication of the initial calibration equation, several additional synthetic calibration studies have been conducted in other laboratories (Fig. 1). The results of a synthetic calibration study conducted at Yale (Zaarur et al., 2013) agree well with the results originally published by the group at Caltech. However, the results of a study conducted at Harvard (Dennis and Schrag, 2010) suggest that the slope of the temperature to Δ_{47} equation is much shallower than the slope determined by the other two groups. The Dennis and Schrag (2010) equation agrees more closely with the theoretical temperature to Δ_{47} relationship determined by Guo et al. (2009). The reason for the discrepancies between the laboratories is not clear, though differences in laboratory protocols may play a role (e.g., Fernandez et al., 2014).

The applicability of a synthetic calibration to any particular naturally occurring carbonate cannot be assumed a priori. Therefore, before any type of carbonate is used in Δ_{47} paleotemperature reconstructions, a modern calibration is required for that particular carbonate. Several calibration studies have been conducted in which naturally occurring modern biogenic carbonates were analyzed, including: surface and deep-sea corals (Ghosh et al., 2006; Thiagarajan et al., 2011; Saenger et al., 2012), otoliths (Ghosh et al., 2007), foraminifera (Tripati et al., 2010; Grauel et al., 2013), snails (Eagle et al., 2013a), mollusks and brachiopods (Came et al., 2007b; Eagle et al., 2013b; Henkes et al., 2013). Most naturally occurring biogenic carbonates (both aragonitic and calcitic) appear to agree broadly with the initial calibration relationship for calcite obtained by Ghosh et al. (2006) and recently confirmed by Zaarur et al. (2013), though there appear to be small differences between taxa (see compilation and discussion by Eiler, 2011). However, two recently published calibration studies – one using modern mollusks (Eagle et al., 2013b) and the other using modern mollusks and brachiopods (Henkes et al., 2013) – yield temperature to Δ_{47} equations that are not consistent with the calibration equation originally published by the group at Caltech (Fig. 1). Instead, these studies yield equations with slopes that are more similar to the one determined by Dennis and Schrag (2010). As suggested by Henkes et al. (2013), the difference between the mollusk/brachiopod equation and the equations determined for other taxa may represent differences in mineral-DIC clumped isotope fractionation between mollusks/brachiopods and other taxa. Alternatively, it may simply reflect recent modifications to laboratory protocols, i.e. the temperature at which acid digestion occurs.

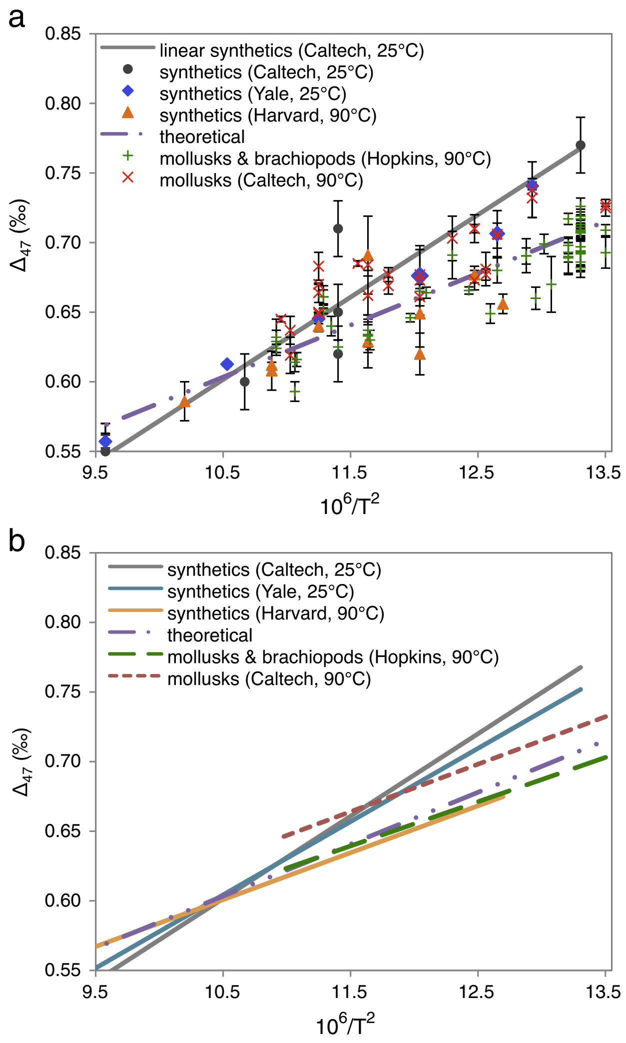

Fig. 1. Previously published calibrations of the Δ_{47} paleothermometer discussed in the text. a) The gray solid line represents the relationship of Ghosh et al. (2006); the gray filled circles represent the synthetics data of Ghosh et al. (2006); the teal filled diamonds represent the synthetics data of Zaarur et al. (2013); the orange filled triangles represent the synthetics data of Dennis and Schrag (2010); the purple dotdash line represents the theoretical relationship of Guo et al. (2009); the green plus symbols represent the mollusk and brachiopod data of Henkes et al. (2013); the red "X"s represent the mollusk data of Eagle et al. (2013b). All error bars are 1 SE. Unreplicated samples are assigned an error of 0.020‰ (Zaarur et al., 2013). b) The gray solid line represents the relationship of Ghosh et al. (2006); the teal solid line represents the relationship of Zaarur et al. (2013); the orange solid line represents the relationship of Dennis and Schrag (2010); the purple dotdash line represents the theoretical relationship of Guo et al. (2009); the dashed green line represents the relationship of Henkes et al. (2013); the dashed red line represents the relationship of Eagle et al. (2013b). The temperatures noted in parentheses are the temperatures at which carbonate samples were digested in phosphoric acid.

Articulated brachiopod fossils are commonly used in the reconstruction of oceanic conditions in the distant geologic past (e.g., Lowenstam, 1961; Bates and Brand, 1991; Grossman et al., 1993; Veizer et al., 1999) because they are abundant in sedimentary archives spanning the entire Phanerozoic, and are especially well represented in Paleozoic strata. Furthermore, articulated brachiopods precipitate multi-layer calcite shells, which are fairly resistant to low-level diagenetic processes (Brand and Veizer, 1980; Brand et al., 2003). Here we present a detailed temperature to Δ_{47} calibration for brachiopods using a suite of thirteen modern specimens that grew at known temperatures. Our objective is