

# Calibration and application of the ‘clumped isotope’ thermometer to foraminifera for high-resolution climate reconstructions

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## Abstract

The reconstruction of past ocean temperatures is fundamental to the study of past climate changes, therefore considerable effort has been invested in developing proxies for seawater temperatures. One of the most recent and promising new proxy is carbonate ‘clumped isotope’ thermometry, in particular because it is based on thermodynamic equilibrium and not on biogeochemical proxies. Here, we present a new calibration of the ‘clumped isotope’ thermometer to foraminifera based on seven species of planktic and benthic foraminifera spanning a growth temperature range of  $\sim 2$ – $28$  °C. We used a newly developed technique for the measurements of small samples to improve the applicability of this method to paleoceanography. Our data have a comparable precision ( $\sim 0.005$ – $0.013$ ‰) and confirm previous calibration studies based on biogenic and inorganic calcite. We discuss possible sources of uncertainty such as over-/underestimation of the calcification temperatures, species-specific vital effects, pH variations between the seawater and the vacuole water of the species and possible kinetic effects on the ‘clumped isotope’ calibration.

To validate our calibration study and test the applicability of our measuring technique to paleoclimate and paleoceanographic studies we measured the isotope composition of *Globigerinoides ruber* (white) at high-resolution in a sediment core covering the last 700 years in the Gulf of Taranto (Mediterranean Sea). The results show that it is necessary to average a relatively large number of analyses to achieve a consistent temperature signal for the detection of small sea surface temperature changes. Although with the current analytical system, ‘clumped isotope’ thermometry is only applicable to the analysis of relatively large SST changes in marine sediments, further technical improvements may make this a very powerful technique for paleoceanographic studies.

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## 1. INTRODUCTION

The stable oxygen and carbon isotope geochemistry of foraminifera is one of the most important tools in paleo-

ceanography and paleoclimatology (Emiliani, 1955; Shackleton, 1967; Ravelo and Hillaire-Marcel, 2007). The oxygen isotopic composition of foraminifera calcite varies as a function of the growth temperature and the isotopic composition of the ambient seawater in which the calcification takes place (e.g., Waelbroeck et al., 2005), thus if the  $\delta^{18}\text{O}$  of seawater ( $\delta^{18}\text{O}_w$ ) is known the calcification temperature can be calculated. However, the oxygen isotope values of seawater can only be estimated for ancient environments,

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leaving a large uncertainty in reconstructed sea surface temperatures (SSTs). ‘Clumped isotope’ paleothermometry (Ghosh et al., 2006) has the potential to solve this long standing problem in paleoceanography.

‘Clumped isotope’ geochemistry is concerned with the state of ordering of heavy isotopes in molecules with more than one rare isotope (Eiler and Schauble, 2004; Wang et al., 2004; Schauble et al., 2006; Eiler, 2007). This method allows determination of the precipitation temperature of calcite via the abundance of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in carbonate, and at the same time to calculate the  $\delta^{18}\text{O}_w$  in which the organism lived (Ghosh et al., 2006; Eiler, 2007). The abundance of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in carbonates is a function of precipitation temperature of the carbonates and has been shown to be independent of the  $\delta^{13}\text{C}$  of the dissolved inorganic carbon (DIC) and the  $\delta^{18}\text{O}_w$  (Ghosh et al., 2006). The first calibration of the ‘clumped isotope’ thermometer was based on the comparison of the  $\Delta_{47}$ -value of  $\text{CO}_2$  released by phosphoric-acid digestion of carbonate to the growth temperature of experimentally precipitated calcite and of different biogenic carbonates from organisms grown at a known temperature (Ghosh et al., 2006; Eiler, 2007). Since that pioneering work, several additional calibrations of biogenic carbonates, such as fish otoliths (Ghosh et al., 2007), mollusks and brachiopods (Came et al., 2007), foraminifera and coccoliths (Tripathi et al., 2010), deep-sea corals (Thiagarajan et al., 2011) and one on tooth enamel bioapatite (Eagle et al., 2010) have been published. These calibrations all showed a remarkably consistent pattern for biogenic carbonates. In contrast, studies on speleothems showed that these inorganically-precipitated carbonates are often out of equilibrium (Affek et al., 2008; Daëron et al., 2011).

All the above calibrations were carried out in the same laboratory at the California Institute of Technology. The only other currently available calibration of the ‘clumped isotope’ thermometer carried out in another laboratory was published by Dennis and Schrag (2010) and is based on inorganically precipitated calcite. This work showed a much shallower slope than all other calibrations but similar to the theoretical predictions of Schauble et al. (2006) and Guo et al. (2009) based on first principles calculations. This questioned the validity of the calibrations based on biogenic carbonates. Dennis and Schrag (2010) suggested that one of the causes for the difference to the Ghosh et al. (2006) calibration could be poor inter-laboratory calibration. However, the work of Dennis et al. (2011) which defined a new absolute reference frame for reporting the analyses of ‘clumped isotopes’ based on  $\text{CO}_2$  equilibrated with waters of different  $\delta^{18}\text{O}$  composition showed that this difference still remains and must be related to analytical and/or experimental issues. Therefore, there is a definite need for additional calibration studies, especially from other laboratories, and different analytical approaches.

The analytical requirements on precision and accuracy for ‘clumped isotopes’ are much higher than for conventional isotope analyses (Eiler, 2007), because for temperatures between 1 °C and 50 °C the range in  $\Delta_{47}$ -values is only between 0.75‰ and 0.5‰, and because  $^{13}\text{C}$ – $^{18}\text{O}$ – $^{16}\text{O}_2$  makes up only ~40 ppm of natural  $\text{CO}_2$  (Eiler and Schauble, 2004). Because the temperature sensitivity of the meth-

od is ~0.004–0.005‰/°C (Ghosh et al., 2006) an external precision of this order is necessary if an uncertainty of  $\pm 1$  °C in the temperature reconstructions is to be reached (Eiler, 2007).

In the original method of Ghosh et al. (2006), which is the commonly used method in the currently active laboratories, relatively large amounts of sample material (8–15 mg) are necessary, which is not suitable for high-resolution studies of climate change in marine sediments, where often only a small amount of sample is available. In an attempt to make this method more applicable to paleoceanography, Schmid and Bernasconi (2010) developed a new automated method for ‘clumped isotope’ measurements on small carbonate samples. They demonstrated that by repeated measurements ( $n = 6$ – $15$ ) of 150–200  $\mu\text{g}$  aliquots of carbonate with a completely automated, commercially-available system a sufficient precision and accuracy, similar to that of large samples, could be reached (Schmid and Bernasconi, 2010). This method should allow producing a high-resolution  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  stratigraphy and at the same time a lower resolution ‘clumped isotope’ reconstruction of temperature and seawater  $\delta^{18}\text{O}$  (Bernasconi et al., 2011). In this work we present a new calibration based on foraminifera that were collected across a temperature gradient ranging between 2 and 28 °C. This calibration was used to verify the calibration of Ghosh et al. (2006) and Tripathi et al. (2010) in an independent way and with different analytical procedures than other laboratories. Furthermore, we present a high-resolution isotope record of a short sediment core covering the last 700 years in the Gulf of Taranto (Mediterranean Sea) to demonstrate the applicability and limitations of the method for paleoceanographic reconstructions from marine sediment cores.

## 2. MATERIAL AND METHODS

### 2.1. Samples

We collected core-top samples of 7 species of foraminifera from 30 different locations (Fig. 1) with growth temperatures ranging from 2 to 28 °C. The detailed information for each station and the different species analyzed is given in Table 1. When direct  $\delta^{18}\text{O}$  measurements of ambient seawater were not available, we used published data from stations as close as possible (Table 1). We analyzed five different planktonic species (*Globigerinoides ruber* (white), *Orbulina universa*, *Neogloboquadrina pachyderma* (sinistral), *Globorotalia inflata* and *Globorotalia truncatulinoides*) and two benthic species (*Uvigerina mediterranea* and *Cibicides pachyderma*).

For the sediment core study the species *G. ruber* (white) was used for ‘clumped isotope’ measurements. The 46 cm long sediment core was dated with  $^{210}\text{Pb}$ - and AMS  $^{14}\text{C}$ -dating. A complete description of the core and the age model calculation is reported in Grauel (2012).

### 2.2. Sample pre-treatment

After freeze-drying, the sediments were wet sieved into size fractions of  $>355 \mu\text{m}$ , 355–250  $\mu\text{m}$ , 250–200  $\mu\text{m}$  and

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