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## Journal Article

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### Publication date:

2018-09-01

### Permanent link:

<https://doi.org/10.3929/ethz-b-000280900>

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### Originally published in:

Geochimica et Cosmochimica Acta 236, <https://doi.org/10.1016/j.gca.2018.03.010>

### Funding acknowledgement:

160046 - Clumped Isotope Thermometry in burial diagenetic systems - part 2: new constraints on the kinetics of  $^{13}\text{C}$ - $^{18}\text{O}$  bond reordering from contact metamorphic aureoles of magmatic intrusions (SNF)



# Coupled Mg/Ca and clumped isotope analyses of foraminifera provide consistent water temperatures

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Received 8 August 2017; accepted in revised form 6 March 2018; available online 16 March 2018

## Abstract

The reliable determination of past seawater temperature is fundamental to paleoclimate studies. We test the robustness of two paleotemperature proxies by combining Mg/Ca and clumped isotopes ( $\Delta_{47}$ ) on the same specimens of core top planktonic foraminifera. The strength of this approach is that Mg/Ca and  $\Delta_{47}$  are measured on the same specimens of foraminifera, thereby providing two independent estimates of temperature. This replication constitutes a rigorous test of individual methods with the advantage that the same approach can be applied to fossil specimens. Aliquots for Mg/Ca and clumped analyses are treated in the same manner following a modified cleaning procedure of foraminifera for trace element and isotopic analyses. We analysed eight species of planktonic foraminifera from coretop samples over a wide range of temperatures from 2 to 29°C. We provide a new clumped isotope temperature calibrations using subaqueous cave carbonates, which is consistent with recent studies. Tandem Mg/Ca– $\Delta_{47}$  results follow an exponential curve as predicted by temperature calibration equations. Observed deviations from the predicted Mg/Ca– $\Delta_{47}$  relationship are attributed to the effects of Fe-Mn oxide coatings, contamination, or dissolution of foraminiferal tests. This coupled approach provides a high degree of confidence in temperature estimates when Mg/Ca and  $\Delta_{47}$  yield concordant results, and can be used to infer the past  $\delta^{18}\text{O}$  of seawater ( $\delta^{18}\text{O}_{\text{sw}}$ ) for paleoclimate studies.  
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**Keywords:** Clumped isotopes; Mg/Ca analysis; Planktonic foraminifera; Paleoceanography; Paleoclimatology

## 1. INTRODUCTION

The temperature of seawater is an important variable needed for paleoclimate reconstruction and numerical climate model simulations. Various proxies of past ocean temperature have been developed including paleo-ecological transfer functions, Mg/Ca, and biomarkers ( $U_{37}^k$ , and  $\text{TEX}_{86}$ ). Among the newest advances in paleothermometry is the application of clumped isotopes (expressed with the parameter  $\Delta_{47}$ ), which refers to the ordering or “clumping” of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in carbonate minerals (for review, see Eiler, 2007, 2011). The formation of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in carbonate minerals is a function of temperature, and is inde-

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pendent of the  $\delta^{18}\text{O}$  of the ambient water or the  $\delta^{13}\text{C}$  of the dissolved inorganic carbon (DIC) (Schauble et al., 2006). Because the measurement of clumped isotopes in carbonates also includes the determination of  $\delta^{18}\text{O}$  of the carbonate ( $\delta^{18}\text{O}_{\text{cc}}$ ) it permits temperature to be determined at the same time as  $\delta^{18}\text{O}$  of seawater ( $\delta^{18}\text{O}_{\text{sw}}$ ).

The first calibration of the clumped isotope paleothermometer using inorganic calcite and corals was reported by Ghosh et al. (2006) who found a range of  $\Delta_{47}$ -values between 0.8‰ and 0.5‰ for temperatures between 1°C and 50°C, with an external uncertainty equivalent to  $\pm 2^\circ\text{C}$ . The uncertainty results mainly from the analytical error in determining  $\Delta_{47}$  (Fernandez et al., 2017). The calibration was later confirmed by two studies that included foraminifera and other biogenic calcites (Tripathi et al., 2010; Grauel et al., 2013). However, the transfer of these calibrations to the Absolute Reference Frame (ARF) of Dennis et al. (2011), which was introduced to improve interlaboratory comparability, has relatively large uncertainties because of the lack of appropriate standards before the reference frame was introduced. Following the introduction of the ARF, a number of calibrations were published with slopes differing significantly from each other, but most recent calibrations (Kele et al., 2015; Bonifacie et al., 2017; Kelson et al., 2017) appear to converge on a common temperature dependence.

The elemental ratio of Mg and Ca in foraminiferal calcite is also temperature-dependent (Rosenthal et al., 1997; Lea et al., 1999; Elderfield and Ganssen, 2000; see Lea, 2014 for review). Many empirical calibration studies and laboratory culture experiments have shown that Mg/Ca of foraminiferal calcite increases exponentially with increasing temperature (Nürnberg et al., 1996). Elderfield and Ganssen (2000) showed that the relationship between Mg/Ca and temperature is similar for different species of planktonic foraminifera, whereas more recent studies have emphasized species-specific calibrations (Dekens et al., 2002; Anand et al., 2003; Weinkauff et al., 2016). In addition, paired measurements of Mg/Ca and  $\delta^{18}\text{O}_{\text{cc}}$  from the same foraminiferal specimens have been used to estimate the  $\delta^{18}\text{O}_{\text{sw}}$  (e.g., Lear et al., 2000, 2015; Anand et al., 2003). The temperature dependence of Mg/Ca is often expressed in the form:

$$\text{Mg/Ca (mmol mol}^{-1}\text{)} = b e^{aT}, \quad (1)$$

where  $a$  and  $b$  are constants and  $T$  is temperature in  $^\circ\text{C}$ . Culture, sediment trap and coretop calibrations have shown that the exponential constant ( $a$ ) varies from  $\sim 0.085$  to  $0.102$ , giving a sensitivity of ca. 9% change in Mg/Ca per  $^\circ\text{C}$  (Nürnberg et al., 1996; Lea et al., 1999; Elderfield and Ganssen, 2000; Anand et al., 2003), whereas ( $b$ ) is species-specific (Elderfield and Ganssen, 2000; Anand et al., 2003; Lea et al., 1999; Barker et al., 2005). Consequently, more recent studies suggest species-specific calibrations of the Mg/Ca with respect to temperature as this provides more accurate estimates of temperature in certain regions (Regenberg et al., 2009).

To complicate matters, planktonic foraminiferal Mg/Ca can be affected by dissolution, Fe-Mn oxide coating, salinity, and seawater Mg/Ca variations, thus hampering tem-

perature reconstructions. High-Mg carbonate will dissolve preferentially resulting in a lower Mg/Ca value (lower apparent temperature) (Regenberg et al., 2014 and references therein). Furthermore, Fe-Mn metal oxide coating on the tests can lead to too high Mg/Ca-based temperatures (Lea et al., 2005), whereas salinity may also influence the Mg/Ca of foraminiferal tests (Ferguson et al., 2008; Hönisch et al., 2013). Considering the many factors that can influence the Mg/Ca in foraminifera (e.g. Lear et al., 2000; Sadekov et al., 2008; Fehrenbacher et al., 2014; Vázquez Riveiros et al., 2016), it is desirable to confirm the estimated temperature with an independent proxy.

Here we combine measurements of Mg/Ca and clumped isotopes from the same calcitic planktonic foraminiferal tests from globally distributed modern coretops to provide independent estimates of calcification temperature. Foraminiferal samples for Mg/Ca and clumped isotope analyses are subject to the same cleaning procedure. Whereas different paleothermometers have been compared previously (e.g. Mg/Ca ratios and alkenones, or alkenones and TEX<sub>86</sub>; Schouten et al., 2002; Leduc et al., 2010), we derive temperatures on the exact same specimens of foraminifera, which should give identical results. We test if the Mg/Ca- $\Delta_{47}$  data fall on the line predicted using the known temperature relationship for each proxy. Furthermore, we show that a clumped isotope regression for planktonic foraminifera agrees with inorganic carbonate calibrations, suggesting that vital effects are not significant for clumped isotopes. Finally, we discuss the potential application and the advantages of this method to fossil specimens for reconstructing more accurate estimates of past temperature and  $\delta^{18}\text{O}_{\text{sw}}$  values.

## 2. MATERIALS AND METHODS

### 2.1. Selection of foraminifera and cleaning procedure for tandem Mg/Ca and clumped analyses

We used existing coretop samples from several sites from the Atlantic, Arctic, Pacific, and Indian Oceans (Fig. 1 and Table S1) to test the relationship between Mg/Ca ratios and  $\Delta_{47}$  values in modern foraminifera. In the North Atlantic the cores were the same as those used previously by Elderfield and Ganssen (2000) (Tables S1 and S2). The samples span a temperature range from 2 to 29°C. Coretops with the potential to yield large ( $>5$  mg) mono-specific samples of foraminifera were selected from the  $>300$   $\mu\text{m}$  size fraction of the sediment except for *Neogloboquadrina pachyderma* (sinistral) where the  $>150$   $\mu\text{m}$  size fraction was chosen to obtain sufficient material. After cleaning the samples consisted of  $\sim 3$  mg of foraminiferal calcite and included 8 different species of surface- and deep-dwelling planktonic foraminifera: *Globigerina bulloides*, *Globigerinoides sacculifer*, *Globorotalia hirsuta*, *Globorotalia inflata*, *Globorotalia menardii*, *Neogloboquadrina dutertrei*, *Neogloboquadrina pachyderma* (s), and *Orbulina universa*.

We devised a cleaning procedure to ensure that the Mg/Ca ratios and  $\Delta_{47}$  values were measured on the exact same specimens of foraminifera. Foraminiferal tests were subjected to a modified version of the cleaning procedure used

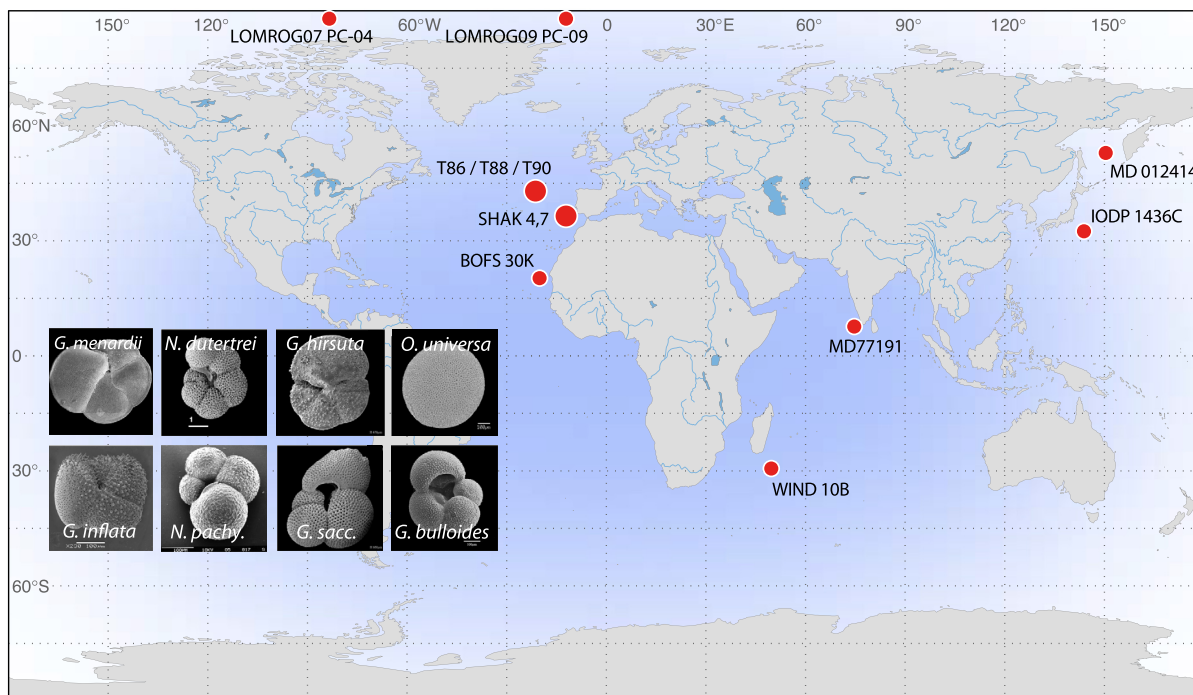


Fig. 1. Location map of coretop samples used in this study. Inset images of planktonic foraminifera exemplify the species studied.

for Mg/Ca (Barker et al., 2003). The main modifications were: (i) the use of larger vials (2.5 ml acid-cleaned vials instead of 0.5 ml ones) to accommodate greater volumes of reagents for the large sample sizes, (ii) substitution of the warm, weak (1%), oxidative step by a cold (room temperature), stronger one (5%  $\text{H}_2\text{O}_2$ ), (iii) post-cleaning removal of any silicates remaining after drying, and (iv) the omission of the dilute acid leaching step. Selected samples were carefully monitored with SEM images of foraminifera following the oxidative cleaning step to ensure that no dissolution or recrystallization had occurred.

The modified cleaning procedure includes the following steps: (i) crushing of the shells; (ii) clay removal using deionized water and methanol in an ultrasonic bath; (iii) removal of organics using 5%  $\text{H}_2\text{O}_2$  at room temperature, buffered with 0.1 M NaOH; (iv) check for potential contamination (e.g. silica grains) under the microscope and removal of contaminants if necessary. After drying at room temperature under vacuum, the samples were powdered between glass plates and split into 7 or more aliquots (120–140  $\mu\text{g}$  each) for clumped isotope analyses, plus one aliquot ( $\sim 250 \mu\text{g}$ ) for Mg/Ca ratio analysis using the method of de Villiers et al. (2002). To the greatest extent possible, the method ensures that the Mg/Ca ratios and  $\Delta_{47}$  values were measured on the same specimens of foraminifera.

## 2.2. Mg/Ca determination

Cleaned foraminifera were analysed for Mg/Ca ratios by inductively coupled plasma optical emission spectrometry (ICP-OES) using an Agilent 5100 instrument. Samples were dissolved in 0.1 M  $\text{HNO}_3$  and centrifuged to remove any

undissolved material. After an initial run to determine Ca concentration, samples were diluted to constant [Ca] (100 ppm). Mg/Ca ratios were determined by the intensity ratio method of de Villiers et al. (2002) using calibration standards prepared according to Greaves et al. (2005). Cleaning efficiency and diagenetic effects were monitored by measuring Fe/Ca, Mn/Ca, Al/Ca, Si/Ca and Ba/Ca.

Instrumental precision for the Mg/Ca ratios is  $\pm 0.51\%$ , determined by replicate analyses of a standard solution containing Mg/Ca ratios of  $1.3 \text{ mmol mol}^{-1}$  and a Ca concentration of 100 ppm. Accuracy of Mg/Ca ratios has been established by interlaboratory calibration (Rosenthal et al., 2004; Greaves et al., 2008). Sample heterogeneity for Mg/Ca ratios has been shown to be much greater than instrumental precision (Barker et al., 2003; Rosenthal et al., 2004). We estimate the reproducibility of planktonic foraminiferal Mg/Ca ratios is  $\sim 8\%$  from replicate analyses of *G. bulloides* picked from an Atlantic core-top sample.

## 2.3. Clumped isotope analysis

Clumped isotope measurements were performed at the Godwin Laboratory for Palaeoclimate Research, University of Cambridge, United Kingdom. The Thermo Scientific MAT253 mass spectrometer is equipped with 7 collectors to simultaneously measure masses 44 through 49. To monitor instrumental background during analysis, we use a cup located in a position corresponding to  $m/z$  46.5 with a  $10^{12} \Omega$  resistor. This setup allows online monitoring of the impact of secondary electrons generated by the large  $m/z$  44 beam on the smaller  $m/z$  beam of interest. Dry, cleaned  $\text{CO}_2$  gas was measured against an in-house reference gas (Grauel et al., 2016), which is preferred over commercially

available reference gases because the in-house gas has a bulk isotopic composition close to the gas produced by phosphoric acid digestion of foraminifera under study (reference gas was produced by acidification of Carrara marble; the isotope values for the solid phase are  $\delta^{13}\text{C}_{\text{VPDB}} = 2.25\text{‰}$  and  $\delta^{18}\text{O}_{\text{VPDB}} = -1.27\text{‰}$ ). Between 6 and 15 aliquots of calcium carbonate were reacted with orthophosphoric acid at 70°C using a Thermo Scientific Kiel IV carbonate device. The cryogenic trapping system of the Kiel device was modified by adding a Porapak trap that is cooled with two Peltier elements to remove organic compounds and isobaric contaminants prior to isotopic measurements (Schmid and Bernasconi, 2010; Schmid et al., 2012; Petersen and Winkelstern, 2016). This trap is cooled to ca. -12°C during each run and baked out for at least 1 h before the next run. For each replicate, the initial beam intensity of  $m/z$  44 was around 20 V and decreased to ca. 12 V over the course of 8 cycles. The mass spectrometer uses standard stainless steel capillaries supplied by Thermo Scientific.

Data were reduced using the evaluation scheme developed by Meckler et al. (2014). Pressure sensitive negative backgrounds on the rare isotopologue masses were determined before each run by performing peak shape scans on all masses at different intensities on  $m/z$  44 (25 V, 20 V, 15 V and 10 V). These negative backgrounds originate from secondary electrons of the  $m/z$  44 beam and by determining the  $m/z$  44 pressure dependence with the background scans we can eliminate the mass spectrometer specific non-linearities observed in  $\Delta_{47}$  versus  $\delta^{47}$  plots (Bernasconi et al., 2013; Meckler et al., 2014; Müller et al., 2017a) (Fig. S1). In addition, the  $m/z$  46.5 intensity monitors the negative background signal originating from the  $m/z$  44 beam online during acquisition. The  $m/z$  44 pressure dependent behavior of the  $m/z$  46.5 signal should correlate with the pressure dependent backgrounds of  $m/z$  47 and in case of distinct behavior can be used to track measurements with contamination. The background is tracked using both the slope and intercept of  $m/z$  46.5 and  $m/z$  47, whereby an increase in the slope indicates contaminants in the instrument.

Conversion of the background corrected raw data into the absolute reference frame (ARF) (Dennis et al., 2011) allows the clumped isotope results to be corrected for mass spectrometer specific scale-compression and thus enables comparison to other laboratories. In order to transfer the PBL-corrected data to the ARF we follow the same procedure outlined by Meckler et al. (2014). The four ETH carbonate standards (ETH-1, ETH-2, ETH-3 and ETH-4) were measured on a daily basis (5–6 replicates of 3 standards in every run of 46 samples) and the values of Bernasconi et al. (in review) were used for correction to the ARF. The  $\Delta_{47}$  values have been corrected by an acid fractionation factor of +0.062‰ for 70°C (Defliese et al., 2015; Müller et al., 2017a) to project the data to an acid reaction temperature of 25°C. The standard measurements and comparison to the standard values from ETH Zürich are reported in the supplemental material.

The long-term performance of our system over the course of 11 months for the four ETH carbonate standards

is 0.034–0.045 1SD (1SE = <0.0025) and is consistent with errors reported by other laboratories. The corrections for the  $^{17}\text{O}$  abundance were made following the recommendations of Daëron et al. (2016).

### 3. RESULTS

#### 3.1. Temperature calibration of $\Delta_{47}$

The Godwin Laboratory clumped isotope calibration (i.e., the regression between  $\Delta_{47}$  and temperature) was established using natural cave carbonates that precipitated subaqueously at known temperatures, ranging from 3 to 47°C (Table 1, Fig. 2). These carbonates grew under conditions that minimize  $\text{CO}_2$ -degassing and evaporation and hence kinetic fractionation effects are negligible owing to an unlimited DIC pool in the water (Kele et al., 2015). All samples consist of calcite, except NAICA-1 which is aragonite.

The  $\Delta_{47}$  values for the six calibration samples range from 0.603‰ to 0.758‰. The standard error ranges from 0.006‰ to 0.009‰. We also report the uncertainties at the 95% confidence level (CL), as suggested by Müller et al. (2017b) and Fernandez et al. (2017). The 95% CL uncertainty varies from 0.013‰ to 0.021‰ (Table 1). The uncertainties of this calibration can be reduced if additional calibration samples and more replicates per sample are measured (Fernandez et al., 2017). The calibration follows a regression line of the form:

$$\Delta_{47} = (0.0448 \pm 0.007) * 10^6/T^2 + (0.154 \pm 0.08), \quad (2)$$

where T is temperature in Kelvin.

Our calibration slope is statistically indistinguishable from the travertine calibration produced at ETH Zürich by Kele et al. (2015) using the same methods as those employed at Cambridge and recalculated using the parameters recommended by Daëron et al. (2016) (Fig. 2). The calibration is also very close (i.e. a ca. 0.013‰ lower intercept) to the recalculated ETH calibration (Kele et al., 2015) and those reported by two recent more elaborate studies that suggest there may indeed be a “universal clumped isotope calibration” (Bonifacie et al., 2017; Kelson et al., 2017). The calibration of Kelson et al. (2017) also used the Brand parameters (Brand et al., 2010; Daëron et al., 2016; Schauer et al., 2016) while Bonifacie et al. (2017) used different parameters. Differences between ETH and Cambridge intercepts might be caused by the limited number of calibration samples and thus temperature range of the Cambridge calibration.

It is encouraging that measurements of clumped isotopes using the same analytical methods and parameters for data processing and carbonate standards at ETH and Cambridge give very similar calibration curves. Although the ETH calibration is largely based on inorganic carbonate samples, we suggest it is also appropriate for biogenic carbonates such as foraminifera (Kele et al., 2015; Grauel et al., 2016; Rodríguez-Sanz et al., 2017, see also discussion).

Table 1  
Summary of stable and clumped isotope data for the cave carbonate samples. The full dataset for all replicates can be found in supplemental Table S4.

SA/STD	Cave name, Country	# replicates	Average $\delta_{45}$	STDEV $\delta_{45}$	SE $\delta_{45}$	Average $\delta_{46}$	STDEV $\delta_{46}$	SE $\delta_{46}$	Average d13C (permil VPDB)	STDEV d13C	SE d13C	Average d18O (permil VPDB)	STDEV d18O	SE d18O	Average $\Delta_{47}$	STDEV $\Delta_{47}$	SE $\Delta_{47}$	95% confidence interval (permil)	known T (°C)	$10^6/T^2$ (K)	TD47 (°C)	External standard error (°C)	
BSP-1	Bärenschacht, Switzerland	21	-9.88	0.042	0.009	-8.08	0.098	0.021	-7.50	0.07	0.01	-9.07	0.07	0.02	-15.95	0.523	0.114						
DSP1	Dark Star, Uzbekistan	11	-1.56	0.051	0.016	-4.93	0.106	0.032	1.35	0.05	0.02	-5.91	0.10	0.03	-9.74	0.196	0.059						
GPC-1	Guano Cave, Tanzania	21	-13.04	0.045	0.010	-3.52	0.087	0.019	-11.08	0.09	0.02	-4.56	0.15	0.03	-7.52	0.405	0.088						
MCP-1	Mawmluh Cave, India	22	-9.76	0.079	0.017	-5.28	0.164	0.035	-7.47	0.08	0.02	-6.30	0.17	0.04	-10.35	0.336	0.072						
NAICA 1	Naica Mine, Mexico	17	-0.61	0.037	0.009	-10.98	0.087	0.021	2.59	0.04	0.01	-11.97	0.08	0.02	-21.17	0.621	0.151						
OWB-1	Oder-Warthe-Bogen, Poland	21	-13.75	0.030	0.007	-6.11	0.070	0.015	-11.73	0.05	0.01	-7.11	0.07	0.01	-12.35	0.300	0.065						
SA/STD	Cave name, Country	Average $\Delta_{47}$	STDEV $\Delta_{47}$	SE $\Delta_{47}$	Average D47 raw	STDEV D47 raw	SE D47 raw	Average RF AC	STDEV RF AC	SE RF AC	95% confidence interval (permil)	known T (°C)	$10^6/T^2$ (K)	TD47 (°C)	External standard error (°C)								
BSP-1	Bärenschacht, Switzerland	0.13	0.554	0.121	-17.71	0.134	0.029	0.707	0.006	0.006	0.013	8.9	12.6	11.5	1.6								
DSP1	Dark Star, Uzbekistan	0.10	0.181	0.055	-6.06	0.142	0.043	0.758	0.008	0.009	0.021	3.2	13.1	-0.9	2.2								
GPC-1	Guano Cave, Tanzania	-0.52	0.372	0.081	-16.57	0.121	0.026	0.638	0.007	0.007	0.015	24.5	11.3	31.1	2.4								
MCP-1	Mawmluh Cave, India	0.17	0.240	0.051	-14.89	0.234	0.030	0.686	0.006	0.007	0.015	18.6	11.7	17.0	1.9								
NAICA 1	Naica Mine, Mexico	0.70	0.784	0.190	-11.16	0.111	0.027	0.603	0.008	0.008	0.018	47.0	9.8	42.7	3.0								
OWB-1	Oder-Warthe-Bogen, Poland	-0.20	0.363	0.079	-19.74	0.085	0.019	0.723	0.004	0.009	0.019	9.1	12.6	7.4	2.2								

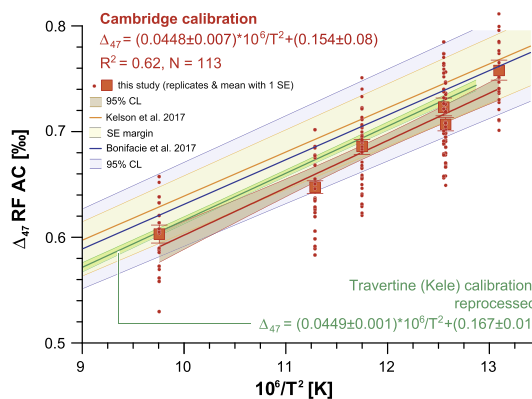


Fig. 2. Cambridge clumped isotope calibration. Comparison of Cambridge  $\Delta_{47}$ -temperature calibration (red line with 95% confidence limits) with the travertine calibration (black line) of Kele et al. (2015), recalculated using the parameters recommended by Daëron et al. (2016). The two calibration regression lines are parallel to each other. The Cambridge calibration is based on subaqueous cave carbonates and spans the temperature range from 3 to 47°C. Temperature is given in Kelvin. RF AC refers to acid fractionation corrected  $\Delta_{47}$  values in the ARF of Dennis et al. (2011). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### 3.2. Coretop foraminifera samples

We analyzed 24 coretop samples, including eight species of planktonic foraminifera, for Mg/Ca ratio and clumped isotopes (Figs. 1 and 3, Table S2). The foraminiferal samples span a wide range of water temperature from 2 to 29°C. The Mg/Ca ratios range from about 0.8 to 6 mmol mol<sup>-1</sup>, whereas  $\Delta_{47}$  values vary from 0.654‰ to 0.741‰. Most paired Mg/Ca- $\Delta_{47}$  values follow the predicted relationship (Fig. 3), supporting the sensitivity of both geochemical thermometers when applied to modern samples. Colder samples often show elevated Mg/Ca and/or  $\Delta_{47}$  values and tend to deviate from the predicted tandem line, similar to previous observations (Tripathi et al., 2010; Grauel et al., 2013).

A significant divergence from the theoretical Mg/Ca- $\Delta_{47}$  relationship indicates a problem with Mg/Ca,  $\Delta_{47}$ , or both. Several samples fall well off the expected line, with two *N. dutertrei* samples exhibiting too low  $\Delta_{47}$  or Mg/Ca values and two samples (1 *N. pachyderma* (s) and 1 *O. universa*) exhibiting too high values. These samples are clearly influenced by factors other than temperature.

### 3.3. Tandem Mg/Ca- $\Delta_{47}$ calibration

The measured  $\Delta_{47}$  values versus Mg/Ca ratios are compared to the expected relationship between the Cambridge clumped isotope calibration and the Mg/Ca-based temperatures calculated with the calibration of Elderfield and Ganssen (2000) (Fig. 3). This combined equation is expressed as:

$$\frac{Mg}{Ca} = a \exp\left(b \sqrt{\frac{c}{\Delta_{47} - d}} - 273.15\right), \quad (3)$$

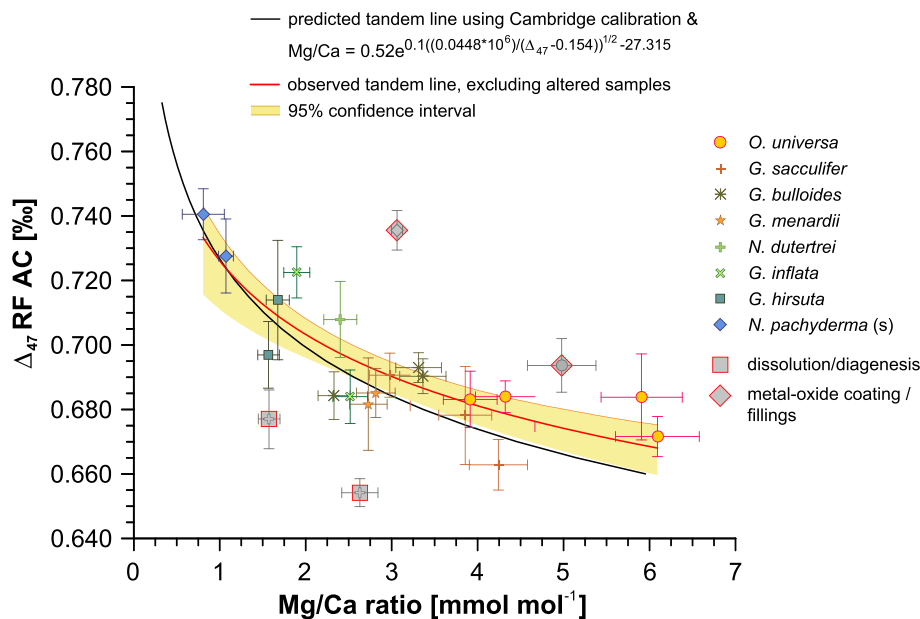


Fig. 3. Comparison of observed and predicted relationship between Mg/Ca and  $\Delta_{47}$ . Black line shows the predicted relationship using the Cambridge calibration:  $\Delta_{47} = (0.0448 * 10^6/T^2) + 0.154$  and the Mg/Ca-T equation of Elderfield and Ganssen (2000):  $Mg/Ca = 0.52 \exp^{0.10T}$  ( $^{\circ}C$ ). Mg/Ca and  $\Delta_{47}$  were measured on identical tests comprising 8 foraminiferal species. The yellow shading represents the 95% confidence interval of all samples measured that were not affected by contamination or dissolution, based on 5000 Monte-Carlo simulations. Diamonds identify samples affected by metal oxide coating or filling, squares indicate samples influenced by dissolution.

where  $a$  is the pre-exponential constant,  $b$  is the sensitivity factor of Mg/Ca per  $^{\circ}C$ ,  $c$  is the slope of the clumped isotope regression,  $d$  is the intercept of the clumped isotope regression.

## 4. DISCUSSION

### 4.1. Relationship between Mg/Ca ratios and $\Delta_{47}$ values

Although a large number of proxies exist for estimating past temperature of the ocean in marine sediments (Müller et al., 1998; Elderfield and Ganssen, 2000; Bijl et al., 2009; Hasenfratz et al., 2017), only a few studies have attempted replication of paleotemperatures with different proxies using the *exact same material*. Paleotemperature proxies measured on different substances from the same samples in a core can disagree for a variety of reasons (e.g., Bijl et al., 2009; MARGO project members, 2009; Grauel et al., 2012). For example, alkenones or TEX<sub>86</sub> may record temperatures at a different depth or season than that of foraminiferal calcite.

The major advantage of our approach is that Mg/Ca ratios and  $\Delta_{47}$  values represent two completely independent temperature proxies that can be measured on the same homogenized samples of foraminiferal calcite; thus, they should yield the same calcification temperature if secondary factors have not altered the shell chemistry. Indeed, our results show that careful selection and cleaning of foraminifera from spatially diverse coretops follow the predicted Mg/Ca- $\Delta_{47}$  relationship (Fig. 3), providing support for the tandem Mg/Ca-clumped isotope approach.

Several processes can result in a divergence from the expected relationship (Fig. 4). Iron-manganese oxide or

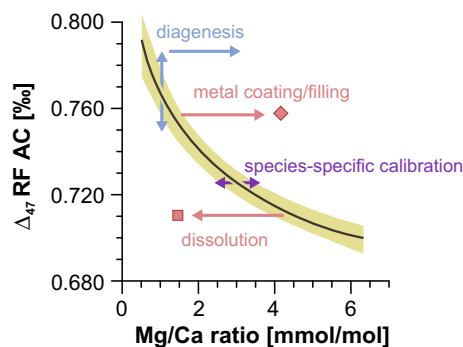


Fig. 4. Schematic diagram of the theoretical relationship of planktonic foraminifera Mg/Ca and  $\Delta_{47}$ . Arrows illustrate the qualitative direction of change expected from processes such as dissolution (square), metal oxide coatings or contamination (diamond), diagenesis and species vital effects that influence Mg/Ca-temperature calibrations.

manganese carbonate coatings contain excess Mg concentrations that result in anomalously high Mg/Ca ratios (Barker et al., 2003, 2005; Pena et al., 2008; Hasenfratz et al., 2017). Reductive cleaning may yield more reliable results for these samples, but we have not tested the effect of reductive cleaning on clumped isotopes. Heating of the sample during cleaning is ill advised; thus, different cleaning procedures need to be applied to aliquots for clumped and Mg/Ca analyses if reductive cleaning is necessary. Dissolution can preferentially remove high-Mg calcite in foraminifera tests, resulting in too low Mg/Ca ratios and temperatures (Brown and Elderfield, 1996; Fehrenbacher and Martin, 2014). If dissolution selectively removes

“warmer” specimens (those with higher Mg/Ca ratios) clumped isotopes would be affected, whereas if dissolution affects high-Mg phases within foraminifera tests the clumped isotope signal would not be affected.

Although we do not observe systematic offsets of individual species, we identify several samples that do not conform to the expected  $\Delta_{47}$ -Mg/Ca relationship (Fig. 3). Two *N. dutertrei* samples exhibit too low  $\Delta_{47}$  or Mg/Ca values and consequently fall below the predicted calibration line, whereas one sample of *N. pachyderma* (s) and one of *O. universa* exhibit too high values and fall above the predicted line.

Clumped isotope temperature ( $T_{\Delta_{47}}$ ) estimates for the *N. dutertrei* outliers are close to the estimated temperature at calcification depth (Fig. 7; Fig. S2A), whereas  $T_{\Delta_{47}}$  is lower than the SST estimates for these samples (Fig. S2B). The Mg/Ca-based temperature estimates ( $T_{\text{Mg/Ca}}$ ) are too cold for both calcification depth and SST (Figs. S2C, D). This suggests that the Mg/Ca ratio has been compromised by dissolution (Regenberg et al., 2014), while the clumped isotope values give the correct temperature at the time of test formation. These two outliers are from cores located at ca. 1.3 km and 1.8 km water depth in the Indian and Pacific Oceans, respectively, near or below the critical depth at which dissolution sets in (Fig. 7 in Regenberg et al., 2014) (Fig. S3).

Two samples that fall clearly above the line (*N. pachyderma* (s) and *O. universa*) (Fig. 3) may have been affected by Fe-Mn oxide or Mn carbonate coatings, or infilling that was insufficiently removed during the cleaning procedure, although this is not supported by elevated indicative elemental ratios (Table S2). Coating of Fe-Mn oxide or Mn carbonate can increase the Mg concentration in foraminiferal tests and such addition would cause abnormally high Mg/Ca ratios (Boyle, 1983; Lea et al., 2005). Fe-Mn coatings or infillings would affect the Mg/Ca ratio-derived temperature estimate, but would not influence the clumped isotopes. This interpretation

is consistent with too high  $T_{\text{Mg/Ca}}$ , but  $T_{\Delta_{47}}$  values that are in line with calcification depth temperatures and SST data (Fig. S2).

The outlying *N. pachyderma* sample is characterized by an unrealistically high Mg/Ca ratio and  $T_{\text{Mg/Ca}}$  for its location in the Arctic (Figs. 3, S2C, D). In contrast,  $T_{\Delta_{47}}$  is only slightly higher than the estimated calcification temperature (Fig. S2). The elemental ratios do not show signs of contamination that might have affected the Mg/Ca signal and it remains unclear what process led to the high Mg/Ca ratios in these samples.

The fact that the outlying *O. universa* sample gives a Mg/Ca temperature that is consistent with its calcification temperature and SST (Figs. S2C, D) suggests that only the clumped isotope system has been compromised. The  $T_{\Delta_{47}}$  value for this outlier is ca. 5°C too low, implying either insufficient replicate analyses or diagenetic alteration via some unexplained process which increases  $\Delta_{47}$ .

## 4.2. Temperature estimates

We test both species-specific calibrations and the multi-species Mg/Ca-T regression equation of Elderfield and Ganssen (2000) to calculate the temperature at the time of calcification (Figs. 5A, B). A cross-plot of clumped isotope ( $T_{\Delta_{47}}$ ) and Mg/Ca ( $T_{\text{Mg/Ca}}$ ) temperatures shows that most samples fall close to the 1:1 line, confirming the feasibility of the tandem Mg/Ca- $\Delta_{47}$  approach. Deviations largely related to the high temperature end but are small considering the confidence limit. If only the analytical error is considered, Mg/Ca measurements provide temperature estimates with a lower error (average ca.  $\pm 1^\circ\text{C}$ ) than clumped isotopes (average ca.  $\pm 2^\circ\text{C}$ ). Using species-specific equations to calculate  $T_{\text{Mg/Ca}}$  results in generally larger deviations from the 1:1 line (Fig. 5A) compared to the multi-species calibration (Fig. 5B). This can be explained by the fact that the samples used here are derived from the same coretops used by Elderfield and Ganssen

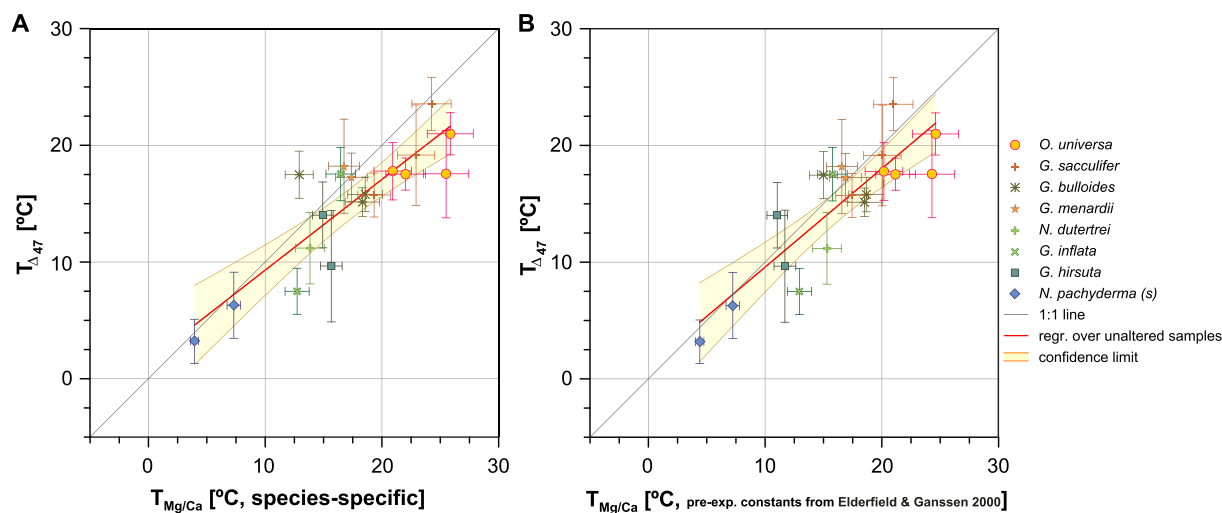


Fig. 5. Comparison of temperatures derived from different Mg/Ca calibrations. (A) Comparison of temperature estimates using the Cambridge equation for  $T_{\Delta_{47}}$  and species-specific pre-exponential constants for  $T_{\text{Mg/Ca}}$  (Table 2). (B) as in (a) but with the single constant of 0.52 (Elderfield and Ganssen, 2000).



(2000). Using the constant ( $b$ ) of 0.52 might be favorable for calculating the calcification temperatures because it is derived from coretop samples that integrate all effects that alter the Mg/Ca signatures prior to and during sedimentation.

Species-specific calibrations are often based on cultured foraminifera or field data that could suffer from restricted temperature ranges of individual species (Anand et al., 2003), species-specific lagged response to SST (Fallet et al., 2010), or differential impact of dissolution on Mg/Ca in foraminifera with different depth habitats (Mulitza et al., 2003). Furthermore, such calibrations might only be valid for specific geographic regions. Because species-specific equations are not available for all extant species or any extinct species, we suggest that using the multi-species pre-exponential constant is a valid test of the tandem method.

Frequently,  $T_{\text{Mg/Ca}}$  values are slightly higher than the annual mean calcification temperature at the water depth derived from the GISS Atlas, whereas  $T_{\Delta 47}$  values agree with calcification temperatures (NOA\_WOA98, Figs. S2A and S2C). Discrepancies could be explained by seasonal calcification bias for individual species, or calcification related to gametogenesis and incorrect assignment of the calcification depth for the foraminifera (see supplemental material).  $T_{\text{Mg/Ca}}$  values show higher scatter and tend to overestimate both calcification depth and sea surface temperatures (Figs. S2C, D).

#### 4.3. $\delta^{18}\text{O}$ of seawater

$\delta^{18}\text{O}_{\text{cc}}$  is dependent on both water temperature and the  $\delta^{18}\text{O}_{\text{sw}}$ . This relationship can be used to estimate the water temperature at the calcification depth, or alternatively the  $\delta^{18}\text{O}_{\text{sw}}$  value, expressed in the form:

$$T (^{\circ}\text{C}) = a + b(\delta^{18}\text{O}_{\text{cc}} - \delta^{18}\text{O}_{\text{sw}}) + c(\delta^{18}\text{O}_{\text{cc}} - \delta^{18}\text{O}_{\text{sw}})^2, \quad (4)$$

where the  $\delta^{18}\text{O}_{\text{cc}}$  value is the equilibrium value of calcite;  $\delta^{18}\text{O}_{\text{sw}}$  is the oxygen isotope value of seawater, and  $a$ ,  $b$ , and  $c$  are constants. Some calibrations use a linear form of the equation where  $c = 0$ .

Many equations with different constants are available, which are derived from both culture experiments and precipitation of inorganic carbonate (Pearson, 2012). We use the equation of Mulitza et al. (2003) because it is based on planktonic foraminifera with a temperature range between 16°C and 31°C (Pearson, 2012). Furthermore, we correct for vital effects using offset values available for different species (Table 2).

Fig. 6 shows the calculated  $\delta^{18}\text{O}_{\text{sw}}$  values using the temperature derived from the Mg/Ca ratio and the  $\Delta_{47}$  value and  $\delta^{18}\text{O}_{\text{cc}}$ . Tandem estimates of the  $\delta^{18}\text{O}_{\text{sw}}$  values obtained from unaltered foraminifera tests fall near the 1:1 line, with *G. inflata*, *G. menardii* and *G. sacculifer* being closest. Large uncertainties associated with the calibrations hamper determination of accurate  $\delta^{18}\text{O}_{\text{sw}}$  values (e.g., Grauel et al., 2013). Additional scatter might be introduced by using

multiple pre-exponential constants for calculating  $T_{\text{Mg/Ca}}$ . We also used a larger size fraction of foraminiferal tests for some species to obtain sufficient mass for the clumped isotope measurement. The  $\delta^{18}\text{O}$  of some foraminifera in coretop samples has been shown to increase with test size (Friedrich et al., 2012). The higher  $\delta^{18}\text{O}_{\text{cc}}$  value translates to higher  $\delta^{18}\text{O}_{\text{sw}}$  value when both Mg/Ca ratios and  $\Delta_{47}$  values are used to calculate temperature.

#### 4.4. A clumped isotope regression for planktonic foraminifera

The Cambridge and ETH clumped isotope calibrations agree very closely (Fig. 2) and span the expected range of SST reflected in the coretop samples. We use the Cambridge clumped isotope calibration to estimate foraminiferal calcification temperature because the foraminifera have been measured using the same method on the same instrument as the cave pearl calibration.

We constructed an independent clumped isotope regression of foraminifera by comparing measured  $\Delta_{47}$  values with calcification depth temperatures of the individual species using the GISS Atlas (Table S2). The derived regression equation is:

$$\Delta_{47} = (0.0315 \pm 0.008) * 10^6/T^2 + (0.313 \pm 0.1), \quad (5)$$

$$N = 158, \quad R^2 = 0.31$$

and spans the temperature range from 2°C to 27°C. The slope of the line is within error of the Cambridge calibration (0.0315 vs. 0.0448) (Fig. 7). The foraminifera regression is only based on a few samples spanning a limited temperature range and should be regarded as verification that the Cambridge calibration can be applied to foraminifera. Whereas almost all foraminifera samples fall on the Cambridge calibration, some samples like *N. pachyderma* fall below the regression. *N. pachyderma* (s) samples have also been reported to give clumped isotope temperatures that were too low compared to inferred calcification temperatures (Grauel et al., 2013). We conclude the Cambridge calibration can be applied to foraminifera, as suggested by previous studies (Eiler, 2007; Tripathi et al., 2010; Grauel et al., 2013; Kele et al., 2015; Rodríguez-Sanz et al., 2017).

#### 4.5. Application to fossil foraminifera

Paired Mg/Ca- $\Delta_{47}$  measurements constitute a powerful tool for identifying altered samples and can be applied to fossil foraminifera to yield reliable paleotemperature estimates. Provided the temperature sensitivities of Mg/Ca ratios and clumped isotopes have not been altered through dissolution or diagenesis, we expect fossil specimens to follow the same theoretical relationship as modern foraminifera. Paleotemperature estimates from samples that fall on the predicted line can be regarded with a high degree of confidence, whereas results that significantly deviate from the expected line indicate either the Mg/Ca ratios,  $\Delta_{47}$  values or both proxies have been affected by secondary effects.

Additional factors could affect the Mg/Ca ratios and  $\Delta_{47}$  values of fossil foraminifera compared to the modern ones

Table 2  
References, species-specific pre-exponential constants and vital offset correction values.

Species	Vital offset correction for $\delta^{18}\text{O}$ (‰, VPDB)	Vital offset reference	Mg/Ca = B exp(AT)		Species-specific constants reference
			B	A	
<i>Globigerina bulloides</i>	0.5	Lin et al., 1997, Paleooceanography 12, 415–427	1.006	0.065	Riveiros et al., 2016, Geochim. Geophys. Geosyst. 17, 1249–1264
<i>Globigerinoides sacculifer</i>	0.6	Rippert et al., 2016, Marine Micropaleontology 128, 14–27	0.74	0.072	Regenberg et al., 2009, EPSL 278, 324–336
<i>Globorotalia hirsuta</i>	0.45	Cleroux et al., 2013, Paleooceanography 12, 1–14	0.409	0.09	Anand et al., 2003, Paleooceanography 18, 1050
<i>Globorotalia hirsuta (dextral)</i>	0.45	Cleroux et al., 2013, Paleooceanography 12, 1–14	0.409	0.09	Anand et al., 2003, Paleooceanography 18, 1050
<i>Globorotalia inflata</i>	0.12	Cleroux et al., 2013, Paleooceanography 12, 1–14	0.72	0.076	Groeneveld and Chiessi, 2011, Paleooceanography 26, P2203
<i>Globorotalia menardii</i>	nil	Kahn et al.1979, Oceanologica Acta 2, 195–208	1.18	0.05	Regenberg et al., 2009, EPSL 278, 324–336
<i>Neogloboquadrina dutertrei</i>	0.26	Cleroux et al., 2013, Paleooceanography 12, 1–14	1.15	0.034	Regenberg et al., 2009, EPSL 278, 324–336
<i>Neogloboquadrina pachyderma (sinistral)</i>	1.5	Pados et al., 2015, Biogeosciences 12, 1733–1752	0.58	0.084	Anand et al., 2003, Paleooceanography 18, 1050
<i>Orbulina universa</i>	0.1	Niebler et al., 1999, in: Fischer & Wefer	0.595	0.09	Anand et al., 2003, Paleooceanography 18, 1050

including burial diagenesis (Winkelstern and Lohmann, 2016) and changing seawater chemistry (Fig. 4). Secondary (inorganic) calcite will typically have higher Mg/Ca, whereas clumped isotopes will depend upon the temperature of recrystallization, which may be higher or lower than the foraminifer calcification temperature. Important factors limiting the application of Mg/Ca ratios of planktonic foraminifera for paleotemperature reconstruction include dissolution, Fe-Mn oxide coatings, and seawater Mg/Ca ratio variations through time. If foraminifera are exposed to undersaturated waters, high-Mg carbonate will dissolve preferentially and lower Mg/Ca ratios, thereby lowering apparent temperatures (Regenberg et al., 2014 and references

therein). Following burial, authigenic Fe-Mn metal oxide may coat the tests and increase the Mg/Ca ratio resulting in higher apparent temperatures (Lea et al., 2005). High salinity (38–39 PS); may also affect Mg/Ca ratios although these salinities are limited to marginal seas (Ferguson et al., 2008; Hönisch et al., 2013).

Long-term variations in Mg/Ca ratios of seawater also affect the Mg/Ca of foraminifera (Evans et al., 2015). It is likely that the Mg/Ca ratio of seawater has increased during the Cretaceous and Cenozoic (Coggon et al., 2010), which introduces ambiguity into Mg/Ca paleothermometry. A change in the Mg/Ca ratio of seawater from the current value of  $5.2 \text{ mmol mol}^{-1}$  would affect foraminiferal

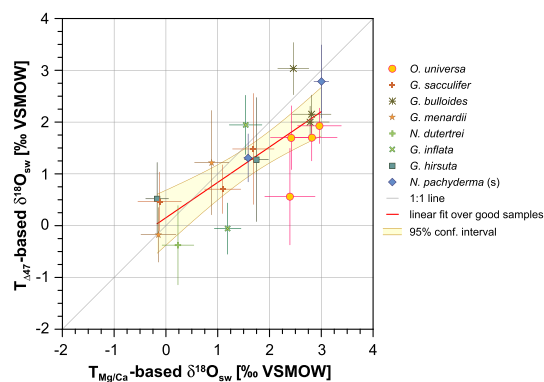


Fig. 6. Comparison of estimates of  $\delta^{18}\text{O}$  in seawater using species-specific  $T_{\text{Mg/Ca}}$  and  $T_{A47}$ .  $\delta^{18}\text{O}_{\text{sw}}$  estimates at the calcification depth are calculated using  $\delta^{18}\text{O}_{\text{cc}}$  corrected for vital effects (Table 2) and the equation  $\delta^{18}\text{O}_{\text{sw}} = ((T - 14.91) + 4.35(\delta^{18}\text{O}_{\text{cc}} + 0.27))/4.35$  from Mulitza et al. (2003). Analytical uncertainties are given assuming 0.25‰ change in  $\delta^{18}\text{O}$  per °C. When considering the associated errors, the slope of the estimates of  $\delta^{18}\text{O}_{\text{sw}}$  calculated using  $T_{\text{Mg/Ca}}$  and  $T_{A47}$  are close to unity.

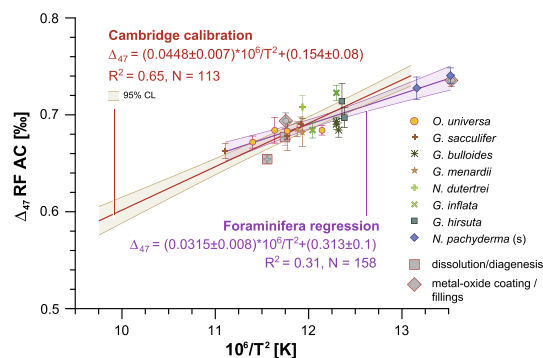


Fig. 7. Clumped isotope calibration for planktonic foraminifera with 95% confidence interval. The foraminifera regression (purple line) is close to the Cambridge cave carbonate calibration (red line). The slope strongly depends on individual samples and is not robust. Samples earlier labeled as affected by dissolution or metal-oxides have not been used for calculating the foraminifera clumped isotope regression. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Mg/Ca but not  $\Delta_{47}$ , resulting in a deviation from the modern Mg/Ca- $\Delta_{47}$  relationship. If the sensitivity of Mg/Ca to temperature is constant or can be estimated (Evans and Müller, 2012), then tandem Mg/Ca- $\Delta_{47}$  analyses might be useful for assessing secular variations in seawater Mg/Ca ratios. With robust  $\Delta_{47}$ -derived calcification temperatures, seawater Mg/Ca ratios (Evans et al., 2018) may be back-calculated and compared to other archives (Coggon et al., 2010). A complication to such an approach is that the sensitivity of Mg/Ca ratios to biogenic uptake may also change as a function of seawater Mg/Ca ratios (Evans et al., 2016).

#### 4.6. Relationship between paired clumped and oxygen isotope measurements

Combining Mg/Ca,  $\Delta_{47}$  and  $\delta^{18}\text{O}_{\text{cc}}$  permits estimation of  $\delta^{18}\text{O}_{\text{sw}}$ , with the potential to deconvolve the signal of temperature and  $\delta^{18}\text{O}_{\text{sw}}$  (ice volume) from  $\delta^{18}\text{O}_{\text{cc}}$  record (e.g., Lear et al., 2000, 2015). The Cenozoic history of glacial ice volume on the continents is a longstanding problem in paleoclimatology that has been difficult to resolve using existing methods. Although it is difficult to derive the absolute value of  $\delta^{18}\text{O}_{\text{sw}}$ , Elderfield et al. (2012) suggested that relative changes in  $\delta^{18}\text{O}_{\text{sw}}$  could be estimated using the sensitivities of Mg/Ca and  $\delta^{18}\text{O}_{\text{cc}}$  to temperature, which are well known:

$$\Delta\delta^{18}\text{O}_{\text{sw}} = \Delta\delta^{18}\text{O}_{\text{cc}} + \frac{\text{Mg}}{\text{Ca}} \frac{S_{\text{O}}}{S_{\text{Mg}}}, \quad (6)$$

where  $\Delta\delta^{18}\text{O}_{\text{sw}}$  is the change in the  $\delta^{18}\text{O}$  of seawater,  $\Delta\delta^{18}\text{O}_{\text{cc}}$  is the change in the  $\delta^{18}\text{O}$  of calcite, and  $S_{\text{O}}$  and  $S_{\text{Mg}}$  are the sensitivities of oxygen isotopes and Mg/Ca to temperature. This simplified expression is only valid for small changes (see supplementary material).

Following a similar approach, we derive the approximate relationship between small changes in paired clumped and oxygen isotope measurements (see supplementary material):

$$\Delta\delta^{18}\text{O}_{\text{sw}} = \Delta\delta^{18}\text{O}_{\text{cc}} + \frac{S_{\text{O}}}{S_{\Delta_{47}}} \frac{T^3}{2} \Delta\Delta_{47}, \quad (7)$$

where  $\Delta\delta^{18}\text{O}_{\text{sw}}$  is the change in the  $\delta^{18}\text{O}$  of seawater,  $\Delta\delta^{18}\text{O}_{\text{cc}}$  is the change in the  $\delta^{18}\text{O}$  of calcite,  $\Delta\Delta_{47}$  is the change in  $\Delta_{47}$ , and  $S_{\text{O}}$  and  $S_{\Delta_{47}}$  are the sensitivities of oxygen isotopes and clumped isotopes to temperature. The sensitivity  $S_{\Delta_{47}}$  is estimated from the slope of the curve in Fig. 2, but at temperature  $T$  (in Kelvin). For example, choosing  $T = 290$  K (17°C) this approximation is valid for the targeted temperature range (0°C and 35°C). The  $S_{\Delta_{47}}$  of the Cambridge calibration is 0.003‰ per °C, which gives a  $S_{\Delta_{47}}/S_{\text{O}}$  sensitivity of 0.012.

The sensitivity ratio ( $S_{\text{O}}/S_{\Delta_{47}}$ ) can also be estimated by the slope of  $\Delta_{47}$  versus  $\delta^{18}\text{O}$  for the coretop planktonic foraminiferal data (Fig. 8) assuming, as a first approximation, a constant  $\delta^{18}\text{O}_{\text{w}}$ , for the modern ocean (i.e. the measured  $\delta^{18}\text{O}_{\text{cc}}$  is solely controlled by temperature). The slope of the  $T_{\Delta_{47}}$  versus  $\delta^{18}\text{O}$  line is similar to available calcite-water  $\delta^{18}\text{O}$  equilibrium equations (Pearson, 2012). The slope  $S_{\Delta_{47}}/S_{\text{O}}$  is 0.012 (Fig. 8) which is similar to the estimated calibration given above.

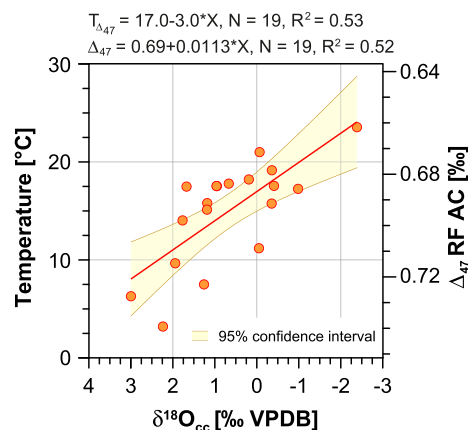


Fig. 8. Regression of measured  $\delta^{18}\text{O}_{\text{cc}}$  and clumped isotopes ( $\Delta_{47}$  RF AC) and temperatures derived using the Cambridge calibration. The slope of  $\delta^{18}\text{O}_{\text{cc}}$  versus  $\Delta_{47}$  gives the sensitivity ( $S_{\text{O}}/S_{\Delta_{47}}$ ) of the  $\delta^{18}\text{O}$ -clumped isotope system. The slope of  $\delta^{18}\text{O}_{\text{cc}}$  versus  $\Delta_{47}$ -derived temperature is -3, which is close to other estimates of the sensitivity of foraminiferal  $\delta^{18}\text{O}_{\text{cc}}$  to temperature (Pearson, 2012).

In paleoclimate studies, it is often the change in temperature or  $\delta^{18}\text{O}_{\text{sw}}$  that is sought rather than the absolute values. Eqs. (5) and (6) allow estimation of the change in the  $\delta^{18}\text{O}_{\text{sw}}$  knowing the sensitivities (slopes) of Mg/Ca,  $\Delta_{47}$  and  $\delta^{18}\text{O}$  to temperature, but is independent of the intercepts of the calibrations. The temperature sensitivity of Mg/Ca for most species of planktonic foraminifera is close to 0.1, whereas the pre-exponential constant varies among species. Similarly, the slopes of the different clumped isotope temperature calibrations are fairly similar but the intercepts vary more widely (Figs. 2 and 7). The propagated errors in estimating  $\delta^{18}\text{O}_{\text{sw}}$  from  $\delta^{18}\text{O}_{\text{cc}}$  and  $\Delta_{47}$  measurements are too large ( $\pm 0.6\%$ ) to be practically useful for paleoclimate studies. We suggest that studies can be designed to measure differences in  $\Delta_{47}$ ,  $\delta^{18}\text{O}$  and Mg/Ca between samples to test for changes in the  $\delta^{18}\text{O}$  of seawater.

An example application is the magnitude of temperature and ice volume change across the Eocene/Oligocene boundary, which has been investigated using both clumped isotopes (Petersen and Schrag, 2015) and Mg/Ca (Lear et al., 2008; Bohaty et al., 2012). Petersen and Schrag (2015) found that  $\Delta_{47}$  values of planktonic foraminifera at ODP Site 689 remain nearly constant across the Eocene/Oligocene boundary, requiring that the large increase in  $\delta^{18}\text{O}$  must be explained entirely by changes in the isotopic composition of seawater ( $\delta^{18}\text{O}_{\text{sw}}$ ). Although the clumped isotope estimate of  $\delta^{18}\text{O}_{\text{sw}}$  change ( $0.75 \pm 0.23\%$ ) agrees within error with several Mg/Ca-based estimates, our method of simultaneous measurement of  $\Delta_{47}$  and Mg/Ca on the same foraminifera would offer a more direct comparison.

The triple-proxy approach (Mg/Ca,  $\Delta_{47}$  and  $\delta^{18}\text{O}_{\text{cc}}$ ) can provide higher confidence in reconstructed changes in temperature and  $\delta^{18}\text{O}$  of seawater if two independent proxies provide the same results. It will be challenging to obtain enough benthic foraminifera for clumped and Mg/Ca analysis, but the sample size required is continuing to be

reduced. For example, we require only  $\sim 2$  mg of cleaned material for both  $\Delta_{47}$  (Meckler et al., 2014) and Mg/Ca analysis (de Villiers et al., 2002) making analysis of benthic foraminifera possible in large volume samples. Further reduction of the required sample size can be achieved with the LIDI (long-integration dual-inlet) approach (Müller et al., 2017b).

## 5. CONCLUSIONS

We demonstrate that paired Mg/Ca ratios and  $\Delta_{47}$  values measured on the same planktonic foraminifera from coretop samples follow expected relationships and provide redundant temperature estimates. Concordant results provide more confidence in derived (paleo)temperature estimates whereas discordant results identify suspect samples that are affected by secondary processes. As both proxies have uncertainties and limitations, obtaining the same temperature from paired analysis is a significant improvement over single-proxy estimates. This approach also avoids the large uncertainties in temperature estimates inherent in the combination of proxies derived from different organisms (coccolithophorids, foraminifera, crenarchaeota, etc.) that may have different seasonal, water-depth and habitat preferences. The combination of two completely independent methods on the exact same foraminiferal calcite provides a robust estimate of water temperatures that is independent of variations of seawater  $\delta^{18}\text{O}$ . Furthermore, this tandem approach aids in the identification of foraminiferal calcite that may have been altered through dissolution or diagenetic alteration. Finally, the approach also allows tandem estimates of the oxygen isotope composition of seawater from the simultaneous measurement of the  $\delta^{18}\text{O}$  of the same shells. The redundancy inherent in the method has the potential to greatly improve confidence in paleoclimate reconstructions.

## ACKNOWLEDGMENTS

Ian Mather provided invaluable technical support for the clumped isotope measurements. Cedric John and Simon Davis (Imperial College London) helped us with heated gas preparations. We thank Gerald Ganssen (Amsterdam Global Change Institute) for use of his sample collection. Ludwig Löwemark (National Taiwan University) and Richard Gyllenkreutz (Stockholm University) kindly provided some Arctic samples and the Taiwan Ocean Research Institute provided the sample from the Okhotsk Sea. Professors Paolo Forti and Jose Maria Calaforra provided the sample NAICA-01. Julio Lompronti is thanked for his support with SEM imaging. Finally, we thank Norbert Marwan (PIK Potsdam), and Niklas Boers (ENS Paris), for fruitful discussions. Harry Elderfield contributed to this study with his deep insights into the (bio)geochemistry of foraminifera. His enthusiasm for paleoceanographic research is deeply felt as a loss for all authors. We dedicate this publication to the memory of our colleague and friend Prof. Harry Elderfield FRS who sadly passed away prior to the final preparation of the manuscript.

## FUNDING

This study was predominantly supported by NERC project ID NE/M003752/1 to D.A.H. and H.E.. S.F.M.B., F. G. and D.A.H. also acknowledge support from the European Union's Horizon 2020 Research and Innovation programme (Marie Skłodowska-Curie grant agreement No. 691037). S.M.B acknowledges support of SNSF project No. 200020\_160046.

## AUTHOR CONTRIBUTIONS

D.A.H., H.E., S.F.M.B. and A.L.G. designed the study. D.A.H. and M.V. selected the cores and sample material. S. F.M.B., J.R., L.L., F.G. and A.L.G. conducted the clumped analyses and M.V. and M.G. made the Mg/Ca analyses. All authors contributed to the interpretation of the results. S.F.M.B. and D.A.H. wrote the manuscript with editorial contributions from all other authors.

## COMPETING INTERESTS

The authors declare no competing financial interests.

## DATA AND MATERIALS AVAILABILITY

All data will be made available online at <http://www.ruhr-uni-bochum.de/sediment/publikationen.html>. Additional data available from authors upon request.

## APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.gca.2018.03.010>.

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Associate editor: Thomas M. Marchitto