

On the combination of the planktonic foraminiferal Mg/Ca, clumped (Δ_{47}) and conventional ($\delta^{18}\text{O}$) stable isotope paleothermometers in palaeoceanographic studies

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Abstract

Assuming that foraminiferal clumped isotope (Δ_{47}) values are independent of seawater salinity and pH, the combination of Mg/Ca, $\delta^{18}\text{O}$ and Δ_{47} values, may in theory allow us to disentangle the temperature, salinity/ $\delta^{18}\text{O}_{\text{sw}}$ and pH signals. Here, we present a new Mg/Ca- Δ_{47} dataset for modern planktonic foraminifera, from various oceanographic basins and covering a large range of temperatures (from -0.8 to 25 °C). These measurements were performed on the same samples and species as the ones used for the foraminiferal Δ_{47} calibration of Peral et al. (2018), allowing comparison between both Mg/Ca and Δ_{47} paleothermometers. There is a good agreement between these two paleothermometers when the Mg/Ca-temperature is corrected for seawater salinity and pH, suggesting that foraminiferal Δ_{47} shows not relationship to salinity nor pH. Our results show, however, that Δ_{47} temperature uncertainties still limit our ability to reconstruct accurately enough pH and $\delta^{18}\text{O}_{\text{sw}}$ from the combination of Mg/Ca, $\delta^{18}\text{O}$ and Δ_{47} .

This article also presents an update of the previously published foraminiferal Δ_{47} calibration (Peral et al., 2018), that can be directly applied to palaeoceanographic studies: $\Delta_{47} = 37.0 \times 10^3 / T^2 + 0.181$.

1. INTRODUCTION

The reconstruction of key physical and chemical ocean water parameters, like seawater temperature, salinity and pH, is critical to understand the processes driving past ocean and climate variations. However, precisely quantifying these parameters remains extremely challenging. Several proxies have been developed to reconstruct paleo-temperatures, but they all suffer from various limitations and biases. In his seminal work on isotopes, Harold Urey suggested that the extent by which ^{18}O was enriched in marine calcium carbonates relative to the water from which it is precipitated, could be used as a past ocean thermometer (Urey, 1947). However, later studies showed that this paleo-thermometer is biased by the isotopic composition of the global ocean ($\delta^{18}\text{O}_{\text{sw}}$) that does not remain constant but reflects the waxing and waning of large continental ice sheets over glacial and interglacial cycles. This signal associated with global changes in continental ice volume strongly imprints paleo- $\delta^{18}\text{O}$ records obtained from marine carbonates (Shackleton, 1967), with additional

contributions from regional modifications of evaporation/precipitation (in a smaller contribution). Thus, it is impossible to accurately reconstruct past ocean temperature using the carbonate $\delta^{18}\text{O}$ -thermometer without an independent knowledge of seawater $\delta^{18}\text{O}_{\text{sw}}$. Furthermore, interspecies differences in the $\delta^{18}\text{O}$ -temperature relationship testify to the importance of physiological processes, also called “*vital*” effects (e.g. Urey et al., 1951). In order to take into account these effects, several authors developed species-specific calibrations (e.g., Bemis et al., 1998; Mulitza et al., 2003).

More recently, several studies showed that the Mg/Ca elemental ratio of foraminiferal calcite can be used to reconstruct paleo-seawater temperatures (Rosenthal et al., 1997; Lea et al., 1999; Elderfield and Ganseen, 2000). Most foraminiferal species build their shells from magnesium-poor calcite, in which the minor amount of Mg that can be substituted to Ca is temperature dependent. The paleoclimatology community had great expectations regarding the combination of foraminiferal $\delta^{18}\text{O}$ and the Mg/Ca-thermometer, which could be measured from the same material allowing theoretically to disentangle temperature and $\delta^{18}\text{O}_{\text{sw}}$ signals. However, the Mg/Ca-thermometry proved to be more complex and challenging than originally expected. First, it appeared that the partitioning coefficient between Mg in seawater and Mg in the crystal matrix is not only thermodynamically controlled by temperature, but also reflects physiological or ecological processes (Rosenthal et al., 1997; Lea et al., 1999; Elderfield and Ganseen, 2000; Lea, 2014), prompting several authors to develop species-specific, empirical Mg/Ca-Temperature calibrations (Nürnberg et al., 1996; Rosenthal et al., 1997; Lea et al., 1999; Erez, 2003). From the first development of the Mg/Ca paleothermometer it was shown that foraminiferal Mg/Ca is influenced by physico-chemical variables other than temperature such as carbonate ion concentration (Elderfield et al., 2006; Rosenthal et al., 2006), as well as salinity (Nürnberg et al., 1996; Lea et al., 1999; Kisakürek et al., 2008; Mathien-Blard and Bassinot, 2009; Gray et al., 2018; Gray and Evans, 2019) and pH (Lea et al., 1999; Gray et al., 2018; Gray and Evans 2019), and - on time-scales longer than ~ 1 Ma - the Mg/Ca ratio of seawater (Evans et al., 2016). In addition, analytical procedures must be carefully considered since cleaning protocols have an effect on the measurement of Mg/Ca within foraminiferal shells (Barker et al. 2003; Pang et al., 2020 and references therein). These secondary influences on foraminiferal Mg/Ca complicate its use as a temperature proxy to such an extent that numerous studies have dealt with the comparison of Mg/Ca based SST estimates with independent paleothermometers.

The carbonate clumped isotope method (noted Δ_{47} hereafter) is one of the most recent paleothermometer, which developed over the last decade. The Δ_{47} approach is based on the quantification of subtle statistical anomalies in the abundance of doubly substituted carbonate isotopologues ($^{13}\text{C}^{18}\text{O}^{16}\text{O}^{16}\text{O}^{2-}$) relative to the random distribution of isotopes (Eiler, 2007, 2011). A slightly higher abundance of ^{13}C - ^{18}O bonds is, for thermodynamical reasons, a function of temperature (Eiler, 2011; Passey and Henkes, 2012; Stolper and Eiler, 2016) and this relationship is independent of the $\delta^{18}\text{O}$ of water in which the calcification occurs (Schauble et al., 2006). Clumped isotope methodological studies have shown no evidence of vital effect (Tripathi et al., 2010; Grauel et al., 2013; Peral et al., 2018; Piasecki et al., 2019; Meinicke et al., 2020) nor salinity effect (Grauel et al., 2013; Peral et al., 2018) on foraminiferal Δ_{47} . Moreover, studies dealing with non-foraminiferal carbonates (Tripathi et al., 2015; Watkins and Hunt, 2015) showed the lack of pH effect (or its negligible influence) on clumped isotope. The absence of major biases would make Δ_{47} one of the most promising paleo-thermometers. However, its use is still limited because of its small temperature sensitivity and the large sample size required to significantly reduce the analytical uncertainties. Obtaining precise and high-resolution Δ_{47} records remains a challenge.

Because of non-thermal effects on $\delta^{18}\text{O}$ and Mg/Ca from foraminifer shells, recent comparisons revealed discrepancies between Mg/Ca- and Δ_{47} -derived temperatures (Peral et al., 2020; Leutert et al., 2020; Meinicke et al., 2021). These discrepancies are not linked to any specific foraminifer species (different species were used in the three studies), nor are they associated to a given oceanic basin (samples from three different regions were studied, the Mediterranean Sea, the Southern Ocean, and the Indian Ocean) or to a time period (the studies covered from the top Pleistocene to 5 million years back). We believe that those discrepancies can be extremely informative as they may chiefly reflect vital effects and the impact of salinity and pH on the Mg/Ca-thermometer, offering the opportunity to disentangle temperature, salinity, and pH from the combination of $\delta^{18}\text{O}$, Mg/Ca and Δ_{47} in planktonic foraminifera. Planktonic foraminiferal $\delta^{18}\text{O}$ depends on temperature and $\delta^{18}\text{O}_{\text{sw}}$, the latter being correlated with the salinity. Carbonate $\delta^{18}\text{O}$ may be combined with Δ_{47} -derived temperature to reconstruct the $\delta^{18}\text{O}_{\text{sw}}$ (Peral et al., 2020). As Mg/Ca is influenced by salinity and pH, pH may be obtained by paring the Mg/Ca ratio with the reconstructed temperature from Δ_{47} and salinity estimates from sea-level or from the combination of $\delta^{18}\text{O}$ - Δ_{47}), following

the equations described in Gray et al. (2018 and 2019). Combining $\delta^{18}\text{O}$, Mg/Ca and Δ_{47} in foraminifera may therefore prove highly useful in palaeoceanographic studies.

The relationship between Mg/Ca and Δ_{47} in planktonic foraminifera has been previously studied to investigate our ability to detect the potential biases associated to Fe-Mn oxide coatings, contamination and/or dissolution of foraminiferal tests (Breitenbach et al., 2018) in order to extract the best paleo-temperature estimates from non-biased measurements. However, the sensitivity of foraminiferal Δ_{47} to salinity and pH has not been given much attention so far and still needs to be examined since a potential dependence of Δ_{47} on these chemo-physical parameters would potentially explain part of the differences observed between the Δ_{47} and the Mg/Ca paleothermometers.

For the present paper, we measured Mg/Ca on the same set of samples and foraminiferal species used in the Δ_{47} calibration of Peral et al. (2018). These data make it possible to explore the sensitivity of foraminiferal Δ_{47} to salinity and pH, and evaluate the potential interest and limits of combining $\delta^{18}\text{O}$, Mg/Ca- and clumped-temperatures to disentangle temperature, salinity- $\delta^{18}\text{O}_{\text{sw}}$, and pH effects. In the process, we took advantage of re-calibrated clumped isotope data following cutting-edge methodological developments to provide a revised version of the planktonic and benthic foraminiferal clumped isotope calibration of Peral et al. (2018), that would be used for future paleoceanographic studies.

2. MATERIALS AND METHODS

2.1. Samples

We used the same samples as those used in Peral et al. (2018), which are core-tops from twelve marine sedimentary cores from different oceanographic basins in the North Atlantic, Southern, Indian and Pacific Oceans (Fig. 1). All core-tops were chronologically constrained and are from the late Holocene (Peral et al., 2018). The location of samples, the water depths of the cores, the studied species and the ages are given in Table 1. We assume no changes in temperature, salinity, and pH over the late Holocene at our core sites and use modern hydrological data (see paragraph 2.4.). Yet, as discussed later, the recent warming and the

addition of anthropogenic CO₂ to the surface ocean likely complicate the comparison of instrumental carbonate system measurements with core-top foraminiferal samples.

The core sites cover a wide range of seawater physico-chemical conditions, with temperatures ranging from -2 to 25 °C, salinity from 33.7 to 36.2 and pH from 7.7 to 8.1. The top 1 cm of each sediment core-top was collected and dried overnight at 50°C. The samples were wet sieved to collect the size fraction larger than 150 μm, and the residues were dried. Nine species of planktonic foraminifera and two species of benthic foraminifera were hand-picked under a binocular.

For the Mg/Ca- Δ_{47} comparison, because of the differing carbonate chemistry controls on Mg/Ca in planktonic and benthic foraminifera (Lea, 1999; Elderfield et al 2006) we exclude the two benthic samples and only provide and discuss Mg/Ca data from the planktonic foraminifera samples. To limit the potential size effects on Mg/Ca, we picked the planktonic foraminifera in narrow size ranges centered around the optimal size of each species (i.e., the size corresponding to the maximum abundance of adult shells). For the clumped-isotope calibration, we include the benthic foraminifera data and a large range of size as was originally done in Peral et al. (2018).

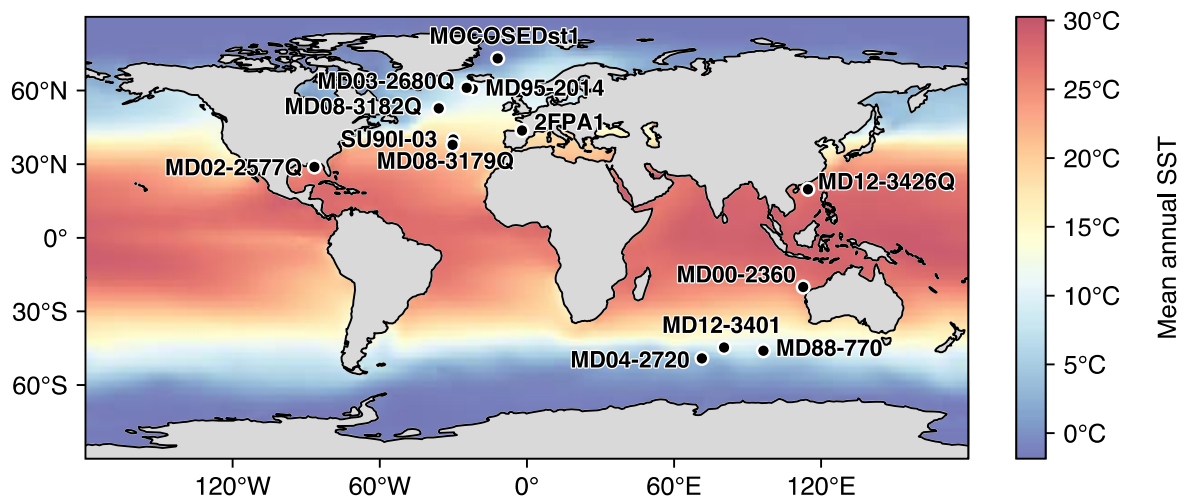


Figure 1: Map of core-top location used in this study, with the mean annual SST from WOA13

2.2. Clumped and conventional stable isotopes

The clumped-isotope data were previously reported by Peral et al. (2018). The methodology (from the cleaning protocol to the measurement) is described in Daëron et al. (2016) and Peral et al., (2018). A summary of the cleaning protocol steps is presented in supplementary material (Fig. S1) For the present paper, we reprocessed our Δ_{47} data in accordance with the new InterCarb - Carbon Dioxide Equilibrium Scale (I-CDES) and the associated data processing methods (Bernasconi et al., 2021; Daëron, 2021).

In previous studies, discrepancies between clumped isotope calibrations had been observed (e.g., Tripathi et al., 2010; Grauel et al., 2013). Thanks to an international effort, several laboratories conducted an intercalibration exercise in order to determine clumped isotope values of carbonate standards (ETH 1-4, IAEA-C1&2 and MERK; Bernasconi et al., 2021). This new standardization approach (I-CDES reference frame) results in internationally agreed calibrations (Anderson et al, 2021; Fiebig et al., 2021).

The Δ_{47} values of our modern foraminifera (Peral et al., 2018) were normalized to the I-CDES reference frame (Bernasconi et al., 2021) using the carbonate standards ETH-1/2/3/4. Data processing was performed using the Δ_{47} crunch library and the new pooled standardization approach, as described in Daëron (2021). The reprocessed Δ_{47} calibration is now compared with the new and/or other recalculated calibrations and used for future paleoceanographic studies. The full dataset is provided in the supplementary material (Table S1).

The Δ_{47} values were converted to temperatures using the Peral et al. re-calculated calibration. The temperature uncertainties were estimated by propagating (i) the external Δ_{47} reproducibility of our analytical sessions of measurements, based on repeated analyses of standards and samples and (ii) the uncertainties associated with respective calibrations. Recently, Anderson et al. (2021) have shown that when using the same standardization and data processing, re-evaluated Δ_{47} -temperature calibrations obtained on various carbonate materials agree within the range of uncertainty. In terms of Δ_{47} -temperature reconstructions, using Peral et al. (2018) re-calculated calibration (this paper), or using the unified calibration from Anderson et al. (2021), yield the same results. We found it important to provide in the present paper a revised calibration equation that is based on cutting-edge approaches of Δ_{47} standardization and processing methods (Bernasconi et al. 2021; Daëron, 2021) to serve for future studies based on the state-of-the-art standard values.

2.3. Mg/Ca analyses and derived temperatures

2.3.1. Mg/Ca measurements

A total of 93 Mg/Ca analyses on 9 species of planktonic foraminifera were performed at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) using a PlasmaQuant ELITE Inductively coupled plasma mass spectrometry (ICP-MS) from Analytik Jena. One milligram of foraminiferal shells was hand-picked for each sample allowing to perform 3 to 4 replicate analyses. We followed the cleaning protocol of Barker et al. (2003). Shells were crushed between two glass plates and the resulting fragments were put into acid-leached micro-vials. Fine material (i.e. clay) was removed through repeated ultrasonic cleaning with 18.2 M Ω water and then ethanol. In order to remove potential organic contaminants, the samples were then oxidized with alkali-buffered 1% H₂O₂ solution for 10 minutes at 100°C. The final cleaning treatment consists in a rapid leaching with 0.001 M HNO₃, before dissolution in 0.15 M HNO₃. Samples are centrifuged immediately after dissolution and transferred to a new acid-leached centrifuge tube, leaving a residual \sim 10 μ l, which helps exclude any remaining undissolved contaminants. Trace metal grade (NORMATOM) acids are used throughout.

A 10 μ l aliquot of each sample was first analyzed in order to determine calcium concentrations. The samples were then diluted to a calcium concentration of 1mM Ca, to match that of the bracketing standards. Mg/Ca ratios were measured using a modified version of the method of Yu et al. (2005) against in-house standards prepared from single elementary solutions. Mg/Ca instrumental precision was determined based on multiple replicates of a standard solution of known Mg/Ca composition, with a long-term precision of 2% (2RSD). Analysis of external standard NIST RM 8301 (Foraminifera) using our method gives a value of 2.65 ± 0.02 (1 Σ E), in excellent agreement with its published value of 2.62 ± 0.14 (Stewart et al., 2020). The data are summarized in Table 2 and the full data set is provided in supplementary material (Table S2).

2.3.2. Mg/Ca-derived temperatures

In order to compare Mg/Ca and clumped-isotope-derived temperatures, we calculated the Mg/Ca-derived temperatures using the multi-species calibration of Anand et al. (2003). The estimated-Mg/Ca temperatures show a large difference when compared with the clumped-isotope-derived temperatures (see supplementary material, Fig. S2). We recalculated the multi-species Anand et al. (2003) calibration using the temperatures from the oxygen isotopic calibration of Kim and O'Neil (1997), which may provide a more robust basis for reconstructing temperature effects (Roche et al., 2018) than the modified, benthic-derived equation of Shackleton (1974) used in the Anand et al. (2003) study (see details in section 2.4.1). Following the same strategy than Anand et al. (2003), we only included the data from the 350 – 500 μm size-range and excluded the data from *Orbulina universa* and *Globigerinella*. We note that, as shown in Anand et al. (2003), the measured $\delta^{18}\text{O}_{\text{calcite}}$ is up to ~ 1 per mil too light in the wintertime compared to the value predicted using the measured sea surface temperature- and salinity-based $\delta^{18}\text{O}_{\text{sw}}$ estimates at the Sargasso Sea sediment trap site. This is likely due to a seasonal change in the $\delta^{18}\text{O}_{\text{sw}}$ -salinity relationship at this site, which potentially introduces a substantial bias to the resulting Mg/Ca equation (Gray et al, 2018). The recalculated equation is presented in Table 3 and shown on supplementary material (Data Processing file).

To the best of our knowledge, we chose the most adequate calibrations, considering the species, the size fraction, the oceanic region, and the cleaning protocol, when possible. Unfortunately, the only available calibration for *Globorotalia menardii* was established using a cleaning protocol with a reductive step (Regenberg et al., 2010), which is known to lower the Mg/Ca ratio of foraminifera compared to the cleaning approach of Barker et al. (2003) that we used for the present paper (e.g. Pang et al., 2020). In the absence of a calibration for *Neogloboquadrina pachyderma* (dextral), we used the same calibration as the one developed for *N. pachyderma* (sinistral) (Vázquez Riveiros et al., 2016). The uncertainties were calculated by propagating the analytical errors, based on the long-term standard deviation of our standards and the uncertainties associated with the respective calibrations.

We also compared our clumped isotope data with Mg/Ca-temperatures corrected for salinity and pH effects using the species-specific equations (Table 3) from Gray and Evans (2019) for *O. universa*, *Globigerinoides ruber* and *Globigerina bulloides*. For the species for which a specific calibration is not available, we used the generic equation of Gray and Evans

(2019). To the best of our knowledge, *N. pachyderma* is not pH sensitive (Tierney et al., 2019). Thus, no correction was applied to the Mg/Ca of this species.

The multi-parameter regression equations of Gray and Evans (2019) provide Mg/Ca as a function of the temperature, the salinity, and the pH of the sea water in which the foraminifera have grown:

$$\text{Mg/Ca} = \exp (a \times (S - a) + c \times T + d \times (\text{pH} - e)) + f$$

Where a, b, c, d, e and f are constants, and T, S and pH are the temperature (in °C), the salinity and the pH of seawater during calcification. To correct the Mg/Ca, we used the modern climatological data extracted from oceanographic atlases for the salinity and the pH, (see details in section 2.4).

In this study, three thermometers are at our disposal: clumped isotope-derived temperatures, oxygen isotopic temperatures and WOA-extracted temperatures. However, to perform the corrected Mg/Ca calibration, two temperatures are required to (i) correct the Mg/Ca values using the equations of Gray and Evans (2019) and (ii) calculate this corrected-Mg/Ca calibration. The clumped isotope temperatures are compared with the corrected Mg/Ca-derived temperatures; we therefore cannot use them. The oxygen isotopic temperatures are used to constrain the clumped-isotope calibration. To limit circular reasoning as much as possible and avoid using the same thermometer to constrain both clumped isotope and corrected Mg/Ca calibrations, we chose to correct the Mg/Ca values (Gray and Evans equations) with the oxygen isotope temperatures, and to constrain the multi-species corrected Mg/Ca calibration with the temperatures extracted from the WOA13 atlas (see the section 2.4 for details about temperature estimation and extraction).

2.4. Independent constraints on temperatures, salinity and pH from Δ_{47} and Mg/Ca ratios

2.4.1. Estimation of calcification temperatures

Temperatures from WOA13 (Locarnini et al., 2013) are extracted for the foraminiferal-Mg/Ca calibration. Because one still does not know well the exact habitat depth and growth season of planktonic species and their spatial variability in relation to nutrient availability and physico-chemical conditions (i.e., Retailleau et al., 2011; Schiebel and Hemleben, 2017), we followed the same approach as Peral et al. (2018). We calculated the average water column

temperature over a range of calcification depths depending on species and core-top location. According to Tolderlund and Be' (1971) and Durazzi (1981), calcification depths in the North Atlantic Ocean range between 0 – 50 m for *G. ruber* and *O. universa*, and the depth range is 0-100m for *G. bulloides*, *G. truncatulinoides*, *G. menardii* and *G. inflata* (Steinke et al., 2005; Numberger et al., 2009, Rebotim et al 2017). For *N. pachyderma*, the living depth is estimated from 0 to 200 m depth (Rebotim et al., 2017). In the Indian Ocean, Duplessy et al. (1981) placed the depth of calcification for all these species within and below the mixed layer, except for *G. ruber* and *G. menardii* which are believed to remain respectively at the surface and within the mixed layer (0–100 m). In the South China Sea, *G. ruber* and *G. menardii* are described as living near the surface and in the top 100 m, respectively (Pflaumann and Jian, 1999). Finally, the living depth of *O. universa* being very poorly constrained to the best of our knowledge, we assume that it lives everywhere at the same depth as in the North Atlantic Ocean (Rebotim et al., 2017). Furthermore, the seasonality of phytoplankton blooms remains poorly constrained in the literature. We thus followed a conservative approach by averaging the monthly mean temperatures (excepted winter months) for each core, with assigned uncertainties reflecting both seasonal and vertical variability, quantified as the standard deviation of all retained monthly temperature data for a given site and a uniform depth over the range of (species-dependent) living depths (from the Python code of Whitaker et al., 2019).

In order to limit uncertainties associated to our imperfect knowledge of planktonic foraminifera ecology, numerous authors have used $\delta^{18}\text{O}$ -derived temperatures instead of atlas temperatures for the calibration of geochemical proxies (e.g. Anand et al., 2003; Mathien-Blard and Bassinot, 2009; Peral et al., 2018; Meinicke et al., 2020). Comparing WOA13 atlas temperatures and foraminifer $\delta^{18}\text{O}$ -derived temperatures obtained using various calibration equations, Peral et al., (2018) suggested the use of the calibration equation of Kim and O'Neil (1997), modified for consistency with the use of an acid fractionation factor (difference of oxygen content in the mineral before and after the reaction with the acid, depending on the mineral and the temperature of reaction) of 1.01025 (Eq. 1) for this dataset. The Kim and O'Neil (1997) calibration is then used to calculate the $\delta^{18}\text{O}$ -derived temperatures in this study.

$$1000 \ln(\alpha_{cc/w}) = 18.03 \times 1000 / T - 32.17 \quad (\text{Eq. 1})$$

Where T is the isotopic temperature in K and $\alpha_{CC/W}$ is the oxygen-18 fractionation factor between calcite and water:

$$\alpha_{CC/W} = (1 + \delta^{18}\text{O}_{C/SMOW} / 1000) / (1 + \delta^{18}\text{O}_{SW/SMOW} / 1000) \quad (\text{Eq. 2})$$

with $\delta^{18}\text{O}_{C/SMOW}$ and $\delta^{18}\text{O}_{SW/SMOW}$ corresponding to foraminiferal calcite and seawater $\delta^{18}\text{O}$, both relative to VSMOW. Following the recommendation of Marchitto et al. (2014), $\delta^{18}\text{O}_c$ values for *Uvigerina* were adjusted by subtracting 0.47 ‰.

Seawater $\delta^{18}\text{O}$ values at each core site were extracted from the gridded data set of LeGrande and Schmidt (2006). The same approach as the WOA-temperature extraction is followed. For benthic foraminifera (re-calibration of clumped isotope versus temperature), the bottom $\delta^{18}\text{O}_{SW}$ values are considered. For the planktonic foraminifera, the mean $\delta^{18}\text{O}_{SW}$ values averaged for the living depth of each species for each oceanic basin is considered. The uncertainties in $\delta^{18}\text{O}_{SW}$ for each core site were defined as the quadratic sum of the site-specific standard deviation of $\delta^{18}\text{O}_{SW}$ within the corresponding water depth and a constant error of 0.20 ‰ assigned to the GISS grid interpolation. Final uncertainties of the oxygen isotopic temperatures are propagated based on the $\delta^{18}\text{O}_{SW}$ uncertainties and the external analytical error on $\delta^{18}\text{O}$ values.

We also compared the reconstructed Mg/Ca-temperatures to $\delta^{18}\text{O}$ -temperatures using mono-specific $\delta^{18}\text{O}$ calibrations (Bemis et al., 1998 for *G. bulloides* and *O. universa*). This comparison is presented in Figure S3 and discussed in paragraph 4.2.

2.4.2. Seawater salinity and pH determination

The seawater salinity values at each core-top location were extracted from the gridded data set of WOA13 (Zweng et al., 2013). The same method was used as for the GISS $\delta^{18}\text{O}_{SW}$ values, we computed average salinity values over the corresponding water depth for each species and oceanic basin. Uncertainties were estimated at each core-top and species site as the quadratic sum of a nominal error of 0.20 arbitrarily assigned to the WOA13 data set and the site-specific standard deviation of salinity.

The seawater pH values at each core-top location and for each species living depth were extracted from the data set of GLODAP 2020 (Olsen et al., 2020). Same to the approach followed for the GISS $\delta^{18}\text{O}_{SW}$ and WOA13 temperature and salinity, we averaged the available

GLODAP 2020 data. An uncertainty of 0.02 is assigned to GLODAP pH data (Olsen et al., 2020). It is notable that the extracted pH data are far from ideal because due to the release of anthropogenic CO₂, the surface ocean has acidified since 1850, lowering the pH relative to the pre-industrial value; whereas the vast majority of foraminifera in the core top samples are likely to be of predominantly preindustrial age or older. However, it is the best method that we have for now, and as the impact of anthropogenic CO₂ is relatively uniform, the underlying spatial variations in pH (the relevant quantity for our analysis) is likely to be somewhat less impacted than the absolute pH values.

The detailed calculations, used in this article, are presented in the supplementary material (Data Processing).

3. RESULTS

3.1. Clumped isotope dataset

The original clumped-isotope calibration of Peral et al. (2018) is recalculated following the latest methodological developments (see section 2.2 for details). The recalculated clumped-isotope data range from 0.6976 ‰ to 0.5917 ‰ and covers a range of temperatures from -2.3 to 25.4 °C (oxygen isotopic temperatures from eq. 1 are used in the whole section; Table 2). As expected, the Δ_{47} values increase with decreasing temperatures; the benthic foraminifera sample from the arctic (*C. wuellerstorfi* – MOCOSED-St1) records the highest Δ_{47} value, while the lowest Δ_{47} value corresponds to one of the warmest planktonic foraminifer samples (*G. ruber* – MD00-2360).

3.2. Raw Mg/Ca dataset

Mg/Ca values have been only obtained for the planktonic foraminifera. Our raw Mg/Ca dataset ranges from 0.8 to 7.7 mmol/mol (Table 2 for the whole section) and covers a range of temperatures from -0.8 to 25.4 °C (WOA13 temperatures for the whole section; Table 2). As expected, the cold-water dwelling foraminifera (*N. pachyderma* s. – MOCOSED st 1) record the lowest Mg/Ca and the warm-water surface dwellers such as *G. ruber* and *O. universa* the highest Mg/Ca values. The very high Mg/Ca of 7.7 mmol/mol for *O. universa* is puzzling, since

this species presumably calcifies at lower temperature than *G. ruber* which recorded a raw Mg/Ca value of 4.3 mmol/mol (sample from MD00-2360). This is likely explained to some extent by the fact that *O. universa* is known to have a large vital effect (Lea, 1999). The raw Mg/Ca ratios measured on the same samples and species, but for different size fractions show a maximum difference of 0.4 mmol/mol between all the size fractions.

3.3. Mg/Ca corrected for salinity and pH

The raw Mg/Ca values are corrected for salinity and pH from atlas data, using the method as described in section 2.3.1. The Mg/Ca corrected for salinity and pH dataset ranges from 1.7 mmol/mol (Table 2) for *G. bulloides*-MD08-3182 that calcified at 8 °C (isotopic temperatures, Table 2), to 6.0 mmol/mol for the warm-water surface dwellers *O. universa* (MD00-2360Q), that calcified at 23.3 °C (lower by 1.7 mmol/mol compared to the raw Mg/Ca values). The corrected Mg/Ca values for the species coming from the same core tops display a consistent relationship with calcification temperatures.

3.4. Comparison of Mg/Ca-derived temperatures (multi-species and mono-species equations) versus $\delta^{18}\text{O}$ and Δ_{47} -derived temperatures

The Mg/Ca-derived temperatures were estimated using the recalculated multi-species calibration of Anand et al. (2003) and compared to the $\delta^{18}\text{O}$ -temperatures (Fig. 2.a) estimated using Kim and O'Neil (1997) equation (eq. 1), as described in section 2.4.1. The Mg/Ca-temperatures for the species *G. bulloides* and *O. universa* are systematically higher than the $\delta^{18}\text{O}$ -derived temperatures, while most of the other species display lower Mg/Ca-derived temperatures (Fig. 2.a). A linear regression only explains 60 % of co-variance between the two thermometers (Fig. 2.a).

Then, the Mg/Ca-derived temperatures reconstructed using the multi-species calibration of Anand et al. (2003) are compared to the Δ_{47} -derived temperatures obtained using the recalculated version of the foraminifer calibration equation of Peral et al. (2018; see section 2.3; Fig. 2.b). As was observed with the $\delta^{18}\text{O}$ -temperatures, the *G. bulloides* and *O. universa* species show higher Mg/Ca-derived temperatures than those derived from Δ_{47} and a linear regression only explains 54 % of co-variance between the two thermometers (Fig. 2.b).

We finally computed Mg/Ca-derived temperatures using mono-species calibrations. These Mg/Ca-temperatures are in better agreement with $\delta^{18}\text{O}$ -derived temperatures (Table 3; Fig. 2.c) and Δ_{47} -derived temperatures (Fig. 2.d.), with regression equations explaining 78% and 74% of co-variance.

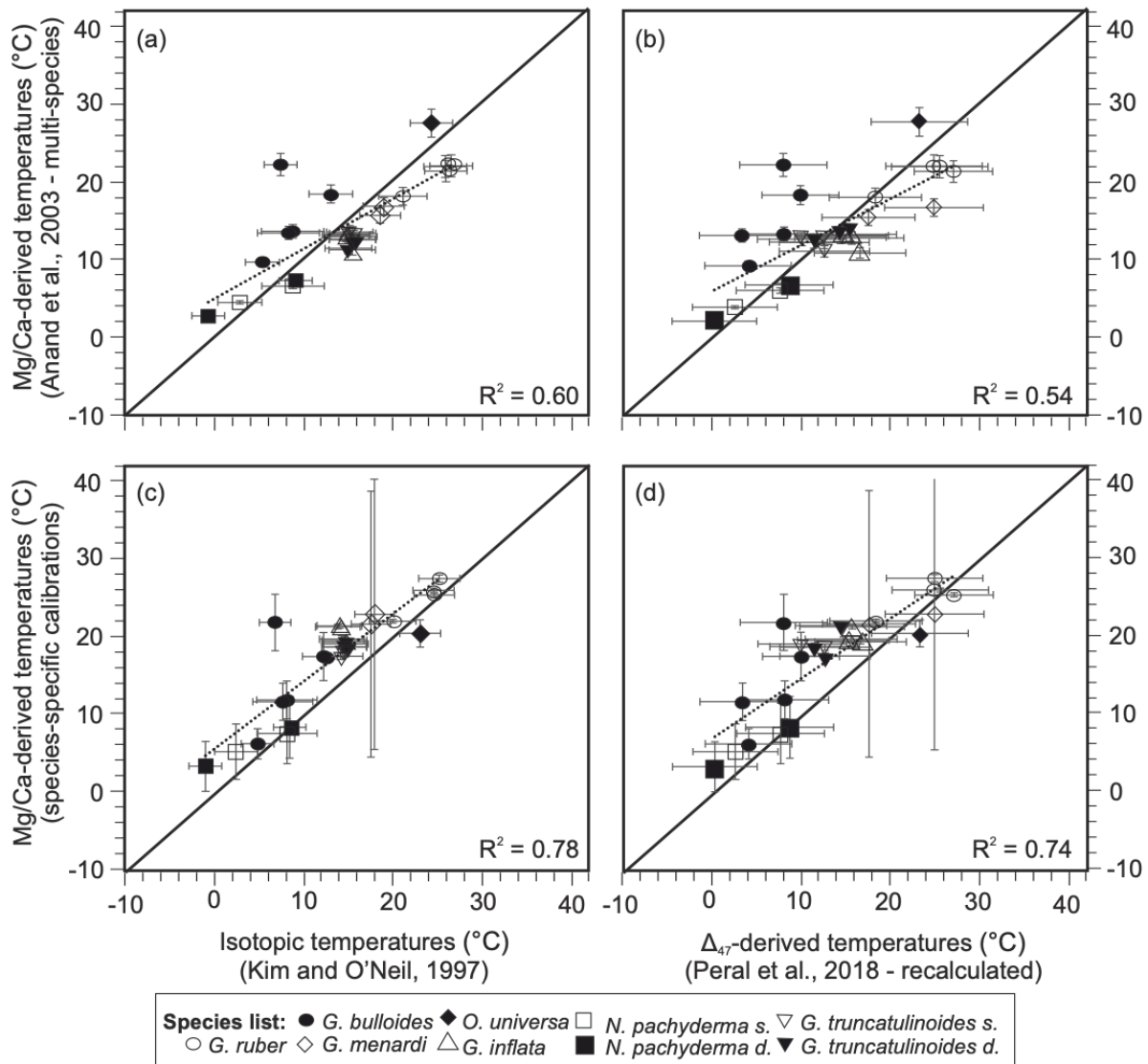


Figure 2: Comparison of temperature estimates obtained on 9 planktonic species. Top panels: reconstructed Mg/Ca temperatures using the recalculated multi-species calibration of Anand et al. (2003) compared to reconstructed $\delta^{18}\text{O}$ temperatures, using Kim and O'Neil (1997) (a) and Δ_{47} -derived temperatures, using recalculated Peral et al. (2018) (b). Bottom panel: reconstructed Mg/Ca derived temperatures using the most adequate mono-specific calibrations compared to reconstructed $\delta^{18}\text{O}$ temperatures, using Kim and O'Neil (1997) (c) and Δ_{47} -derived temperatures, using recalculated Peral et al. (2018) calibration (d). Dotted

black lines are linear regressions, the black solid lines are the 1:1 line. Uncertainties are at $2\Sigma E$.

3.5. Comparison of Δ_{47} values versus raw and corrected Mg/Ca values

The Δ_{47} values (recalculated from the raw data of Peral et al., 2018) are compared to the raw Mg/Ca values (Fig. 3.a – without *O. universa*), and the Mg/Ca values corrected only for seawater salinity (i.e. setting d constant to zero in the correction equations from Gray and Evans, 2019) (Fig. 3.b), and corrected for seawater salinity and pH salinity (Fig. 3.c). To compute the corrected Mg/Ca values, the salinity and pH values from the atlas, and temperatures derived from calcite $\delta^{18}O$ (Fig. 3.b and c) are used. The samples of *N. pachyderma* are not corrected and their raw values are plotted in all the figures.

The raw Mg/Ca data (without corrections) show a poor agreement with the Δ_{47} values (Fig. 3.a; $R^2 = 0.52$). When the Mg/Ca values are corrected, a better agreement is observed between the Mg/Ca values corrected for “salinity” or “salinity + pH” and the Δ_{47} values (respectively: $R^2 = 0.74$ in Fig. 3.b and $R^2 = 0.77$ in Fig. 3.c).

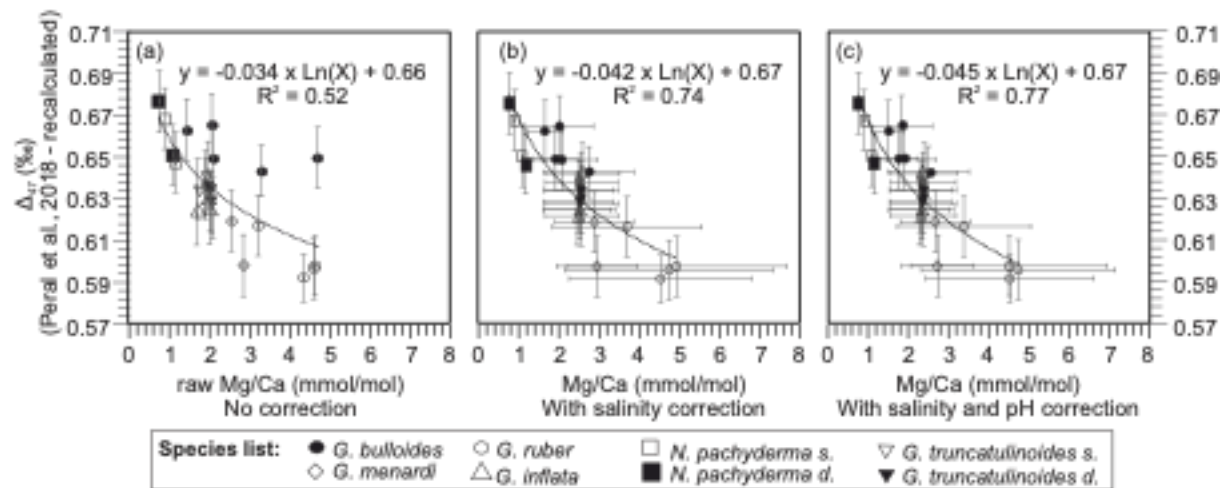


Figure 3: Comparison of our recalculated foraminiferal Δ_{47} values with raw Mg/Ca values (uncorrected) (a), with Mg/Ca-corrected for salinity only (b) and with Mg/Ca-corrected for salinity and pH (c). The Mg/Ca values are corrected using the equations from Gray and Evans (2019), the salinity and pH from the atlas and the oxygen isotopic temperatures. The black dotted logarithmic regressions are plotted for all the plots. All the uncertainties are at $2\Sigma E$.

3.6. Multi-species corrected Mg/Ca calibration

To improve the comparison between Mg/Ca- and Δ_{47} -derived temperatures, we test to correct the Mg/Ca-derived temperatures. In order to correct the Mg/Ca-derived temperatures, we calculated a corrected-Mg/Ca calibration. We used our Mg/Ca values corrected with the temperatures estimated from $\delta^{18}\text{O}$ and the salinities and the pH from the atlas for each site (see details in section 2.2). The multi-species-Mg/Ca equation is constrained by the WOA13 temperatures (Table 3). Firstly, the raw Mg/Ca is plotted against the WOA13-temperatures. An exponential regression only explains 52 % of both thermometers' covariance (Fig. 4.a). When the corrected-Mg/Ca values are used, the data exhibit a better fit with an exponential regression (Fig. 4.b, $R^2 = 94\%$). Also, interestingly, it is noticeable that the temperature sensitivity in this calibration is around 6%, which is consistent with the values that Gray and Evans (2019) suggest as the universal temperature sensitivity.

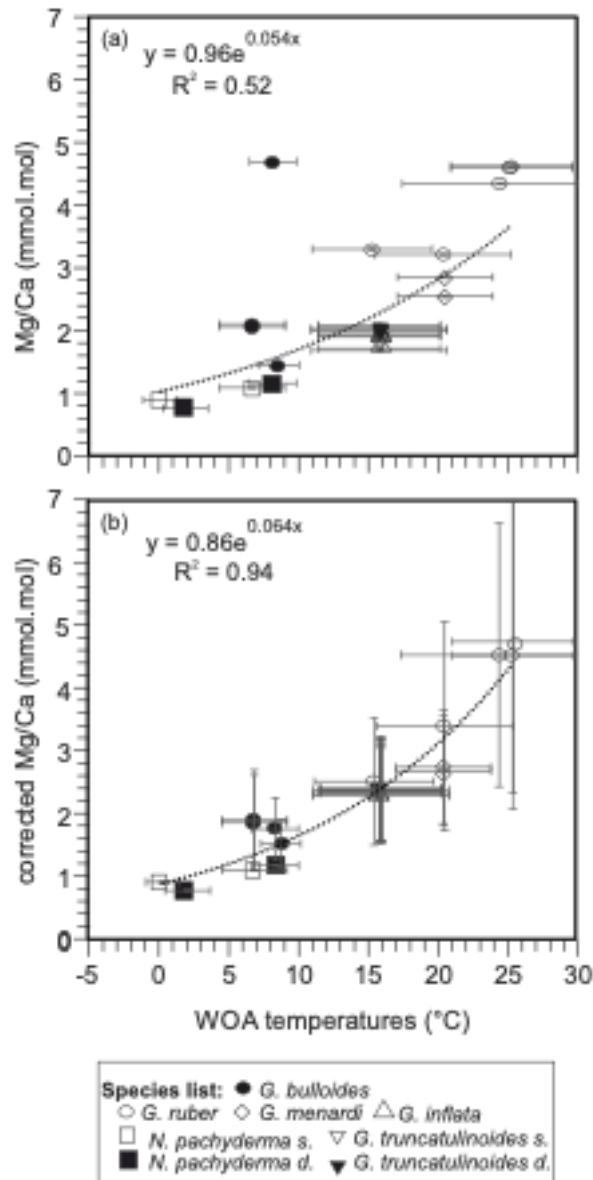


Figure 4: Raw foraminifer Mg/Ca core top data are plotted against the WOA13 temperatures, excluded *O. universa* (a). The corrected Mg/Ca ratios for seawater salinity and pH (respectively from isotopic temperatures, WOA13 and GLOPAD 2020 atlas), except for *N. pachyderma* (no pH effect), are plotted against WOA13 temperatures without *O. universa* (b). All the uncertainties are at 2 SE.

4. DISCUSSION

4.1. Updated foraminiferal clumped-isotope calibration

The efforts of clumped-isotope community have led to the establishment of an international standardization and a uniform measurement data processing, allowing robust/accurate comparisons between Δ_{47} measurements performed in different laboratories (Bernasconi et al., 2021, and Fig. 5 therein). Following the newest methodological advancements in clumped isotope – new standard values and data processing (see details in section 3.2) - (Bernasconi et al., 2021; Daëron, 2021), we recomputed the multi-foraminiferal species calibration from Peral et al. (2018) (Fig. 5). The total least square regression yields the following relationship:

$$\Delta_{47} = A \times 10^3 / T^2 + B \quad \text{eq. 3}$$

where

$$A = 37.0$$

$$B = 0.181$$

To compute the formal standard errors for this regression, we reformulate the equation 3 in terms of the barycenter of our $(1/T_0^2)$ values, so that parameters A and B_0 are statistically independent:

$$\Delta_{47} = A*(T^{-2} - T_0^{-2}) + B_0 \quad \text{eq. 4}$$

where

$$A = 37.0 \text{ (SE = 2.0)}$$

$$B_0 = 0.636 \text{ (SE = 0.0025)}$$

$$T_0 = 285.1 \text{ K}$$

The previous conclusions of Peral et al. (2018) are still valid – i.e., no species-specific, apparent foraminiferal size and salinity effects. This updated calibration is compared with the unified calibration of Anderson et al. (2021) and the precise inorganic calibration of Fiebig et al. (2021) (Fig. 5). A good agreement (in the range of 0.3 – 1.3 °C, within the calibrations uncertainties) is observed between the three calibrations. This agreement between biogenic (this study) and inorganic (Anderson et al., 2021; Fiebig et al., 2021 and the slow-growing Laghetto Basso and Devils Hole calcite (Daëron et al., 2019; Anderson et al., 2021)) carbonates confirms that the use of similar standardization (Bernasconi et al., 2021; Daëron, 2021) solves the discrepancy between the calibrations (Anderson et al., 2021; Fiebig et al., 2021). This observation allows a direct application of this calibration to foraminifera for

palaeoceanographic studies; this recalculated version of the calibration by Peral et al. (2018) should be used instead of the original version for future paleoceanographic studies.

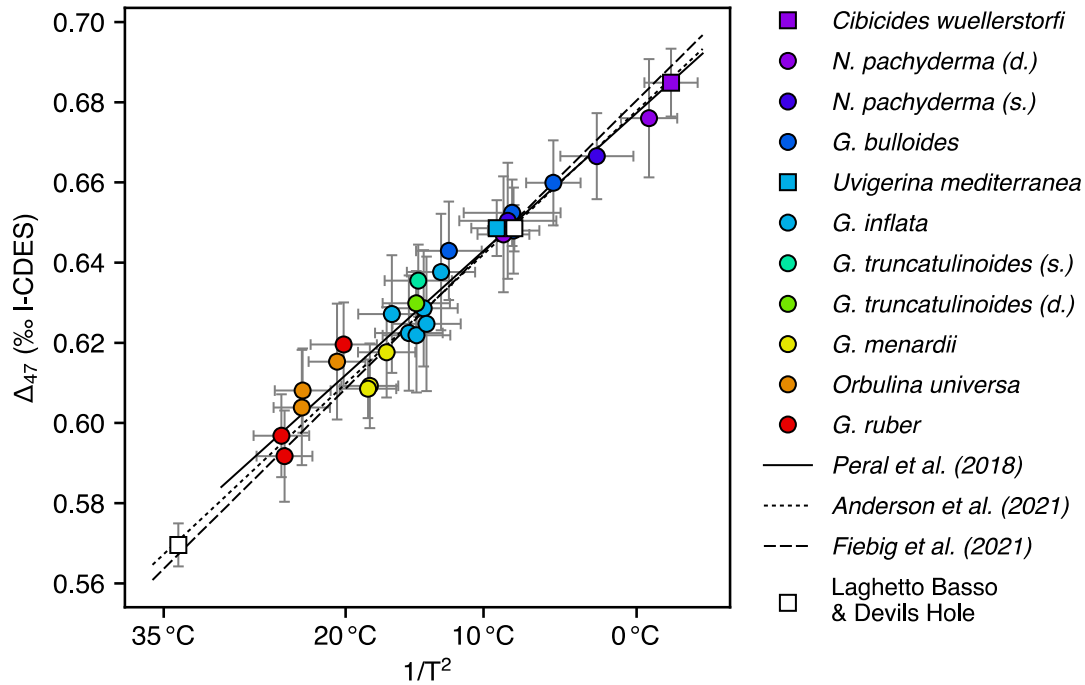


Figure 5: Recalculated Δ_{47} values (mean and 2SE) compared to oxygen isotopic temperatures (mean and 2SE) obtained with Kim and O’Neil (1997) for planktonic (circle) and benthic (square) foraminifera samples, combining all size fractions (modified from Peral et al., 2018). The new calibration regression corresponds to the black line (Peral et al., 2018 recalculated). The recalculated foraminiferal calibration is compared to the slow-growing calcite from Laghetto Basso and Devils Hole (from Anderson et al., 2021) and to calibrations of Anderson et al. (2021) and Fiebig et al. (2021)

4.2. Species specific effects in Mg/Ca-temperatures vs Δ_{47} -temperatures

By comparing various paleothermometers we are able to better constrain the limitations of each of the methods and, within the framework of these limitations, try to extract as much meaningful climatic information as possible by combining those proxies.

The plot of Mg/Ca-temperatures vs Δ_{47} -derived temperatures (Fig. 2.b) shows a larger scattering around the 1:1 line than the plot displaying Mg/Ca-temperatures vs $\delta^{18}\text{O}$ -derived temperatures (Fig. 2.a). This larger scattering likely results from the higher uncertainties in the

clumped-isotope-derived temperatures. The use of species-specific calibrations for Mg/Ca-derived temperature improves the fit with the Δ_{47} -derived temperatures, compared to the use of a multi-species calibration (Fig. 2.d vs Fig. 2.b). No species-specific calibration is necessary for clumped isotope as Δ_{47} thermometer does not appear to be affected by species-specific effects (Tripathi et al., 2010; Grauel et al., 2013; Peral et al., 2018; Meinicke et al., 2020).

Despite the use of optimal size fractions and species-specific Mg/Ca calibrations, the Mg/Ca-derived temperatures are systematically warmer than $\delta^{18}\text{O}$ - and Δ_{47} -derived temperatures (Fig. 2.b&d – linear regression lines). This is coherent with previous observations in paleoceanographic studies (Peral et al., 2020; Leutert et al., 2020). No significant improvement is observed when species-specific calibrations are used to reconstruct temperatures from *G. bulloides* and *O. universa* $\delta^{18}\text{O}$ (Bemis et al., 1998) (Figure S3).

The large difference found between the Mg/Ca values of *O. universa*, and the values of other species likely results from vital effects. The species *O. universa* was excluded from the multi-species calibration of Anand et al. (2003) for this reason. However, it is interesting to notice that clumped isotope in *O. universa* seems to reconstruct accurate temperatures (Peral et al., 2018). For a better comparison between our Δ_{47} and Mg/Ca values, the *O. universa*-MD00-2360 sample was not taken into account in the rest of the present paper.

G. bulloides Mg/Ca data result in temperatures as high as 20 °C, showing up to 12 °C difference with the two isotopic thermometers. Such a discrepancy in our dataset likely results from the complexity of the *G. bulloides* morphotype, which appear to encompass various genotypes with different depth and ecological preferences (Osborne et al., 2020). Possible differences in their vital effects will need to be addressed in future studies. A second explanation would be the dependence of Mg/Ca values on salinity and pH (Nürnberg et al., 1996; Kisakürek et al., 2008; Mathien-Blard and Bassinot, 2009, Gray et al., 2018; Gray and Evans, 2019). It is valid if the foraminiferal- Δ_{47} thermometer is not affected by the salinity and the pH of the seawater. It has been shown that the Δ_{47} in foraminifera is not affected by salinity (Tripathi et al., 2010; Peral et al., 2018), however, the pH dependence of the foraminiferal Δ_{47} thermometer has never previously been studied.

4.3. Sensitivity of foraminiferal Δ_{47} to salinity and pH

The relationship between foraminiferal Δ_{47} and raw Mg/Ca has been previously examined by Breitenbach et al. (2018). These authors showed that the clumped isotope-Mg/Ca comparison could help identify potential problems and biases of the Mg/Ca-thermometer resulting from Fe-Mn oxide coatings, clay contamination and/or foraminiferal test dissolution.

Our foraminifera samples are in a good state of preservation and do not suffer from dissolution (SEM pictures available in Peral et al., 2018). Additionally, the Fe/Ca and Mn/Ca values are always low in our dataset, below the thresholds that lead to suspect a contamination problem (Boyle and Keigwin (1985); see supplementary material Table S2). Once *O. universa* is excluded, the relatively poor correlation between Mg/Ca and clumped isotope (Fig. 3a; $R^2=0.52$) chiefly results from not taking into account the salinity and pH effects on Mg/Ca, as clearly demonstrated by the fact that the correlation improves significantly between Δ_{47} and “salinity” (Fig. 3.b; $R^2 = 0.74$) and “salinity + pH” -corrected Mg/Ca data (Fig. 3.c; $R^2 = 0.77$).

The strong correlations between clumped isotope data and salinity and pH-corrected Mg/Ca (Fig. 3c, $R^2=0.77$) tend to support the long thought suggestion that Δ_{47} is not strongly affected by salinity (Tripathi et al., 2010; Peral et al., 2018) and pH.

4.4. Salinity and pH effects on reconstructed Mg/Ca vs Δ_{47} temperatures

As the Δ_{47} seems to not be dependent on salinity and pH, and by correcting the Mg/Ca-temperatures, the difference observed in Figure 2 should be explained. Using the new corrected multi-species calibration (Fig. 4), the corrected Mg/Ca values are converted into temperatures and compared to the Δ_{47} -derived temperatures (Fig. 6). A good agreement is observed between both thermometers (Fig. 6). The regression line is very close to the line 1:1 and can explain 83% of the co-variance between thermometers (Fig. 6). Comparing the Fig. 6 with the Fig. 2.d shows that the corrections for salinity and pH improve the covariance between the two thermometers by 9%, and thus significantly improve the agreement between the two thermometers. Our results thus concur with observations from the geological record, that improved agreement between Δ_{47} , and Mg/Ca temperature is observed when the influences of pH and salinity on Mg/Ca are accounted for (Leutert et al, 2020; Meinicke et al 2021) and demonstrate the importance of correcting the Mg/Ca values

for non-thermal influences (Gray et al., 2018; Gray and Evans, 2019). However, it is noticeable that the Mg/Ca-derived temperatures are still slightly warmer in the colder part of our dataset (< 10 °C). This difference can be explained by the difficulty to correctly estimate the living environmental conditions of the species or by the requirement of species-specific corrected Mg/Ca calibrations, or by adding species/genotype-specific equations for the other most commonly used species in palaeoceanographic and genotype of well know species such as *G. bulloides* (Osborne et al., 2020).

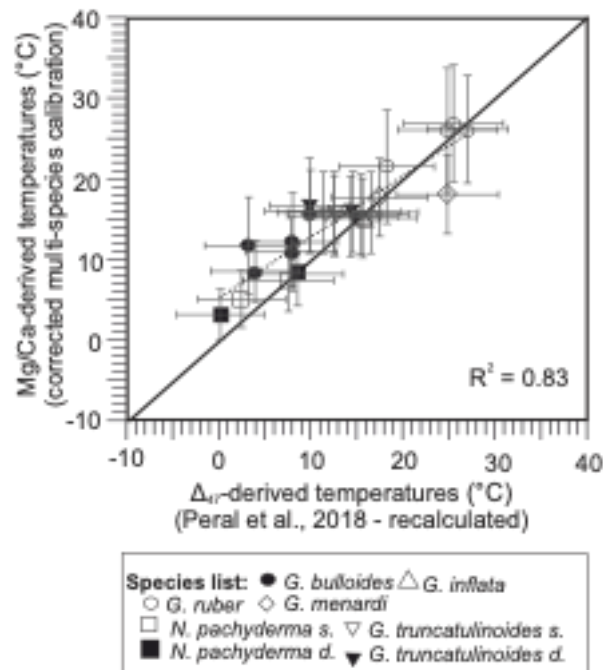


Figure 6: Mg/Ca values, corrected for salinity and pH (respectively from WOA13 and GLOPAD2020 atlas) using the $\delta^{18}\text{O}$ -derived temperature, is converted into temperatures by using the multi-species corrected Mg/Ca calibration and compared to the Δ_{47} -derived temperatures using the recalculated Peral et al. (2018) calibration. The dotted linear regression, excluding *O. universa*, is plotted. A line 1:1 is plotted in black; uncertainties are at $2 \Sigma E$.

4.5. The potential of combining Mg/Ca ratio, $\delta^{18}\text{O}$ and Δ_{47} for palaeoceanographic studies

The combination of $\delta^{18}\text{O}$ and Δ_{47} in foraminifera has been previously studied to accurately reconstruct the signal of $\delta^{18}\text{O}_{\text{sw}}$ even during glacial-interglacial scales (Peral et al., 2020). Next, the comparison between Mg/Ca and Δ_{47} systematically shows differences between the two thermometers in modern and fossil foraminifera. Recently, Breitenbach et

al. (2018) showed that combining Mg/Ca and clumped isotopes data may help to detect possible dissolution and metal coating biases on the Mg/Ca-thermometer. When samples are not biased by contamination, dissolution or diagenesis, the combination of these two proxies can be used to estimate long-term variations in seawater Mg/Ca (Evans et al., 2018; Meinecke et al., 2021). In the present study, we showed that salinity and pH are the key factors that result in apparent discrepancies between clumped isotope and non-corrected Mg/Ca. Because of the multi-parameter dependency of foraminiferal $\delta^{18}\text{O}$, Δ_{47} and Mg/Ca, the combination of these paleo-thermometers could provide us with more than estimates of past ocean temperatures. When temperature can be derived accurately from the clumped isotope, then the pH could be reconstructed from Mg/Ca using the Gray and Evans equation (2019) and injecting the clumped isotope temperature and salinity estimated from sea level (Gray et al., 20129) or from TEX86 data (Leutert et al., 2020) or reconstructed from its relationship with $\delta^{18}\text{O}_{\text{sw}}$.

We tested such an approach with our core-top database. Firstly, the $\delta^{18}\text{O}_{\text{sw}}$ was reconstructed by pairing $\delta^{18}\text{O}$ and Δ_{47} and using equation 1 (Kim and O'Neil, 1997). Then salinity was reconstructed using modern, salinity- $\delta^{18}\text{O}_{\text{sw}}$ relationships (section 2.4; supplementary material Fig. S4, at our site locations). Finally, we used our raw Mg/Ca, the estimated salinities and the clumped isotope temperatures to reconstruct pH values from the equations of Gray and Evans (2019). The reconstructed pH is compared to the pH extracted from the atlas, by plotted their difference against the different species (Fig. 7). The differences in pH, from the same species and coming from different core tops, present a relatively good agreement within the error bars (Fig. 7), but the uncertainties are very large relative to expected pH changes in the geological past (see discussion below). The foraminifers in core tops are predominantly of pre-industrial age or older than the pre-industrial age but will also contain some "modern" foraminifers. The Atlas pH is "modern" and thus contains a substantial influence of anthropogenic CO_2 , which has lowered surface ocean pH globally (see below). The reconstructed pH of the foraminifers for each of the core tops will be equivalent to the average pH covering the time range during which the foraminifers have grown and is thus not equivalent to the pH within the Atlas. The differences between reconstructed and Atlas pH data may also be explained by the assumption that we made on the living depth and seasonality of each samples/species on $\delta^{18}\text{O}_{\text{sw}}$ and pH from the atlases.

Despite the potential of this approach, it is notable that the uncertainties of pH are large (at $2\Sigma E$ in Fig. 7b). The associated uncertainties in the reconstructed pH range between 0.23 and 0.39, which is high for paleoceanographic reconstruction of pH and conversion to atmospheric CO₂ concentration (e.g. pH variations are on the order of 0.15 over G-IG cycles (e.g. Gray and Evans, 2019), and pH changes over the Eocene-Oligocene boundary are around 0.2 units (Leutert et al., 2020)). Interestingly, the uncertainties are mainly dominated by the uncertainties in the clumped isotope-derived temperatures. Smaller uncertainties of the Δ_{47} would result in smaller uncertainties of the reconstructed pH. The Δ_{47} uncertainties can be reduced by measuring more replicates or by improvements in mass spectrometry. Additionally, another limitation of this approach is the salinity reconstruction that we applied in this study. It requires either to assume that, in the past, the relation between $\delta^{18}O_{sw}$ and salinity was the same as the one of today. A direct application of the $\delta^{18}O$ and Δ_{47} combination is therefore not straightforward and other methods of salinity reconstruction may be used (Gray and Evans, 2019; Leutert et al., 2020).

Further studies are needed on species-specific equations for the dependence of Mg/Ca on salinity and pH, on mass spectrometry to reduce the amount of material and associated temperature uncertainties in Δ_{47} , on the relationship between $\delta^{18}O_{sw}$ and salinity today and in the past. Nevertheless, the systematic use of Mg/Ca, $\delta^{18}O$ and Δ_{47} ratios is useful to better understand the limits of these proxies and would help in their interpretations in paleoceanographic studies. Finally, pairing these paleothermometers with the boron isotope pH proxy (i.e., Foster and Rae, 2016), which requires knowledge of temperature to calculate K_B and pH, would allow for multiple independent constraints on past variations in pH and temperature.

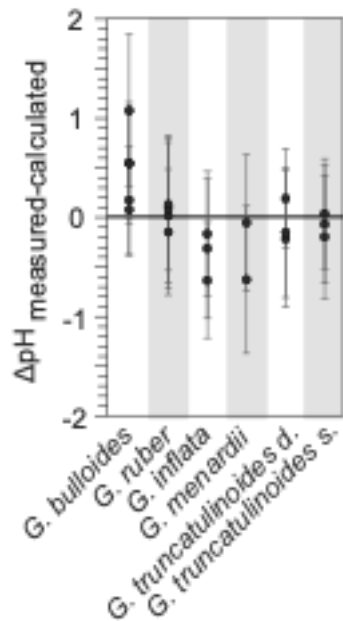


Figure 7: the difference for all the species from our dataset (excepted *O. universa* and *N. pachyderma*) between the extracted pH from the atlas (GLOPAD 2020) and the reconstructed pH, using the equations from Gray and Evans (2019) with the raw Mg/Ca, the Δ_{47} -derived temperatures, and the combination of $\delta^{18}\text{O}$ and Δ_{47} -derived temperatures to reconstruct the $\delta^{18}\text{O}_{\text{sw}}$. The uncertainties correspond to the uncertainties associated with the reconstructed pH (2SE)

5. CONCLUSION

The improved agreement observed between Mg/Ca and Δ_{47} when Mg/Ca values are corrected for salinity and pH suggests that the foraminiferal clumped isotopes are only temperature dependent. As such, the combination of the foraminiferal Mg/Ca, $\delta^{18}\text{O}$ and Δ_{47} , could allow the temperature (Δ_{47} thermometer), salinity (by combining $\delta^{18}\text{O}$ and Δ_{47} , to reconstruct the $\delta^{18}\text{O}_{\text{sw}}$ and then, the salinity) and pH (the only remaining unknown information) of the past seawater to be determined. However, at present, the application of this approach is nontrivial. In particular, the current temperature uncertainty estimates from Δ_{47} result in pH uncertainties on the order of expected changes in the geological record. Furthermore, the species-specific Mg/Ca pH sensitivity (Gray and Evans, 2019) adds an additional complication when applying the approach to extinct species. Finally, we present an update of foraminiferal clumped-isotope calibration of Peral et al., 2018, that corresponds to

the latest methodological developments (data processing and standardization) and can be directly applied to palaeoceanographic studies.

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Author contributions

MP and FB have designed the study. MP wrote the manuscript, and all co-authors help in the writing. MD provided the python code to reprocess the clumped-isotope calibration. FB, DB, MD and WG provided assistance in the interpretation of the clumped-isotope and/or Mg/Ca data. JB, FJ, CK, EM and CW helped in the selection of the marine sediment cores and foraminifer species. MP hand-picked the foraminiferal samples. MP and HR cleaned the samples for the Mg/Ca measurements and HR and WG performed the Mg/Ca measurements.

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Table 1: Core top locations and water depth with species considered in this study and chronological.

Cores	Latitude (°)	Longitude (°)	Water depth (m)	Species	Core-top cal. yrs BP (95% CL)	References
MOCOSDSt1	73.04	-11.93	1839	<i>Cibicides wuellerstorfi</i> ; <i>N. pachyderma s</i>	6317 (+150/-94) *	(1)
MD04-2720	-49.13	71.36	750	<i>N. pachyderma d</i>	n.a.	
MD12-3401	-44.69	80.4	3445	<i>G. bulloides</i>	< 4000 **	(2)
MD95-2014	60.59	-22.08	2397	<i>G. bulloides</i>	715 (+94/-149) *	(1)
MD08-3182Q	52.71	-35.94	1355	<i>N. pachyderma s</i> ; <i>G. bulloides</i>	500 (+40/-53) *	(3)
MD03-2680Q	61.06	-24.55	1812	<i>N. pachyderma d</i>	402	(4)
2FPA1	43.67	-2.00	664	<i>Uvigerina mediterranea</i>	< 4000 ***	(1)
SU90I-03	40.05	-30	2475	<i>G. bulloides</i>	2013 (+125/-120) *	(1)
MD08-3179Q	37.86	-30.3	2036	<i>G. ruber</i> ; <i>G. inflata</i> ; <i>G. truncatulinoides s</i> ; <i>G. truncatulinoides d</i>	4403 (+153/-121) *	(1)
MD12-3426Q	19.73	114.61	3630	<i>G. menardii</i> ; <i>O. universa</i>	1755 (+159/-139) *	(1)
MD00-2360	-20.08	112.67	980	<i>G. menardii</i> ; <i>O. universa</i> ; <i>G. ruber</i>	3622 (+135/-137) *	(1)
MD02-2577Q	28.84	-86.67	4076	<i>G. menardii</i> ; <i>O. universa</i> ; <i>G. ruber</i>	1107 (+110/-105) *	(1)

* Age determined by radiocarbon dating

** Age determined by stratigraphic control

*** Age determined by presence of Rose Bengal

(1) Peral et al., 2018; (2) Vazquez Riveiros et al., 2016; (3) Kissel et al., 2013 and (4) Kissel et al., 2009

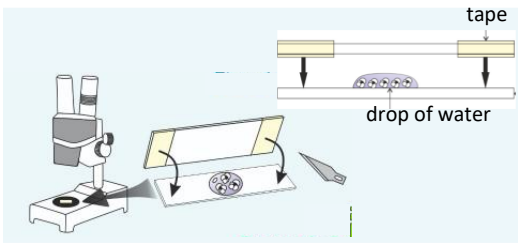
Table 2: Summary of the main results used in this study. In green the data coming from the Mg/Ca ratios, in blue the ones from oxygen-isotopic values, in yellow the ones from the clumped isotope and in orange from Ocean Atlas. The samples/species are represented with the optimal size fraction, the raw and corrected (for salinity and pH using the equation from Gray and Evans, 2019) Mg/Ca ratio, recalculated $\delta^{18}\text{O}$ and the Δ_{47} for each species. The temperatures from WOA13 (Locarnini et al., 2013), from $\delta^{18}\text{O}$ using Kim and O'Neil (1997), from the Mg/Ca calibrations: multi-species (Anand et al., 2003), mono-species (see Table 3), corrected for salinity and pH multi-species (equation from this study) and from Δ_{47} . Seawater $\delta^{18}\text{O}$ and pH from WOA13 (Zweng et al., 2013) and GLODAP 2020 (Olsen et al., 2020), respectively with the reconstructed $\delta^{18}\text{O}_{\text{sw}}$ and pH and their differences are also compared. The sensitivity of Mg/Ca to salinity and pH is also reported. *G. trunca* means *G. truncatulinoides* and *N. pachy* is *N. pachyderma*.

Core	Species	Size fraction	raw			cor			$\delta^{18}\text{O}_{\text{c}}$			Δ_{47}			T WOA 13		T O-isotope		T Mg/Ca multi-species		T Mg/Ca mono-species		T Mg/Ca corrected		T Δ_{47}		estimated $\delta^{18}\text{O}_{\text{sw}}$ (‰)		pH GLODAP2020		estimated pH		Sensitivity Dif. pH to salinity and pH (%)
			Mg/Ca	SD	#	Mg/Ca with WOA	SD	#	‰	SE	‰	SE	#	T(°C)	sT	T(°C)	sT	T(°C)	sT	T(°C)	sT	T(°C)	sD	‰	sD	‰	sD	‰	sD				
MD08-3182	<i>G. bulloides</i>	250-315	2.1	0.006	4	1.7	0.28	1.8	0.1	0.649	0.007	4	6.8	1.9	8.3	0.9	13.5	0.4	11.8	1.2	12.3	3.1	8.0	1.5	0.27	0.42	8.1	0.02	7.9	0.3	0.16	9.2	
MD08-3182	<i>G. bulloides</i>	315-355	2.1	0.006	4	1.7	0.28	1.9	0.1	0.665	0.007	4	6.8	1.9	7.9	0.9	13.3	0.4	11.5	1.2	11.8	3.0	3.3	1.4	-0.72	0.41	8.1	0.02	7.6	0.3	0.53		
MD12-3401	<i>G. bulloides</i>	250-315	1.5	0.006	3	1.8	0.25	2.0	0.1	0.663	0.007	4	8.7	0.7	5.1	0.9	9.5	0.3	6.15	1.0	8.4	1.9	4.0	1.4	-0.39	0.42	8.1	0.02	8.0	0.2	0.06		
MD95-2014	<i>G. bulloides</i>	315-355	4.7	0.006	3	1.8	0.28	2.1	0.1	0.649	0.007	4	8.3	0.8	7.0	0.9	22.3	0.7	21.7	1.8	11.0	2.2	8.0	1.5	0.61	0.42	8.1	0.02	7.0	0.4	1.06		
SU90-03	<i>G. bulloides</i>	250-315	3.3	0.006	4	3.0	0.91	1.6	0.1	0.643	0.006	6	15.4	2.15	12.4	0.9	18.5	0.6	17.3	1.5	16.8	3.0	9.9	1.1	0.51	0.34	8.1	0.02	7.6	0.3	0.53	7.6	
MD08-3179	<i>G. inflata</i>	355-400	2.0	0.008	3	3.1	0.70	1.2	0.1	0.629	0.007	4	15.9	2.4	14.2	0.9	13.1	0.4	21.3	0.1	15.4	2.5	14.4	1.5	1.10	0.42	8.1	0.02	8.3	0.3	-0.18		
MD08-3179	<i>G. inflata</i>	400-450	1.7	0.008	4	3.1	0.70	1.1	0.1	0.622	0.007	4	15.9	2.4	14.7	0.9	11.1	0.3	19.1	0.1	15.9	2.5	16.5	1.5	1.46	0.42	8.1	0.02	8.8	0.3	-0.65		
MD08-3179	<i>G. inflata</i>	450-500	2.0	0.008	4	3.1	0.70	1.2	0.1	0.625	0.009	3	15.9	2.4	14.0	0.9	13.0	0.4	21.1	0.1	15.2	2.5	15.6	1.9	1.43	0.50	8.1	0.02	8.4	0.4	-0.33		
MD00-2360	<i>G. menardii</i>	355-400	2.9	0.004	4	3.2	0.72	-0.4	0.1	0.598	0.008	4	20.4	1.7	18.1	0.9	16.9	0.6	22.7	8.6	18.2	2.5	24.8	1.8	1.75	0.44	8.1	0.02	8.8	0.4	-0.64	9.1	
MD00-2360	<i>G. menardii</i>	400-450	2.6	0.004	4	3.2	0.72	-0.3	0.1	0.619	0.007	4	20.4	1.7	17.7	0.9	15.6	0.5	21.5	8.5	17.8	2.4	17.5	1.6	0.30	0.43	8.1	0.02	8.2	0.3	-0.07		
MD00-2360	<i>G. ruber</i>	250-315	4.3	0.008	3	4.1	1.84	-1.8	0.1	0.592	0.006	7	24.4	3.5	24.8	0.9	21.5	0.7	25.2	0.1	24.9	3.5	27.0	1.2	0.79	0.32	8.1	0.02	8.3	0.3	-0.16		
MD02-2577	<i>G. ruber</i>	250-315	4.6	0.008	4	4.5	1.64	-1.3	0.1	0.596	0.007	4	25.4	2.2	24.7	0.9	22.1	0.7	25.8	0.1	25.6	3.8	25.5	1.7	0.91	0.43	8.1	0.02	8.1	0.4	0.00		
MD02-2577	<i>G. ruber</i>	315-355	4.6	0.008	4	4.5	1.64	-1.5	0.1	0.598	0.007	4	25.4	2.2	25.4	0.9	22.2	0.7	27.3	0.2	26.2	3.9	24.8	1.7	0.65	0.43	8.1	0.02	8.0	0.4	0.07		
MD08-3179	<i>G. ruber</i>	250-315	3.2	0.008	4	3.5	1.2	-0.1	0.1	0.617	0.007	4	20.5	2.4	20.2	0.9	18.2	0.6	21.8	0.1	21.6	3.5	18.3	1.6	0.67	0.42	8.1	0.02	8.0	0.3	0.11		
MD08-3179	<i>G. trunca (d.)</i>	355-400	2.0	0.006	4	2.5	0.65	1.1	0.1	0.642	0.007	4	15.9	2.2	14.9	0.9	12.8	0.4	18.9	0.2	16.1	2.6	10.0	1.5	0.00	0.42	8.1	0.02	7.9	0.3	0.17	7.6	
MD08-3179	<i>G. trunca (d.)</i>	400-450	2.1	0.006	4	2.5	0.65	1.1	0.1	0.625	0.007	4	15.9	2.2	14.5	0.9	13.5	0.4	19.5	0.2	15.7	2.5	15.5	1.6	1.30	0.43	8.1	0.02	8.3	0.4	-0.23		
MD08-3179	<i>G. trunca (d.)</i>	450-500	2.1	0.006	3	2.5	0.65	1.1	0.1	0.628	0.007	4	15.9	2.2	14.8	0.9	13.3	0.4	19.4	0.2	16.0	2.5	14.6	1.6	1.04	0.42	8.1	0.02	8.3	0.3	-0.17		
MD08-3179	<i>G. trunca (s.)</i>	355-400	1.9	0.006	4	2.5	0.65	1.1	0.1	0.638	0.007	4	15.9	2.2	14.7	0.9	12.5	0.4	18.6	0.2	16.0	2.5	11.4	1.5	0.34	0.42	8.1	0.02	8.1	0.3	0.02		
MD08-3179	<i>G. trunca (s.)</i>	400-450	1.9	0.006	4	2.5	0.65	1.1	0.1	0.634	0.007	4	15.9	2.2	14.8	0.9	12.4	0.4	18.5	0.2	16.0	2.5	12.6	1.5	0.58	0.42	8.1	0.02	8.2	0.3	-0.08		
MD08-3179	<i>G. trunca (s.)</i>	450-500	1.7	0.006	4	2.5	0.65	1.2	0.1	0.634	0.007	4	15.9	2.2	14.3	0.9	11.3	0.4	17.4	0.2	15.5	2.5	12.6	1.5	0.69	0.42	8.1	0.02	8.3	0.3	-0.21		
MD03-2680	<i>N. pacht (d.)</i>	200-250	1.2	0.008	4	1.2	0.01	1.7	0.1	0.647	0.007	4	8.3	0.8	8.6	0.9	7.0	0.2	8.3	2.0							8.6	1.5	0.36	0.42	8.0	0.02	
MD04-2720	<i>N. pachy (d.)</i>	200-250	0.8	0.008	4	0.8	0.01	3.2	0.1	0.676	0.008	4	2.0	0.82	-0.8	0.9	2.4	0.0	3.2	1.6							0.2	1.4	-0.09	0.41	8.1	0.02	
MD08-3182	<i>N. pachy (s.)</i>	200-250	1.1	0.006	3	1.1	0.01	1.8	0.1	0.65	0.007	4	6.8	1.9	8.3	0.9	6.3	0.2	7.5	1.9							7.6	1.4	-0.16	0.42	8.1	0.02	
MOCOSD	<i>N. pachy (s.)</i>	200-250	0.9	0.006	3	0.89	0.01	2.9	0.1	0.668	0.007	4	0.2	0.61	2.6	0.9	4.2	0.1	5.2	1.8							2.6	1.4	0.08	0.41	7.8	0.02	
MD00-2360	<i>O. universa</i>	500-560	7.8	0.004	4	8.9	11.6	-1.4	0.1	0.602	0.007	4	20.4	3.5	23.2	0.9	27.8	0.9	20.3	0.9	35.9	10.8	23.2	1.7	0.34	0.43	8.1	0.02	8.3	1.25	-0.16	5.2	

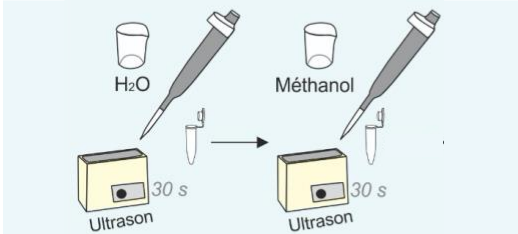
Table 3: Summary of all the Mg/Ca calibration used in this study: mono-specific species calibrations, calibration with salinity and pH corrections and the salinity and pH corrected multi-species calibration

Recalculated multi-species calibration from Anand et al., 2003					
Mg/Ca = B*exp(A*T)					
		Values	SE		
	A	0.0913	0.003		Recalculated in this study
	B	0.6109	0.002		
Mono-specific calibrations					
Mg/Ca = B*exp(A*T)					
		Values	SE	Size fraction	
<i>G. menardii</i>	A	0.091	0.012	355-400	Regenberg et al., 2009
	B	0.36	0.31		
<i>O. universa</i>	A	0.085	0.002	NA	Lea et al., 1999
	B	1.38	0.05		
	A	0.09		350-500	
	B	0.595	0.042		
<i>G. ruber</i>	A	0.09		250-350	Anand et al., 2003
	B	0.449	0.006		
	A	0.09		350-500	
	B	0.395	0.009		
<i>N. pachyderma s</i>	A	0.084	0.006	200-250	Vasquez Riveiros et al., 2016
	B	0.58	0.084		
<i>G. inflata</i>	A	0.09		350-500	
	B	0.299	0.005		
<i>G. truncatulinoides d.</i>	A	0.09		350-500	Anand et al., 2003
	B	0.359	0.008		
<i>G. truncatulinoides s.</i>	A	0.09		350-500	
	B	0.359	0.008		
<i>G. bulloides</i>	A	0.081	0.005	250-315	Elderfield and Ganssen. 2000 North Atlantic
	B	0.81	0.04		
	A	0.061	0.005	250-315	Elderfield and Ganssen. 2000 Southern Ocean
	B	0.996	0.038		
Mono-specific calibrations with SSS and pH corrections					
Mg/Ca=exp(A*(S - B) + C*T + D*(pH - E) + F					
		Values	SE		
<i>G. ruber</i>	A	0.036	0.006		
	B	35			
	C	0.061	0.005		
	D	-0.87	0.1		
	E	8	0		
	F	0.03	0.03		
<i>G. bulloides</i>	A	0.036	0.006		
	B	35			
	C	0.061	0.005		
	D	-0.88	0.12		
	E	8	0		
	F	0.21	0.04		Gray and Evans. 2019
<i>O. universa</i>	A	0.036	0.006		
	B	35			
	C	0.061	0.005		
	D	-0.51	0.11		
	E	8	0		
	F	0.77	0.48		
Multi-species	A	0.036	0.006		
	B	35			
	C	0.061	0.005		
	D	-0.73	0.07		
	E	8	0		
	F	0			
Salinity and pH-corrected multi-species calibrations					
Mg/Ca = B*exp(A*T)					
		Values			
	A	0.0624			This study
	B	0.8784			

Step 1



Step 2



Step 3



Cleaning protocol for clumped isotope in foraminifera

Step 1: Crush the foraminifera

Gently crush foraminifera between two glass slides to open all chambers

Step 2: remove clay

Add milliQ water
Remove the water
Ultrasonic bath for 30s
Repeat 3 times or more until water remains clear and colourless

Add methanol
Ultrasonic bath for 30s
Remove the methanol
Repeat 2 time or more until the methanol remains clear and colourless

Remove the maximum of the methanol

Step 3: Dry

Dry at room temperature under a fume hood. Microtubes should be open but covered with aluminum foil to avoid dust contaminants

Equipment:

Microtubes, gloves, fume hood, microscope, 4 beaker (for water & dirty water and for methanol & dirty methanol), pipette and pipette tip (change for each sample or each step)

Figure S1: summary of the cleaning protocol steps for clumped isotope in foraminifera

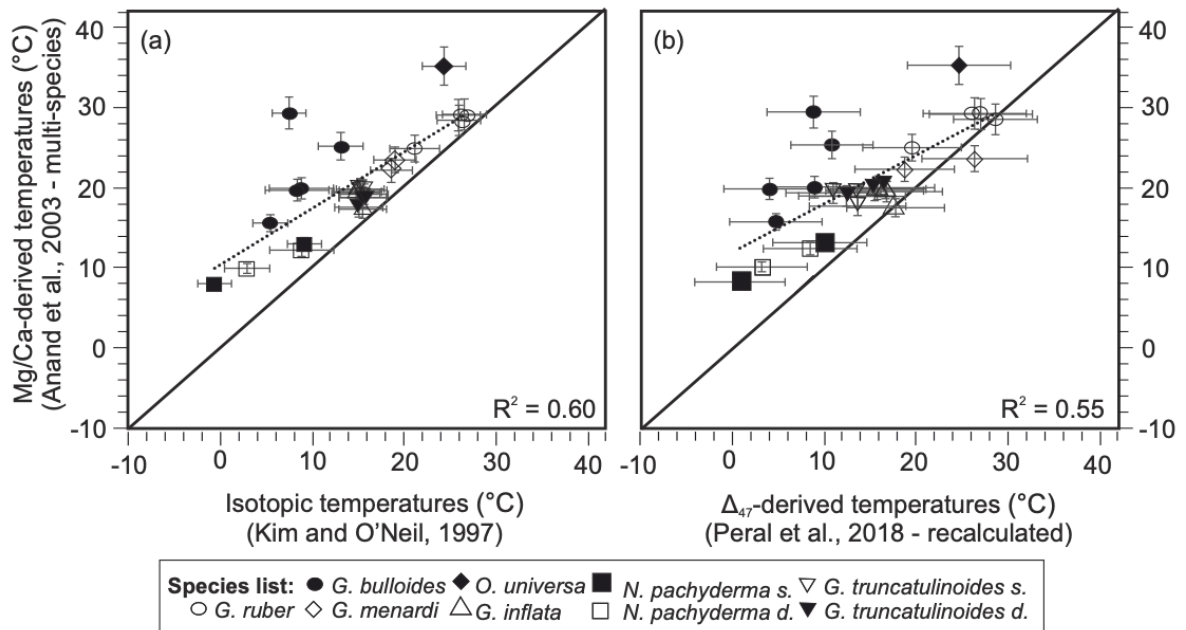


Figure S2: reconstructed Mg/Ca temperatures using the original multi-species calibration of Anand et al. (2003) compared to reconstructed $\delta^{18}\text{O}$ temperatures, using Kim and O'Neil (1997) (a) and Δ_{47} -derived temperatures, using recalculated Peral et al. (2018) (b) for 9 planktic foraminifera. The linear regressions are the dotted black lines, a line 1:1 is in black, and the uncertainties are at 2 SE.

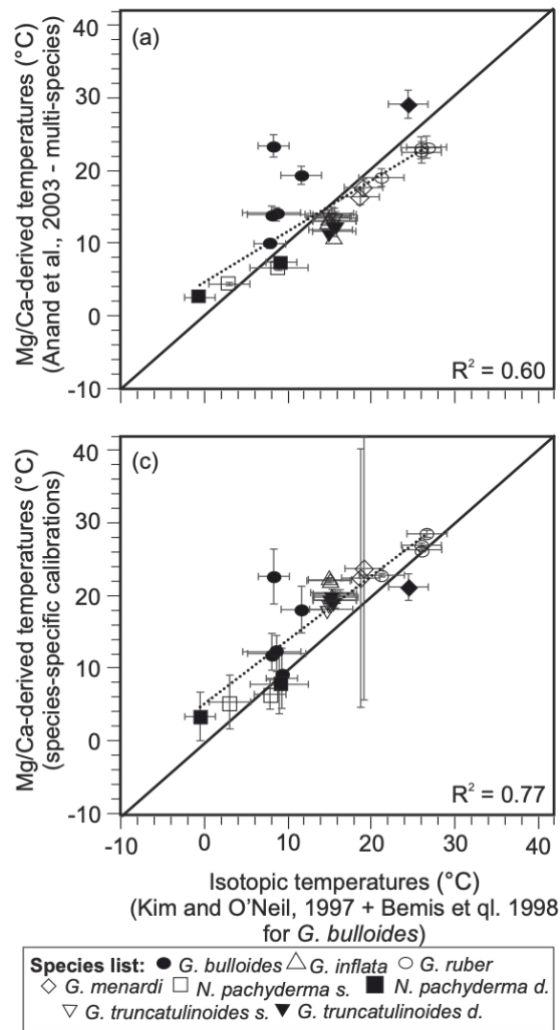


Figure S3: reconstructed Mg/Ca temperatures using the recalculated multi-species calibration of Anand et al. (2003) compared to reconstructed $\delta^{18}\text{O}$ temperatures, using Kim and O'Neil (1997) (a) and reconstructed Mg/Ca derived temperatures using the most adequate mono-specific calibrations compared to reconstructed $\delta^{18}\text{O}$ temperatures, using Kim and O'Neil (1997) and Bemis et al. (1998) calibration for *G. bulloides* (b). The linear regressions are the dotted black lines, the 1:1 line is the black solid line, and the uncertainties are at 2 SE.

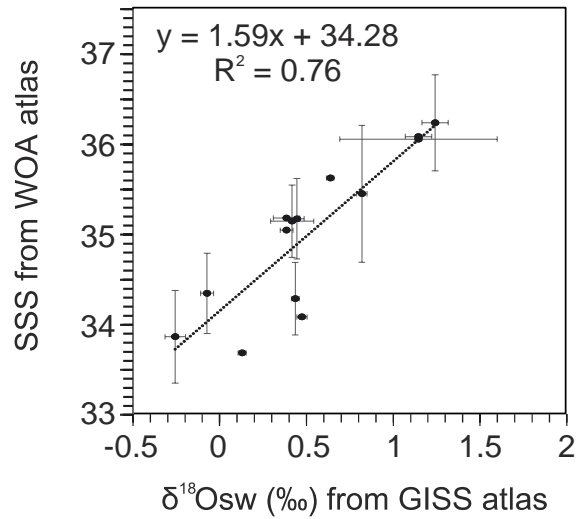


Figure S4: relationship between the seawater salinity from WOA 13 and the $\delta^{18}\text{O}$ of the seawater from GISS atlas for all our samples defined as core/species. For benthic foraminifera we used the available bottom data and planktonic foraminifera we integrated data withing the column water corresponding to the known living depths of each specie (see details in Peral et al., 2018). The linear regressions are the dotted black lines, a line 1:1 is in black, and the uncertainties are at 2 SE.