

Assessing the reliability of foraminiferal Mg/Ca thermometry by comparing field-samples and culture experiments: a review

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Trace elements incorporated into foraminiferal test carbonate are commonly used as palaeoproxies. For instance, benthic and planktonic Mg/Ca ratios are frequently used for reconstructing bottom and sea surface temperature (SST) changes, respectively. However, over the past few decades it has been shown that the incorporation of Mg²⁺ into foraminiferal calcite is controlled by more than one environmental parameter, with significant variations of their sensitivities between culture and field-based studies. Opinions differ as to whether the laboratory conditions during culturing experiments or the natural conditions during field sampling (core-tops, sediment traps and plankton tows) better trace the wealth of information with improved accuracy. Laboratory culture experiments that isolate the effects of individual environmental parameters have been used to identify secondary controls on Mg uptake into planktonic foraminifer tests. However, field-based data (core-top sediments and plankton tows) from high salinity super-saturated settings have shown the additional presence of high-Mg inorganic precipitates leading to significant salinity (S) biases on the Mg/Ca palaeothermometer. Testing such synergistic effects between temperature, salinity and calcite saturation state would require an experimental design where all these parameters are varied systematically, but such experiments have yet to be conducted. Since the synergistic effects cannot presently be ruled out through culturing experiments, it is imperative to initially confirm the amplitude and geographic distribution of the detectable diagenetic precipitations (Scanning Electron Microscopy analysis) through field-based work, further quantify their importance (discrimination of distinct diagenetic stages and quantification of the diagenetic imprint) and finally estimate its potential effect on Mg/Ca-*T* calibration (e.g., overgrowth-corrected species-specific calibration equations). The example of the marginal high-salinity settings, among others, clearly highlights that the optimal use of Mg/Ca as a palaeotemperature proxy urgently requires the complementarity of both culture- and field-based data. To this end, we here present advantages and disadvantages to each approach. These insights reinforce the potential of the combined use of culture- and field-based foraminiferal studies, where possible, in order to minimize the observed inconsistencies, and to advance Mg/Ca thermometry by both providing a framework for better understanding the nature of Mg/Ca dependence on seawater temperature, and the effects of complicating factors.

Key words: Mg/Ca palaeothermometry, core-top sediments, sediment traps, plankton tows, laboratory culture experiments, palaeoceanography.

INTRODUCTION

Foraminiferal Mg/Ca thermometry is a rapidly developing and widely used tool for palaeoceanographic reconstruction (e.g., [Lea et al., 2000](#); [Anand et al., 2003](#); [Hoogakker et al., 2009](#); [Kontakiotis et al., 2011](#); [Martínez-Botí et al., 2011](#); [Honisch et al., 2013](#); [Hertzberg and Schmidt, 2013](#); [Lea, 2014](#); [Antonarakou et al., 2015](#); [Spero et al., 2015](#)). The geochemistry of foraminiferal

tests reflects the environmental conditions in which the foraminifera grew and therefore contribute in reconstructing past ocean climate. More explicitly, the planktonic foraminiferal fossil record is of great importance to our understanding palaeoceanography and regional or global climatic change through time, as they are sensitive indicators of surface and near-surface water conditions. On the other hand, Mg/Ca in benthic foraminiferal species has been used for example to recognize deep-sea temperature (*T*) changes ([Martin et al., 2002](#); [Marchitto et al., 2007](#)) and Cenozoic evolution of global ice volume ([Lear et al., 2002](#)). Unfortunately, data interpretation and palaeoenvironmental reconstructions still remain very challenging, reflecting the incomplete knowledge of the ecology, physiology and life cycles in modern foraminifers, which can only be obtained through field and laboratory observations (e.g., [Bijma et al., 1990](#); [Spero et al., 1997, 2015](#); [Russell et al., 2004](#)).

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Mg/Ca palaeothermometry has the potential of recording relatively small ocean T changes, which is particularly useful when studying high-frequency climate changes during the Pleistocene (Lea et al., 2000; Medina-Elizalde and Lea, 2005; Rodríguez-Sanz et al., 2012; Regoli et al., 2015; Lynch-Stieglitz et al., 2015; Lear et al., 2015), and is based on the premise that seawater temperature is the primary control on Mg^{2+} incorporation into foraminiferal tests during calcification. The underlying basis for Mg/Ca thermometry, as corroborated by both thermodynamics and physiological processes, is that the substitution of Mg in calcite is endothermic and therefore is favoured at higher temperatures (Lea et al., 1999; Erez, 2003; Bentov and Erez, 2006; Lea, 2014). However, it has also been shown that the process is controlled by other environmental parameters. Because foraminiferal Mg/Ca ratios are controlled by calcification physiology (Erez, 2003; Bentov and Erez, 2006), empirical calibration studies are essential to determine the T sensitivity, as well as the roles of any other contributing factors, such as salinity (e.g., Nürnberg et al., 1996; Lea et al., 1999; Ferguson et al., 2008; Kisakürek et al., 2008; Groeneveld et al., 2008; Duenas-Bohórquez et al., 2009; Hoogakker et al., 2009; Arbuszewski et al., 2010; Hönisch et al., 2013), carbonate ion concentration (e.g., Rosenthal et al., 2006; Elderfield et al., 2006; Alison et al., 2010; Raitzsch et al., 2010), inorganic diagenetic overprint (e.g., Kontakiotis et al., 2011; van Raden et al., 2011; Boussetta et al., 2011; Sabbatini et al., 2011), and likely others. It is necessary to pay close attention on these environmental parameters, because insufficient knowledge of them can compromise use of foraminiferal Mg/Ca ratios in confidently reconstructing past temperatures.

During recent decades, this “palaeothermometer” has undergone a period of phenomenal growth, and it has quickly taken its place as one of the most useful means palaeoceanographers have to study past climates. The initial milestones, such as the first attempt to deduce glacial tropical SSTs using Mg/Ca (Hastings et al., 1998), the first calibrations made on cultured whole shells (Lea et al., 1999), or the first detailed sediment trap calibrations (Anand et al., 2003; Martínez-Botí et al., 2011), was followed by new ones focusing mostly on its confident use on targeted key (morpho)species (e.g., *Globigerinoides ruber*) on both short (modern or late Quaternary; Steinke et al., 2005; Thirumalai et al., 2014; Antonarakou et al., 2015) and longer time scales over the past 17 My (Wara et al., 2005; Medina-Elizalde and Lea, 2005; Medina-Elizalde et al., 2008; Lear et al., 2015). Especially for the modern material (core-tops, plankton tows and sediment traps), in which the Mg/Ca signal is complicated by the combined influence of environmental parameters (e.g., salinity, calcite saturation state; Kisakürek et al., 2008; Hoogakker et al., 2009; Kontakiotis et al., 2011; van Raden et al., 2011; Hönisch et al., 2013; Hertzberg and Schmidt, 2013; Hertzberg et al., 2016) and/or biological processes (Hathorne et al., 2009; Wit et al., 2010; Bolton et al., 2011; Nehrke et al., 2013; Spero et al., 2015), progress has been rapid because of improvements in analytical instrumentation and methods (Haley and Klinkhammer, 2002; Benway et al., 2003; Klinkhammer et al., 2004; Rosenthal et al., 2004; Greaves et al., 2008; Mortyn et al., 2011). Moreover, the progress has been made in elucidating the impact of changing seawater Mg/Ca ratios on Mg/Ca palaeothermometry (Medina-Elizalde et al., 2008; Hasiuk and Lohmann, 2010; Broecker and Yu, 2011; Evans and Müller, 2012; Evans et al., 2015; Higgins and Schrag, 2015; Lear et al., 2015) could prove crucial in the successful application of this proxy to the global palaeoclimatic reconstructions across a wide range of time periods.

This study does not aim to reinterpret or evaluate previous work. It is primarily a synthesis of published data, as well as a summary of considerations applicable to Mg/Ca thermometry. The purpose is not to conclude which approach is better, but rather to highlight that each approach fittingly complements the other. Although remarkable progress has been made in this field, we present in detail the major advantages and limitations (Table 1) and aim to contribute to the understanding of the functioning and reliability of the foraminiferal Mg/Ca- T proxy. Therefore, we compare Mg/Ca of natural populations and cultured specimens in order to determine whether culture data results can be applied to natural specimens. We provide a unique perspective on possible future research directions to address several key unresolved questions in Mg/Ca thermometry.

LABORATORY AND FIELD CONTRADICTION

The establishment of empirical relationships in laboratory and field approaches is an important step towards the understanding of the proxy and its soundness in palaeoceanographic reconstruction. Moreover, the comparison between culture- and field-grown foraminifera leads to the discovery of limitations as well, which make a significant contribution to the continuing development of Mg/Ca thermometry and its application to palaeoceanography. Especially for the recently developed proxies, such as the Mg/Ca palaeothermometer, it is desirable to investigate these in more detail. Important aspects are the calibration of species that are particularly suitable for manipulation in laboratory settings, and which are also ubiquitous in palaeoceanographic field studies due to their ability to cope with environmental variability.

In both cases, although field based studies indicate T as the dominant control on Mg/Ca, they present significant variations due to the existence and degree of the main complicating factors affecting Mg/Ca. For instance, the percentage change in Mg/Ca per °C in planktonics ranges from 4 to 43% (e.g., Lea et al., 2000; Dekens et al., 2002; Anand et al., 2003; Ferguson et al., 2008), suggesting a higher sensitivity than in culture (4%/psu – Lea et al., 1999; $8 \pm 2\%$ /psu – Kisakürek et al., 2008). Similarly, through culture experiments salinity (S) was shown to exert no impact (Toyofuku et al., 2000, 2011; Diz et al., 2012) or a significantly slighter (4–11%/psu – Lea et al., 1999; 5 ± 3 –7%/psu – Nürnberg et al., 1996; $6 \pm 2\%$ /psu – Kisakürek et al., 2008; Duenas-Bohórquez et al., 2009; 3–5%/psu – Dissard et al., 2010a) influence than that from core-top (15–59% – Ferguson et al., 2008; 15% – Mathien-Blard and Bassinot, 2009; $27 \pm 4\%$ – Arbuszewski et al., 2010) or plankton tow (16% – Martínez-Botí et al., 2011) studies. The seawater carbonate ion concentration CO_3^{2-} that is known to affect the Mg/Ca ratios in foraminiferal calcite also shows contradictory results between field and culture studies. Although field studies and laboratory experiments indicate the same influence (low carbonate ion saturation results in decreased Mg^{2+} incorporation) on planktonic foraminifera (Kisakürek et al., 2008; Duenas-Bohórquez et al., 2009), this effect on benthic foraminifera remains inconclusive, since the field studies consider deep-water species showing a negative effect on Mg/Ca ratios (Elderfield et al., 2006; Rosenthal et al., 2006; Yu and Elderfield, 2008), but culturing experiments consider shallow-water benthic foraminifera and indicate the absence of a clear influence of CO_3^{2-} (Allison et al., 2010; Dissard et al., 2010b). This differential response of the CO_3^{2-} influence remains unexplained, and might be attributed to specific physiological responses of environmental factors that are correlated to

CO_3^{2-} but are less measurable (e.g., the presence of symbionts and/or respiration; Jørgensen et al., 1985). However, such detailed observations clearly demonstrate that a much better knowledge of the nature and extent of Mg/Ca variability must be obtained in order to develop a fuller understanding of the cause(s) of the Mg/Ca variability and finally to explain the apparent discrepancy between field- and culture-based studies, a problem that has plagued all previous palaeoceanographic efforts with this proxy system.

ADVANTAGES AND LIMITATIONS

CULTURING EXPERIMENTS

Culture experiments differ significantly from natural conditions in important ways that may affect quantitative comparisons against field studies. Culture-based calibrations offer the great advantage that foraminifera are calcified under controlled laboratory conditions, where each environmental factor can be manipulated independently (Table 1). For instance, they calcify under prescribed and accurately measured temperatures, which are constrained during the experiment; therefore it is an independent variable. This is not the case for core-top or plankton tow or trap studies, where T must be estimated using either a climatological atlas or some derivation of the calcification temperature attained from foraminiferal ^{18}O ($^{18}\text{O}_c$) and ^{18}O of seawater ($^{18}\text{O}_{sw}$) (Elderfield and Ganssen, 2000; Anand et al., 2003). In these cases, T itself becomes a dependent variable

(Table 1) and may introduce greater error into the calibration than the measurement of Mg/Ca ratios (Anand et al., 2003).

Moreover, live culturing is an important means by which species-specific biological effects on trace element uptake can be unraveled and the vital effects can be determined (Table 1). For example, factors that are known to influence foraminifera, such as light, temperature, salinity, and pH, can be varied systematically by experimentation (Nürnberg et al., 1996; Mashiotta et al., 1999; Lea et al., 1999) to better understand their impacts on Mg^{2+} uptake. Direct experimentation removes much of the ambiguity associated with the calibration, and moreover offers unique opportunities to identify and explore many of the factors affecting test geochemistry. With this regard, culture data provide an important means by which sediment observations can be interpreted. In several cases, culturing has elucidated previously unknown influences on foraminiferal shell geochemistry that could not be recognized by other approaches (Nürnberg et al., 1996; Mashiotta et al., 1997; De Nooijer et al., 2014). Because microhabitat effects are minimized and the water chemistry is kept constant across the range of temperatures (T_s), the culture experiments address key uncertainties in the field based calibrations (e.g., elimination of any post-depositional dissolution and diagenetic effects, which are potentially attributed to core-top samples). Moreover, experiments are performed without sediment, which has the advantage of minimizing geochemical gradients or exchange of trace elements (Table 1).

However, potential disadvantages of culture calibrations are that laboratory conditions may not realistically reproduce the natural environment to ensure natural chamber growth

Table 1

Advantages and limitations of culture experimental vs. field-based sampling approaches in critical assessment and calibration of foraminiferal Mg/Ca thermometry (see into the text for specific citation details)

			Advantages	Limitations
			Laboratory conditions	Culture experiments
Marine conditions	Sediments	Core-tops	<ol style="list-style-type: none"> 1. Directly handle the foraminiferal material, which is representative of a complete life cycle 	<ol style="list-style-type: none"> 1. Temperature must be estimated (dependent variable) 2. Post-depositional diagenetic (dissolution and overgrowth) effects 3. Biological influences (vital effects) cannot be determined 4. Represented shell material of mixed age with a complex history
			Water column	Sediment traps
	Plankton tows	<ol style="list-style-type: none"> 1. Regional coverage 2. Not necessary the assumption of oxygen isotopic equilibrium to arrive at calcification temperatures 3. A variety of in-situ environmental variables (e.g., temperature) against which Mg/Ca can be compared 		

(Barker et al., 2005), and therefore they are limited by the lack of physico-chemical gradients usually encountered by the vertically migrating foraminifera (Martínez-Botí et al., 2011). Moreover, during culturing experiments only a limited number of species can be studied, and only under very restricted ecological conditions (Table 1). Such conditions rely on the specific foraminiferal diet (e.g., Russell et al., 2004, and Duenas-Bohórquez et al., 2009, fed foraminifera only with *Artemia salina* nauplius) and the time interval of the experiment (it is usually ended as soon as individuals underwent gametogenesis). Such limitations in mimicking the natural processes or in comparing to other means of calibration still linger and raise questions regarding the applicability of laboratory calibration work.

PLANKTON TOW, SEDIMENT TRAP AND CORE-TOP CALIBRATIONS

A prerequisite for palaeoceanographic application of culture calibrations is a demonstration that the T sensitivity of foraminiferal material is retained from chamber formation through the development of gametogenic calcite and crust, the effects of dissolution, to residence at the sea bed (Elderfield and Ganssen, 2000). Core-top calibrations integrate all these processes, and therefore are valuable since they are based on material that will eventually form the sedimentary record, having gone through a complete life cycle including the above mentioned gametogenesis and secondary calcite formation (Barker et al., 2005). As a consequence, core-top calibrations have the great advantage to directly handle the material that is buried to form the palaeoceanographic record (Table 1) and their importance stems from the similar characteristics of the material used for calibration and subsequent applications in the sedimentary record (Mortyn and Martínez-Botí, 2007).

Nevertheless, there are also disadvantages and limitations, as this approach may be affected by secondary diagenetic effects, such as partial dissolution and overgrowth (Table 1), which, at times, render difficult the establishment of a reliable link between Mg/Ca and SST (e.g., Dekens et al., 2002; Regenberg et al., 2007, 2009, 2014; Sadekov et al., 2010; Kontakiotis et al., 2011; Sabbatini et al., 2011; Fehrenbacher and Martin, 2014). For example, partial dissolution of foraminiferal calcite tends to cause a decrease in Mg/Ca; since the solubility of carbonate tends to increase with depth at any location, core-top material from greater depths will be particularly prone to Mg/Ca alteration. Moreover, complications occur in calibrating the results and in establishing the link with SST, if the samples used have undergone early and/or post-depositional alteration. In that case, the information on the bulk foraminiferal geochemical composition altered by diagenesis combines the actual biogenic calcite signal and the composition of the inorganic precipitates. This is problematic, because the diagenetic calcite, in terms of overgrowth, may mask the primary oceanographic signal of planktonic foraminiferal tests and distort the Mg/Ca-based SST estimates.

Another potential artefact of the core-top approach seems to be that such calibrations cannot be used to separate and attribute individual biological influences, or to determine how vital effects might affect Mg^{2+} uptake (Lea, 1999; Table 1). This issue is particularly relevant for applications on the subspecies (morphotype) level, which shows distinct ecology with different biological lifestyles (e.g., habitat preferences, seasonal production maxima, stratification, salinity – Numberger et al., 2009; Antonarakou et al., 2015) and presents a different degree of response to the diagenetic processes (Antonarakou et al., 2012) reflected both in their stable isotope compositions (Kawahata,

2005; Löwemark et al., 2005; Antonarakou et al., 2015) and Mg/Ca geochemistry (Steinke et al., 2005; Bergami et al., 2008; Antonarakou et al., 2015). Such speciation can complicate field-based calibrations because of the possibility of distinct species-specific relationships, and therefore it is clear that a better understanding of the shell chemistry of the morphotypes is essential for meaningful palaeoenvironmental reconstructions (Steinhardt et al., 2015; Antonarakou et al., 2015).

The analysis of living foraminifera collected from the water column, using both plankton tow and moored sediment traps is an alternative way to calibrate and validate the Mg/Ca proxy. According to Pak et al. (2004), the sediment trap material, in combination with *in situ* and simultaneous measurements of T and other properties, bridges the gap between culturing of foraminifera and core-top calibrations. Sediment traps present the advantage that the timing/rate of foraminiferal production is known, so direct comparison between the geochemical signal and the *in situ* and simultaneous instrumental record is possible (Table 1). Furthermore, trap material is also valuable because it most closely represents the material entering the sedimentary record without actually reaching the sediment surface. On the other hand, depth-discrete tows from the water column afford three main advantages: (1) the advantage of regional coverage, (2) the fact that it is not necessary to assume oxygen isotopic equilibrium to arrive at calcification T_s , and (3) there is a variety of *in situ* environmental variables, temperature among others, against which Mg/Ca can be compared (Martínez-Botí et al., 2011; Table 1). Especially, if a reliable temperature estimate can be made for water column samples (e.g., ^{18}O -derived T_s – Anand et al., 2003; Martínez-Botí et al., 2011), this may provide one of the most robust approaches to Mg/Ca thermometry calibration. Collectively, calibrations based on water column samples have the great advantage that the season of growth is known and therefore better constraints can be made on the specific T_s used in calibrations; but because environmental conditions often change, using field data from the water column to quantify the influence of variations in any single parameter is the more difficult approach. Spatial and temporal integration of material may bias calibrations based on sediment traps and plankton tows (Table 1).

COMPARATIVE POTENTIALS AND THEIR PALAEOCEANOGRAPHIC IMPLICATIONS

A central issue in the temperature calibration of planktonic foraminiferal Mg/Ca remains the stenotopic character of the proxy carriers themselves, which limits the calibration T range obtainable for any given species in the field and raises questions regarding the application of laboratory calibration work carried out under conditions without an apparent analogue in the foraminifer's habitat range. The issue becomes even more complex when potential artefacts, such as salinity and calcite saturation state, act as secondary controls on Mg/Ca ratios and confound its use as a T -proxy for palaeoceanographic reconstructions. Therefore, in the following discussion we present sensitivity analyses to the S and overgrowth effects.

This serves as a timely complement to recent field and culture studies, in which the potential significance of both S and diagenesis on Mg/Ca ratios is discussed (e.g., Kisakürek et al., 2008; Ferguson et al., 2008; Kontakiotis et al., 2011; Sabbatini et al., 2011; Hönisch et al., 2013; Antonarakou et al., 2015). We present an extensive multi-format view (culture, core-top and plankton tow samples) of the palaeoceanographically significant planktonic foraminifer species *Globigerinoides ruber* and

(sub) species-specific (in terms of both colour variants and distinct morphotypes in its white chromotype) response to the S and overgrowth effects across a broad range of oceanographic regions in the context of published calibration data, highlighting particular features of each approach. We especially focus on *G. ruber* since it seems to be the most appropriate species for the S effect due to its continuous presence occupying many overlapping segments of the entire S range, it is a sensitive species to manipulations during culturing experiments (Hemleben et al., 1989; Kisakürek et al., 2008) as well to carbonate diagenesis in high salinity settings (Kontakiotis et al., 2011; Boussetta et al., 2011; Sabbatini et al., 2011; Antonarakou et al., 2012), and because it is well instrumentally validated (Mortyn et al., 2011).

THE SALINITY EFFECT

The salinity effect appears weaker in culture experiments than field observations. As Mathien-Blard and Bassinot (2009) and Dissard et al. (2010a) have proposed for *G. ruber* and *A. tepida* respectively, the S effect on Mg/Ca in culture experiments can be addressed through the analysis of the last chambers, which calcified during the course of the experiment. The weaker Mg/Ca sensitivity to S deduced from culture experiments (Lea et al., 1999; Kisakürek et al., 2008) compared to that deduced from core-tops (Ferguson et al., 2008; Mathien-Blard and Bassinot, 2009; Arbuszewski et al., 2010) may indicate that during the later stages of shell development, the incorporation of Mg²⁺ into the calcite lattice is less affected by S than during the early stages. This discrepancy may simply suggest that growth conditions during culture experiments create a stress on individual specimens, which alters somewhat the calcification processes and masks the real sensitivity of Mg²⁺ incorporation to S. This discrepancy indicates that the field-based study is probably the most promising approach to examine and evaluate the absolute S influence on foraminiferal Mg/Ca ratios. On the other hand, if the laboratory experiments use values of physical-chemical parameters within the tolerance ranges of the studied species, it would be an advantage to minimize stressful conditions that could potentially affect foraminiferal Mg²⁺ incorporation, and thus to fully evaluate the S factor and develop a more reliable and sensitive *T* proxy. However, merging both the results from field studies with recent findings from laboratory experiments, the S effect could be fully determined and an additional realistic mechanism could be proposed to explain why S affects shell Mg/Ca.

In our attempt to cover most of the S range in the global oceans and moreover to impart a more universal character to our analysis, in terms of the S effect, we use in our comparison samples from the lower salinity Indian (Sadekov et al., 2008, 2009; Mohtadi et al., 2009, 2010a, b, 2011), Pacific (Oppo et al., 2005, 2009; McConnell and Thunell, 2005; Benway et al., 2006; Steinke et al., 2006; Bolton et al., 2011) and Atlantic (Rosenthal and Boyle, 1993; Lea et al., 2000, 2003, 2006; Dekens et al., 2002; Anand et al., 2003; Schmidt et al., 2004; Farmer, 2005; Weldeab et al., 2005; Newton et al., 2006; LoDico et al., 2006; Lund and Curry, 2006; Richey et al., 2007, 2009; Cléroux et al., 2008; Mathien-Blard and Bassinot, 2009; Steph et al., 2009; Regenberget al., 2009; Arbuszewski et al., 2010; Haarmann et al., 2011; Martínez-Botí et al., 2011; Friedrich et al., 2012; Antonarakou et al., 2015) oceans, as well as the more saline Red (Kisakürek et al., 2008; Mathien-Blard and Bassinot, 2009) and Mediterranean seas (Ferguson et al., 2008; Kontakiotis et

al., 2011; Wit et al., 2010; Sabbatini et al., 2011; Boussetta et al., 2011; Kontakiotis, 2016). In all regions, this proxy includes samples from both the high salinity subtropical gyre and the lower salinity equatorial regions. Moreover, the plurality of core-top samples from semi-enclosed basins (Mediterranean Sea, Red Sea, Arabian Sea, Caribbean Sea), where S shows a much greater gradient than in the open ocean, and the cultured samples also contribute to extend our analysis further to the lower and upper S limits. Thus, the compiled data span a large range of S values, from 30.4 to 44.3 psu. In the case of the Mediterranean Sea samples, we further accounted for diagenetic alteration, where presented, by excluding all core-top samples suggested to be impacted by high-Mg overgrowths (Ferguson et al., 2008; Kontakiotis et al., 2011; Sabbatini et al., 2011; Boussetta et al., 2011).

A suite of 741 samples (670 core-tops, 63 plankton tows/sediment traps, spanning a large latitudinal gradient – from 47.5°N to 42.0°S; Appendix 1*; and 8 cultured samples) was compared, with both core-top and plankton tow samples showing similar geographic distribution in all basins. Regarding the discrimination between the two colour variants, all *G. ruber* “pink” (p) data come from the Atlantic Ocean and the Mediterranean Sea, since this variant presently only lives there (Aurahs et al., 2009, 2011). On the contrary, this geographic restriction does not seem to exist for the *G. ruber* “white” (w), since it can adapt to more oligotrophic waters and lives in all the oceans. However, although literature data for *G. ruber sensu stricto* are globally abundant, relevant data for *G. ruber sensu lato* are mostly restricted to particular regions (Indonesian Sea, South China Sea and Caribbean Sea).

The combined data set consists of *G. ruber* specimens that are ubiquitous in palaeoceanographic studies and have been frequently used for the calibration of the Mg/Ca tracer using published field and cultured data. Both its colour varieties have an excellent fossil record, while the divergences in morphologically distinct species (morphotypes) can be tracked and mirrored in sediment or water column samples. An important aspect of this application is that it helps to investigate the amplitude of the overlapping or the scattering observed between the three different approaches (core-tops, plankton tows/sediment traps, culture experiments) examined here and among the studied colour variants and/or morphotypes.

An implicit limitation of this approach is that many of the planktonic foraminifera migrate vertically in the water column, potentially compounding the signals they record. Although the planktonic foraminifera occupy several ecological niches, which may oversimplify the true variability, we minimize the problem exclusively using *G. ruber* coloured-variants and morphotypes, that live and calcify over a narrow depth range (0–50 m; Wang, 2000; Anand et al., 2003; Farmer et al., 2007; Mortyn et al., 2011; Richey et al., 2012; Hönisch et al., 2013; Antonarakou et al., 2015; Kontakiotis, 2016), also assuring a high degree of accountability between this work and the other published studies that assess the secondary influence of S on the Mg/Ca thermometer.

Taking into account the findings of Hertzberg and Schmidt (2013) for *G. ruber* Mg/Ca palaeothermometry, we use the average depth of 30 m for the ¹⁸O_{sw} estimation since a number of studies have shown that the preferred depth habitat of *G. ruber* is ~0–30 m (e.g., Schmuker and Schiebel, 2002; Waelbroeck et al., 2005; Kuroyanagi et al., 2008; Numberger et al., 2009; Grauel and Bernasconi, 2010; Mortyn et al., 2011; Hönisch et al., 2013; Hertzberg and Schmidt, 2013; Antonarakou et al., 2015;

* Supplementary data associated with this article can be found, in the online version, at doi: 10.7306/gq.1272

Kontakiotis, 2016) and the appropriate calibration equations (Dekens et al., 2002) for the dissolution correction depending on the location ($Mg/Ca = 0.38 \exp 0.09 [SST - 0.61 (\text{core depth km})]$ for the Atlantic and $Mg/Ca = 0.38 \exp 0.09 [SST - 0.61 (\text{core depth km}) - 1.6]$ for Indian and Pacific oceans). The Dekens et al. (2002) dissolution correction was preferred instead of that from Regenberg et al. (2006) since the latter includes samples only from the Caribbean Sea, while the former integrates over a wider area, including samples from the Atlantic and the Pacific oceans. However, it is worth noting that the Dekens et al. (2002) dissolution-corrected calibration equations may not be the best in situations where diagenesis appears to be the controlling dissolution factor, rather than the CO_3^{2-} of bottom waters. However, we are not able to distinguish the source of dissolution (preferential dissolution of high-Mg foraminiferal calcite in undersaturated bottom waters or productivity-induced dissolution under different nutrient regimes) in all the studied samples, and moreover the Rosenthal and Lohmann (2002) calibration equation does not apply in this case, as it requires shell weight measurements for each sample.

For the majority of the samples, where there are available ^{18}O data, and for the calculation of the $^{18}O_{sw}$ values, we used the gridded data set of LeGrande and Schmidt (2006), due to its regional character. Using the data library clone at http://granger.ldeo.columbia.edu/%28data/free/alexeyk/LeGrandeSchmidt2006/calculated_d18O.nc.%29readfile/.d18o/depth/30-VALUE/ we gathered $^{18}O_{sw}$ data for each core site at 30 m water depth. Isotopic temperatures were determined with the Bemis et al. (1998) low-light isotopic temperature equation. The expected Mg/Ca ratios were determined by substituting calculated isotopic T_s into the Anand et al. (2003) Mg/Ca-SST calibration equation, with the only exceptions for the locations where calcite dissolution can occur. This includes samples (1) where the core depths fall below the lysocline and (2) from the high-productivity equatorial upwelling regions (even at core depths above the lysocline), where there is evidence for significant shell dissolution (e.g., Hertzberg and Schmidt, 2013). Following the results of Hertzberg and Schmidt (2013), such a combination of calibration equations improves the correlation with S. Finally, the “excess” Mg/Ca in all cases was calculated, defined as the difference between the measured and the expected Mg/Ca ratio at the $^{18}O_{sw}$ -corrected T (where there are available $^{18}O_c$ data) or SST-derived from the World Ocean Atlas (Locamini et al., 2010; where there are no available $^{18}O_c$ data). Since ^{18}O data are not available for all samples, conclusions from this comparison should be interpreted with caution.

“Excess” Mg/Ca, which quantifies T -independent Mg/Ca variability, has been plotted against S (Figs. 1 and 2). Linear regressions show a generally poor correlation between these variables on all field-grown foraminifera with respect to culture calibrations. As readily seen in Figure 1, the core-top data overlap well with the sediment trap/plankton tow data. In agreement with the recent findings of Martínez-Botí et al. (2011), Mg/Ca ratios in plankton tow foraminifera co-vary with core-tops, although the former show more scattered values. This discrepancy might be explained by the more universal character of the core-top data, since they are geographically distributed in all oceans, extending our calibration in a greater S range. Notably, the plankton-tow values are significantly higher than those expected from core-tops with the same S values. This discrepancy cannot be attributed to the lack of gametogenic calcite, since *G. ruber* does not form this type of calcite (Ni et al., 2007), but it could be explained by the existence (or absence) of symbionts that might have altered the Mg/Ca ratios in plankton tow samples. Moreover, we observe a change in slope of the Mg/Ca-SSS relationships over the range of the calibration, sug-

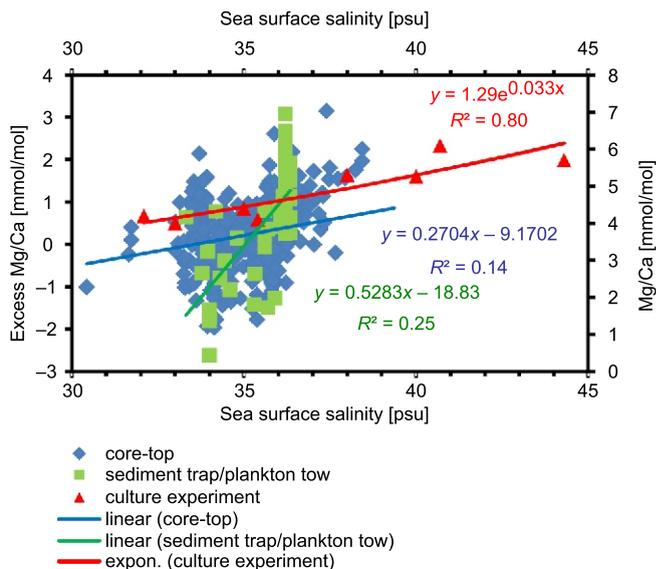


Fig. 1. Excess Mg/Ca in *G. ruber* tests from core-top (blue diamonds) and plankton tow/sediment trap (green squares) observations, and Mg/Ca ratios from laboratory cultures (red triangles) against the mean-annual sea surface salinity (SSS) (Antonov et al., 2010)

Excess Mg/Ca is defined as the part of the Mg/Ca signal that cannot be explained by average annual SST and $^{18}O_{sw}$ at the core sites. The blue and green lines define the linear regressions through the core-top and plankton tow/sediment trap data respectively. The red line is the exponential regression through the combined *G. ruber* (w+p) culture data of Hönisch et al. (2013) and Kisakürek et al. (2008)

gesting variable S sensitivities. The most plausible explanation is that the “original” water column signal contains a range of ontogenetic stages of planktonic foraminifera, which do not always show the adult characters (Brummer et al., 1987; Martínez-Botí et al., 2011). Consequently, it is likely that their absence will lead plankton-tow samples to different Mg/Ca ratios than those demonstrated from core-tops, using “whole-test” foraminifera collected from surface sediments. Moreover, the number of plankton-tow samples is significantly smaller than the number of core-top samples used in our data set.

In order to highlight the association patterns between colour variants/morphotypes and excess Mg/Ca, a correspondence analysis of the relative correlation to SSS of these types has been carried out (Fig. 2). In the particular case of *G. ruber*, two different pairs of lines have been created. One compares data for the white and the pink varieties and the other compares *sensu stricto* versus *sensu lato* morphotype data. R^2 values for both the core-top and plankton tow/sediment trap samples are <0.48 and most of them are <0.10 , with the only exception of *G. ruber* (p) sediment trap/plankton tow data where the uniquely high R^2 value is due to only 2 data points. A simple visual examination of the different plots of Figure 2 already suggests these poor correlations, as samples are either scarce (s.s. and s.l. data from the water column) or present a degree of scatter that does not allow a good regression to be obtained (s.s. and s.l. data from sediments). Throughout the analysed S range, the spreading of the samples shows a comparable pattern in both chromotypes, with *G. ruber* (p) slightly less scattered than *G. ruber* (w). The additional split of the data between the two *G. ruber* (w) morphotypes shows opposite patterns, with *G. ruber* s.s. positively correlated and *G. ruber* s.l. negatively correlated

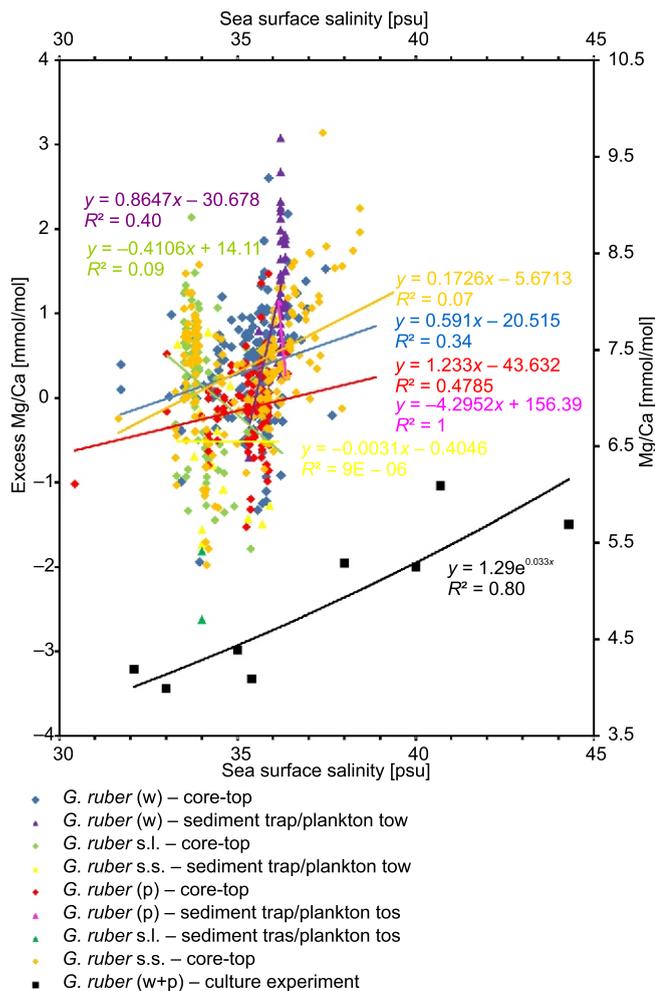


Fig. 2. The T -independent “excess Mg/Ca” in *G. ruber* tests recalculated for all the published field-based data sets presented here, and compared to data from laboratory cultures spanning a large salinity range from 30.4 to 44.3 psu

“Excess Mg/Ca” was calculated as the difference between measured and expected shell Mg/Ca values using a combination of the Dekens et al. (2002) or Anand et al. (2003) Mg/Ca-SST equations and the Bemis et al. (1998) low-light oxygen isotope temperature equation. Specific corrections to dissolution were also applied depending on the water depth and geographic distribution of core-top or plankton tow/sediment trap samples (explained in the text). Laboratory experiment data are symbolized by squares, plankton-tow/sediment trap data as triangles, and core-top data as diamonds. Sub-specific split was applied to the combined Mg/Ca data set in the context of both *G. ruber* chromotypes (white and pink) and morphotypes (*sensu stricto* and *sensu lato*). The coloured lines represent the linear regressions, while the equations and the correlation coefficients of each case are also shown and highlight the S effect

with S. The negative correlation to S is due to a worse fit of the tow Mg/Ca data to the calibration curve at higher salinities, implying lower residuals at higher salinities. However, the fact that these samples come exclusively from marginal basins (e.g., Caribbean Sea, South China Sea, Indonesia; Steinke et al., 2006; Sadekov et al., 2008; Mohtadi et al., 2011; Bahr et al., 2013) implies that it should be further evaluated in different regions from the open ocean. This unexplained divergence could probably be explained either by the different size fraction adopted between the previous studies or by the biomineralisation changes during the life cycle of each morphotype, even

to sub-specific physiological responses of calcification to salinity. In this regard, in agreement with the recent study of Antonarakou et al. (2015), this study not only justifies the separate treatment of the two chromotypes for palaeoenvironmental reconstructions, but also highlights the different degree of the S effect among *G. ruber* morphotypes when colour is invariant.

THE DIAGENESIS EFFECT

The influence of diagenesis can be reflected by three main and distinct diagenetic processes by which foraminiferal test wall structure and morphology can be modified: partial dissolution, overgrowth and recrystallisation (Edgar et al., 2015). All three can potentially act to offset the original geochemistry of foraminiferal tests post-mortem, either in the water column or at beneath the sea-floor (Pearson and Burgess, 2008; Sadekov et al., 2010). Although the former has been widely studied for the Mg/Ca palaeothermometer through water depth transects, size-normalized dissolution proxies, X-ray tomography and bulk sedimentological parameters (e.g., Lea et al., 2000, 2006; Dekens et al., 2002; Rosenthal and Lohmann, 2002; Regenberg et al., 2006, 2014; Fehrenbacher et al., 2006; Mekik et al., 2007; Huang et al., 2008; Fehrenbacher and Martin, 2011, 2014; Johnstone et al., 2011), this is not the case for the other two. Recrystallisation (neomorphism), which refers to the replacement of primary by new crystals of the same mineral (calcite) species (Folk, 1965), is often gradual and very localized, which means that many rounds of dissolution and re-precipitation may be applied in order for a new crystal to be formed, and consequently it is very difficult to be traced in modern material. Indeed, deep-sea sites containing recrystallised foraminifera are relatively rare in the geological record (Schrag et al., 1995; Kozdon et al., 2013; Edgar et al., 2013, 2015; Fantle and Higgins, 2014; Fantle, 2015; Voigt et al., 2015) and are most frequent associated with sites proximal to continents or they are usually limited to continental sections of Paleocene to Pliocene age (e.g., Sexton et al., 2006a, b; Drinia et al., 2007, 2008; Pearson and Burgess, 2008; Pearson et al., 2015; Karakitsios et al., 2016). This is in accordance with results of numerical modelling experiments implying that most calcite recrystallisation occurs during the early stages of burial (in the first 10 Myr; Rudnicki et al., 2001; Fantle et al., 2010; Fantle, 2015). However, in addition to burial depth and sediment age, lithology (including sediment porosity and permeability) and sedimentation rates also play important roles in controlling the rate of carbonate recrystallisation. For instance, clay-rich sediments (e.g., core-tops, down-core sediments) often yield “glassy” foraminifera, because the low permeability of clays limits post-depositional recrystallisation (Pearson et al., 2001; Sexton et al., 2006a; Pearson and Burgess, 2008). Finally, the overgrowth effect, in terms of high-Mg rhombohedral inorganic precipitates, alters the Mg/Ca content of foraminiferal shells, questioning the reliability of this proxy especially in high-salinity supersaturated settings.

With regard to the Mediterranean Sea and Red Sea, there is clear evidence that the precipitation of diagenetic crust on planktonic foraminifera can affect the fidelity of Mg/Ca records. Progress on documenting the precipitation of high-Mg calcite overgrowths from different sub-basins of the Mediterranean Sea has recently occurred (Kontakiotis et al., 2011; van Raden et al., 2011; Boussetta et al., 2011; Sabbatini et al., 2011) due to improvements in analytical instrumentation (e.g., LA-ICPMS, FT-TRA), emphasizing several aspects of the overgrowth effect, such as the mechanism, the degree of the diagenetic alteration and its species-specific potential response. These inor-

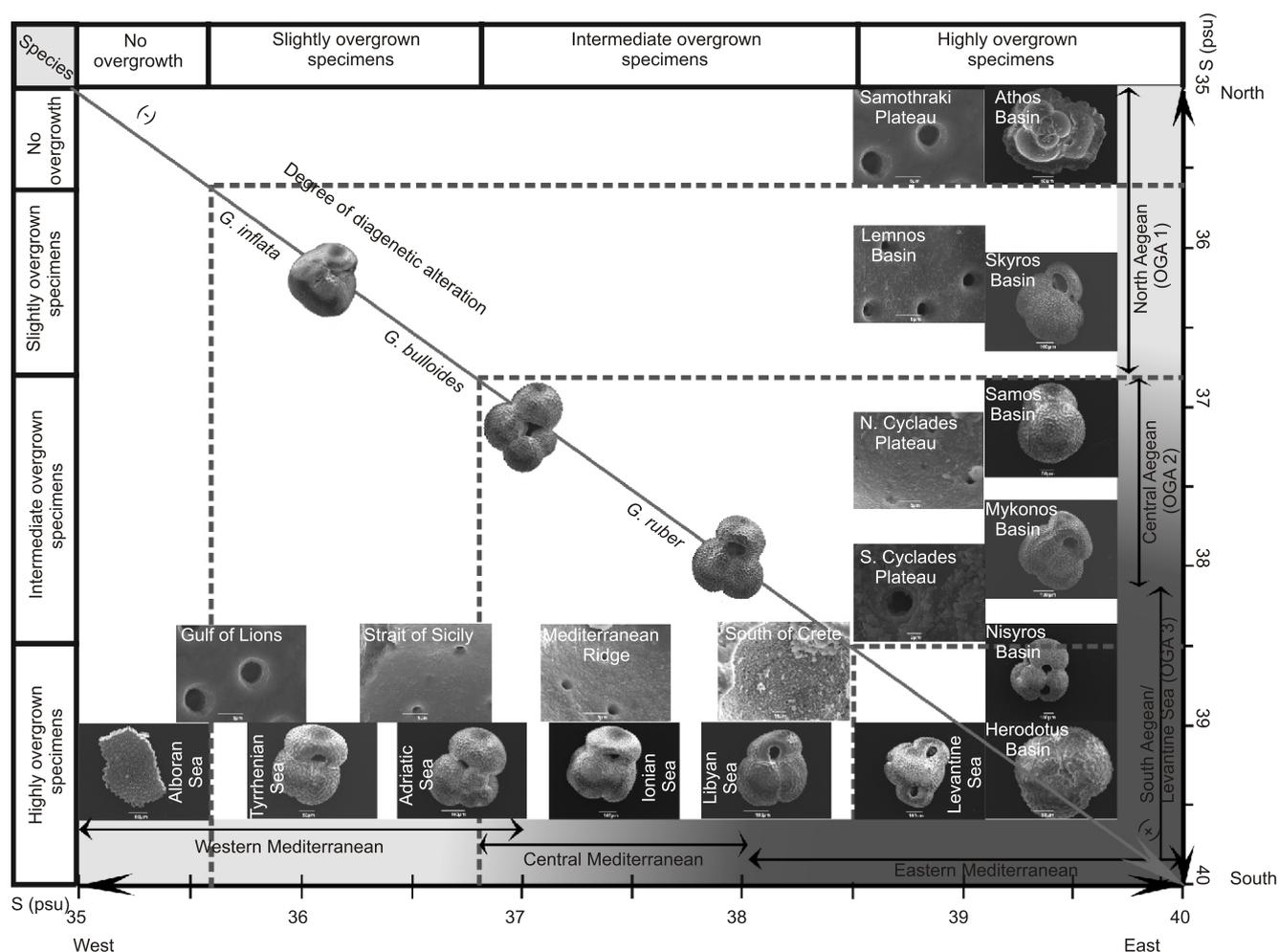


Fig. 3. Schematic representation of the overgrowth effect on planktonic foraminifera Mg/Ca ratios from the entire Mediterranean Sea

The horizontal and vertical axes contain high-resolution *G. ruber* SEM images (internal and external parts of the tests) from different sub-basins of two (W–E and N–S) transects along the Mediterranean Sea. According to recent observations of Antonarakou et al. (2012), diagenesis indicative of three stages are also shown. The arrow shows the gradually increased degree of diagenetic alteration on a NW–SE direction in terms of both geographic distribution (Kontakiotis et al., 2011; Antonarakou et al., 2012) and species-specific determination (van Raden et al., 2011). Scale bars are indicated on each image

ganic calcites can be easily distinguished from the biogenic calcite qualitatively and quantitatively by SEM (it typically consists of more equant and larger in shape and size crystals than their biogenic counterparts, due to lower surface free energy, often growing with radially directed c-axes; Zhang and Dawe, 2000; Hover et al., 2001; Crudeli et al., 2004) and geochemistry (it contains ~15% of MgCO_3 and constitutes up to 20% of the total shell calcite; Sabbatini et al., 2011) analyses. Therefore, this effect can be easily assessed, providing the researchers with important information which will potentially lead to a global multivariate calibration including such a correction factor.

As a likely illustration of this, Figure 3 shows the strong heterogeneity of the diagenetic imprint on *G. ruber* shells among different basins of the Mediterranean Sea (in both N–S and W–E transects). In the N–S transect along the eastern Mediterranean, we exclusively use new SEM data in our comparison from the samples analyzed in the studies of Kontakiotis et al. (2011) and Antonarakou et al. (2012) due to their higher diagenetic potential (their Mg/Ca values range from 3.35 to 21.61 mmol/mol). However, there are also considerable challenges. The absolute magnitude of the Mg/Ca change is much

smaller in lower salinity and calcite saturation state regions, and therefore differently overgrown specimens have been recorded along the eastern Mediterranean (Antonarakou et al., 2012). Separating these parameters and designating the different diagenetic stages for several species, even for different morphotypes of the same species, in conjunction with the geographical distribution of the analysed core-top samples will undoubtedly be a major and very promising research area in the future. If it becomes possible to differentiate these stages and to additionally correlate the diagenetic alteration with genetic data, the amount of information potentially extracted from the trace element data will substantially increase and a more precise reconstruction of the SST could be achieved.

SUMMARY AND CONCLUSIONS

The points outlined above could potentially lead to differences between various calibrations. Specifically, field based studies using core top sediment samples (Elderfield and Ganssen, 2000; Dekens et al., 2002) and time series sediment

trap samples (Anand et al., 2003; McConnell and Thunell, 2005) have generated calibration equations for multiple species of planktonic foraminifera from different regions and over different T ranges. Further uncertainties may be caused by differences in analytical procedures and/or sample preparation between different laboratories (Rosenthal et al., 2004; Greaves et al., 2008). Nevertheless, results attained using very different approaches are remarkably consistent. Modern calibrations may be expressed by an exponential relation of the form: $Mg/Ca = a \cdot \exp^{b \cdot T}$, where a and b are the pre-exponential and exponential constants, respectively.

Additionally, during the last two decades most researchers (in both culture- and field-based studies), in their attempt to account for the influence of the secondary factors that have a disproportionately large influence on Mg/Ca ratios, produced calibration equations that include, besides T , a correction term such as a depth-related dissolution artifact (Dekens et al., 2002; Mekik et al., 2007), a salinity correction factor (Groeneveld et al., 2008; Mathien-Blard and Bassinot, 2009), and a carbonate ion content (CO_3^{2-}) correction, or a combination of them (Kisakürek et al., 2008; Arbuszewski et al., 2010; Khider et al., 2015). All of these new insights and applications reinforce the view that the maximum potential of this “palaeothermometer” in reconstructing past ocean-climate interactions has not yet been reached. However, additional work is required to address the apparent discrepancies between field-based discoveries, on the one hand, and culture study results on the other hand. Perhaps a combined data set from all these approaches could pro-

duce a new, more global, palaeotemperature equation calibration with the dual benefit of improved SST estimates, as well as the ability to estimate errors due to changes in some of the additional influential factors. Given that some species (e.g., *G. truncatulinoides*; McKenna and Prell, 2004) cannot be easily cultured in the laboratory, the Mg/Ca- T calibration in this case must be determined using individuals collected from either the water column or the sediments. In addition to the “synthetic approach”, the comparison provided in this study also underlines the need for (sub)species-specific calibrations, taking into account the significant vital, salinity and overgrowth effects, which differentially affect the Mg/Ca- T calibration of each species. Ultimately, further calibration work involving parallel measurements of fossil and live-collected or cultured samples is urgently required to resolve this issue and thus allow us to access the wealth of information on different oceanic environments. The generation of records from different sites worldwide would minimize the potential uncertainties, and a consistency in observed trends in Mg/Ca for different planktonic and benthic Foraminifera would also validate our interpretations.

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