Element/Ca ratios in Nodosariida (Foraminifera) and their potential application for paleoenvironmental reconstructions

Laura Pacho[1]; Lennart de Nooijer[1]; Gert-Jan Reichart[1,2]

[1] Royal Netherlands Institute for Sea Research (NIOZ) and Utrecht University, Texel.
[2] Department of Geosciences, Utrecht University, Utrecht.

Correspondence to: Laura Pacho Sampedro (laura.pacho.sampedro@nioz.nl), Lennart de Nooijer (lennart.de.nooijer@nioz.nl), Gert-Jan Reichart (gert-jan.reichart@nioz.nl).

Abstract. The chemical composition of foraminiferal shells is a well-known tool in paleoceanography to reconstruct past environments and climate. Their application is based on the relation between environmental variables and the concentration of elements incorporated or stable isotope fractionation during calcification. The vast majority of these so-called proxy-relationships are based on the foraminiferal order of the Rotaliida, that for example, encompass all living planktonic species. However, there are more orders of foraminifera with calcifying members, some of which that have fundamentally different biomineralization pathways, such as the Nodosariida, the Polymorphinida and the Vaginulinida. All these belong to the class of the Nodosariata and produce calcite shells, which may serve as carriers of paleo-environmental and climate signals. The microstructures of these shells and overall morphology of these foraminifera strongly deviate from the Rotaliida, suggesting that their elemental and stable isotopic composition do not necessarily respond similarly to environmental parameters. A potential advantage of the Nodosariata is that they appear considerably earlier in the fossil record (Carboniferous) than the Rotaliida (Jurassic), thereby possibly extending the range of foraminifer-based paleoceanographic reconstructions considerably. To test the potential application of Nodosariata foraminifera as paleoproxies, we investigated incorporation of 5 elements in 11 species as a function of environmental parameters from a transect sampled in the Gulf of Mexico. Their element composition (B/Ca, Na/Ca, Mg/Ca, Sr/Ca and Ba/Ca) shows a distinct geochemical signature for these foraminifera different to that of members of other foraminiferal orders. Results also show an increase in Mg/Ca values with increasing temperature, similar to that know for the Rotaliida, which suggest that Nodosariata shells might be useful for paleotemperature reconstructions. The difference in Mg/Ca-temperature calibration in Nodosariata compared to Rotaliida, with the large differences in their morphology, shell's microstructures and overall geochemical composition, suggests that the Mg/Ca to

temperature relationship is partly independent of the exact calcification mechanism. We compare Mg/Ca-temperature sensitivities across foraminiferal orders and describe a relationship between the average Mg/Ca and the sensitivity of the Mg/Ca-temperature calibration. For other elements, the variability across orders is smaller compared to that in Mg/Ca, which results in more similar El/Ca-environmental calibrations.

1. INTRODUCTION

Reconstructing past climates is an integral part of predicting the impact of the ongoing rise in atmospheric CO_2 levels on the Earth's future climate. The expected temperature increase for a doubling in $p CO_2$ (the so-called climate sensitivity) has, for instance, been estimated by comparing past seawater temperatures and carbon dioxide levels (Rosenthal et al., 2017; D'Arrigo et al., 2006; Mann et al., 1998). Reconstructions of such parameters rely on accurate and precise tools that can be applied to past episodes in Earth's history with conditions similar to those expected in the future. In this context, foraminifera are popular tools as they are proxy signal carriers for constraining past seawater temperature and pH. Field and culturing studies have shown the dependence of the chemical composition of their shells on the seawater chemistry and physics in which they calcified. For example, the amount of incorporated Mg (expressed as the shell's Mg/Ca) increases exponentially with temperature (Nürnberg et al., 1996) and can hence be used to reconstruct past changes in bottom water temperature using benthic foraminifera (Lear et al., 2002) and sea surface temperature using planktonic foraminifera (Hastings et al., 1998; Lea et al., 2000).

The incorporation of Mg into the calcite of most foraminifera is, however, much lower compared to calcite precipitated inorganically from seawater (Morse et al., 2007). This offset and the observed differences in Mg/Ca values between species (Wit et al., 2012) is hypothesized to be caused by the strong biological control that foraminifera exert on the chemistry of the calcifying fluid from which they form their shells (Erez, 2003; Nooijer et al., 2014). This biological control and the resulting inter-species variability in calcite chemistry has highlighted the need for species-specific calibrations (Wit et al., 2017; Allen et al., 2016). With this in mind, Mg/Ca and other proxies based on foraminiferal shell composition, including Na/Ca for salinity (Dämmer et al., 2020; Bertlich et al., 2018; Wit et al., 2013) and $\delta^{11}B$ for seawater pH (Foster and Rae, 2016; Rae et al., 2011; Spivack et al., 1993) have been developed and successfully applied. Another complicating factor when applying foraminiferal proxy signals is the dependency of element incorporation and isotope fractionation on more than one environmental parameter.

For example, shell Mg/Ca values are also affected by the marine inorganic carbon system (Evans et al., 2016), salinity (Raitzsch et al., 2010; Dissard et al., 2010) and the [Mg^{2+}] of the seawater (Evans and Mller, 2012). Ideally, proxy application would therefore include multiple elements to reconstruct a single parameter. Or alternatively, use multiple proxy relationships to simultaneously reconstruct multiple environmental parameters.

Our knowledge of the controls on foraminiferal shell geochemistry is almost exclusively based on results obtained from Rotaliida. These foraminifera are characterized by multilocular shells composed of bilamellar calcite (Reiss, 1957, 1963) that can be optically radial or granular. The popularity of using members of this order is partly due to the fact that they encompass all extant planktonic foraminiferal species, while the diversity and overall high abundance of benthic Rotaliida add to their popularity for reconstructions of bottom water conditions. Few studies investigated element incorporation in the Miliolida, which have a fundamentally different calcification mechanism (ter Kuile et al., 1989; De Nooijer et al., 2009; Debenay, J.-P., Guillou, J.-J., Geslin, E., Lesourd, M. and F., 1998). The composition of their calcite is markedly different from that of the Rotaliida, with for example markedly high Mg/Ca (Toyofuku et al., 2000a; van Dijk et al., 2017b) and more depleted $\delta^{25}Mg$ values (Dämmer et al., 2021).

Reconstructions based on Rotaliida could theoretically span the last ~190 Ma since they first occur in the fossil record in the Pliensbachian (Haynes, 1981b). The order of Nodosariata evolved calcification much earlier in the Permian (Haynes, 1981a) and their application would therefore roughly double the age for which paleoceanographic reconstructions could be made using foraminiferal shell chemistry. They separated from the Rotaliida and Miliolida likely before the Cambrian (Pawlowski et al., 2003) and are currently found in many marine habitats and are easily recognizable by their uniserial chamber arrangement (Haynes, 1981a). Their walls are fibrous, composed of conical bundles of one to tens of µm in length, specific to the Nodosariata and therefore suggest a unique biomineralization mechanism (Dubicka et al., 2018). Despite such differences, their stable oxygen isotopic composition is relatively small (Dubicka and Wierzbowski, 2021) and the small carbon isotope difference between the two types of foraminifera suggest a difference in their depth habitats.

So far, the Nodosariata elemental composition has not been studied and therefore, we analyzed element incorporation such as Na/Ca, Mg/Ca, Sr/Ca, B/Ca and Ba/Ca of different species collected along a depth transect in the Gulf of Mexico.

Accompanying environmental data (temperature, salinity, etc.) allow us to detect any dependencies of the incorporation of elements on these parameters and compare them to existing calibrations for Rotaliida foraminiferal species.

2. MATERIAL AND METHODS

2.1 Sampling location

Commented [LPS6]: Editor Chiara Borrelli

80 In February 2020, sediment samples were collected from the continental margin in the northern Gulf of Mexico using research vessel *Pelagia* (expedition 64PE467). Samples were collected along a transect close to the outflow of the Atchafalaya River, at depths of 105m, 272m and 619m (Fig. 1). From box cores, smaller sub-cores were collected on deck and subsequently sliced (with a resolution of 0.5 cm for the upper two centimeters and in 1 cm-slices down to a depth of 10 cm). The sediment was stored in ethanol, with Rose Bengal (rB) (2 g/L) added to stain the cytoplasm of living foraminifera.

85 From the overlying water of the box cores, vials were filled for analysis of DIC (dissolved inorganic carbon) and TA (total alkalinity) after filtering over 0.4 µm filters. For both analyses, 5 mL vials were filled with seawater and stored at 4 °C after addition of 15 µL of $HgCl_2$ to prevent biological alteration of the inorganic carbon system. The samples were analyzed after returning to the laboratory using a QuAAtro Continuous Flow Analyser. DIC samples were acidified and the carbon dioxide that was formed was dialyzed over a membrane that reduces the phenolphthalein indicator and was spectrophotometrically

90 recorded at 550nm (Stoll et al., 2001). For TA, a slightly acid buffered solution of Potassium Hydrogen Phthalate was added to the sample after which the intensity at 590nm was recorded (Sarazin et al., 1999). Values obtained for DIC and TA were consistent with the ones obtained from earlier expeditions (Sirois, 2017). Bottom water temperature and salinity were taken from CTD casts at the same station where the sediment samples were taken approximately 4 meters above the sea floor. Values for all inorganic carbon system parameters can be estimated using two measured parameters, since any combination of two

95 such parameters will allow calculating all others, including dissolved CO_2 (Zeebe et al., 1999), performed with $PyCO_2SYS$ (Lewis, E; Wallace, D; Allison 1998), using the recent published Python script (Humphreys et al., 2022).

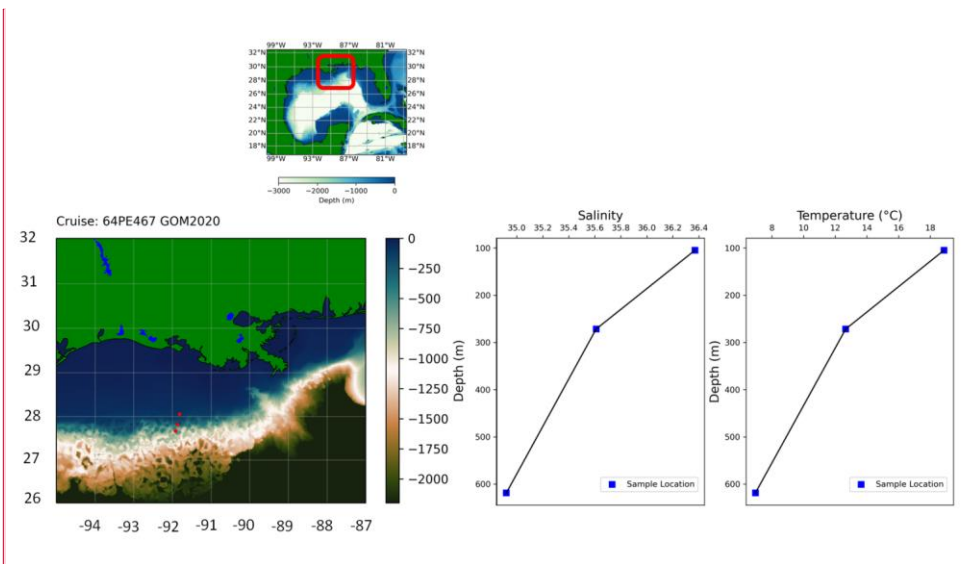



Figure 1: Left: sampling location in the Gulf of Mexico (GEBCO, 2022). Right: salinity and temperature data from CTD at bottom sample.

Position	Station	Depth (m)	Temperature (°C)	Salinity	DIC (µmol/Kg)	TA (µmol/Kg)	pCO$_2$ (ppm)	pH	[CO$_3^{2-}$] (µmol/Kg)	[HCO$_3^-$] (µmol/Kg)	fCO$_2$ (ppm)	ΩCa
91.812W/ 28.052N	A100	104.7	18.87	36.37	2151.7	2334.7	621.60	7.88	135.84	1995.29	619.46	3.16
91.862W/ 27.812N	A300	271.64	12.66	35.61	2144.9	2277	623.25	7.86	102.47	2017.51	620.93	2.32
91.92W/ 27.665N	A600	618.8	6.96	34.92	2202.1	2300.7	616.54	7.84	82.51	2089.71	614.07	1.7

100

Table 1: Chemical and physical seawater parameters at the stations where foraminifera were collected. Temperature, salinity, DIC and TA were measured; the other parameters (pCO$_2$ and all parameters to the right of pCO$_2$) were calculated.

2.2 Sample preparation

Commented [LPS9]: Editor Chiara Borrelli

105 Samples were washed using sieves with mesh sizes of 63 µm and 150 µm and dried in an oven at 60°C. When selecting the specimens, rB-stained foraminifera were separated from non-stained specimens to allow detection of possible post-mortem alteration of the primary geochemical signal. The foraminifera were cleaned after isolation from the sediment by immersion in a solution of 1% H_2O_2 and 0.1M NH_4OH, and three consecutive rinses with double deionized water. During the latter step, the Eppendorf tubes were placed in an ultrasonic bath to remove any particles adhering to the shells. In this way, 188

110 individuals were prepared for single-chamber geochemical analysis using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS).

2.3 Analytical procedure

Commented [LPS10]: Editor Chiara Borrelli

Specimens were ablated for 50 seconds in a NWR193UC TV2 dual volume chamber using circular spots of 80 µm set at a repetition rate of 6 Hz, using an energy density of 1.00 ± 0.05 J/cm^2. The 193 nm wavelength of the LA-ICPMS used is deep

115 ultra violet (193 nm), which is excellently suited for ablating carbonates (Reichart, 2003). The aerosol produced during the ablation was transported to a quadrupole ICP-MS (Thermo Fisher Scientific iCAP-Q) on a helium flow with a flow rate of 0.6 L/min, with 0.4 L/min Argon make-up gas being added before entering the ICP torch. Calibration was performed against USGS MACS-3 (synthetic calcium carbonate) pressed powder standard with ^{43}Ca as an internal standard. Scanned masses include ^{11}B, ^{23}Na, ^{25}Mg, ^{27}Al, ^{43}Ca, ^{88}Sr and ^{138}Ba. Standard reference material for quality control was NFHS-2-NP (Boer et al., 2022).

120 Data reduction was performed using an adapted version of the data reduction software SILLS (Signal Integration for Laboratory Laser Systems,(Boer et al., 2022; Marcel Guillong, Christopher Latkoczy, Jung Hun Seo and A, 2008)) in Matlab. Repeatability based on RSDs of measurements of NFHS-2-NP in this study (n=8) is 4% for Na/Ca, 1% for Mg/Ca and 2% for Sr/Ca. For all specimens, two to three spot analysis were performed on the final chamber (Fig. 2). The average element/calcium ratio was calculated from the entire profile of the foraminifera chamber wall with a delay of 3 seconds after

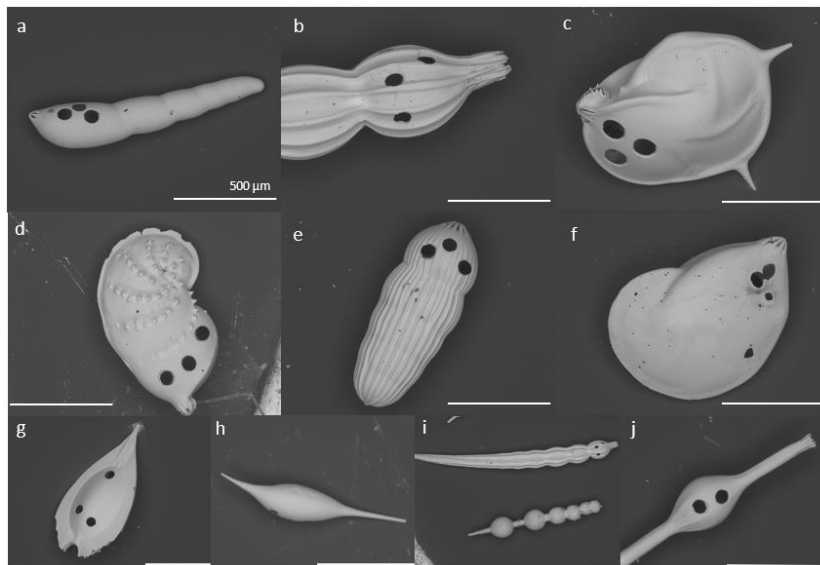
125 firing the laser. The end point of the profile, where the laser penetrates the chamber wall, was calculated in the adapted Matlab application based on a drop of 30% of the ^{43}Ca intensity. This end point of the profile was visually checked using laser ablation screen shots continuously made and stored every 2 seconds.

Commented [LPS11]: Dr. Reinhard Kozdon:
It sounds as if the repeatability is based on data from a different analytical session (Boer et al., 2022) using NFHS-2-NP standard. However, this study used the MACS-3 standard for calibration. What is the repeatability on MACS-3?

Commented [LPS12]: Dr. Reinhard Kozdon:
What type of laser was used, what was the wavelength (193 nm?). In addition, I had to google the NFHS-2-NP standard. Please add some info. Did the authors perform a standard-sample-standard bracketing approach? I assume they did, but I wasn't able to find this in the description.

Since they were not correlated and the occasional high Mg/Ca was not accompanied by high Al/Ca, the elevated Mg/Ca could not be attributed to contamination (e.g. by clay particles or a recrystallized phase at the surface of the shells, Fig. S1; Fig. S2; Fig. S3; Fig. S4) we did not remove any of the original data points. Instead, we statistically tested for outliers to identify El/Ca ratios that are outside the expected distribution given the data. These outliers (n =25) are highlighted in the figures and in- or excluding them was found to have an insignificant effect on the reported regressions.

Laser ablation system sample cell	NIOZ
Wavelength	193nm
Pulse duration	4 ns
Laser fluence	1 J/cm²
Laser spot size	60 µm
Laser repetition rate	6 Hz
Carrier gas flow rate (He)	0.6 L/min

Table 2: Characteristics and method for the LA-ICPMS analyses.

Commented [LPS13]: Dr. Ellen Thomas:
Others might prefer somewhat different methodology (e.g., rose bengal staining, absence of reductive cleaning, check for clay contamination), but in my opinion the methodology is acceptable since clearly described, so readers can take into account how measurements were made. Statistical data analsyis is also well described and looks good.

Commented [LPS14]: Dr. Reinhard Kozdon:

LA-ICPMS analyses of foraminifera shells are not trivial, and many papers have been published, discussing different approaches of analysis and methodologies to process the data. I am not able to find many information within this manuscript. For example, was the entire LA-ICPMS profile
integrated, and the average element/Ca ratios calculated? Was the intrashell variability monitored, while the laser milled through the chamber wall? There could be some additional information in this signal. Where there any criteria for cut-off? (e.g., laser penetrates the chamber wall – at what point to end integration of the data).

Figure 2: Nodosariata species studied. (a): *Dentalina* **spp.; (b)** *Nodosaria flintii***; (c)** *Lenticulina calcar***; (d)** *Vaginulinopsis baggi***; (e)** *Pseudoglandulina comatula***; (f)** *Lenticulina calcar***; (g)** *Fissurina radiata***; (h)** *Procerolagena* **sp.(i)** *Nodosaria flintii* **up and** *Amphicoryna* **sp. bottom; (j)** *Grigelis semirugosus***. (The SEM images were taken after LA-ICPMS, holes in the pictures are a consequence of the analyses and they were placed in the most recent chamber). All scale bars are 500 µm, the size of the ablation craters are all 80 µm (Closest picture of the aperture in Fig. S5).**

2.4 Statistical analyses

For the three species present at all depths sampled we performed an ordinary least sum of squares regression analysis to test dependency of the elements incorporated on environmental parameters. For Mg/Ca and temperature, an exponential response model was assumed, while assuming a linear response model for Na/Ca and salinity. For B/Ca and the inorganic carbon parameters, a linear response model was assumed. Prior to regression analysis, outliers were identified based on studentized residuals using the package "statsmodels" for python and applying the method "sidak" from the Holm-Šídák method with one-step correction (Seabold and Perktold, 2010). Identified outliers are highlighted in the figures: their presence or absence had only a marginal effect on the regression analysis.

When plotting the results, the analytical error was plotted for individual analyses (which mostly falls within the size of the sample marker), the standard deviation for the sample to identify the variability within the sample as well as the standard error (SE), to show confidence interval for the estimate of the average. Standard deviation (SD) and SE are related according to SE=SD/$\sqrt{(n° \ measurements)}$).

Since all data are derived from three locations, in addition to the regression analysis, a two-tailed t-test, was performed to test whether the variances of the El/Ca between locations significantly differed.

3. RESULTS

3.1 Average El/Ca in Nodosariata species

Combining the data from all stations shows that the average El/Ca in the individual Nodosariata species varies between 6.65 to 13.2 mmol/mol for Na/Ca, between 5.94 and 20.1 mmol/mol for Mg/Ca and between 1.09 and 1.81 mmol/mol for Sr/Ca (Table 2) (for more information about variability for two species within the same genus Table S2). For all measured Mg/Ca of

Commented [LPS15]: Dr. Ellen Thomas:
Nodosariata taxonomy is complex, and definitely not full examined; in general, the names cited with images in fig. 2 seem OK, except for 2d: *Lenticulina papillosa*, which species is a densely coiled spiral, not unrolling. A species with a uniserial part is *Vaginulinopsis baggi* McLean 1955.
(hZps://www.marinespecies.org/aphia.php?p=taxdetails&id=896255)

Commented [LPS16]: Dr. Reinhard Kozdon:
It seems that 2-3 analysis were placed in the final chamber (Fig. 2). Please add this information here.

Commented [LPS17]: Dr. Ellen Thomas:
In 'fundamentally distinct morphology' (line 197), I would like to see the very typical apertural morphology mentioned in addition to the chamber arrangement, because the aperture is easily recognizable for non-foram specialists.

And editor Chiara Borrelli.

Commented [LPS18]: Dr. Reinhard Kozdon:
Line 135: the package

Commented [LPS19]: Dr. Reinhard Kozdon:
Line 136: Dot before "Identified" missing.

Commented [LPS20]: Dr. Ellen Thomas:
In view of the fact that such analyses usually combined different morphospecies of e.g. *Lenticulina*, could the authors specifically comment on differences in El/Ca by species within the same genus?

a single species, the SD is on average 3.01 mmol/mol, where it is 1.07 mmol/mol for Na/Ca, and 0.14 mmol/mol for Sr/Ca.

This translates to a relative variability in El/Ca within a species of 19.6% for Sr/Ca, % for Na/Ca and 56% for Mg/Ca.

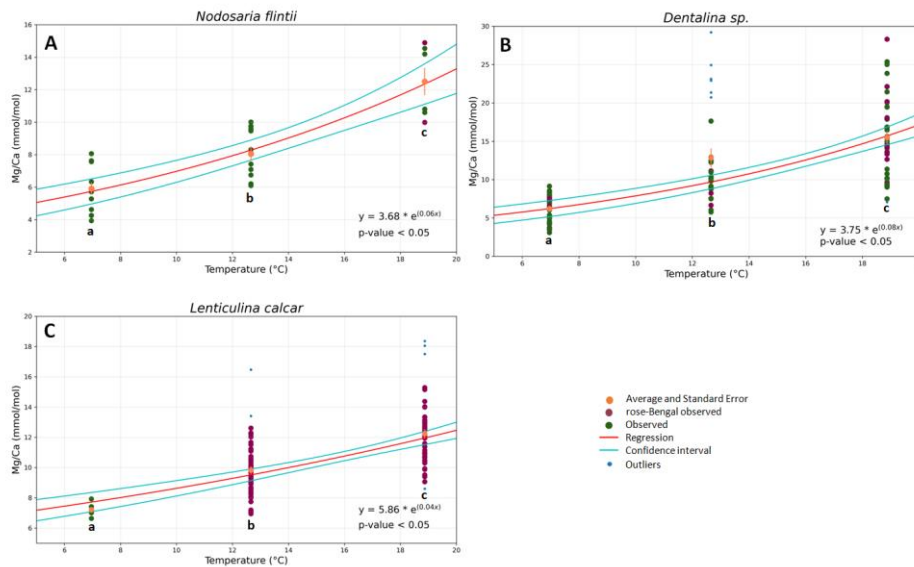
For the Nodosariata Ba/Ca varies considerably, between 2.5 and 4.6 μmol/mol, with an average SD of 1.2 μmol/mol, which corresponds to a 71% variability. The B/Ca data varies between 51 and 83 μmol/mol, with a modest variability in the Nodosariata, with an average SD of 9.8 (or 31.2%) per species.

Species	Na/Ca (mmol/mol)	SD	Mg/Ca (mmol/mol)	SD	Sr/Ca (mmol/mol)	SD	Ba/Ca (μmol/mol)	SD	B/Ca (μmol/mol)	SD	Number of measurements/specimens
Amphycorina sp.	8.50	± 0.74	5.94	± 0.79	1.20	± 0.07	3.18	± 0.74	53.37	± 5.67	52/19
Nodosaria flintii	8.22	± 0.85	8.08	± 2.91	1.30	± 0.14	3.78	± 1.85	53.09	± 10.13	30/10
Dentalina spp.	9.28	± 1.63	11.74	± 6.49	1.33	± 0.19	4.63	± 2.88	66.73	± 17.84	107/35
Fissurina radiata	6.65	± 0.41	7.42	± 2.92	1.09	± 0.07	2.53	± 0.25	53.98	± 6.64	5/2
Grigelis semirugosus	10.85	± 1.50	11.78	± 4.04	1.57	± 0.13	2.85	± 0.79	62.21	± 6.20	32/12
Lenticulina calcar	10.71	± 1.19	10.87	± 2.43	1.58	± 0.15	2.50	± 1.10	82.72	± 15.06	104/33
Lenticulina denticulifera	10.03	± 1.21	11.31	± 2.82	1.54	± 0.18	3.45	± 1.40	67.29	± 16.87	85/27
Vaginulinopsis baggi	9.50	± 0.81	8.81	± 1.88	1.54	± 0.08	2.73	± 0.64	51.12	± 6.54	58/20
Procerolagena gracillini	10.47	± 1.35	8.64	± 0.93	1.81	± 0.25	2.85	± 0.76	64.36	± 3.84	6/2
Pseudoglandulina comatula	13.21	± 0.93	20.06	± 3.19	1.60	± 0.07	4.28	± 1.58	80.04	± 9.38	38/13
Oolina spp.	10.01	± 1.20	12.14	± 4.75	1.39	± 0.24	2.88	± 0.66	58.12	± 9.96	8/2

Table 3: Element incorporation average and SD for eleven species spanning 188 analyzed specimens of Nodosariata.

3.2 Impact of temperature on Mg/Ca and salinity on Na/Ca

Mg/Ca correlates positively with temperature in *Nodosaria flintii*, *Dentalina* spp. and *Lenticulina calcar* over a 12 °C range studied here (for more information about the variability between living and non-living species variability Table S1). Lowest and highest values for Mg/Ca were found in *Dentalina spp.*, ranging from 3.09 mmol/mol at 6.96 °C to 29.2 mmol/mol at

18.87 °C (Fig. 3b and Table 3). For *Nodosaria flintii*, Mg/Ca ranges from 3.93 mmol/mol to 14.9 mmol/mol (Fig. 3c and Table 3) and for *Lenticulina calcar* Mg/Ca increases from 6.6 to 18 mmol/mol (Fig. 3 and Table 3). Despite the differences in absolute values, the sensitivity of changes in Mg/Ca as a function of temperature is similar for the three species, with *Dentalina* spp. having a slightly higher Mg/Ca-temperature sensitivity than the other two species (Table 3).

Commented [LPS23]: Dr. Reinhard Kozdon:
Line 157: over a the

Commented [LPS24]: Dr. Reinhard Kozdon:
Figures 3, 4: please write rose-Bengal observed (or living) instead of rB observed

175

Figure 3. Correlations between Mg/Ca and temperature for three species of Nodosariata. Dots in blue show the outliers that were omitted before regression analysis based on studentized residuals. Red points are individuals living when sampled (i.e. stained with rose-Bengal) and green points are non living individuals when sampled. Red line indicates the result of the exponential OLS regression using both stained and non stained specimens, cyan lines indicate the 95% confidence interval of the regression.

180 Results also show a significant positive increase in Na/Ca with salinity for two species, *Dentalina* spp. and *Nodosaria flintii*, despite the relatively small range in salinities between sites (1.45 units). For *N. flintii*, average Na/Ca varied between 6.7 and 10 mmol/mol, which is similar to the increase of 5.6 to 13 mmol/mol by *Nodosaria flintii* (Fig.4).

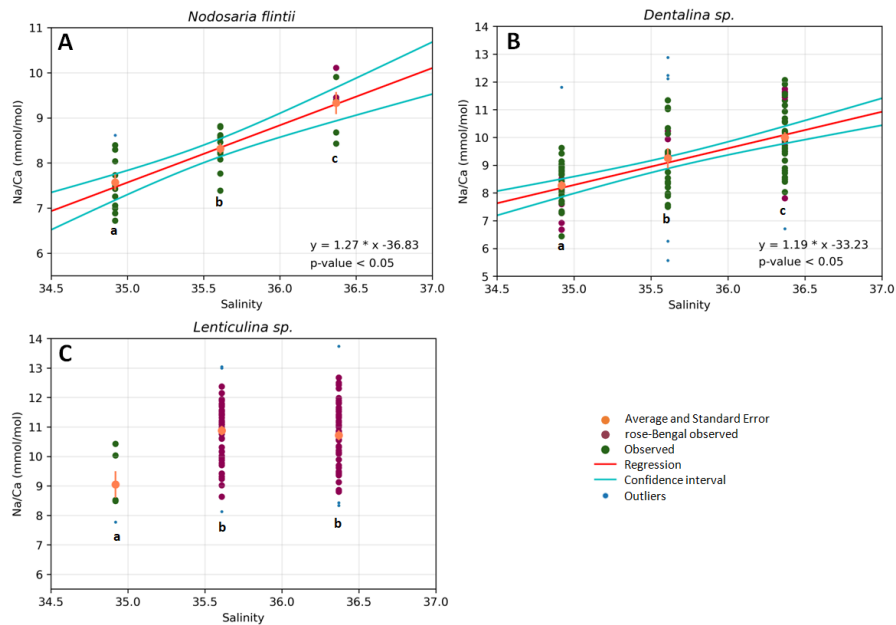



Figure 4: Correlations between Na/Ca and salinity for three species of Nodosariata. Outliers are shown in blue that were omitted before regression analysis (panels A and B) based on studentized residuals. Red points are individuals living when sampled (stained with rose-Bengal) and data in green are non-stained individuals. Red lines in A and B indicate the result of the linear OLS regression using both the stained and non-stained specimens and the two cyan lines indicate the 95% confidence interval of the regression.

For *Lenticulina* sp., no regression was found between salinity and Na/Ca (panel C); 'a' and 'b' indicate significant differences in the averages between the three groups of datapoints (i.e. the average Na/Ca at lowest salinity is significantly different from the average Na/Ca in the other two sampled stations).

4. DISCUSSION

4.1 Element incorporation in Nodosariata shells

The average values of Na/Ca, Sr/Ca and Ba/Ca of the Nodosariata are similar to those observed in planktonic (Barker et al., 2005) and many benthic Rotaliida (Lear et al., 2002; Elderfield et al., 2006), whereas Miliolida have considerably lower Na/Ca and higher Sr/Ca and Ba/Ca (Van Dijk et al., 2017). In addition, the Nodosariata's Mg/Ca, is higher (5-30 mmol/mol; Fig. 3) than those in planktonic and many low Mg/Ca benthic Rotaliida (Allen et al., 2016; Barker et al., 2005; Lowenstein and Hönisch, 2012). Many larger benthic, tropical Rotaliida and most Miliolida, have an order of magnitude higher Mg/Ca values (Evans et al., 2018; Toyofuku et al., 2000b) compared to those observed for the Nodosariata. The Nodosariata's B/Ca values are considerably lower compared to those reported for other foraminiferal species (Rae et al., 2011). A similar low B/Ca value was found for the rotaliid *Operculina umbonatus* (Rae et al., 2011), but this species has much higher Mg/Ca compared to the species measured here (Fig. 3). Together, our measurements imply that the Nodosariata have a unique El/Ca signature that can easily be distinguished from that of the other calcifying foraminiferal orders (Rotaliida, Miliolida, etc.), despite overlap of some ratios with those of some other species.

This order or class specific signature of the shell's composition supports a fundamental differences in their calcification mechanisms (Dubicka et al., 2018; Dubicka and Gorzelak, 2017). Such a difference is also suggested with a fundamentally distinct morphology (i.e. chamber arrangement), as well as the μm scale structures observed within the chamber walls. The chamber walls of the Nodosariata show a lamellar and fibrous texture, while Rotaliida show a granular texture (Dubicka et al., 2018). Such differences in the shell's microstructure coincide with the here observed contrasting Mg/Ca values, similar to what was already reported for comparisons between other pairs of foraminiferal orders (van Dijk et al., 2016; Bentov and Erez, 2006). Deep evolutionary branching between Nodosariata and Rotaliida and the large difference in time of first fossil occurrence further supports the hypothesis that they evolved their biomineralization mechanism independently. With different seawater chemical conditions(van Dijk et al., 2016; Tanner et al., 2020) at the time when Nodosariata and Rotaliida evolved calcification biomineralization mechanisms may well reflect contrasting selective pressures, which in turn is reflected by the shells' Mg/Ca ratios.

Although they have a long geological and evolutionary history, El/Ca variability in the elemental-to-calcium ratio within the Nodosariata is remarkably small compared to that observed in e.g. the Rotaliida. The Mg/Ca values vary between the different families -the Lagenidae, Nodosariidae, Ellipsolagenidae and the Vaginulinidae- not significantly (one-way ANOVA, p-value

Commented [LPS26]: Dr. Ellen Thomas:
line 203: 'large difference *in time* of first fossil occurrence' - please add 'in time'

Commented [LPS27]: Dr. Ellen Thomas:
line 206:' *El/Ca* variability ...is remarkably small'; please add 'El/Ca' or 'chemistry of shell carbonate', to make this clear (in fact, morphological variability is rather large)

> 0.05 and F=1.082). Also, for the other elements no significant difference in the average elemental ratios is observed between species and thus, between families. This does not exclude the existence of species or families within the Nodosariata that may

220 have a different elemental signature than those reported here as we investigated 3 species only. Still, the analyzed species span 3 different orders within the Nodosariata. The relative uniformity in shell carbonate composition across the orders may indicate that the calcification mechanism invented by the Nodosariata is very well suited for a wide range for seawater chemical conditions. Alternatively, the relatively low species diversity of the present day Nodosariata compared to that during the Jurassic (Haynes, 1981a) may reflect a selective loss of calcification mechanisms due to past changes in ocean chemistry

225 and/or physics, possibly related to past climate variability. Such a hypotheses on the potential interplay between calcification and climate can be tested by comparing the El/Ca of extinct species from a suite of eras to that of species living today. (Haynes, 1981b, a) (Evans et al., 2013; Maeda et al., 2017) (Toyofuku et al., 2011; Barrientos et al., 2018).

4.2 Effect of environment in the element incorporation

4.2.1 Na/Ca versus salinity

230 Na/Ca correlates with salinity in 2 of the Nodosariata species investigated: *Dentalina* spp. and *Nodosaria flintii* (Fig. 4). Sensitivities of Na/Ca to salinity relationships appear somewhat higher than those reported for Rotaliida species (Wit et al. 2013; Geerken et al. 2019; Allen et al. 2016; Mezger et al. 2016; Hauzer et al. 2021) (Table 4). Parallel to the increasing number of reports on the correlation between Na incorporation and salinity, there is discussion of what precisely controls foraminiferal Na/Ca, which could be $[Ca^{2+}]$ (Hauzer et al., 2018) as well as the $[Na^+]_{sw}$ and/or salinity (Wit et al., 2013). In

235 addition, it may be that Na incorporation is affected by precipitation rates as well, such as indicated by inorganic experiments showing that Na-incorporation is affected by saturation state (Devriendt et al., 2021). Although poorly constrained in foraminifera (Geerken et al. 2022), environmental factors may affect the rate at which foraminifera precipitate their calcite, making the relationship between Na/Ca and an environmental parameter indirect. Still, the consistent increase in Na/Ca with salinity in many Rotaliida foraminifera and the here reported correlations for two Nodosariata species (Fig 4; Table 4), suggests

240 a more direct coupling between seawater $[Na^+]$ and or $[Ca^{2+}]$ and underscores the robustness of this proxy.

Order	Species	Sensitivity (mmol/mol)	Paper
Nodosariida	*Nodosaria flintii*	1.27	This study
Nodosariida	*Dentalina* sp	1.19	This study
Rotaliida low Mg	*Ammonia tepida*	0.22	Wit et al., 2013
Rotaliida low Mg	*Ammonia tepida*	0.064	Geerken et al., 2019
Planktonic Rotaliida	*G. ruber*	0.074	Allen et al., 2016
Rotaliida med Mg	*Amphistegina lessonii*	0.077	Geerken et al., 2019
Planktonic Rotaliida	*G. ruber*	0.66	Mezguer et al., 2016
Planktonic Rotaliida	*G. sacculifer*	0.6	Mezguer et al., 2016
Rotaliida High Mg	*Operculina ammonoides*	0.33	Hauzer et al., 2021

Table 4: Comparison of sensitivities of Na/Ca versus salinity of benthic foraminifera from this study and Rotaliida with different Mg incorporation ratios.

245 **4.2.2   Mg/Ca versus temperature**

The Mg/Ca-temperature relationships found for the Nodosariata species reported here (Fig. 3) is likely also affected by different bottom water [CO_3^{2-}] at the sampled stations (Sadekov et al., 2014). The effect of saturation state on Mg-incorporation was found to be approximately 40 mmol/mol for a range of ~1000 µmol [CO_3^{2-}]/kg seawater in culturing experiments (Dissard et al., 2010; Yu et al., 2019; van Dijk et al., 2017a). This would amount to a change of approximately 2 mmol/mol Mg/Ca over

250   the total change at the three locations studied here, assuming that the sensitivity of Mg-incorporation as a function of [CO_3^{2-}] in the Nodosariata is similar to that in Rotaliida. This would reduce the change in Mg/Ca as a function of temperature by less than 10% and hence this would only have a very modest impact on the here reported Mg/Ca-temperature sensitivities (Fig. 3). For each of the three species that were found at all three stations, Mg/Ca increased exponentially with temperature (Fig 3). The application of these calibrations for Nodosariata for reconstructing past temperature can be challenging since using the

Commented [LPS28]: Dr. Reinhard Kozdon:
Line 242 range instead of change?

255 chemical composition of fossil shells this far back in time requires careful assessment of the calcite diagenetic overprints. Furthermore changes in $[Mg^{2+}]_{sw}$ and $[Ca^{2+}]_{sw}$ in the past can affect the incorporation of Mg into the calcite, nevertheless few studies have been developing new proxies to better understand these changes for both $[Mg^{2+}]_{sw}$ (Pogge von Strandmann et al., 2014; van Dijk et al., 2016) and $[Ca^{2+}]_{sw}$ (Nambiar et al., 2023).

The Mg/Ca-temperature sensitivities are slightly lower than those reported for most Rotaliida species. On average, Mg/Ca

260 increases by 6% per °C in the Nodosariata species analyzed here (Fig. 3), while in many planktonic species Mg/Ca increases by 10% per °C (Barker et al., 2005). Low-Mg/Ca benthic rotaliids display an increase of approximately 8% in Mg/Ca per °C (Lear et al., 2002; Raitzsch et al., 2010; Russell et al., 2004). High-Mg/Ca benthic Rotaliida species, on the other hand increases by only 2% (Maeda et al., 2017), which is similar to the slopes of those reported for Miliolida (de Nooijer et al., 2017; Toyofuku et al., 2000a).

265 Combining sensitivities for the different groups of foraminifera and their average Mg/Ca and comparing them to those of inorganically precipitated calcites (Morse et al., 2007; Wit et al., 2012), suggests a negative relation between Mg-incorporation and sensitivity to temperature (Fig. 5). The relative increase in Mg/Ca with temperature is smaller for species incorporating relatively much Mg in their calcite and vice versa. Highest Mg/Ca ratios are found in inorganically precipitated calcites (Morse et al., 2007) in which the increase of Mg/Ca is approximately 2 % for a 1 °C temperature increase. For species incorporating

270 equally much Mg (e.g. *Operculina ammonoides* (Evans et al., 2013)*)*, the slope of the Mg/Ca-temperature calibration is similar, while for species like *Ammonia tepida* (incorporating 50-100 times less Mg in their shell), the increase is approximately 7% per 1 °C temperature increase (Fig. 5).

This suggests that the observed high sensitivity of Mg/Ca to temperature in the low Mg/Ca species actually consists of two factors: an inorganic temperature dependent fractionation and a biomineralization-related partitioning, which is also

275 temperature dependent. The large difference in Mg/Ca between foraminifera (Wit et al., 2012) has been suggested to reflect the efficiency to lower the Mg/Ca in the calcifying fluid, either achieved by active Mg^{2+}-removal (Elderfield et al., 1996; Spero et al., 2015) or by selective inward Ca^{2+} transport (Toyofuku et al., 2017). Foraminiferal species with calcite Mg/Ca ratios close to those found in inorganic precipitation experiments may well lack such a mechanism and the increase in Mg/Ca with temperature hence matches that found in inorganic precipitation experiments. The species that are capable of lowering the

Commented [LPS29]: Dr. Reinhard Kozdon:

The fact that Nodosariata appear in the Carboniferous provides researchers with the opportunity to extend the range of foraminifera-based climate reconstructions significantly (the authors are also mentioning this in the abstract as a motivation for this study). However, how realistic would it be to find Carboniferous shells that are well-enough preserved for paleoclimate reconstructions? Any prior studies assessing the preservation of these shells? I think this needs several sentences of discussion.

Commented [LPS30]: Dr. Reinhard Kozdon:

Also, there are many studies discussing the evolution of seawater Mg/Ca over time - this is relevant for the accuracy of the Mg/Ca temperature proxy in 'deep-time'. I believe that the discussion-section of this manuscript would benefit by the addition of a few sentences addressing this topic.

Please add some discussion of past seawater Mg/Ca and the implication on 'deep-time'

280 Mg/Ca in the fluid from which they calcify, incorporate consistently more Mg at increased temperatures (Fig. 5). This suggests

that foraminiferal Mg/Ca-temperature relationships are determined by two components (Dämmer et al., 2021). The first

component is the biological control on Mg partitioning and the second component is the thermodynamic effect of temperature

on Mg/Ca. In foraminiferal species where the first component is absent (i.e. when they precipitate from a seawater like fluid),

the second component determines the Mg/Ca-temperature sensitivity. For species that lower the Mg^{2+} in the fluid from which

285 they precipitate their calcite, the biological component dominates the Mg/Ca-temperature calibration. The relatively large

variability in the low Mg/Ca species may be explained by small environmental factors (e.g. salinity or water depth) or by

processes that are part of the calcification mechanism (e.g. Rayleigh fractionation, organic templates) that may vary slightly

between species. The Nodosariata studied here have similar Mg/Ca, but differ in their sensitivities (Fig. 5), which may well

reflect the environmental and/ or calcification-related differences between species. (Elderfield et al., 1996; Branson et al.,

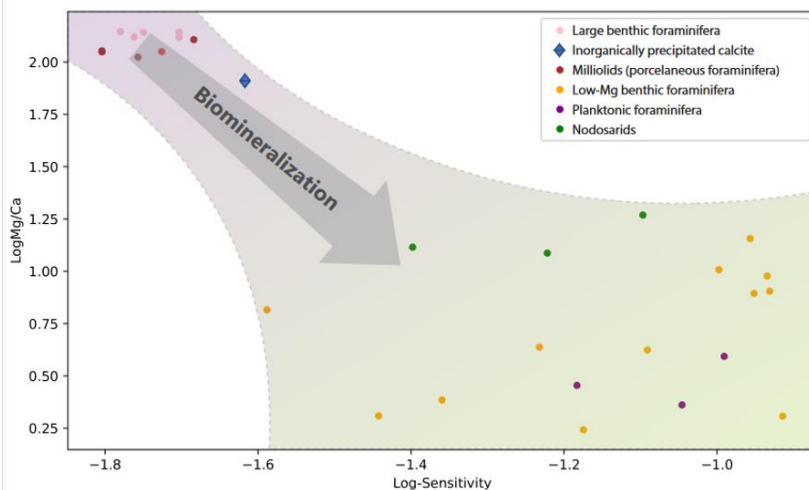
290 2018).

Commented [LPS31]: Dr. Ellen Thomas:
Figure 5: please use different signature for inorganically precipitated calcite, to make that stand out.

Figure 5: Comparison between the sensitivity and the average Mg/Ca for different groups of foraminifera. Results for the Nodosariata are from this study, all other Mg/Ca-temperature calibrations are from previous studies (Toyofuku et al., 2011; Douglas

295 and Staines-Urias, 2007; Barrientos et al., 2018; Rosenthal et al., 1997; Quillmann et al., 2012; Raitzsch et al., 2008; Lea et al., 1999; Anand et al., 2003; Barker et al., 2005; Rosenthal et al., 2011; Kristjánsdóttir et al., 2007; Lear et al., 2002; Evans et al., 2013; Maeda et al., 2017; Wit et al., 2012; Morse et al., 2007; Toyofuku et al., 2000a; de Nooijer et al., 2017; Knorr et al., 2015)**. Species towards the lower right corner are increasingly affected by biomineralization. These calibrations were used to calculate and plot the Mg/Ca at 20 °C.**

5. CONCLUSION

300 The chemical composition of the shells of various Nodosariata species collected in the Gulf of Mexico was found to be clearly different from those of other foraminiferal orders. Their Mg/Ca was between 6 and 20 mmol/mol and their Na/Ca was relatively high compared to ratios for most planktonic Rotaliida species. Sr/Ca and B/Ca were comparable to those found in other foraminiferal species. In two of the species studies, the Na/Ca increased linearly with salinity. Between families of the Nodosariata analyzed, the El/Ca was relatively similar. The Nodosariata's Mg/Ca is correlated to temperature and could thus

305 serve as a sea water temperature proxy. Compared to Rotaliida and Miliolida orders our analysis show a relation between the species' Mg/Ca and its sensitivity to changes in temperature. When more Mg is incorporated, it is less sensitive to changes in temperature and vice versa. This suggest the interaction between two components that together determine the Mg/Ca: the capacity of a species to control the Mg/Ca of the calcite and the thermodynamic effect of temperature on Mg incorporation.

DATA AVAILABILITY

310 DOI:10.25850/nioz/7b.b.lf

> **Commented [LPS32]:** Dr. Ellen Thomas and Dr. Reinhard Kozdon
>
> Now data in an open-access platform.

AUTHOR CONTRIBUTIONS

Conceptualization, Gert-Jan Reichart and Lennart de Nooijer; generated geochemical proxy analyses, Laura Pacho; Interpretation of the data, Laura Pacho, with the support of the co-authors; Writing, Laura Pacho with the support of the co-authors. Gert-Jan Reichart secure funding for the project.

315 ## COMPETING INTERESTS

The contact author has declared that none of the authors has any competing interests.

ACKNOWLEDGEMENTS

We are grateful to the captain and crew on board of RV Pelagia expedition 64PE467 to the Gulf of Mexico. To Frans Jorissen for providing help with the identification of foraminifera. To Wim Boer for the LA-ICPMS analyses and Karel Baker for the

320   DIC and TA analyses.

FINANCIAL SUPPORT

This work was carried out under the program of the Netherlands Earth System Science Centre (NESSC), financially supported by the Ministry of Education, Culture and Science (OCW).

References

325   Allen, K. A., Hönisch, B., Eggins, S. M., Haynes, L. L., Rosenthal, Y., and Yu, J.: Trace element proxies for surface ocean conditions: A synthesis of culture calibrations with planktic foraminifera, Geochim. Cosmochim. Acta, 193, 197–221, https://doi.org/10.1016/j.gca.2016.08.015, 2016.

Anand, P., Elderfield, H., and Conte, M. H.: Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series, Paleoceanography, 18, https://doi.org/10.1029/2002pa000846, 2003.

330   Barker, S., Cacho, I., Benway, H., and Tachikawa, K.: Planktonic foraminiferal Mg/Ca as a proxy for past oceanic temperatures: A methodological overview and data compilation for the Last Glacial Maximum, Quat. Sci. Rev., 24, 821–834, https://doi.org/10.1016/j.quascirev.2004.07.016, 2005.

Barrientos, N., Lear, C. H., Jakobsson, M., Stranne, C., O'Regan, M., Cronin, T. M., Gukov, A. Y., and Coxall, H. K.: Arctic Ocean benthic foraminifera Mg/Ca ratios and global Mg/Ca-temperature calibrations: New constraints at low temperatures,

335   Geochim. Cosmochim. Acta, 236, 240–259, https://doi.org/https://doi.org/10.1016/j.gca.2018.02.036, 2018.

Bentov, S. and Erez, J.: Impact of biomineralization processes on the Mg content of foraminiferal shells: A biological perspective, Geochemistry, Geophys. Geosystems, 7, https://doi.org/10.1029/2005GC001015, 2006.

Bertlich, J., Nürnberg, D., Hathorne, E. C., De Nooijer, L. J., Mezger, E. M., Kienast, M., Nordhausen, S., Reichart, G. J., Schönfeld, J., and Bijma, J.: Salinity control on Na incorporation into calcite tests of the planktonic foraminifera Trilobatus

340   sacculifer - Evidence from culture experiments and surface sediments, Biogeosciences, 15, 5991–6018, https://doi.org/10.5194/bg-15-5991-2018, 2018.

Boer, W., Nordstad, S., Weber, M., Mertz-Kraus, R., Hönisch, B., Bijma, J., Raitzsch, M., Wilhelms-Dick, D., Foster, G. L., Goring-Harford, H., Nürnberg, D., Hauff, F., Kuhnert, H., Lugli, F., Spero, H., Rosner, M., van Gaever, P., de Nooijer, L. J., and Reichart, G.-J.: New Calcium Carbonate Nano-particulate Pressed Powder Pellet (NFHS-2-NP) for LA-ICP-OES, LA-
345   (MC)-ICP-MS and µXRF, Geostand. Geoanalytical Res., 46, 411–432, https://doi.org/https://doi.org/10.1111/ggr.12425, 2022.

Branson, O., Redfern, S. A. T., Elmore, A. C., Read, E., Valencia, S., and Elderfield, H.: The distribution and coordination of trace elements in Krithe ostracods and their implications for paleothermometry, Geochim. Cosmochim. Acta, 236, 230–239, https://doi.org/10.1016/j.gca.2017.12.005, 2018.

350   D'Arrigo, R., Wilson, R., and Jacoby, G.: On the long-term context for late twentieth century warming, J. Geophys. Res. Atmos., 111, 1–12, https://doi.org/10.1029/2005JD006352, 2006.

Dämmer, L. K., de Nooijer, L., van Sebille, E., Haak, J. G., and Reichart, G. J.: Evaluation of oxygen isotopes and trace elements in planktonic foraminifera from the Mediterranean Sea as recorders of seawater oxygen isotopes and salinity, Clim. Past, 16, 2401–2414, https://doi.org/10.5194/cp-16-2401-2020, 2020.

355   Dämmer, L. K., van Dijk, I., de Nooijer, L., van der Wagt, B., Wilckens, F. K., Zoetemelk, B., and Reichart, G. J.: Temperature Impact on Magnesium Isotope Fractionation in Cultured Foraminifera, Front. Earth Sci., 9, 1–13, https://doi.org/10.3389/feart.2021.642256, 2021.

Debenay, J.-P., Guillou, J.-J., Geslin, E., Lesourd, M., and R. and F.: De plaquettes rhomboedriques / k la surface d ' un test porcelane de foraminifere actuel, Geobios, 31, 295302, https://doi.org/10.1016/S0016-6995(98)80013-2, 1998.

360   Devriendt, L. S., Mezger, E. M., Olsen, E. K., Watkins, J. M., Kaczmarek, K., Nehrke, G., Nooijer, L. J. De, and Reichart, G.: ScienceDirect Sodium incorporation into inorganic CaCO3 and implications for biogenic carbonates, Geochim. Cosmochim.

Acta, https://doi.org/10.1016/j.gca.2021.07.024, 2021.

van Dijk, I., de Nooijer, L. J., Hart, M. B., and Reichart, G.-J.: The long-term impact of magnesium in seawater on foraminiferal mineralogy: Mechanism and consequences, Global Biogeochem. Cycles, 30, 438–446, https://doi.org/https://doi.org/10.1002/2015GB005241, 2016.

van Dijk, I., de Nooijer, L. J., Wolthers, M., and Reichart, G. J.: Impacts of pH and [CO32−] on the incorporation of Zn in foraminiferal calcite, Geochim. Cosmochim. Acta, 197, 263–277, https://doi.org/10.1016/j.gca.2016.10.031, 2017a.

van Dijk, I., de Nooijer, L. J., Boer, W., and Reichart, G. J.: Sulfur in foraminiferal calcite as a potential proxy for seawater carbonate ion concentration, Earth Planet. Sci. Lett., 470, 64–72, https://doi.org/10.1016/j.epsl.2017.04.031, 2017b.

Van Dijk, I., Nooijer De, L. J., and Reichart, G. J.: Trends in element incorporation in hyaline and porcelaneous foraminifera as a function of pCO2, Biogeosciences, 14, 497–510, https://doi.org/10.5194/bg-14-497-2017, 2017.

Dissard, D., Nehrke, G., Reichart, G. J., and Bijma, J.: The impact of salinity on the Mg/Ca and Sr/Ca ratio in the benthic foraminifera Ammonia tepida: Results from culture experiments, Geochim. Cosmochim. Acta, 74, 928–940, https://doi.org/10.1016/j.gca.2009.10.040, 2010.

Douglas, R. and Staines-Urias, F.: DIMORPHISM, SHELL Mg/Ca RATIOS AND STABLE ISOTOPE CONTENT IN SPECIES OF BOLIVINA (BENTHIC FORAMINIFERA) IN THE GULF OF CALIFORNIA, MEXICO, J. Foraminifer. Res., 37, 189–203, https://doi.org/10.2113/gsjfr.37.3.189, 2007.

Dubicka, Z. and Gorzelak, P.: Unlocking the biomineralization style and affinity of Paleozoic fusulinid foraminifera, Sci. Rep., 7, 1–6, https://doi.org/10.1038/s41598-017-15666-1, 2017.

Dubicka, Z. and Wierzbowski, H.: Can oxygen and carbon isotope ratios of Jurassic foraminifera be used in palaeoenvironmental reconstructions ?, 577, https://doi.org/10.1016/j.palaeo.2021.110554, 2021.

Dubicka, Z., Owocki, K., and Gloc, M.: Micro- and nanostructures of calcareous foraminiferal tests: Insight from

representatives of Miliolida, Rotaliida and Lagenida, J. Foraminifer. Res., 48, 142–155, https://doi.org/10.2113/gsjfr.48.2.142, 2018.

385   Elderfield, H., Bertram, C. J., and Erez, J.: A biomineralization model for the incorporation of trace elements into foraminiferal calcium carbonate, Earth Planet. Sci. Lett., 142, 409–423, https://doi.org/10.1016/0012-821x(96)00105-7, 1996.

Elderfield, H., Yu, J., Anand, P., Kiefer, T., and Nyland, B.: Calibrations for benthic foraminiferal Mg/Ca paleothermometry and the carbonate ion hypothesis, Earth Planet. Sci. Lett., 250, 633–649, https://doi.org/10.1016/j.epsl.2006.07.041, 2006.

Erez, J.: The Source of Ions for Biomineralization in Foraminifera and Their Implications for Paleoceanographic Proxies, Rev.
390   Mineral. Geochemistry Search Dropdown Menu, 54, 115–149, https://doi.org/10.2113/0540115, 2003.

Evans, D. and Mller, W.: Deep time foraminifera Mg/Ca paleothermometry: Nonlinear correction for secular change in seawater Mg/Ca, Paleoceanography, 27, 1–11, https://doi.org/10.1029/2012PA002315, 2012.

Evans, D., Müller, W., Oron, S., and Renema, W.: Eocene seasonality and seawater alkaline earth reconstruction using shallow-dwelling large benthic foraminifera, Earth Planet. Sci. Lett., 381, 104–115, https://doi.org/10.1016/j.epsl.2013.08.035, 2013.

395   Evans, D., Wade, B. S., Henehan, M., Erez, J., and Müller, W.: Revisiting carbonate chemistry controls on planktic foraminifera Mg / Ca: Implications for sea surface temperature and hydrology shifts over the Paleocene-Eocene Thermal Maximum and Eocene-Oligocene transition, Clim. Past, 12, 819–835, https://doi.org/10.5194/cp-12-819-2016, 2016.

Evans, D., Müller, W., and Erez, J.: Assessing foraminifera biomineralisation models through trace element data of cultures under variable seawater chemistry, Geochim. Cosmochim. Acta, 236, 198–217, https://doi.org/10.1016/j.gca.2018.02.048,
400   2018.

Foster, G. L. and Rae, J. W. B.: Reconstructing Ocean pH with Boron Isotopes in Foraminifera, Annu. Rev. Earth Planet. Sci., 44, 207–237, https://doi.org/10.1146/annurev-earth-060115-012226, 2016.

GEBCO: "The GEBCO_2022 Grid - a continuous terrain model of the global oceans and land." NERC EDS British

Oceanographic Data Centre NOC. doi: doi:10.5285/e0f0bb80-ab44-2739-e053-6c86abc0289c, 2022.

405 Geerken, E., de Nooijer, L. J., Roepert, A., Polerecky, L., King, H. E., and Reichart, G. J.: Element banding and organic linings within chamber walls of two benthic foraminifera, Sci. Rep., 9, 3598, https://doi.org/10.1038/s41598-019-40298-y, 2019.

Geerken, E., de Nooijer, L., Toyofuku, T., Roepert, A., Middelburg, J. J., Kienhuis, M. V. M., Nagai, Y., Polerecky, L., and Reichart, G. J.: High precipitation rates characterize biomineralization in the benthic foraminifer Ammonia beccarii, Geochim. Cosmochim. Acta, 318, 70–82, https://doi.org/10.1016/j.gca.2021.11.026, 2022.

410 Hastings, D. W., Russell, A. D., and Emerson, S. R.: Foraminiferal magnesium in globeriginoides sacculifer as a paleotemperature proxy, Paleoceanography, 13, 161–169, https://doi.org/10.1029/97PA03147, 1998.

Hauzer, H., Evans, D., Müller, W., Rosenthal, Y., and Erez, J.: Calibration of Na partitioning in the calcitic foraminifer Operculina ammonoides under variable Ca concentration: Toward reconstructing past seawater composition, Earth Planet. Sci. Lett., 497, 80–91, https://doi.org/https://doi.org/10.1016/j.epsl.2018.06.004, 2018.

415 Hauzer, H., Evans, D., Müller, W., Rosenthal, Y., and Erez, J.: Salinity Effect on Trace Element Incorporation in Cultured Shells of the Large Benthic Foraminifer Operculina ammonoides, Paleoceanogr. Paleoclimatology, 36, https://doi.org/10.1029/2021PA004218, 2021.

Haynes, J. R.: The Nodosariida BT - Foraminifera, edited by: Haynes, J. R., Palgrave Macmillan UK, London, 180–203, https://doi.org/10.1007/978-1-349-05397-1_9, 1981a.

420 Haynes, J. R.: The Rotaliida (Smaller) BT - Foraminifera, edited by: Haynes, J. R., Palgrave Macmillan UK, London, 236–273, https://doi.org/10.1007/978-1-349-05397-1_12, 1981b.

Humphreys, M. P., Lewis, E. R., Sharp, J. D., and Pierrot, D.: PyCO2SYS v1.8: Marine carbonate system calculations in Python, Geosci. Model Dev., 15, 15–43, https://doi.org/10.5194/gmd-15-15-2022, 2022.

Knorr, P. O., Robbins, L. L., Harries, P. J., Hallock, P., and Wynn, J.: Response of the miliolid Archaias angulatus to simulated

425   ocean acidification, J. Foraminifer. Res., 45, 109–127, https://doi.org/10.2113/gsjfr.45.2.109, 2015.

Kristjánsdóttir, G. B., Lea, D. W., Jennings, A. E., Pak, D. K., and Belanger, C.: New spatial Mg/Ca-temperature calibrations for three Arctic, benthic foraminifera and reconstruction of north Iceland shelf temperature for the past 4000 years, Geochemistry, Geophys. Geosystems, 8, https://doi.org/10.1029/2006GC001425, 2007.

ter Kuile, B., Erez, J., and Padan, E.: Mechanisms for the uptake of inorganic carbon by two species of symbiont-bearing 430   foraminifera, Mar. Biol., 103, 241–251, https://doi.org/10.1007/BF00543354, 1989.

Lea, D. W., Mashiotta, T. A., and Spero, H. J.: Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing, Geochim. Cosmochim. Acta, 63, 2369–2379, https://doi.org/10.1016/S0016-7037(99)00197-0, 1999.

Lea, D. W., Pak, D. K., and Spero, H. J.: Climate impact of late quaternary equatorial Pacific sea surface temperature variations, 435   Science (80-.)., 289, 1719–1724, https://doi.org/10.1126/science.289.5485.1719, 2000.

Lear, C. H., Rosenthal, Y., and Slowey, N.: Benthic foraminiferal Mg/Ca-paleothermometry: A revised core-top calibration, Geochim. Cosmochim. Acta, 66, 3375–3387, https://doi.org/10.1016/S0016-7037(02)00941-9, 2002.

Lewis, E; Wallace, D [1]; Allison, L. J. [2]: Lewis_wallace, https://doi.org/doi.org/10.2172/639712, 1998.

Lowenstein, T. K. and Hönisch, B.: The Use of Mg/Ca as a Seawater Temperature Proxy, Paleontol. Soc. Pap., 18, 85–100, 440   https://doi.org/DOI: 10.1017/S1089332600002564, 2012.

Maeda, A., Fujita, K., Horikawa, K., Suzuki, A., Yoshimura, T., Tamenori, Y., and Kawahata, H.: Evaluation of oxygen isotope and Mg/Ca ratios in high-magnesium calcite from benthic foraminifera as a proxy for water temperature, J. Geophys. Res. Biogeosciences, 122, 185–199, https://doi.org/10.1002/2016JG003587, 2017.

Mann, M. E., Bradley, R. S., and Hughes, M. K.: Global-scale temperature patterns and climate forcing over the past six 445   centuries, Nature, 392, 779–787, https://doi.org/10.1038/33859, 1998.

Marcel Guillong, Christopher Latkoczy, Jung Hun Seo, D. G. and C. A. and A, H.: Determination of sulfur in fluid inclusions by laser ablation ICP-MS, J. Anal. At. Spectrom., https://doi.org/10.1039/B807383J, 2008.

Mezger, E. M., de Nooijer, L. J., Boer, W., Brummer, G. J. A., and Reichart, G. J.: Salinity controls on Na incorporation in Red Sea planktonic foraminifera, Paleoceanography, 31, 1562–1582, https://doi.org/10.1002/2016PA003052, 2016.

450   Morse, J. W., Arvidson, R. S., and Lüttge, A.: Calcium carbonate formation and dissolution, Chem. Rev., 107, 342–381, https://doi.org/10.1021/cr050358j, 2007.

Nambiar, R., Hauzer, H., Gray, W. R., Henehan, M. J., Cotton, L, Erez, J., Rosenthal, Y., Renema, W., Müller, W., and Evans, D.: Controls on potassium incorporation in foraminifera and other marine calcifying organisms, Geochim. Cosmochim. Acta, 351, 125–138, https://doi.org/10.1016/j.gca.2023.04.020, 2023.

455   de Nooijer, L. J., van Dijk, I., Toyofuku, T., and Reichart, G. J.: The Impacts of Seawater Mg/Ca and Temperature on Element Incorporation in Benthic Foraminiferal Calcite, Geochemistry, Geophys. Geosystems, 18, 3617–3630, https://doi.org/10.1002/2017GC007183, 2017.

De Nooijer, L. J., Toyofuku, T., and Kitazato, H.: Foraminifera promote calcification by elevating their intracellular pH, Proc. Natl. Acad. Sci. U. S. A., 106, 15374–15378, https://doi.org/10.1073/pnas.0904306106, 2009.

460   Nooijer, L. J. De, Spero, H. J., Erez, J., Bijma, J., and Reichart, G. J.: Earth-Science Reviews Biomineralization in perforate foraminifera, Earth Sci. Rev., 135, 48–58, https://doi.org/10.1016/j.earscirev.2014.03.013, 2014.

Nürnberg, D., Bijma, J., and Hemleben, C.: Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures, Geochim. Cosmochim. Acta, 60, 803–814, https://doi.org/10.1016/0016-7037(95)00446-7, 1996.

Pawlowski, J., Holzmann, M., Berney, C., Fahrni, J., Gooday, A. J., Cedhagen, T., Habura, A., and Bowser, S. S.: The evolution
465   of early Foraminifera, Proc. Natl. Acad. Sci., 100, 11494–11498, https://doi.org/10.1073/pnas.2035132100, 2003.

Quillmann, U., Marchitto, T. M., Jennings, A. E., Andrews, J. T., and Friestad, B. F.: Cooling and freshening at 8.2 ka on the

NW Iceland Shelf recorded in paired δ18O and Mg/Ca measurements of the benthic foraminifer Cibicides lobatulus, Quat. Res., 78, 528–539, https://doi.org/DOI: 10.1016/j.yqres.2012.08.003, 2012.

Rae, J. W. B., Foster, G. L., Schmidt, D. N., and Elliott, T.: Boron isotopes and B/Ca in benthic foraminifera: Proxies for the
470   deep ocean carbonate system, Earth Planet. Sci. Lett., 302, 403–413, https://doi.org/10.1016/j.epsl.2010.12.034, 2011.

Raitzsch, M., Kuhnert, H., Groeneveld, J., and Bickert, T.: Benthic foraminifer Mg/Ca anomalies in South Atlantic core top sediments and their implications for paleothermometry, Geochemistry, Geophys. Geosystems, 9, https://doi.org/10.1029/2007GC001788, 2008.

Raitzsch, M., Duenas-Bohórquez, A., Reichart, G. J., De Nooijer, L. J., and Bickert, T. T.: Incorporation of Mg and Sr in
475   calcite of cultured benthic foraminifera: Impact of calcium concentration and associated calcite saturation state, Biogeosciences, 7, 869–881, https://doi.org/10.5194/bg-7-869-2010, 2010.

Reichart, G.: Single foraminiferal test chemistry records the marine environment, *Geology*, 31, 355–358, https://doi.org/10.1130/0091-7613, 2003.

Reiss, Z.: Occurrence of Nezzazata in Israel, Micropaleontology, 3, 259–262, 1957.

480   Reiss, Z.: Comments on Wall Structure of Foraminifera, Micropaleontology, 9, 50, https://doi.org/10.2307/1484605, 1963.

Rosenthal, Y., Boyle, E. A., and Slowey, N.: Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography, Geochim. Cosmochim. Acta, 61, 3633–3643, https://doi.org/10.1016/S0016-7037(97)00181-6, 1997.

Rosenthal, Y., Morley, A., Barras, C., Katz, M. E., Jorissen, F., Reichart, G. J., Oppo, D. W., and Linsley, B. K.: Temperature
485   calibration of Mg/Ca ratios in the intermediate water benthic foraminifer Hyalinea balthica, Geochemistry, Geophys. Geosystems, 12, https://doi.org/10.1029/2010GC003333, 2011.

Rosenthal, Y., Kalansky, J., Morley, A., and Linsley, B.: A paleo-perspective on ocean heat content: Lessons from the

Holocene and Common Era, Quat. Sci. Rev., 155, 1–12, https://doi.org/10.1016/j.quascirev.2016.10.017, 2017.

Russell, A. D., Hönisch, B., Spero, H. J., and Lea, D. W.: Effects of seawater carbonate ion concentration and temperature on
490   shell U, Mg, and Sr in cultured planktonic foraminifera, Geochim. Cosmochim. Acta, 68, 4347–4361,
https://doi.org/10.1016/j.gca.2004.03.013, 2004.

Sadekov, A. Y., Bush, F., Kerr, J., Ganeshram, R., and Elderfield, H.: Mg/Ca composition of benthic foraminifera Miliolacea
as a new tool of paleoceanography, Paleoceanography, 29, 990–1001, https://doi.org/10.1002/2014PA002654, 2014.

Sarazin, G., Michard, G., and Prevot, F.: A rapid and accurate spectroscopic method for alkalinity measurements in sea water
495   samples, Water Res., 33, 290–294, https://doi.org/10.1016/S0043-1354(98)00168-7, 1999.

Seabold, S. and Perktold, J.: Statsmodels: Econometric and Statistical Modeling with Python, Proc. 9th Python Sci. Conf., 92–
96, https://doi.org/10.25080/majora-92bf1922-011, 2010.

Sirois,   S.:   RB   17-04   GOMECC-3:   Gulf   of   Mexico   Ecosystems   and   Carbon   Cycle   Cruise,
https://repository.library.noaa.gov/view/noaa/16758, 2017.

500   Spero, H. J., Eggins, S. M., Russell, A. D., Vetter, L., Kilburn, M. R., and Hönisch, B.: Timing and mechanism for intratest
Mg/Ca   variability   in   a   living   planktic   foraminifer,   Earth   Planet.   Sci.   Lett.,   409,   32–42,
https://doi.org/10.1016/j.epsl.2014.10.030, 2015.

Spivack, A. J., You, C.-F., and Smith, H. J.: Foraminiferal boron isotope ratios as a proxy for surface ocean pH over the past
21 Myr, Nature, 363, 149–151, https://doi.org/10.1038/363149a0, 1993.

505   Stoll, M. H. C., Bakker, K., Nobbe, G. H., and Haese, R. R.: Continuous-flow analysis of dissolved inorganic carbon content
in seawater, Anal. Chem., 73, 4111–4116, https://doi.org/10.1021/ac010303r, 2001.

Tanner, T., Hernández-Almeida, I., Drury, A. J., Guitián, J., and Stoll, H.: Decreasing Atmospheric CO2 During the Late
Miocene   Cooling,   Paleoceanogr.   Paleoclimatology,   35,   e2020PA003925,

https://doi.org/https://doi.org/10.1029/2020PA003925, 2020.

510   Toyofuku, T., Kitazato, H., Kawahata, H., Tsuchiya, M., and Nohara, M.: Evaluation of Mg/Ca thermometry in foraminifera: Comparison of experimental results and measurements in nature, Paleoceanography, 15, 456–464, https://doi.org/https://doi.org/10.1029/1999PA000460, 2000a.

Toyofuku, T., Suzuki, M., Suga, H., Sakai, S., Suzuki, A., Ishikawa, T., de Nooijer, L. J., Schiebel, R., Kawahata, H., and Kitazato, H.: Mg/Ca and δ18O in the brackish shallow-water benthic foraminifer Ammonia "beccarii," Mar. Micropaleontol.,
515   78, 113–120, https://doi.org/10.1016/j.marmicro.2010.11.003, 2011.

Toyofuku, T., Matsuo, M. Y., De Nooijer, L. J., Nagai, Y., Kawada, S., Fujita, K., Reichart, G. J., Nomaki, H., Tsuchiya, M., Sakaguchi, H., and Kitazato, H.: Proton pumping accompanies calcification in foraminifera, Nat. Commun., 8, 1–6, https://doi.org/10.1038/ncomms14145, 2017.

Wit, J. C., Nooijer, L. J. De, Barras, C., Jorissen, F., and Reichart, G. J.: A reappraisal of the vital e ff ect in benthic foraminifera
520   on Mg / Ca ratios : species specific uncertainty relationships, 4947–4977, https://doi.org/10.5194/bgd-9-4947-2012, 2012.

Wit, J. C., De Nooijer, L. J., Wolthers, M., and Reichart, G. J.: A novel salinity proxy based on na incorporation into foraminiferal calcite, Biogeosciences, 10, 6375–6387, https://doi.org/10.5194/bg-10-6375-2013, 2013.

Wit, J. C., de Nooijer, L. J., Haig, J., Jorissen, F. J., Thomas, E., and Reichart, G. J.: Towards reconstructing ancient seawater Mg/Ca by combining porcelaneous and hyaline foraminiferal Mg/Ca-temperature calibrations, Geochim. Cosmochim. Acta,
525   211, 341–354, https://doi.org/10.1016/j.gca.2017.05.036, 2017.

Yu, Z., Lei, Y., Li, T., Zhang, S., and Xiong, Z.: Mg and Sr uptake in benthic foraminifera Ammonia aomoriensis based on culture and field studies, Palaeogeogr. Palaeoclimatol. Palaeoecol., 520, 229–239, https://doi.org/10.1016/j.palaeo.2019.02.001, 2019.

Zeebe, R. E., Bijma, J., and Wolf-Gladrow, D. A.: A diffusion-reaction model of carbon isotope fractionation in foraminifera,

530 Mar. Chem., 64, 199–227, https://doi.org/10.1016/S0304-4203(98)00075-9, 1999.