



500 million years of foraminiferal calcification

L.J. de Nooijer^{a,*}, L. Pacho Sampedro^a, F.J. Jorissen^b, J. Pawlowski^c, Y. Rosenthal^d,
D. Dissard^e, G.J. Reichart^{a,f}

^a NIOZ - Royal Netherlands Institute for Sea Research, Texel, the Netherlands

^b UMR CNRS 6112 LPG-BIAF, Angers University and Nantes Université, France

^c Institute of Oceanology, PAS, Sopot, Poland

^d Rutgers, New Brunswick, USA

^e IRD/UMR LOCEAN, Nouméa, New Caledonia

^f Utrecht University, Utrecht, the Netherlands

ARTICLE INFO

Keywords:

Foraminifera
Evolution
Paleoclimate

ABSTRACT

Ongoing ocean acidification affects marine calcification, although the scope and magnitude of this impact is essentially unknown. Here, we investigate the evolutionary origin of shell building in foraminifera to understand the long-term interplay between ocean carbon chemistry and calcification. Our analysis of shell chemical composition reveals multiple, independent origins for foraminiferal calcification throughout the Phanerozoic. Differences between orders reflect the different physiological controls employed by foraminifera to take up Ca^{2+} and inorganic carbon from seawater for CaCO_3 precipitation. With the long timespan involved, variability in seawater chemistry provided contrasting environments for calcification to arise, resulting in the diverse calcification strategies that exist today. This, in turn, explains the opposite responses of shell building to carbon perturbations. Our results call for adopting an evolutionary perspective when predicting the impact of perturbations on marine calcification and thereby, on the global carbon cycle.

1. Introduction

Marine calcification is predicted to collapse with ongoing ocean acidification (e.g. Kleypas et al., 1999; Van de Waal et al., 2013). Since CaCO_3 production adds one mole of CO_2 for every mole of calcite or aragonite precipitated, calcification and atmospheric CO_2 are linked in a carbon-climate feedback loop. With reports showing that calcification can also be promoted by increased dissolved CO_2 (e.g. Iglesias-Rodriguez et al., 2008; Fujita et al., 2011), the net contribution of marine calcification to the ocean's inorganic carbon inventory of the near future, is challenging to predict. Studying marine calcification in a geological and evolutionary context may provide an understanding of the dependency of marine calcification on marine inorganic carbon chemistry, and may also offer an explanation for the inter-species variability in calcification responses.

The Phanerozoic eon (>500 million years) is characterized by multiple, long-term as well as short-term, changes in climate and seawater chemistry. During all of this period, foraminifera have been present in marine habitats and left a fossil record that provides us with a long-term

record of climate change. As one of the major marine calcifiers, their continuous production of shells has affected the global carbon cycle and thereby, Earth's climate. Key to understanding their impact is the interplay between their calcification strategy and seawater chemistry, which can only be provided by a reconstruction of the evolution of calcification. This, in turn, starts by appreciating the enormous genetic, morphological and fossil diversity in foraminifera.

With the advent of molecular biology, foraminiferal phylogenetic analyses (Pawlowski et al., 2003, 2013; Sierra et al., 2022) have confirmed the kinships within this phylum as was suggested by comparisons of the shells' microstructures (Loeblich and Tappan, 1984; Tappan and Loeblich, 1988). This correspondence between genetics and wall structure essentially places calcification in the centre of foraminiferal evolution. Calcification pathways in foraminifera are hypothesized to involve selective ion transporters that lead to specific elemental signatures of the shell (Erez, 2003; Bentov and Erez, 2006; De Nooijer et al., 2009, 2014). Consequently, the carbonate elemental composition of a foraminiferal wall primarily reflects its calcification strategy. The Mg concentration in foraminiferal shells is particularly indicative since

* Corresponding author.

E-mail address: Lennart.de.nooijer@nioz.nl (L.J. de Nooijer).

<https://doi.org/10.1016/j.earscirev.2023.104484>

Received 13 March 2023; Received in revised form 24 May 2023; Accepted 15 June 2023

Available online 17 June 2023

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it reflects the ability to actively overcome the inhibition of calcite growth by Mg^{2+} (Zeebe and Sanyal, 2002; Segev and Erez, 2006). To identify variability in calcification strategies and compare these with phylogenetic relationships, we collected over 6500 published ratios of Li, B, Na, Mg, Sr, Ba and U to Ca and compared them within and between four orders of calcifying foraminifera: Nodosariida, Miliolida, Rotaliida and Robertinida. Only data from living specimens –either from core tops or experiments- were selected and used for comparison. For the two orders for which geochemical data were not yet available, the Spirillinida and Carterinida, we provided new elemental composition data and added them to the comparison.

2. Materials and methods

2.1. Literature data

Geochemical data for the largest possible variety of foraminifera are here compiled from available publications. Due to the dominance of reports on rotaliid geochemistry, and particularly Mg/Ca, we did not attempt summarizing all literature for this group. Instead, we primarily aim to include as many (super)families as possible. Published element ratios include those from controlled growth experiments as well as from studies from the natural environment.

For all taxonomic classifications, the WORMS database was used (Hayward et al., 2022). This includes the indexing at the level of the species, genus, family, superfamily, class and order, which is based on (Pawlowski et al., 2013; Holzmann and Pawlowski, 2017; Loeblich and Tappan, 1987; Loeblich and Tappan, 1992). Occasionally, additional taxonomic information was copied into the dataset (e.g. ‘pink’ or ‘white’ for *G. ruber*).

2.2. El/Ca in Spirillinida and Carterinida

Since there is no published El/Ca for the Spirillinida and the Carterinida, we selected specimens of *Spirillina* sp. from core-top samples from the Gulf of Mexico, rose Bengal-stained and collected in January 2020 and *Carterina spiculotesta* collected in July 2021 at Noumea, New Caledonia. Specimens of the latter species were sampled alive at 50 m depth in New Caledonian lagoon, they were considered living during sampling due to their color and attachment to the substrate (i.e. rock surface). Specimens were rinsed with MilliQ and ablated according to (De Nooijer et al., 2017). In total, 3 specimens of *Spirillina* sp. and 6 specimens of *C. spiculotesta* were measured.

2.3. El/Ca in Nodosariida

Specimens of Nodosariida were sampled from The Gulf of Mexico in 2020 at three different depths (105, 270 and 620 m). The sediment samples were stained with rose Bengal (1 g/L ethanol) to identify living specimens, which were then cleaned by organic matter removal using a solution of 1% H_2O_2 and 0.1 M NH_4OH . After rinsing with double deionized water, specimens were dried and ablated using a circular, 60 μm spot in helium environment as a repetition rate of 5 Hz and an energy density of 1 J/cm². Contamination of the surface by remaining clay particle was identified by high Al/Ca (> 0.4 mmol/mol) and discarded from the database. In total, 141 specimens of Nodosariida were measured and added to the database (Pacho et al., in prep.).

2.4. Statistical analysis

All existing and new data were combined into one database. Statistical treatments were performed in Python using the Spyder environment and the matplotlib, numpy, pandas, scipy and statsmodels packages. To avoid bias by (experimental) results obtained from very much offset Mg/Ca_{sw} ratios, only data were selected for Mg/Ca_{sw} between 4 and 6. For a similar reason, results from extreme salinities (> 50

and < 25) and carbonate chemistries (DIC <1750 and > 3000) were removed prior to data processing. Since incorporation of elements affect incorporation of other elements as well (e.g. Mewes et al., 2015), experimental data with very high El/Ca (e.g. Ba/Ca_{sw} > 0.06 mmol/mol; De Nooijer et al., 2017) were also removed from the database.

Prior to Principal Component Analysis, all data were normalized and centred to account for the large differences in absolute values for the different El/Ca's. Normalization and centering were done on the complete dataset.

3. Results

Our analysis shows that foraminifera have distinct El/Ca fingerprints that clearly follow the division at the order-level (Fig. 1). While Na/Ca and Sr/Ca vary moderately (about one order of magnitude or less, respectively), Mg/Ca varies by three orders of magnitude. Other elements, as far as data are available, also display distinct differences between foraminiferal orders (fig. S1 - S3). The dataset also shows clear differences in Mg/Ca within the rotaliids, with a high and low Mg/Ca cluster that reflects the phylogeny within this order. The rotaliid species precipitating calcite with intermediate and high Mg/Ca (> 25 mmol/mol) all belong to the Calcarinidae and Nummulitidae, which are more closely related to each other than to the other rotaliid families (Holzmann and Pawlowski, 2017; fig. S4).

Due to the underrepresentation of some orders (e.g. Carterinida and Spirillinida), it is challenging to find a chemical ‘fingerprint’ based on multiple El/Ca. However, when using five El/Ca, the orders are all clearly distinguishable from each other (fig. S5). When directly comparing El/Ca (Fig. 1; fig. S1-S2) as well as applying principal component analyses (fig. S5), we show that the Nodosariida are relatively homogenous in their El/Ca and clearly different from the Miliolida, Carterinida and Rotaliida. The Miliolida form a distinct cluster, with a combination of high Mg/Ca and low Na/Ca. The Robertinida have a relatively high Na/Ca and low Mg/Ca values, while variability in Sr/Ca covaries less with foraminiferal phylogeny. The Rotaliida are the foraminiferal order with the largest variability in El/Ca, which is mainly due to the high El/Ca values found within three rotaliid families (Fig. 2).

4. Discussion

4.1. The polyphyletic nature of calcification

We argue that if calcification had preceded the early branching amongst foraminifera, orders would geochemically resemble each other the way they do genetically. However, our analysis reveals a mismatch between order-level genetic kinship and similarity in geochemical fingerprints and excludes a common, calcifying ancestor (Fig. 3). Genetically closely related orders can have very different geochemical composition (e.g. Miliolida and Spirillinida), while some pairs with similar El/Ca can be genetically very distant (e.g. Nodosariida and Robertinida). Instead, calcification pathways have likely been invented multiple times in the course of foraminiferal evolution. This has been suggested before for individual orders and was based on morphological and microstructural diversity (Mikhalevich, 2004, 2014, 2021; Dubicka, 2019), as well as molecular data (Pawlowski et al., 2013; Holzmann and Pawlowski, 2017; Sierra et al., 2022).

Within orders, however, geochemistry remains similar compared to the variability observed between orders. This suggests a similar biomineralization mechanism and hence a common calcifying ancestor for each of the different orders. The exception to this pattern are the Rotaliida, with a large group precipitating low-Mg/Ca calcite and only a few families that build shells with high-Mg/Ca calcite (Fig. 2). This distinction in Mg/Ca signifies the rise of larger, tropical and symbiont-bearing Rotaliida in the Cretaceous (e.g. Hottinger, 1982) when Mg/Ca of the seawater was much lower than during the evolution of the first (low-Mg/Ca) rotaliid foraminifera (Fig. 3).

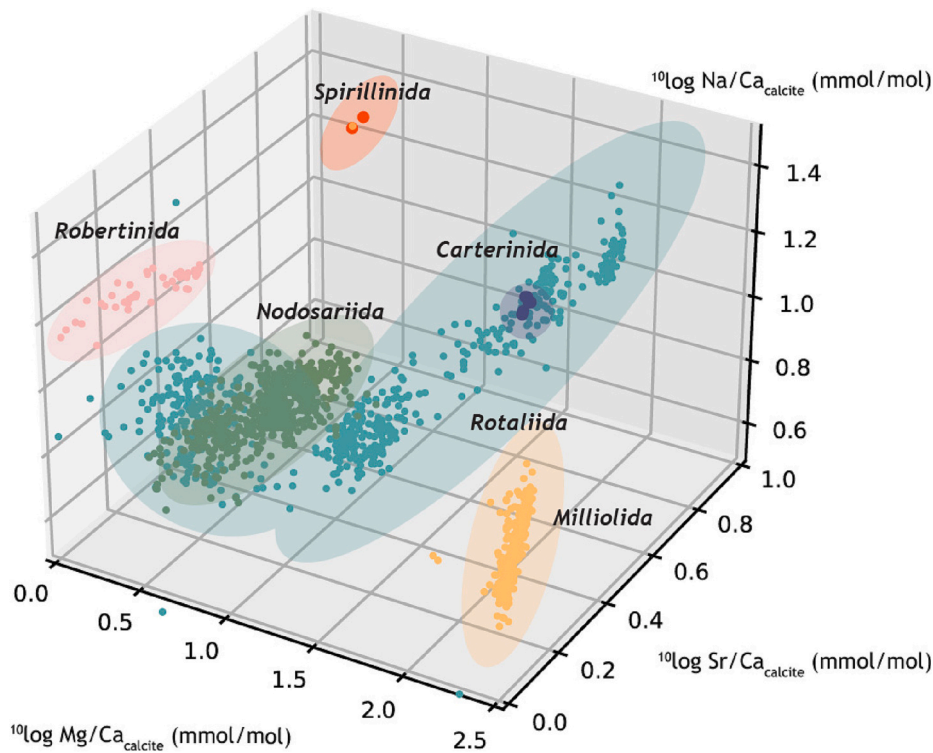


Fig. 1. Mg/Ca, Na/Ca and Sr/Ca across the six calcifying foraminiferal orders. Due to the skew in the published element/Ca, their concentrations in foraminiferal shells is plotted on a logarithmic scale. A transparent oval is added for each order to indicate the volume occupied by the data. Newly supplied data (i.e. for the Carterinida and Spirillinida) are plotted as larger circles.

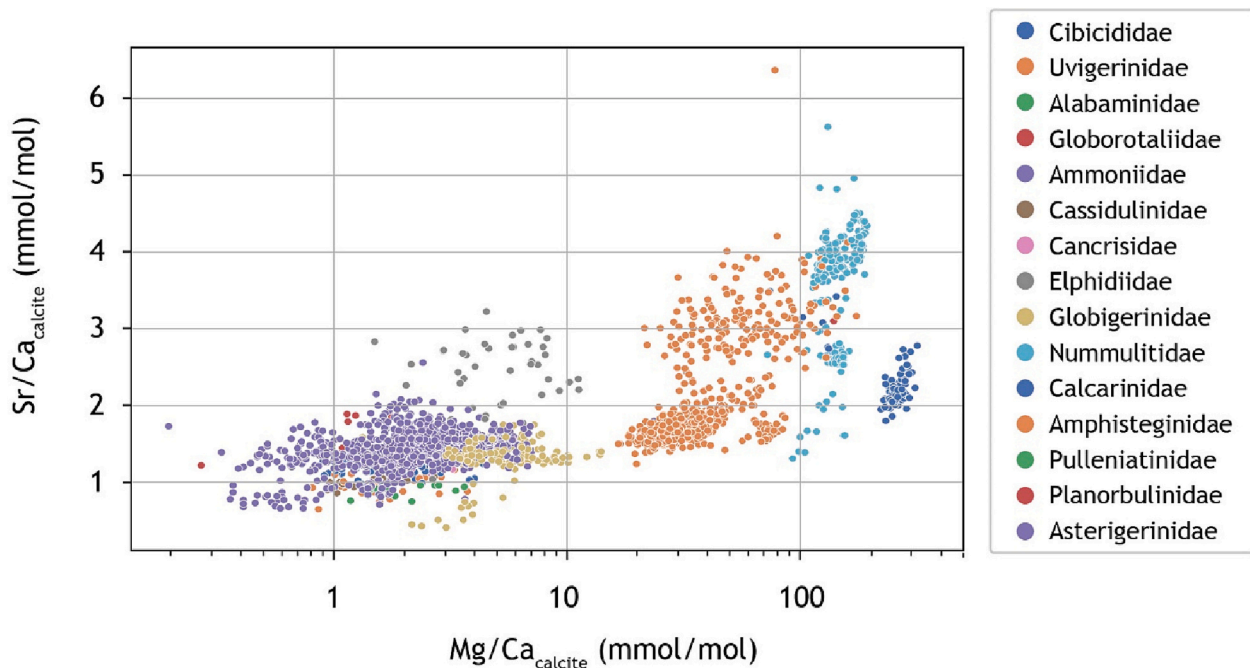


Fig. 2. Variability in geochemistry within the Rotaliida. Calcite Mg/Ca versus Sr/Ca is grouped per family indicating a clustering of elemental composition per rotaliid family.

Variability in Mg/Ca amongst foraminiferal orders and within the Rotaliida, relates to the unique role of Mg^{2+} in foraminiferal calcification (Zeebe and Sanyal, 2002). Since Mg is one of the most abundant cations in seawater, strongly inhibiting calcite nucleation and growth, it is hypothesized that many species calcify using a Mg-discriminating

mechanism (Segev and Erez, 2006; Dämmer et al., 2021). Our results suggest that such a mechanism is present in most of the Rotaliida, including all planktonic foraminifera, as well as in the Robertinida, Spirillinida and Nodosariida (Fig. 1). In the Carterinida, Milioliida and some rotaliid families, this mechanism is either absent or plays a minor

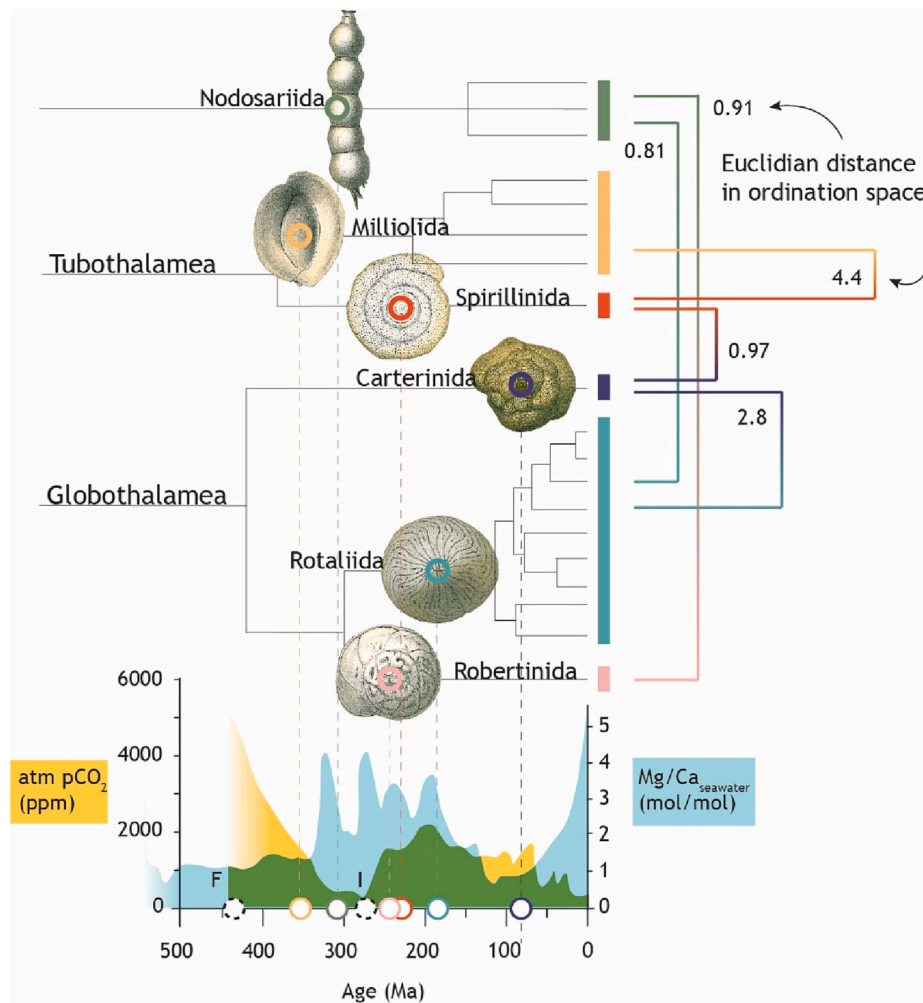


Fig. 3. A simplified foraminiferal evolutionary tree with emphasis on calcifying orders. The first fossil occurrences of calcifying members of these six orders are represented by circles (Loeblich and Tappan, 1964; Rettori et al., 1994; Gräfe, 2005; Vachard et al., 2010). The exact timing of the divergence is uncertain for most orders, and thus the dates are indicated tentatively here (Tappan and Loeblich, 1988; Holzmann and Pawlowski, 2017; Groussin et al., 2011; Rigaud et al., 2015). According to genetic similarity (Holzmann and Pawlowski, 2017), the Spirillinida are close to the Miliolida, whereas Nodosariida form a separate lineage. For the three orders with the highest diversity (i.e. Miliolida, Nodosariida and Rotaliida), evolution of families is indicated (based on Holzmann and Pawlowski, 2017; Habura et al., 2006; Hayward et al., 2022). For the other three orders, no attempt is made to indicate the diversity on family-level due to an absence of phylogenetic data and/or a detailed fossil record. The Euclidian distances in the ordination space between orders (as calculated on the basis of the principal component analysis of El/Ca ratios; fig. S5) are presented on the right side of the evolutionary tree. Larger numbers indicate dissimilar average El/Ca between groups: a Euclidian distance of 0 would indicate identical geochemistry. The (dis)similarity of only some pairs of orders are indicated here. Reconstructed Mg/Ca of seawater (in blue; Stanley and Hardie, 1998) has been copied below the evolutionary tree, and so is the proxy-based CO₂ reconstruction for the Phanerozoic (in yellow; Royer et al., 2004). The first fossil occurrences of the Involutinida (I) and Fusulinida (F) are indicated on the time line.

role during calcification. Banding in many elements is characteristic for the calcite of rotaliid shells (refs) and is absent in that of miliolids (Roepert et al., 2022). The precipitation of alternating high- and low-Mg/Ca, B/Ca, S/Ca, etc. hints to a specific ‘vital effect’ (Erez, 2003) in the Rotaliida and likely relates to the bilamellar mode of calcification in this group (Reiss, 1957). Variability in the thickness and intensity of these bands between species may explain part of the total variability observed (Fig. 1). Similarly, microscale heterogeneity in El/Ca in other orders may hence provide an explanation for the variability observed between orders. Additional controls on Mg incorporation and potential explanations for the variability between orders in other elements include ion selectivity of organic compounds present during calcification (Branson et al., 2016), Rayleigh fractionation (Elderfield et al., 1996; Marchitto et al., 2018) and CaCO₃ precipitation rate (Busenberg and Plummer, 1985; Devriendt et al., 2021).

The independent emergences of calcification likely explain the order-specific microstructures of the shell. The Nodosariida, for example, have a shell consisting of two converging layers of conical crystals (Dubicka et al., 2018), whereas the Miliolida precipitate small needles that are agglutinated in an organic matrix during chamber formation (Berthold, 1976). The calcite of the rotaliids consists of lamellae (Reiss, 1957) formed by micro-sized crystals (Yin et al., 2021), similar to that of the Robertinida, which differ from the other five orders by precipitating aragonite. The similarity in morphology and relatively short period between their first fossil occurrences, does not exclude the possibility that these two orders share a common, calcifying ancestor and that climate or environmental changes caused the evolutionary diversion of

these two orders. The Spirillinida have a distinct ‘monocrystalline’ calcite (Dubicka, 2019) and the Carterinida make their shell by precipitating elliptical spicules increasing in size with every chamber added (Deutsch and Lipps, 1976). The consistency of these microstructural features as well as the overall morphology within orders throughout the fossil record (Vachard et al., 2010) suggests that the biomineralization mechanisms remained very similar after they first appeared.

Our analysis also reveals that the variability in Mg/Ca, Sr/Ca and Na/Ca primarily depends on the taxonomic level. For example, within Rotaliida the relative spread (expressed as standard deviation) in Mg/Ca is almost 250%, while it varies on average by only 15% within a species. The order-level variability in Sr/Ca and Na/Ca is lower (41% and 56%) than that of Mg/Ca, but decrease to 9 and 11%, respectively, on species level (fig. S4). The consistent decrease in the variability of El/Ca towards smaller taxonomic units supports the theory that each order has a biomineralization mechanism responsible for its El/Ca signature that remained relatively constant over long geological periods of time. The only exception to this within-order consistency in El/Ca, are the rotaliid families Nummulitidae and Calcarinidae that precipitate calcite with a Mg/Ca over 50 mmol/mol (Fig. 1; Fig. 2).

4.2. The interplay between calcification and climate

The recognition of fundamentally different biomineralization mechanisms within foraminifera also explains the contrasting responses of calcification to dissolved CO₂ concentrations (Keul et al., 2013).

Recent studies showed that rotaliid foraminifera may actually perform better at elevated $p\text{CO}_2$ and total dissolved inorganic carbon (DIC) concentrations (e.g. Kawahata et al., 2019). The integration of pH manipulation by these foraminifera (De Nooijer et al., 2009) to promote availability of carbonate ions, renders the calcification mechanism by these groups less dependent on changes in external saturation state (as suggested for planktonic species: Zarkogiannis et al., 2022). Miliolid foraminifera, on the other hand, may lack such a mechanism and are thus more sensitive to changes in saturation state (Hikami et al., 2011).

Such order-specific sensitivities to environmental conditions may well be reflected in their habitat preferences. Nodosariida for example, are rare in shallow waters, whereas most high-Mg/Ca Rotaliida are confined to tropical, shallow habitats (refs). Since saturation state depends on water depth and temperature, distribution of foraminiferal orders may partly reflect their (in)ability to actively raise the saturation state at the site of calcification. Similarly, the presence of photosynthetic symbionts, in planktonic species and large, tropical Rotaliida and Miliolida, may help to increase the saturation state at the site of calcification. This may explain calcification despite high seawater $[\text{Mg}^{2+}]$ and hence, high Mg/Ca in larger benthic rotaliids and miliolids. The precipitation of relatively low Mg/Ca-calcite by planktonic, symbiont-bearing species highlights the necessity to determine the timing of acquiring symbionts relative to the evolution of a calcification mechanism.

The different calcification strategies developed by the six foraminiferal orders are linked to the seawater chemistry at the time they evolved calcification. The Mg/Ca of the shells of the foraminifera is inversely correlated to the Mg/Ca of the seawater when they first appeared in the fossil record. Both the Miliolida and the Carterinida precipitate calcite with a high Mg/Ca (Fig. 1), likely indicating precipitation from a more seawater-like calcifying fluid. This in turn may well reflect the absence of the need to actively discriminate against Mg^{2+} during shell-building due to the relatively low seawater $[\text{Mg}^{2+}]$ in the Carboniferous (Miliolida) and the Cretaceous (Carterinida). The Rotaliida, Robertinida and the Spirillinida with their relatively low shell Mg/Ca indicate precipitation from a calcifying fluid containing less Mg compared to Ca with respect to the surrounding seawater. This active discrimination against Mg^{2+} is in phase with the moderately high Mg/Ca of seawater during the Triassic and Jurassic (Stanley and Hardie, 1998; Fig. 3). Interestingly, the two rotaliid families precipitating high-Mg/Ca calcite (Fig. 1, Fig. 3) first appear in the Palaeocene (Boudagher-Fadel, 2018), when seawater Mg/Ca was relatively low (Fig. 3). The Nodosariida have an intermediate Mg/Ca (Fig. 1) and first appeared in the Carboniferous with a reconstructed seawater Mg/Ca between that of the low- and the high-Mg/Ca foraminifera. Finally, aragonite of the Robertinida fits the general aragonite over calcite dominance shown by marine calcifying organisms in periods with highest seawater Mg/Ca (e.g. Stanley and Hardie, 1998; Hardie, 1996; Porter, 2010). This is also true for the extinct Involutinida precipitating aragonite, who were thriving during the Permian when seawater Mg/Ca was approximately 4 mol/mol (Fig. 2).

The second environmental parameter that directly affects calcification is the seawater inorganic carbon chemistry. The first fossil occurrence of the Rotaliida (Gräfe, 2005) is during the high CO_2 -world of the early Jurassic (Royer et al., 2004) that was characterized by a high $[\text{Ca}^{2+}]$ (Stanley and Hardie, 1988) and low sea surface saturation state (Ridgwell, 2005). The active pH regulation of these foraminifera fully fits such an environment: with low $[\text{CO}_3^{2-}]$, but abundant DIC, elevation of the internal pH would be the most cost-effective way to calcify (De Nooijer et al., 2009; Zeebe and Sanyal, 2002; Toyofuku et al., 2017). Modelled and proxy-based Phanerozoic CO_2 reconstructions vary in absolute concentrations (Royer et al., 2004; Witkowski et al., 2018), but agree with the overall trend. The environment at the time the Nodosariida appear in the fossil record (late Carboniferous) was characterized by relatively high saturation state due to low atmospheric CO_2 (Ridgwell, 2005). All other orders evolved in a period when CO_2 was higher

than today, but not as high as during the Silurian/Devonian (Royer et al., 2004). It should be noted that the Carterinida appear much later in the fossil record than the other orders (Fig. 2), in a period with a similar low Mg/Ca_{sw} and low DIC as when the early calcifying miliolids appeared. The similarity in calcite chemistry between these groups may indicate that they independently developed a similar calcification mechanism, despite their phylogenetic distance (Fig. 3).

Essentially, calcification turns seawater-dissolved calcium and carbon into crystalline CaCO_3 . The availability of these ions, however, has changed tremendously over the course of the Phanerozoic (Fig. 3) and it is therefore not surprising that the history of marine calcification is intimately linked to changes in the global carbon- and calcium cycles. We show that the extensive fossil record of foraminifera can be understood by recognizing that, even within this phylum, a multitude of calcification strategies exist. The waxing and waning of foraminiferal groups (Thomas, 2003; Hönisch et al., 2012; Fig. 4) inherently reflects the evolutionary success of the calcification strategy of the various orders. We argue that this also applies to the current perturbation of the global carbon cycle: quantifying the overall response of marine calcification to the rise in $p\text{CO}_2$ and drop in oceanic pH is only possible by acknowledging the evolutionary history of marine calcification.

5. Conclusions

The six orders of foraminifera that make their shells of calcium carbonate, have their own, unique geochemical fingerprint. The variability in elemental composition (Mg/Ca, Na/Ca, Sr/Ca, etc.) is relatively small within each of the calcifying groups compared to that across the whole phylum. Moreover, we show that this variability scales with taxonomic units (i.e. it is progressively smaller in families, genera and species). Particularly Mg/Ca is variable amongst foraminifera, indicating that some groups have evolved a mechanism to actively lower the Mg concentration in the calcifying fluid and thereby mitigate the inhibition on calcium carbonate nucleation and growth by Mg^{2+} . Combined with published phylogenetic data and the fossil record of foraminifera, our results suggest that calcification by foraminifera is polyphyletic (i.e. that it was invented multiple times independently). This also explains the variety in their shells' microstructures, inferred calcification mechanisms and their alteration in dominance in the geological record. The latter essentially reflects the interplay between climate (i.e. CO_2) and seawater chemistry (ocean's Mg^{2+} and Ca^{2+} concentrations) and the evolution of biomineralization. This in turn, underscores the necessity to include an evolutionary perspective when predicting success of marine calcification in a changing ocean.

Author contributions

Conceptualization: LdN
 Methodology: LdN, LPS, DD
 Investigation: LdN, FJJ, JP, YR, GJR
 Visualization: LdN, FJJ, GJR
 Writing – original draft: LdN, LPS, DD, FJJ, JP, YR, GJR

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Lennart de Nooijer reports financial support was provided by NIOZ Netherlands Institute for Sea Research. Lennart de Nooijer reports a relationship with NIOZ Netherlands Institute for Sea Research that includes: employment. Lennart de Nooijer has patent - pending to -.

Data availability

The complete dataset is available at <https://doi.org/10.4121/20236473>. All literature used is listed in the

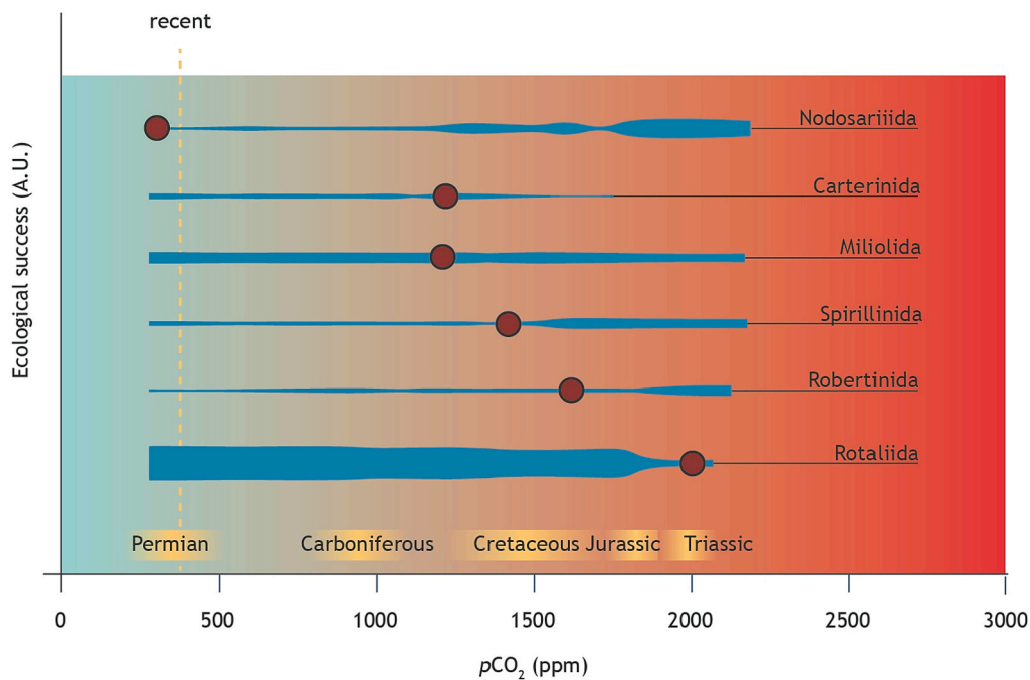


Fig. 4. The ecological success of the six extant foraminiferal orders as a function of past CO₂ levels. The relative abundance in the fossil record (Hohenegger and Piller, 1975; Rigaud and Blau, 2016) was compared to the reconstructed global pCO₂ (Royer et al., 2004). The Nodosariida were relatively abundant in periods with high pCO₂, whereas the rotaliids thrived in low-CO₂ periods. Abundances of the Carterinida are tentatively indicated here as there is very little information on their past abundances. Their record is interpreted as persistence since their appearance in the fossil record (Cretaceous) in relatively low numbers. Current-day CO₂ is indicated as a dashed line. Red circles indicate the pCO₂ at the time of first appearance in the fossil record for each order (Fig. 3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

supplementary data and the complete code used to analyze the data is copied in the supplement.

Acknowledgments

We would like to thank Oscar Branson for valuable comments on an earlier version of this manuscript. 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) (grant no. 024.002.001).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.earscirev.2023.104484>.

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