



1 Monthly element/Ca trends and inter chamber variability in two planktic Foraminifera 2 species: Globigerinoides ruber albus and Turborotalita clarkei from a hypersaline 3 oligotrophic sea 4 5 Noy Levy<sup>1,2</sup>, Adi Torfstein<sup>1,3</sup>, Ralf Schiebel<sup>2</sup>, Natalie Chernihovsky<sup>1,3</sup>, Klaus Peter 6 Jochum<sup>2</sup>, Ulrike Weis<sup>2</sup>, Brigitte Stoll<sup>2</sup>, Gerald H. Haug<sup>2,4</sup> 7 8 9 1) The Fredy & Nadine Herrmann Institute of Earth Sciences, Hebrew University of Jerusalem, Jerusalem 91904, Israel. 10 11 2) Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany. 12 3) Interuniversity Institute for Marine Sciences, Eilat 88103, Israel. 13 4) Department of Earth Sciences, ETH Zurich, Sonneggstrasse 5, 8092 Zurich, Switzerland November 9, 2024 14 15 16 Correspondence to: Noy Levy (noy.levy2@mail.huji.ac.il) 17 18 19 Abstract 20 21 Environmental and biological factors influence the trace element composition (element/Ca) of 22 planktic foraminifer shells. Consequently, the element/Ca measured in these shells (tests) are 23 utilized as proxies to reconstruct past oceanic and climatic conditions. As single shell analyses 24 are increasingly used in paleoceanographic research it is important to understand how proxy 25 systematics change between species, individuals of the same species in a given population, and 26 among chambers of a single individual during its life cycle. Here we present a time series of 27 the chemical composition of planktic foraminifers retrieved using sediment traps between June 28 2014 and June 2015 at the northern part of the Gulf of Agaba (aka Gulf of Eilat). Laser ablation 29 ICP-MS element/Ca measurements were performed on single shells and chambers of 30 Globigerinoides ruber albus and Turborotalita clarkei, collected monthly from five water 31 depths (120 m, 220 m, 350 m, 450 m, and 570 m). Sediment trap samples were paired with 32 corresponding data on water column hydrography and chemistry. Pooled means of measured 33 element/Ca display species-specific and element-specific behavior, with generally higher





34 values for T. clarkei phenotypes ('big' and 'encrusted') in comparison to G. ruber albus. Some 35 element/Ca values measured in water column specimens, such as Al/Ca, vary significantly 36 from core-top specimens. A unique finding is a prominent increase in element/Ca around 37 March-April 2015, during maximum water column mixing, mostly apparent in T. clarkei and 38 to a lesser extent in G. ruber albus. This spring element/Ca increase is observed in most 39 measured elements and is further associated with an increase in inter-chamber variability 40 (ICV). Inter-chamber element/Ca patterns show element enrichment/depletion in the most 41 recently precipitated (final, F0) chamber in comparison to the older chambers (penultimate (F-42 1), antepenultimate (F-2), etc.). Element/Ca in F0 may also be less sensitive to surrounding 43 environmental conditions. For example, the Mg/Ca of the F-1 and F-2 chambers of G. ruber 44 albus display a positive relationship with mixed layer temperatures while F0 does not. To 45 overcome this effect, we suggest using pooled means from non-F0 fractions as environmental 46 records and paleo proxies. 47 These results highlight the complexity of proxy systematics that rises from the variability in 48 element/Ca measured among different species and between chambers, caused by ecological 49 conditions and other processes in the water column including physical, chemical, and

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#### 1. Introduction

biological effects.

## 1.1 Planktic foraminifera as traces of the past environment

Planktic Foraminifera (PF) shells are useful archives for studying the history of Earth's climate and oceans, as their calcareous shells reflect the environmental conditions during their formation (Berggren et al., 1995; Rosenthal, 2007; Schiebel & Hemleben, 2017; Kucera, 2007; Katz et al., 2010; Gupta, 1999; Davis et al., 2020, and others). Various element/Ca measured in PF tests have been closely linked to ambient seawater temperature (e.g., Mg/Ca; Rosenthal et al., 2004), salinity (e.g., Na/Ca; Mezger et al., 2016; Gray et al., 2023), pH and the carbonate system (e.g., B/Ca; Babila et al., 2014; Henehan et al., 2015; Haynes et al., 2019), productivity (e.g., Ba/Ca; Fritz-Enders et al., 2022), and chemical weathering (e.g., Ti/Ca; Amaglio et al., 2025, among others. In the past, the use of these proxies relied on bulk analysis of the entire shell or multiple shells. However, in recent years there has been an increase in the use of high-resolution analytical techniques, such as Laser Ablation (LA) ICP-MS and electron microprobe analyses in paleoceanographic studies (Davis et al., 2020). The element/Ca measurements of



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single specimens (Individual Foraminifer Analysis, IFA) revealed high variability between individuals of the same population as well as significant intra-shell variability (i.e., inter chamber variability, ICV) (Sadekov et al., 2008; Fehrenbacher et al., 2020; Hupp & Fehrenbacher, 2024; Fischer et al., 2024; Davis et al., 2020, and references therein). The associated changes in the geochemical signatures of PF shells are poorly understood and despite the analytical advancements, there are still knowledge gaps in our understanding of proxy systematics in single shell and single chamber of PF species although they are potentially related to the observed shell and chamber element/Ca variability, the life cycles and reproductive modes of many species, as they calcify their shell chambers one at a time. There is also a lack of detailed description and understanding of proxy systematics in description of the dynamics of small-sized species such as T. clarkei, which have been largely overlooked in previous studies despite their significant contribution to the settling PF tests (export flux), as observed in the northern Red Sea (Chernihovsky et al., 2018). Furthermore, specific marine regions, such as in oligotrophic, subtropical basins, particularly in deep-water column environments, are not well-established in terms of their spatial and temporal dynamics (Schiebel & Hemleben, 2017).

## 1.2 Planktic Foraminifer population dynamics in The Gulf of Aqaba

The Gulf of Aqaba (GOA) is considered an open ocean proxy environment (Chase et al., 2011). It is an oligotrophic basin where the main lithogenic flux is derived from dust. During summer (April-September), a ~200 m deep thermocline separates nutrient-depleted surface waters (~25°C) from the nutrient-rich deep layer (~21°C). In winter/spring (October-April), the thermocline gradually erodes due to surface cooling (Figs. 1a and 1e; Meeder et al., 2012), which can lead to the development of a deep mixed layer. Although the depth of the mixed layer varies annually with climatic conditions, the long-term mean mixing depth is approximately 300-400 m, and deep mixing can extend to the sea floor while it typically reaches maximum depth by late March. The regional terrestrial climate is hyper-arid (mean annual rainfall <30 mm) and the main sources for terrigenous material to the GOA are dust storms originating from the Sahara and Arabian Deserts, as well as rare localized floods (Katz et al., 2015; Chase et al., 2011; Ganor et al., 2001; Torfstein et al., 2017).





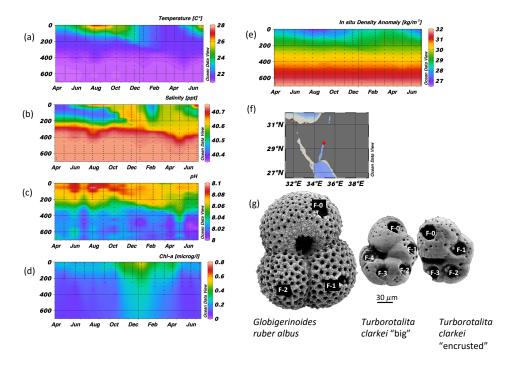


Figure 1: Time series of temperature (a), salinity (b), *p*H (c), Chlorophyll-a concentration (d), and in situ density anomaly (e), measured in the Gulf of Aqaba between April 2014 and June 2015 by the National Monitoring Program (NMP, Shaked & Genin, 2016). Y-axis is depth (m); A map of the Gulf of Aqaba (f); and (g) scanning electron micrographs of the three morphospecies (exhibiting ablation holes in each chamber (labelled), from Levy et al., 2023).

Planktic foraminifera fluxes in the GOA demonstrate strong seasonality, with low fluxes during the summer months, gradually increasing during the autumn-winter, coeval with decreasing sea-surface temperatures and deepening of the mixed layer in the GOA that drives advection of nutrient-replete subsurface waters into the mixed layer. This in turn triggers an increase in primary productivity, expressed by enhanced chlorophyll-a concentrations and high PF fluxes (Chernihovsky et al., 2018, 2020).

Spinose species constitute the majority of the PF assemblage. The smaller size fraction, 63-125 μm, is 86% from the total flux and is dominated by *T. clarkei*. The 125-500 μm size-fraction (~13 %) is dominated by the species *G. ruber albus*, while less than 1% of the shells are in the range of 500-1000 μm, dominated by *O. universa* (Chernihovsky et al., 2018).

Globigerinoides ruber albus and T. clarkei inhabit different dwelling-depths and have diverse life strategies. Globigerinoides ruber albus is a surface dweller and is photo-symbiont





bearing, while *T. clarkei* tends to dwell below the mixed layer depth and is barren of photosymbionts (Rebotim et al., 2017; Schiebel & Hemleben, 2017; Levy et al., 2023). Furthermore, it has been suggested that *G. ruber albus* and *T. clarkei* do not share the same dietary preferences: *G. ruber albus* being more carnivorous than the detritivorous *T. clarkei* which may forage at the exported matter below the pycnocline (Schiebel & Hemleben, 2017). In the GOA, *T. clarkei* has two phenotypes: *T. clarkei* 'big', which all of its test chambers are fully recognizable and their surface is relatively smooth and *T. clarkei* 'encrusted' with a less smooth shell surface and is smaller than the 'big' type (Levy et al., 2023).

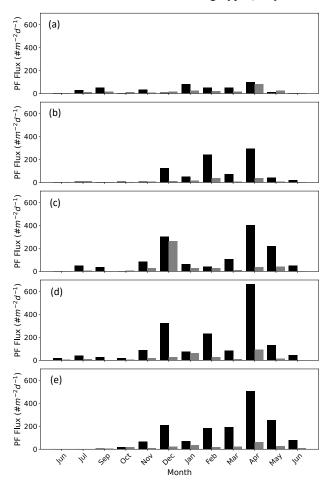


Figure 2: PF fluxes in the Gulf of Aqaba between June 2014 and June 2015 presented according to the size fractions  $>63-125~\mu m$  (black bars) and  $>125-500~\mu m$  (grey bars) at the different sediment trap depths a) 120 m, b) 220 m, c) 340 m, d) 450 m, and e) 570 m. Data from Chernihovsky et al. (2018).





In this study, we investigate the range of element values, year-round trends and interchamber element/Ca variability in *G. ruber albus* and *T. clarkei* tests collected in sediment traps at various water column depths from the GOA. We assess whether the chambers record temporal-seasonal patterns, and the implications for using single chamber data for geochemical proxies (Mg/Ca, B/Ca, Na/Ca). Understanding inter-chamber variability sheds light on biomineralization processes and environmental factors that occur during different stages of the organism's life cycle. This in turn improves the calibration of element/Ca as proxies for reliable reconstruction of past oceanic and climatic conditions. Focusing on PF from the GOA provides critical insights into the use of foraminiferal element/Ca as proxies in a warm and hyper-saline oligotrophic environment.

#### 2. Methodology

#### 2.1. Sampling and oceanographic data

A bottom-tethered mooring has been deployed continuously since January 2014 near Station A, northern GOA (29° 28'95' N, 34° 56'22' E, ~605 m water depth) (Torfstein et al., 2020). Five KC Denmark cylinder sediment traps were mounted vertically and located at depths of 120 m, 220 m, 350 m, 450 m, and 570 m. The trap samples were collected at a monthly resolution. Furthermore, PF samples from the sediment interface were collected using a box core ('core top'). Further detailed description of the mooring, sampling, sample processing, and trapping efficiencies can be found in Chernihovsky et al. (2018) and Torfstein et al. (2020). Here, we report the findings derived from the PF tests collected between June 2014 and June 2015. Water column physical and chemical parameters are routinely collected at Station A by the Israel National Monitoring Program (NMP, Shaked & Genin, 2016). This includes sea surface and water column temperature (°C), salinity, oxygen concentration (μmol/l), alkalinity (meq/kg), *p*H, and chlorophyll-a concentration (μg/l). The mixed layer depth (MLD) is defined as the water depth where the density anomaly (σ0) is equal to, or above, the water density of the surface water column plus a density threshold of 0.125 kg/m³ (Sprintall & Tomczak, 1992).

2.2. Species classification and preparation for LA-ICP-MS





We examined the shell chemical properties of two flux dominating PF species *T. clarkei* and *G. ruber albus* (i.e., sensu stricto, white). For *T. clarkei* we examined two morphotypes: 'big' and 'encrusted'. Identification and nomenclature of the PF taxa followed Schiebel & Hemleben (2017), Morard et al. (2019), and Brummer & Kucera (2022). Three individuals were picked from each sediment trap depth during each month between June 2014 and June 2015. Preliminary preparation and cleaning steps are detailed by Chernihovsky et al. (2018). Reductive and oxidative cleaning had been avoided to retain original signals related to the different encrustation processes and preserve all calcite layers added to the shell during ontogeny (Schiebel & Hemleben, 2017; Jochum et al., 2019). Specifically, the shell *T. clarkei* is prone to loss of material during reductive and oxidative treatment as it has very thin shells with a width ranging 1.9-3.6 µm (Levy et al., 2023). Single chamber measurements were performed to asses inter chamber variability (ICV), on individual shells (individual foraminifer analysis; IFA) using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) on 156 specimens in total. Samples were glued to glass slides using a methyl-hydroxy-propyl-cellulose (MHPC 1:100), positioned with the umbilical side up.

# 2.3. LA-ICP-MS and data processing

Analyses of the calcium-normalized elements for B, Na, Mg, Al, Ti, Mn, Fe, Co, Sr, Ba, Nd, Pb, Th, and U were conducted using a 200 nm wavelength NWR femtosecond (fs) LASER system from ESI, combined with a sector-field Thermo Element-2 ICP mass spectrometer (Jochum et al., 2014). Measurements were performed using a 15 Hz pulse repetition rate (PRR), at low fluence (0.1–0.6 J/cm²), and 18 seconds dwelling time. A 30 μm diameter spot size was selected, as it is the maximum diameter for analysis fitting in a single chamber of the small *T. clarkei*. The microanalytical synthetic reference material MACS-3 for carbonate, NIST-612, and NIST-610 were used for calibration. NIST-612 was used for the tuning of the ICP-MS (Jochum et al., 2019).

The measurement precision (1 relative standard deviation in percent; 1 RSD) yield uncertainties for references materials between  $\sim 5\text{-}17~\%$  for the calcium-normalized elements (Supplementary table 1). Single spot measurements were made on each chamber of the individual shells. Chambers are labelled F0 (final chamber), F-1 (final minus one), F-2, and so on, for the penultimate, antepenultimate, and further chambers, respectively. We calculated averages and standard deviations of element/Ca of single individuals (calculated from all single





190	chamber element /Ca in one shell) and relative standard errors of element/Ca of pooled
191	measurements for a specific morphotype.
192	3. Results:
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194	3.1. Depth-averaged values of element/Ca measured in G. ruber albus and T. clarkei
195	shells using LA-ICP-MS
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197	Generally, the means of Mg/Ca, Sr/Ca, B/Ca, Na/Ca and Ba/Ca in G. ruber albus indicate that
198	the composition of tests, from most water depths is similar to that of core-top samples (Figs.
199	3a-3d, 3j). In contrast, Al/Ca, Ti/Ca, Mn/Ca, Fe/Ca, Nd/Ca, Th/Ca, and U/Ca (Figs. 3e-3i, 3k,
200	3m, 3n) in the tests from sediment interface were higher than in the water column, and lower
201	in case of Co/Ca and Pb/Ca (Figs. 3i, 3l).



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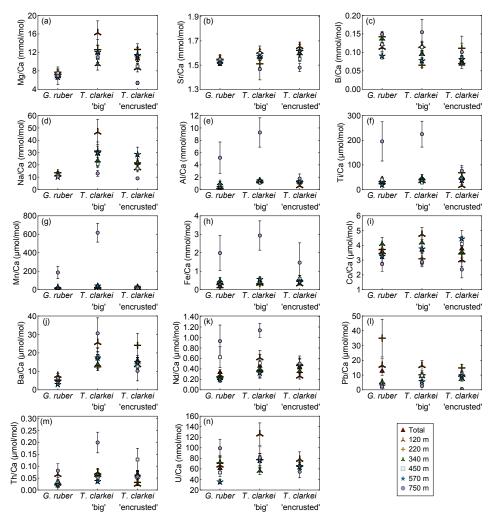


Figure 3: Pooled mean values of the calcium-normalized element ratios of *G. ruber albus*, *T. clarkei* 'big' and *T. clarkei* 'encrusted' shells, derived from sediment traps located at different water depths (120 m to 570 m) and a core top sample (750 m) from the Gulf of Aqaba. Error bars represent 1 sigma relative standard error  $(SD/\sqrt{n})$ .

Furthermore, *T. clarkei* tends to demonstrate higher values and higher variability compared to *G. ruber albus*. Compared to the core-top samples, *T. clarkei* from the water column also exhibit relative enrichment in Al/Ca, Ti/Ca, Mn/Ca, Fe/Ca, Nd/Ca, B/Ca, and Th/Ca (*T. clarkei* 'big'), and depletion in Co/Ca, Pb/Ca, Sr/Ca, and Mg/Ca (*T. clarkei* 'encrusted') (Fig. 3).

3.2. Shell-bound element/Ca time series trends in G. ruber albus and T. clarkei shells





Pooled mean values of Mg/Ca in *G. ruber albus* taken from all water column depths in the GOA reflect MLD temperatures (Fig. 10). Single chamber Mg/Ca over water column depths in *G. ruber albus* range between 2.01 mmol/mol (340 m; June 2015) and 18.49 mmol/mol (340 m; July 2014), with lower/higher values during winter/summer months, respectively (Figs. 4a-4e). A unique observation is an increase in Mg/Ca seen during spring (March-April), i.e., months with maximum surface water column mixing, at some water depths (220 m, 340 m, 450 m; Figs. 4b-4d). Accompanied with the Mg/Ca increase is a clear increase in ICV as evident by the divergence of chamber values. Generally, it appears that Mg/Ca is lower in F0 chambers (orange dotted line) compared to preceding chambers. Mg/Ca in *T. clarkei* 'big' range between 4.00 mmol/mol (340 m; June 2015) and 77.02 mmol/mol (220 m; March 2015) and between 4.06 mmol/mol (570 m; December 2014) and 51.22 mmol/mol (120 m; April 2015) in *T. clarkei* 'encrusted', respectively.

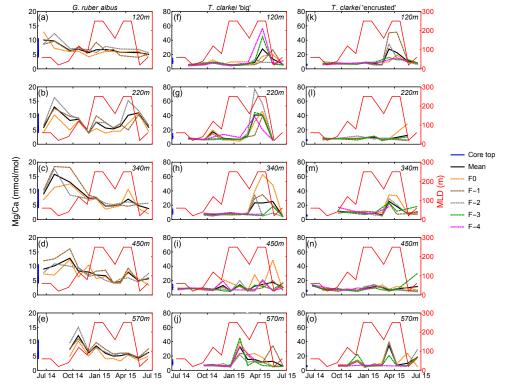


Figure 4: Time series of Mg/Ca values measured from the shells of *G. ruber albus* (a-e), *T. clarkei* 'big' (f-j) and *T. clarkei* 'encrusted' (k-o), derived from sediment traps located at





different water depths (120-570 m). Mg/Ca of core top are marked by a blue bar along the left y-axes.

Sr/Ca in *G. ruber albus* range between 1.25 mmol/mol (570 m; January 2015) and 2.27 mmol/mol (340 m; November 2014) (Figs. 5a-5e). Single chamber Sr/Ca in *T. clarkei* 'big' range between 0.94 mmol/mol (340 m; January 2015) and 2.76 mmol/mol (220 m; April 2015) and for *T. clarkei* 'encrusted' between 0.54 mmol/mol (340 m; April 2015) and 2.92 mmol/mol (570 m; June 2015), respectively (Figs. 5f-5j, and 5k-5o). *Turborotalita clarkei* 'big' and *T. clarkei* 'encrusted' display more ICV than *G. ruber albus*, with peaking Sr/Ca in numerous chambers around April 2015 (Figs. 5f-5o). During the spring months of 2015, Sr/Ca values range between 1.45-2.04 mmol/mol in *G. ruber albus*, 1.32-2.76 mmol/mol in *T. clarkei* 'big' and 0.54-2.27 mmol/mol in *T. clarkei* 'encrusted', respectively (Fig. 5; Fig. S1).

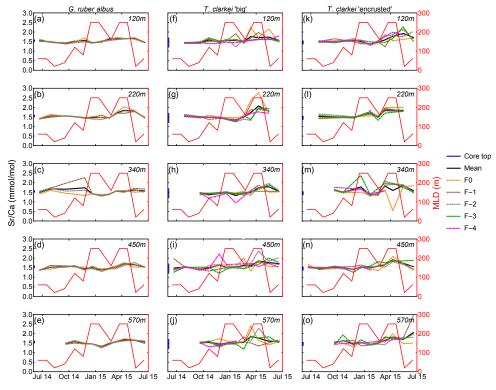


Figure 5: Time series of Sr/Ca values measured from the shells of G. ruber albus (a-e), T. clarkei 'big' (f-j) and T. clarkei 'encrusted' (k-o), derived from sediment traps located at different water depths (120 m - 570 m).





B/Ca values range between 0.03 mmol/mol (570 m; January 2015) to 0.35 mmol/mol (120 m; June 2015) in *G. ruber albus*, with higher values during summer and spring and lower values during the winter (Figs. 6a to 6e). B/Ca measured in the final chamber, F0, are systematically lower compared to F-1 and F-2 values. Unlike most other element ratios, B/Ca values in both phenotypes of *T. clarkei* are similar to the range measured in *G. ruber albus*. In both *T. clarkei* phenotypes, lower B/Ca values were measured during the winter months, most prominently in January. The B/Ca values of *T. clarkei* 'big' range between 0.01 mmol/mol to 0.53 mmol/mol with some higher values during spring (Figs. 6f to 6j). B/Ca values in *T. clarkei* 'encrusted' range between 0.01 mmol/mol to 0.47 mmol/mol. Generally, B/Ca ICV is higher in *T. clarkei* than *G. ruber albus*, especially during spring.

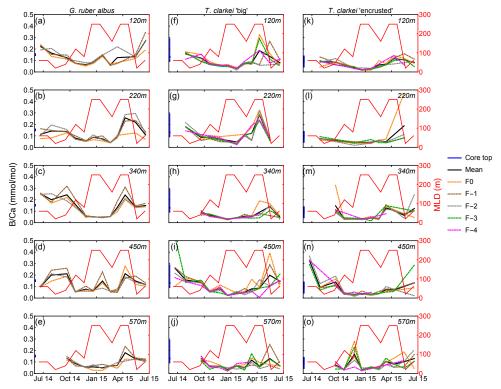


Figure 6: Time series of B/Ca values measured from the shells of *G. ruber albus* (a-e), *T. clarkei* 'big' (f-j) and *T. clarkei* 'encrusted' (k-o), derived from sediment traps located at different traps from 120 m to 570 m water depths.





Na/Ca in *G. ruber albus* ranges between 6.60 mmol/mol (220 m; June 2014) to 64.14 mmol/mol (220 m; April 2015) with a median value of 10.43 mmol/mol (Fig. 7; Fig. S1). Na/Ca in *T. clarkei* 'big' ranges from 6.23 mmol/mol (570 m; September 2014) to 426.54 mmol/mol (220 m; March 2015) with a median value of 12.33 mmol/mol. Na/Ca in *T. clarkei* 'encrusted' ranges between 5.43 mmol/mol (570 m; September 2014) to 176.91 mmol/mol (570 m; March 2015) with a median value of 12.41 mmol/mol. *Globigerinoides ruber albus* has a low ICV during spring, while *T. clarkei* 'big' and 'encrusted' phenotypes display higher ICV during the same time interval. All morphotypes include significant excursions in Na/Ca with high values in *G. ruber albus* during January and April at 220m (Fig. 7b), and high Na/Ca in both *T. clarkei* phenotypes at multiple depths and seasons (Figs. 7f-7j and 7k-7o). In particular, *T. clarkei* phenotypes show significant Na/Ca excursions during March-April and ICV (Figs. 7f-7o).

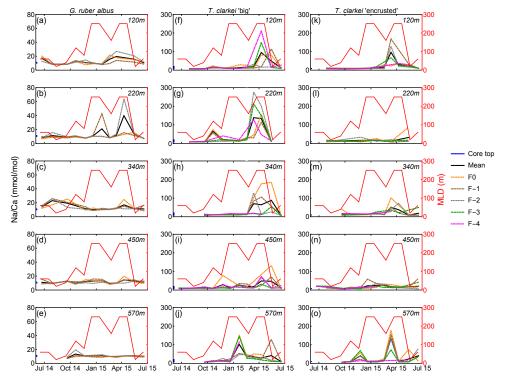


Figure 7: Time series of Na/Ca values measured from the shells of *G. ruber albus* (a-e), *T. clarkei* 'big' (f-j) and *T. clarkei* 'encrusted' (k-o), derived from sediment traps located at different water depths (120 m – 570 m).

Ba/Ca in *G. ruber albus* ranges from 0.73  $\mu$ mol/mol (120 m; November 2014) to 36.81  $\mu$ mol/mol (340 m; June 2015). Ba/Ca in *T. clarkei* 'big' ranges from 0.39  $\mu$ mol/mol (120 m;





June 2015) to 246.54 μmol/mol (450 m; March 2015). Ba/Ca in *T. clarkei* 'encrusted' ranges from 0 μmol/mol (April 2015) to 171.41 μmol/mol (340 m; March 2015) (Fig. 8; Fig. S1). The three morphotypes display varied ICV, although *T. clarkei* shows more prominent ICV during spring months (Figs. 8f-8o) than *G. ruber albus* (Figs. 8a-8e).

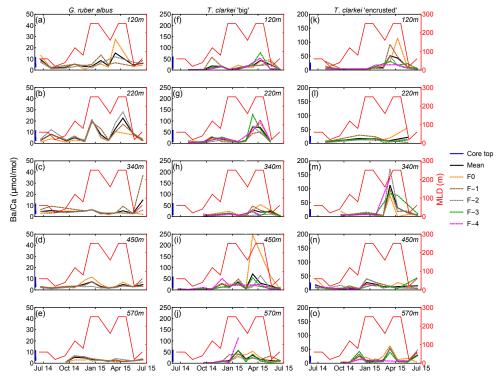


Figure 8: Time series of Ba/Ca values measured from the shells of *G. ruber albus* (a-e), *T. clarkei* 'big' (f-j) and *T. clarkei* 'encrusted' (k-o), derived from sediment traps located at different water depths (120 m – 570 m).

## 3.3. Relationships between element/Ca of the different PF species in the GOA

A Spearman correlation matrix was applied to assess the numerical relationships of the element/Ca in the three analyzed PF phenotypes (Fig. 9; Tab. S2). The *T. clarkei* types exhibit similar pattern of relationships, with minor differences mainly in correlation strength (Fig. 9a, 9b). In general, *T. clarkei* shows more significant relationships than *G. ruber albus*, while, *G. ruber albus*, display different relationships to those of the two *T. clarkei* types. In *T. clarkei*, Mg/Ca displays relatively strong relationships with Na/Ca, Ba/Ca, and Al/Ca (Fig. 9b, 9c). Sr/Ca, B/Ca, Co/Ca and Nd/Ca do not display significant relationships to other elements in *G. ruber albus* as well as in *T. clarkei* 'big' and *T. clarkei* 'encrusted'.





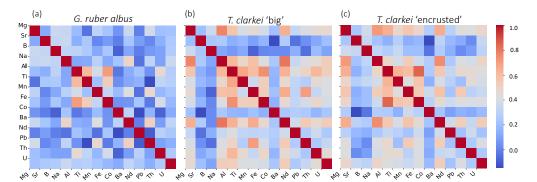


Figure 9: Spearman correlation Matrix of the different trace element Ca normalized abundances in *G. ruber albus* (a), *T. clarkei* "big" (b) and, *T. clarkei* "encrusted" (c).

For both *T. clarkei* 'big' and *T. clarkei* 'encrusted', Na/Ca significantly correlates with Al/Ca, Mn/Ca, and Ba/Ca, the later showing the strongest relationships in *T. clarkei* 'big' (r = 0.82, Fig. 9b; Tab. S2). Relationships between Al/Ca, Ti/Ca, Mn/Ca, Fe/Ca, Ba/Ca and Th/Ca are generally stronger in *T. clarkei* 'big' than in *T. clarkei* 'encrusted', except for Al/Ca and Fe/Ca, which are stronger related in *T. clarkei* 'encrusted' (r = 0.85; Tab. S2) than in *T. clarkei* 'big' (r = 0.74; Tab. S2). Unlike *G. ruber albus*, the U/Ca in *T. clarkei* exhibit relatively strong relationships with Ba/Ca, Na/Ca and Al/Ca (in *T. clarkei* 'big') and Mg/Ca (in *T. clarkei* 'encrusted', Fig. 9c) while in *G. ruber albus*, U/Ca is poorly related to the other elements (Fig. 9a).

## 4. Interpretation

4.1 Inter chamber variability (ICV)

Shell-bound element/Ca display varying trends across different chambers depending on the specific element ratios, and varying over water depth and time (Figs. 4-8). Typically, most PF reproduction-cycles span about a month with individual chambers forming within several hours (Bé et al., 1977), while the time interval between chamber formation can range from hours to weeks (Schiebel & Hemleben, 2017, and references therein). Setting aside the March-April time-interval where PF shells show exceptionally high ICV, *G. ruber albus* generally exhibits lower values (e.g., Mg/Ca, B/Ca), and less ICV compared to *T. clarkei* 'big' and 'encrusted'. The residence of *G. ruber albus* in the relatively homogenous and narrow living environment



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in the surface mixed layer (Schiebel & Hemleben, 2017; Thirumalai et al., 2014; and others), could explain relatively lower ICV. In contrast, *T. clarkei* dwell in the dynamic region near/under the thermocline (Schiebel & Hemleben, 2017; Levy et al., 2023) over a wider dwelling depth horizon, and may experience more heterogeneous environmental conditions which may result in higher ICV.

The secondary crust observed on *T. clarkei* 'encrusted' morphotypes, which covers all chambers of the tests analysed here, does not significantly alter element/Ca when compared to *T. clarkei* 'big', unlike the crust of *Neogloboquadrina dutertrei* (Jonkers et al., 2012). This suggests that the secondary calcite layer in *T. clarkei* 'encrusted' does not play a major role in element incorporation or ICV and is affected by the same mechanisms which control the formation of the ontogenetic calcite, and thus would facilitate application of our finding to the interpretation of fossil *T. clarkei* 'encrusted' in paleoceanography and paleoclimate reconstructions.

The ultimate chamber (F0) presents different systematics compared to the preceding chambers in both T. clarkei and G. ruber albus (Fig. S11). In T. clarkei (both 'big' and 'encrusted'), the F0 typically exhibits higher values of B/Ca, Na/Ca, Mg/Ca, and Al/Ca compared to the previous chambers. In contrast, G. ruber albus displays relatively lower values in F0 for the same ratios highlighting species-specific differences in chamber formation (Fig. S11). Interestingly, Sr/Ca does not follow the same pattern. In T. clarkei 'big' the Sr/Ca distribution mirrors the trends of other elements, while F0 in G. ruber albus and T. clarkei 'encrusted' shows an even distribution of Sr/Ca, likely reflecting the relatively constant Sr/Ca values in the water column during the lifespan of a single test. These observations in G. ruber albus are consistent with previous studies that measured Mg/Ca in individual chambers (Bolton et al., 2011; Davis et al., 2020; Fischer et al., 2024). The contrasting systematics of F0 leading to elevated ICV in the ultimate chamber compared to the previous chambers was previously suggested to be associated with a chamber wall that is not fully calcified (Schiebel & Hemleben, 2017; Bolton et al., 2011; Fischer et al., 2024). Differences in F0 systematics between T. clarkei and G. ruber albus could be driven by species-specific calcification processes, though further research is needed to clarify this issue. Additionally, it is important to consider potential biases in small chambers such as F-4 in T. clarkei morpho-species, where methodological challenges (e.g., laser spots hitting sutures) may skew element/Ca measurements. Consequently, we conclude that the exclusion of F0 and F-4 will enhance the reliability of reconstructions of the marine environment in studies of downcore records.





The contrasting results of the correlation matrixes of the three morphospecies, suggests species-specific mechanisms while calcifying their shells. The Mg/Ca in *T. clarkei* which strongly correlates with Na/Ca, Ba/Ca, and Al/Ca (Fig. 9c), suggests more than one environmental process affects Mg/Ca in the tests as the other element/Ca are considered proxies to different environmental characteristics such as salinity, productivity, and terrigenous input (Chang et al., 2015; Mesa-Fernández et al., 2022; Beasley, et al., 2021). Similar to *G. ruber albus*, in the *T. clarkei* types Sr/Ca, B/Ca, Co/Ca and Nd/Ca do not display statistically significant relationships to other elements making them suitable proxies for distinct and independent environmental properties.

In *G. ruber albus*, Mg/Ca, Sr/Ca and B/Ca show no significant relationships with other element ratios, indicating that independent processes likely govern their proxy systematics (Fig. 9c). Similarly, Co/Ca, Nd/Ca and U/Ca also do not correlate with other element/Ca. While Na/Ca and Ba/Ca exhibit some degree of correlation, as do Mn/Ca and Pb/Ca, the lithophilic elements, Al/Ca, Ti/Ca, which are considered proxies for terrigenous dust input (Chang et al., 2015;

Mesa-Fernández et al., 2022; Beasley, et al., 2021), as well as, Fe/Ca, and Th/Ca, all show a

relative strong correlation. Their correlation implies they can be used together for reconstructing terrigenous input to the water column. Among the lithophilic elements, Th/Ca

display a relatively weaker relationship, suggesting a potential effect of additional processes

such as scavenging (Anderson et al., 1983; François et al., 2004; Costa et al., 2020).

4.2 Relationships of element ratios of the three PF morphotypes

# 4.3 Mg/Ca as a proxy for sea surface temperature

Shell-bound Mg/Ca of calcareous foraminifera have been extensively utilized as a paleothermometer (e.g., Nürnberg et al., 1996; Sadekov et al., 2009). Many of these Mg-temperature calibrations rely on whole-test or pooled-mean Mg/Ca values to reconstruct past sea surface temperatures (Spero et al., 2003; Ganssen et al., 2010; and others). Several studies have measured intra-test and inter-test Mg/Ca in an effort to produce Mg-temperature calibrations using single chamber measurements of *G. ruber* (Sadekov et al., 2008; Bolton et al., 2011; Davis et al., 2020; Levy et al., 2023; Fischer et al., 2024). Previous work on sediment trapderived specimens of *T. clarkei* and *G. ruber albus* from the GOA indicated that *T. clarkei* is not suitable for temperature reconstructions, due to its presumed deep dwelling-depth below the thermocline together with its high sensitivity to water column mixing events. However, while *G. ruber albus* shows exceptionally high pooled mean Mg/Ca values in the GOA in comparison to other ocean regions, it also exhibits seasonal variations that indicate effective





applicability as a paleothermometer (Levy et al., 2023). Due to the high seawater salinity of
 the GOA, a local calibration curve was proposed (Eq. 1; Levy et al., 2023).

$$\frac{\text{Mg}}{\text{Ca}} = 0.39(\pm 0.30) \cdot e^{0.12(\pm 0.03)T} \tag{1}$$

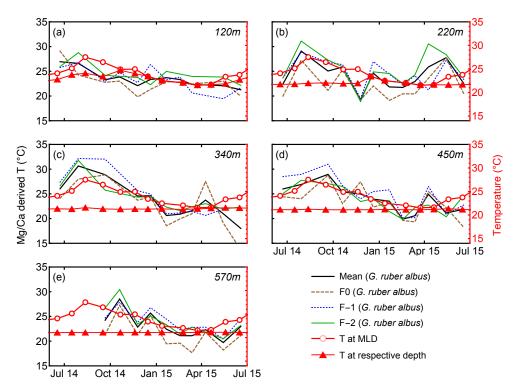


Figure 10: *G. ruber albus* Mg/Ca-derived temperatures versus measured temperatures (red). The calculated temperatures were derived from Eq. 1 for individual chambers. See also Levy et al. (2023).

Inter-chamber variability (ICV) has been shown to affect the local Mg/Ca temperature calibration (Eq. 1) of *G. ruber albus* (Levy et al., 2023; Fig. 10). Generally, Mg/Ca-derived temperatures from chambers F-1 and F-2 correspond closely with mixed layer depth (MLD) temperatures. However, beneath the photic zone, Mg/Ca of all three chambers F0, F-1, and F-2 of the *G. ruber albus* specimens exhibit poor fits with measured temperatures (Fig. 10). Given that *G. ruber albus* calcifies its shell in the photic zone (Schiebel and Hemleben, 2017), these findings support the use of Mg/Ca as a paleothermometer (Nürnberg et al., 1996). The Mg/Ca-





derived temperatures from chamber F0 show lower Mg/Ca temperatures of the MLD than chambers F-1 and F-2 (Fig. 10). Although Mg/Ca data from chambers F-1 and F-2 appear suitable for reconstructing temperatures and demonstrate agreement with MLD temperature trends, the high ICV in *G. ruber albus* is evidently too great to accurately reflect ambient temperatures using this calibration. Therefore, and based on these new observations, we suggest that optimal Mg/Ca-temperature calibration (Eq. 1) should be based on the pooled mean of the F-1 and F-2 chambers at all depths.

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4.2 B/Ca as a proxy for pH

B/Ca in some PF species has been suggested to be a proxy for *p*H (Yu et al., 2007; Allen et al., 2011). Comparing chamber B/Ca of both *G. ruber albus* and *T. clarkei* (both 'big' and 'encrusted') alongside *p*H at various water column depths in the GOA reveals contrasting results. While B/Ca in *G. ruber albus* exhibits seasonality (Fig. 6), with lower values during winter months, it does not appear to be consistent with the *p*H of respective water depth nor the MLD (Fig. 11). This inconsistency suggests that B/Ca in *G. ruber albus* from the GOA is not a reliable recorder of ambient water *p*H. Similarly, Henehan et al. (2015) and Naik & Naidu (2014) reported that B/Ca of open ocean core-top samples and down-core sediment samples do not display a *p*H relationship.

Alternatively, B/Ca in G. ruber albus may be sensitive to salinity and micro-environments produced by PF symbionts with pH levels which are distinct from the ambient water column. Culture experiments have shown that B/Ca is affected by salinity and increases with increasing salinity (Allen et al., 2012). However, only small salinity changes occur in the GOA (Fig. 1), which argue against a strong B/Ca-salinity relationship that would result in a B/Ca seasonal trends. It was suggested that photo-symbionts such as dinoflagellates in G. ruber albus create micro-environments with pH levels, which are distinct from ambient seawater, to accommodate for their photosynthetic activity, and indicate that B/Ca is more affected by pH in those microenvironments than the water column pH (Hönisch et al., 2021; Babila et al., 2014). An additional observation for the G. ruber albus B/Ca values is that they are relatively high in comparison to values from other studies. The relatively high salinity in the GOA (~41), combined with the photosymbiont activity in G. ruber albus may explain the elevated B/Ca values (Henehan et al., 2015; Hönisch et al., 2021; Babila et al., 2014). In contrast to G. ruber albus, B/Ca in the photosymbiont barren T. clarkei may indeed record the changes in pH (Fig. 11) of seawater at its ambient dwelling depth, possibly shifting between the deeper water column depth horizons where pH changes are evident. Indeed, based on the



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fluxes of T. clarkei (Chernihovsky et al., 2018; Fig. 2), the B/Ca of T. clarkei in the sediment record likely represent the pH beneath the thermocline and within the deep-water column horizons for specimens that lived from early winter through spring. In particular, pH at 340 m appears to correlate with the B/Ca trends of T. clarkei types. For B/Ca-pH calibrations utilizing the pooled mean of data from the chambers F-1, F-2, and F-3 is recommended, while excluding F0 F-4 **ICV** the and chambers where more is 11). apparent (Fig.

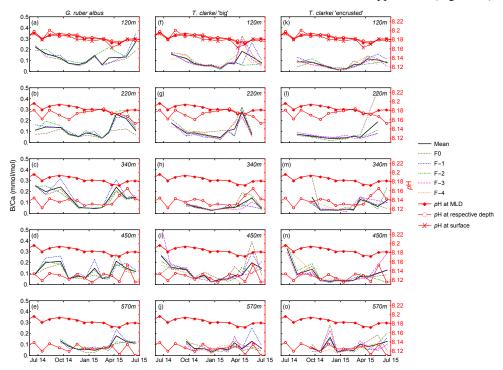


Figure 11: Single chamber B/Ca and in situ pH measured at MLD depth (empty red circles) and 120 m water depth for *G. ruber albus*, *T. clarkei* 'big' and *T. clarkei* 'encrusted'.

4.3 Na/Ca as a proxy for salinity and Ba/Ca as an indicator for productivity Cultured individuals and samples from the surface Caribbean and the Gulf of Guinea of live *T. sacculifer* indicate that Na/Ca can be used as a proxy for salinity, without temperature dependence, however, a species-specific calibration might be required (Bertlich et al., 2018). Despite the high variability of PF Na/Ca values in the GOA during water column mixing (Fig. 7), salinity remains high and relatively constant, ranging between 40.4-40.7. Consequently, a local Na/Ca-salinity calibration shows no significant relationship for any of the three PF morphotypes.





Na/Ca values in PF from the GOA are notably higher compared to other regions. Gray *et al.* (2023) explored the relationship between Na/Ca and salinity in *G. ruber albus* collected from sediment traps, plankton tows, culture samples, and core top samples, contributing to the ongoing discussions regarding the reliability of Na/Ca as a proxy for salinity in both planktic and benthic foraminifera (Allen et al., 2016; Geerken et al., 2018; Mezger et al., 2016, 2018; Gray et al., 2023, and references therein). They concluded that the measurement method (i.e., 'solution' ICP-MS vs. LA-ICP-MS) influences the values of Na/Ca and in turn the relationship with salinity, i.e., weak in solution-based compared to significant in laser ablation-based, at salinity over 36.

Comparing Na/Ca of *G. ruber albus* from the shallowest sediment trap (120 m) in the GOA with the Na/Ca of *G. ruber albus* plankton tows-samples from the GOA deployed and collected in January 2010 and October 2013 (Gray et al., 2023), both measured using LA-ICP-MS, generally reveals similar results, excluding the high-value excursions observed in some single chamber measurements (Fig. 7). *Turborotalita clarkei* in the GOA exhibits elevated Na/Ca values in both 'big' and 'encrusted' compared to *G. ruber albus*. Unlike *G. ruber albus*, there is relatively higher variability between water depths as well as significantly higher values in March, April, and May associated with water column mixing (Fig. 7). During these mixing events, nutrient-rich, high salinity (~40.7) water ascend upward. Therefore, the Na/Ca of *T. clarkei* may serve as a proxy for water column stability, i.e., stratification vs. mixing.

The Ba/Ca in the three morpho-species show a relatively strong correlation with Na/Ca (0.74 and 0.82 in *T. clarkei* 'big' and 'encrusted' respectively, and 0.54 in *G. ruber albus*, the second highest ratio and exceeded only by the 0.57 of Pb/Ca). Ba/Ca is presumably unaffected by temperature, salinity, and pH (Hönisch et al., 2011). In non-spinose species, Ba/Ca typically shows positive relationships with productivity and potentially can be used as an indicator of river run-off (Fritz-Endres et al., 2022; Hönisch et al., 2011; Weldeab et al., 2014). Although floods in the catchment area of the GOA are brief and occur only few times each year (Katz et al., 2015), significant Ba/Ca perturbations during water column mixing may reflect nutrient-rich water admixing to the surface water (Fig. 8).

#### 5. Discussion:

## 5.1 Temporal and vertical dynamics of element/Ca in the GOA

Trace element incorporation into the calcium carbonate shells of planktic foraminifera during calcification is controlled by environmental and ecological factors in the water column such as





temperature, salinity, pH, the carbonate system, dust and terrigenous inputs, as well as whether a species harbor photosymbionts (Schiebel & Hemleben, 2017; and others). Shells of G. ruber albus, T. clarkei 'big' and T. clarkei 'encrusted' from the GOA show species-specific behavior and offer new insights into how these species respond to the vertical and temporal variations in the water column. For most elements, the smaller T. clarkei specimens display higher trace element ratios than the larger G. ruber albus, suggesting more efficient trace element incorporation to the shell or implying that its habitat deeper in the water column has conditions which result in higher trace element incorporation (Fig. 3). Some element ratios such as Mg/Ca, Sr/Ca, B/Ca, Na/Ca (for G. ruber albus) and Ba/Ca for both G. ruber albus and T. clarkei 'encrusted', show overlap between specimens from the water column and from core-tops (Fig. 3), confirming the robustness of downcore-based records allowing to further consider these element/Ca recorders of the water column as paleo-proxies.

While water depth likely influences element/Ca through variations in physical and chemical conditions, the observed inter-chamber variability (ICV) and element/Ca differences between species cannot be attributed to any single environmental parameter. Nonetheless, elements such as Al/Ca, Ti/Ca, Mn/Ca, and Fe/Ca for all species, and Mg/Ca, Sr/Ca, Na/Ca, and Ba/Ca for *G. ruber albus* alone, demonstrate consistent behavior across the water column, suggesting that depth-related factors do not significantly alter calcification mechanisms. This supports the use of pooled mean values for specimens over multiple sediment traps spread over depths (Levy et al., 2023). Interestingly, most element/Ca peak during water column mixing in March-April 2015 for all three morphotypes analyzed here, accompanied by larger ICV (Figs. 4-8). Mg/Ca in *G. ruber albus* and Sr/Ca in all three species show less pronounced excursions, while other trace element ratios (e.g., Co/Ca, U/Ca) exhibit more variability and more extreme values (Figs. S5 and S10). These observations can reflect: i) primary calcite structure alterations driven by environmental shifts and life cycle changes, ii) secondary mineralization (e.g., barite, Amorphous Calcium Carbonate, ACC) (Torres et al., 2010; Evans et al., 2020 and references therein), and iii) fluid inclusions within the shell structure (Gray et al., 2023).

All of these relationships do possibly concern the ontogenetic PF calcite, since SEM imaging of GOA specimens did not reveal secondary minerals or overgrowth on shell calcite (Levy et al., 2023). Moreover, the enrichment of multiple trace elements across species suggests that secondary minerals are unlikely to be responsible for these trends. Discrepancies between Na/Ca in plankton tow versus core-top samples in the Red Sea (Mezger et al., 2018), as well as higher Na/Ca values measured by LA-ICP-MS compared to solution ICP-MS, have been linked to early diagenesis of Na-enriched phases like spines, ACC, or fluid inclusions





(Gray et al., 2023). However, spines and ACC were ruled out for GOA samples, as all of the specimens had lost their spines before analysis and ACC was not detected via SEM. Given that most element/Ca in GOA shells are elevated relative to PF data from elsewhere, fluid inclusions may be a contributing factor (Gray et al., 2023). However, more research is required to investigate whether fluid inclusions are evident in PF shells from the GOA. In the absence of fluid inclusions, environmental changes, particularly during water column mixing, are considered to be the primary drivers of the observed trace element/Ca enrichments in the GOA.

5.2 Water column and sediment signal correlation: Implications to Paleoceanographic studies

Several element ratios (e.g., Al/Ca, Ti/Ca, Mn/Ca, Fe/Ca, Nd/Ca, U/Ca, Co/Ca, and Th/Ca) exhibit discrepancies between water column and core-top specimens (Fig. 3). Some, like Co/Ca, have lower values in surface sediment than the water column, while others, like Fe/Ca show higher values. Differences between sediment trap samples and core-top samples may stem from differential diagenetic processes that affect element/Ca in specimens taken from the water column and the sea floor. For example, diagenetic processes can lead to Mn accumulation and higher Mn/Ca in PF from the core top (McKenzie, 1980; Steiner et al., 2017). Conversely, core-top PF samples may show lower ratios due to the release of these metals into pore water over time (e.g., Co/Ca, Fig. 3i). This release can alter the elemental composition, potentially skewing paleoenvironmental reconstructions. Understanding these processes is crucial for accurately interpreting geochemical data from both sample types.

Despite the offsets of Al/Ca and Ti/Ca between core top and water column specimens, they nevertheless may be utilized to trace the origins of terrigenous inputs and identify periods of dust deposition in the geological record (Torfstein et al., 2017; Martinez-Garcia et al., 2011). Our data reveal significant seasonal excursions in Al/Ca and may demonstrate the use of Al/Ca and Ti/Ca in PF tests as proxies for dust or terrigenous input to the ocean (Fig. S3).

Core top element/Ca values that fall within the same range of values of the sediment trap specimens (Mg/Ca, Sr/Ca, B/Ca, Na/Ca, and Ba/Ca; Fig. 3) suggest that they could reflect water column conditions. The high temporal variability in many of these element/Ca data, together with the varying PF population dynamics throughout the year (Fig. 2) may be considered when approaching PF from sediment cores. Seasonal trends in element/Ca are often obscured by the spring mixing event. However, exceptions to this are observed in Mg/Ca for *G. ruber albus* (Fig. 4; Levy et al., 2023) and B/Ca for *T. clarkei* (Fig. 6), where clear seasonal patterns emerge. A key limitation of reconstructing past environments from element/Ca in PF





shells is the challenge of disentangling seasonal effects from other more episodic environmental signals. However, by identifying water column mixing events through positive element/Ca excursions and elevated ICV, which are evident across all three species (Figs. 4-8), it may be possible to identify the time intervals over which environmental changes are reconstructed. This could allow for more accurate reconstructions of shifts in temperature, carbonate chemistry, and nutrient availability during specific mixing events, improving our understanding of past ocean conditions.

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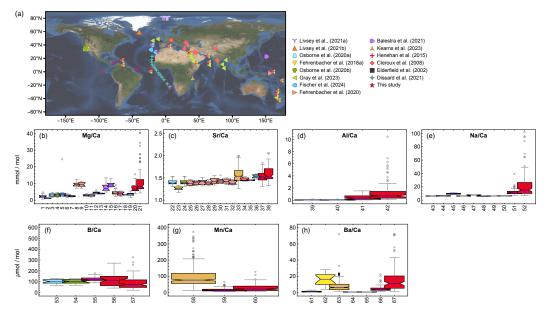
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5.3 Regional comparison of geochemical conditions and PF element/Ca

The Mg/Ca, Al/Ca, and Na/Ca in PF from the GOA generally exceed those reported from other regions (Fig. 12b – 14e). Sr/Ca values, while reaching up to 2.2 mmol/mol during spring, have an average of 1.5 mmol/mol, consistent with previous studies (Fig. 12c; Kisakürek et al., 2008; Cleroux et al., 2008; Elderfield et al., 2002; Brown & Elderfield, 1996; Dissard et al., 2021). The high Mg/Ca range in the GOA versus typical open-ocean levels (0.5-5 µmol/mol) is attributed to elevated salinity (~ 41 compared to mean ocean values of 34.7), which is also evident by the high Na/Ca. The high Al/Ca values and their large variation may be attributed to the close proximity of GOA to terrestrial input. Ba/Ca in the GOA are significantly higher than the values reported in prior studies from Atlantic Ocean core samples and culture experiments (Hönisch et al., 2011; Lea & Boyle, 1991), representing a roughly ten-fold difference. These discrepancies likely stem from two factors: (1) higher salinity in the GOA increases the availability of cations and trace element incorporation into foraminifera shells, and (2) higher-resolution measurements here which reveal chamber-specific elemental ratios, where early chambers (F-1 and F-2) exhibit higher values than final chambers, leading to more accurate, chamber-level data compared to bulk measurements. Combined, these factors explain the elevated values relative to global reports.







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Figure 12. Global comparison of major and trace element-to-calcium ratios. (a) sample global map, (b) Mg/Ca of N. pachyderma, G. bulloides, G. ruber white, N. dutertrei, O. universa, P. obliquiloculata, T. sacculifer and T. clarkei derived from various sources (plankton tows/nets, sediment traps, cores) and measured by Laser Ablation (LA)-ICP-MS, solution-ICP-MS (SOL) and Electron micro-probe analyses (EPMA). (c) Sr/Ca of G. bulloides, G. ruber white, N. dutertrei, O. universa, P. obliquiloculata, T. sacculifer and T. clarkei derived from various sources (plankton tows/nets, sediment traps, cores) and measured by LA-ICP-MS and solution-ICP-MS. (d) Al/Ca of G. bulloides, G. ruber white and T. clarkei derived from sediment traps and measured by LA-ICP-MS. (e) Na/Ca of G. ruber white and T. clarkei from various sources (plankton tows/nets, sediment traps, cores and cultured samples) and measured by LA-ICP-MS and solution-ICP-MS. (f) B/Ca of G. bulloides, G. ruber white and T. clarkei derived from sediment traps and measured by LA-ICP-MS. (g) Mn/Ca of G. ruber white and T. clarkei derived from cores and sediment traps and measured by LA-ICP-MS. (h) Ba/Ca of G. ruber white, N. dutertrei and T. clarkei derived from various sources (plankton tows/nets, sediment traps, cores and cultured samples) and measured by LA-ICP-MS. See table 1 for detailed description of methods.





#	Element/Ca	Reference	Species	Collecting	Measuring
				method	method
1	Mg/Ca	Livsey et al. (2021a)	N. pachyderma	Plankton	LA
				tows / nets	
2	Mg/Ca	Livsey et al. (2021b)	N. pachyderma	Sediment	LA
				traps	
3	Mg/Ca	Osborne et al. (2020)	G. bulloides	Sediment	LA
				trap	
4	Mg/Ca	Osborne et al. (2020b)	G. bulloides	Sediment	LA
				trap	
5	Mg/Ca	Fischer et al. (2024)	G. ruber	Plankton	LA
				tows / nets	
6	Mg/Ca	Fehrenbacher et al.	N. dutertrei	Core	LA
		(2020)			
7	Mg/Ca	Fehrenbacher et al.	N. dutertrei	Core	SOL
		2020			
8	Mg/Ca	Fehrenbacher et al.	O. universa	Core	LA
		(2020)			
9	Mg/Ca	Fehrenbacher et al.	O. universa	Core	SOL
		(2020)			
10	Mg/Ca	Fehrenbacher et al.	<i>P</i> .	Core	LA
		(2020)	obliquiloculata		
11	Mg/Ca	Fehrenbacher et al.	<i>P</i> .	Core	SOL
		(2020)	obliquiloculata		
12	Mg/Ca	Fehrenbacher et al.	T. sacculifer	Core	LA
		(2020)			
13	Mg/Ca	Fehrenbacher et al.	T. sacculifer	Core	SOL
		(2020)			
14	Mg/Ca	Balestra et al. (2021)	O. universa	Plankton	EPMA
				tows / nets	
15	Mg/Ca	Balestra et al. (2022)	O. universa	Plankton	EPMA
				tows / nets	
16	Mg/Ca	Kearns et al. (2023)	G. ruber	Core	LA





17	Mg/Ca	Cleroux et al. (2008)	G. ruber	Core	SOL
18	Mg/Ca	Elderfield et al.	G. ruber	Core	SOL
10	ivig/Ca	(2002)	G. Tuber	Corc	SOL
10	Mg/Ca	<u> </u>	Taganlifan	Plankton	LA
19	Mg/Ca	Dissard et al. (2021)	T. sacculifer		LA
				tows / nets	
20	Mg/Ca	This study	G. ruber	Sediment	LA
				trap	
21	Mg/Ca	This study	T. clarkei	Sediment	LA
				trap	
22	Sr/Ca	Osborne et al. (2020)	G. Bulloides	Sediment	LA
				trap	
23	Sr/Ca	Fehrenbacher et al.	N. dutertrei	Plankton	LA
		(2018a)		tows / nets	
24	Sr/Ca	Osborne et al. (2020b)	G. bulloides	Sediment	LA
				trap	
25	Sr/Ca	Fehrenbacher et al.	N. dutertrei	Core	LA
		(2020)			
26	Sr/Ca	Fehrenbacher et al.	N. dutertrei	Core	SOL
		(2020)			
27	Sr/Ca	Fehrenbacher et al.	O. universa	Core	LA
		(2020)			
28	Sr/Ca	Fehrenbacher et al.	O. universa	Core	SOL
		(2020)			
29	Sr/Ca	Fehrenbacher et al.	<i>P</i> .	Core	LA
		(2020)	obliquiloculata		
30	Sr/Ca	Fehrenbacher et al.	<i>P</i> .	Core	SOL
		(2020)	obliquiloculata		
31	Sr/Ca	Fehrenbacher et al.	T. sacculifer	Core	LA
		(2020)	<del></del>		
32	Sr/Ca	Fehrenbacher et al.	T. sacculifer	Core	SOL
	21/ 04	(2020)	1. Succunjei	2010	202
33	Sr/Ca	Kearns et al. (2023)	G. ruber	Core	LA
	Sr/Ca	Cleroux et al. (2008)	G. ruber	Core	SOL
34	SI/Ca	Cieroux et al. (2008)	G. ruber	Core	SOL

https://doi.org/10.5194/egusphere-2025-1929 Preprint. Discussion started: 12 June 2025 © Author(s) 2025. CC BY 4.0 License.





35	Sr/Ca	Elderfield et al. (2002)	G. ruber	Core	SOL
36	Sr/Ca	Dissard et al. (2021)	T. sacculifer	Plankton tows / nets	LA
37	Sr/Ca	This study	G. ruber	Sediment trap	LA
38	Sr/Ca	This study	T. clarkei	Sediment trap	LA
39	Al/Ca	Osborne et al. (2020)	G. Bulloides	Sediment trap	LA
40	Al/Ca	Osborne et al. (2020b)	G. bulloides	Sediment trap	LA
41	Al/Ca	This study	G. ruber	Sediment trap	LA
42	Al/Ca	This study	T. clarkei	Sediment trap	LA
43	Na/Ca	Gray et al. (2023)	G. ruber	Core	SOL
44	Na/Ca	Gray et al. (2023)	G. ruber	Cultured	SOL
45	Na/Ca	Gray et al. (2023)	G. ruber	Plankton tows / nets	LA
46	Na/Ca	Gray et al. (2023)	G. ruber	Plankton tows / nets	SOL
47	Na/Ca	Gray et al. (2023)	G. ruber	Sediment trap	LA
48	Na/Ca	Gray et al. (2023)	G. ruber	Sediment trap	SOL
49	Na/Ca	Gray et al. (2023)	G. ruber mixed	Core	SOL
50	Na/Ca	Gray et al. (2023)	G. ruber sl	Core	SOL
51	Na/Ca	This study	G. ruber	Sediment trap	LA
52	Na/Ca	This study	T. clarkei	Sediment trap	LA





52	D/C	0.1 (2020)	C D 11 : 1	G 1: 4	т .
53	B/Ca	Osborne et al. (2020)	G. Bulloides	Sediment	LA
				trap	
54	B/Ca	Osborne et al. (2020b)	G. Bulloides	Sediment	LA
				trap	
55	B/Ca	Henehan et al. (2015)	G. ruber	Core	SOL
56	B/Ca	This study	G. ruber	Sediment	LA
				trap	
57	B/Ca	This study	T. clarkei	Sediment	LA
				trap	
58	Mn/Ca	Kearns et al. (2023)	G. ruber	Core	LA
59	Mn/Ca	This study	G. ruber	Sediment	LA
				trap	
60	Mn/Ca	This study	T. clarkei	Sediment	LA
				trap	
61	Ba/Ca	Fehrenbacher et al.	N. dutertrei	Cultured	LA
		(2018a)			
62	Ba/Ca	Fehrenbacher et al.	N. dutertrei	Plankton	LA
		(2018a)		tows / nets	
63	Ba/Ca	Kearns et al. (2023)	G. ruber	Core	LA
64	Ba/Ca	Hönisch et al. (2011)	G. bulloides	Cultured	SOL
65	Ba/Ca	Hönisch et al. (2011)	O. universa	Cultured	SOL
66	Ba/Ca	This study	G. ruber	Sediment	LA
				trap	
67	Ba/Ca	This study	T. clarkei	Sediment	LA
				trap	
		1	1	1	

Table 1: detailed description of the different species, measurement methods and sample origin used for the compilation in figure 12. LA stands for Laser Ablation (LA)-ICP-MS, SOL is solution-ICP-MS and EPMA is Electron micro-probe analyses.

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6. Summary and conclusions:



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Data availability

Author contributions

added following acceptance).



We investigated the effects of inter-chamber variability on the proxy systematics in the hyper saline oligotrophic GOA using single chamber LA ICP-MS analysis measured on two fluxdominating planktic foraminifer (PF) species G. ruber albus and T. clarkei with its two phenotypes 'big' and 'encrusted'. We observed how element/Ca varies in PF chambers as a function of environmental changes in order to then be used as proxies for past oceanic and climatic reconstruction. The results show that some element/Ca exhibit temporal and seasonal variations related to environmental conditions in the water column such as Mg/Ca in G. ruber albus as a temperature proxy, and B/Ca in T. clarkei as a proxy of pH. Although other element/Ca values display more limited variability (e.g., Na/Ca) they may still be of use as paleo-proxies when combined in global calibration studies. Water column mixing has been shown to have a significant effect of element/Ca positive excursions in the analyzed G. ruber albus, and two T. clarkei morphotypes, which may limit the use of some element ratios as proxies, or alternatively, be used as a proxy for water column mixing. Generally, pooled-mean values of element/Ca in the PF tests in the GOA are speciesspecific and element-specific, and are elevated compared to other regions (e.g., Mg/Ca, Al/Ca, Na/Ca). However, the final chamber F0 is different in comparison to the preceding chambers F-1 and F-2, suggesting that the element composition of F0 may be biased and unreliable in terms of recording environmental conditions. Our findings indicate that high-resolution analytical techniques, such as LA ICP-MS enable studying single chamber compositions and variations. Although pooled mean values of specimens over various water depths are recommended for their incorporation as proxies, ICV can also be used as a tracer of environmental factors. Exploring different biochemical or physiological mechanisms which are responsible for the element/Ca variations between species and chambers are critical to shed light on how element/Ca are incorporated to the PF shells. Despite these limitations, the results provide valuable insights into the complex behavior of element/Ca in PF shells.

Tabular supplementary data generated in this study can be found at PANGAEA (DOI: will be

https://doi.org/10.5194/egusphere-2025-1929 Preprint. Discussion started: 12 June 2025 © Author(s) 2025. CC BY 4.0 License.



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648 NL, AT, and RS designed the study; NL, BS, UW, and KPJ, performed the measurements; 649 NL, NC, AT, and RS analyzed the data; NL, RS and AT wrote the manuscript draft; NL, RS, 650 AT and GH reviewed and edited the manuscript. 651 652 The authors declare that they have no conflict of interest. 653 654 Acknowledgments We wish to acknowledge the IUI marine crew and B. Yarden for their assistance in field work 655 656 and sample handling. The National Monitoring Program are thanked for their support and sharing results and E. Levy for fruitful discussions. We are thankful for the three anonymous 657 658 reviewers whom their comments significantly improved this manuscript. This work was 659 supported by Israel Science Foundation grant 834/19 (to AT), a Minerva PhD Fellowship 660 stipend (to NL) and a scholarship from the Advance School for Environmental Studies, HUJI (to NL). 661 662





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