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Sodium incorporation in foraminiferal calcite: An evaluation of the Na/Ca salinity proxy and evidence for multiple Na-bearing phases



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ABSTRACT

The ratio of sodium to calcium (Na/Ca) in foraminiferal calcite has been proposed as a proxy for salinity, yet relatively little is known about the incorporation of sodium into the shells of foraminifera. Ongoing debates include the location of Na in the calcite crystal lattice, the possibility that at least some Na might be complexed with organics, and the influence of spines/spine bases. We present new Na/Ca measurements, determined using both solution and laser ablation ICP-MS, of the planktonic foraminifera *Globigerinoides ruber* (white) from plankton tows and sediment traps spanning a wide salinity range (32.5–40.7 salinity units), laboratory cultures under varying carbonate chemistry, and globally-distributed core-top samples. Our results show that Na/Ca in recently living foraminifera measured by laser ablation ICP-MS is elevated by up to 5 mmol/mol (~85%) relative to the same samples measured by solution ICP-MS (the same comparison for Mg/Ca shows excellent agreement between the techniques). Na/Ca in recently living foraminifera measured by laser ablation ICP-MS displays a significant relationship with salinity above ~36 salinity units with a slope of ~0.7 mmol/mol/salinity unit; however, only a weak relationship is observed between salinity and Na/Ca measured by solution ICP-MS. We propose that Na is incorporated in at least two discrete phases; a primary phase within the CaCO₃ mineral, and a (or likely multiple) secondary phase(s). Possibilities for these secondary phases include residual metastable CaCO₃, fluid inclusions, high Na/Ca spine bases, and organics. These secondary phases contribute to spatially-resolved analyses (i.e. laser ablation ICP-MS) of recently living foraminifera but are removed by crushing/oxidative cleaning for solution ICP-MS, and during early diagenesis, as evidenced by the agreement between laser analysis of core-top samples and Na/Ca measured by solution. The amount of one of these secondary phases, or the amount of Na within this phase, appears to vary as a function of salinity, and is likely the principal driver of the previously observed steep Na/Ca-salinity relationship in recently living foraminifera analysed by laser ablation. Overall, we find salinity, temperature, carbonate chemistry, and bottom water saturation state (Ω_{calcite}) all have a significant but relatively weak effect on Na/Ca in the primary calcite phase. As such, Na/Ca in planktonic foraminifera recovered from sediment cores is unlikely to find widespread utility as a salinity proxy.

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1. Introduction

Along with magnesium, sodium (Na) is one of the two most abundant cations incorporated in foraminiferal calcite (mol/mol), with a typical concentration of ~1500 ppm in planktonic (Bender et al., 1975; Delaney et al., 1985) and benthic (Wit et al., 2013; de Nooijer et al., 2014; Hauzer et al., 2018) foraminifera. Understanding what controls the incorporation of Na into the shells of

foraminifera has recently received more attention following several studies arguing that the Na/Ca of biogenic marine carbonates may have utility as a salinity proxy (e.g. Wit et al., 2013), or as a means of reconstructing past variations in seawater [Ca] over longer geological timescales (Hauzer et al., 2018).

The use of Na/Ca in biogenic calcites to trace past salinity variations was first suggested by Rucker & Valentine (1961) and Gordon et al. (1970), who analysed oysters and barnacle shells, respectively. More recently, detailed laboratory culture experiments such as those of Wit et al. (2013) found a positive Na/Ca-salinity relationship in the benthic foraminifera *Ammonia tepida*, with a slope of 0.22 mmol mol⁻¹ per salinity unit (throughout we refer to salinity units on the Practical Scale). However, as discussed below, subsequent studies have reported different Na/Ca-salinity slopes even within the same species when other experimental parameters are varied (Geerken et al., 2018), indicating that Na incorporation into foraminifera is unlikely to be a simple function of salinity alone.

Recent studies of Na/Ca in the planktonic foraminifers *Globigerinoides ruber* and *Trilobatus sacculifer* resulted in Na/Ca-salinity sensitivities that differ by approximately one order of magnitude, as well as very different absolute Na/Ca values. The study of Allen et al. (2016), in which *G. ruber* (pink) were cultured under varying salinity, yielded Na/Ca values of ~6–7 mmol mol⁻¹ and a Na/Ca-salinity sensitivity of ~0.07 mmol mol⁻¹ per salinity unit. In contrast, the study of Mezger et al. (2016) based on *G. ruber* (white) collected along a transect of plankton tows along a large salinity gradient resulted in higher overall Na/Ca values (~8–11 mmol mol⁻¹), and a salinity sensitivity of 0.66 mmol mol⁻¹ per salinity unit, one order of magnitude higher than Allen et al. (2016). The large differences in both the absolute Na/Ca values and the derived sensitivities of Na/Ca to salinity in these studies indicates there are other major influences on Na incorporation into foraminiferal shells that are not understood. Comparative *T. sacculifer* data from these two studies indicate that the discrepancy discussed above is apparent across multiple species of planktonic foraminifera. Furthermore, Bertlich et al. (2018) report an intermediate slope for *T. sacculifer*, closer to that of the cultured benthic foraminifera ($m = 0.12$). Lastly, adding to the complexity of this emerging picture, Mezger et al. (2018) report no significant Na/Ca-salinity relationship for either *T. sacculifer* or *G. ruber* in core-top samples from the Red Sea, whereas a trend between Na/Ca salinity had previously been observed in plankton tow samples taken along the same transect. Mezger et al. (2018) suggested that these differences might relate to the analysis of spines in studies which collected samples via plankton tow, which are typically not present in core-top shells; however, the presence/absence of spines would not explain the difference between the slope of Bertlich et al. (2018) and the absence of a slope reported by Allen et al. (2016), as the analysis was carried out using an Electron Probe Microanalyzer (EPMA), thus largely avoiding spines.

An alternative explanation for the disagreement between the existing planktonic foraminifera Na/Ca data is that Mezger et al. (2016), Allen et al. (2016), and Bertlich et al. (2018) all use different analytical techniques, reporting results from laser-ablation ICP-MS, solution ICP-MS, and EPMA plus ICP-OES, respectively. Uncertainty remains over both where Na is situated in the calcite lattice, and whether significant amounts of Na are present in more than one phase within the shells of foraminifera. It is possible that the different pre-analytical cleaning procedures, sampling techniques, and standardisation between these methodologies result in systematic offsets. For example, different domains may be sampled to differing extents, or organic material or ions situated in interstitial sites may be removed or leached to differing degrees prior to analysis.

Based on inorganic calcite precipitation experiments, Kitano et al. (1975), White (1978), and Okumura and Kitano (1986) suggested that as a monovalent cation, Na may occupy an interstitial

site, rather than substituting for Ca within the calcite lattice. More recently, the location of Na in interstitial sites was questioned by Yoshimura et al. (2017) who suggested divalent substitution of Na⁺ in place of Ca²⁺ into the carbonate lattice based on synchrotron X-ray spectroscopy. Finally, Branson et al. (2016) demonstrated that the primary organic sheet within the tests of foraminifera is enriched in Na, raising the possibility that a significant amount of the Na measured in foraminifera is bound to or associated with intra-shell organic material.

Here, we address the discrepancies in the relationship between foraminiferal Na/Ca and salinity in existing studies, and whether the Na/Ca of fossil planktonic foraminifera reliably reflect variations in salinity. We compare the results of paired laser-ablation and solution ICP-MS measurements of Na/Ca in cultured, sediment trap, plankton tow, and core top samples of *G. ruber* (white). By analysing sample splits using both laser-ablation and solution ICP-MS, and by constraining the effect of potential analytical biases between the techniques, we assess whether Na in foraminiferal tests may be hosted in multiple phases, before determining the environmental controls on Na incorporation into these phases.

2. Materials and methods

We present new Na/Ca data from *G. ruber* (white) collected by a series of sediment traps and plankton tows from the Bay of Bengal, Arabian Sea, and Red Sea, that span a salinity gradient from 32.5 to 40.7 (Fig. 1). A subset of these samples (Table 1) was measured by both solution ICP-MS and laser ablation ICP-MS (LA-ICP-MS) in order to determine whether the differences in results between previous studies are analytically derived (we note that although derived from the same samples, different populations of individual foraminifera were analysed by the two techniques). We also present the results of a solution-laser ICP-MS comparison experiment, investigating to what extent differences between LA and solution ICP-MS can arise as a consequence of possible analytical biases resulting from standardisation/matrix effects. In addition, we present data of *G. ruber* (white) cultured under varying carbonate chemistry, as well as globally distributed core-top samples in order to assess any potential effect of seawater temperature, carbonate chemistry, and post-depositional dissolution on Na/Ca.

2.1. Arabian Sea and Bay of Bengal sediment trap samples

We utilised 51 samples from sediment trap deployments NBBT09 (17.383°N, 89.700°E; 1450 m water depth), CBBT06 (11.033°N, 84.433°E; 899 m sediment trap depth), SBBT09 (5.400°N, 86.767°E; 886 m sediment trap depth), and JGOFS AS02-M5 (10.003°N, 65.005°E; 2363 m sediment trap depth) (Honjo et al., 2000; Unger et al., 2003). For each of the samples, salinity was calculated using WOA 2013 monthly climatologies (Locarnini et al., 2013), assuming a *G. ruber* habitat depth of 0–50 m. These sediment trap deployments form a transect spanning a salinity gradient of 32.5 to 36.5 (Fig. 1). Further details about these samples and the method used to calculate salinity are given in Gray et al. (2018). The sample locations are given in Table S1 and the hydrographic data, morphotype, size fraction, as well as the Na/Ca values are given in Table S2.

2.2. Gulf of Eilat tows

Foraminifera were collected from the northernmost Red Sea (Gulf of Eilat) at 20 m water depth by plankton drift tows at a location with a bathymetry of >300 m, during January 2010 and October 2013. The salinity of the northernmost Gulf of Eilat at the time of collection ranged between 40.32 and 40.65. Foraminifera

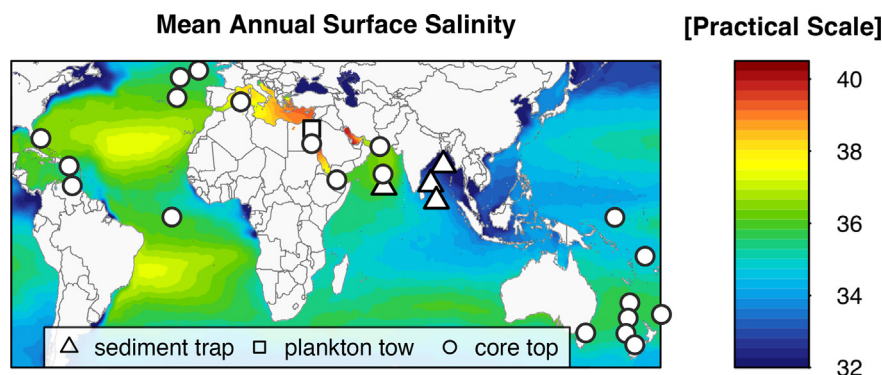


Fig. 1. Location of sediment trap, core-top, and plankton tow samples used in this study overlaid on WOA18 mean annual salinity on the Practical Scale (Zweng et al., 2018). See Table S1 for sample locations.

Table 1
Summary of samples with paired solution and laser ablation ICP-MS Na/Ca analysis.

Sample	Type	Salinity*	Solution-ICP-MS	LA-ICP-MS	n
			Na/Ca (mmol/mol) ¹	Na/Ca (mmol/mol) ²	
CBBT06	Trap	33.7 ± 0.1	5.8 ± 0.1	7.7 ± 0.7	24
SBBT09	Trap	34.2 ± 0.1	5.9 ± 0.2	7.6 ± 0.5	20
JGOFS AS02-M5	Trap	36.1 ± 0.3	6.4 ± 0.2	7.6 ± 0.5	31
Gulf of Eilat	Tow	40.5 ± 0.2	6.2 ± 0.2	10.3 ± 1.70	21
Culture [‡]	Culture	37.0	5.8 ± 0.2	8.5 ± 1.15	118
OCE25-50BC [†]	Coretop	36.5	5.4 ± 0.1	5.7 ± 0.3	40

The sediment trap/plankton tow data are for *G. ruber sensu stricto* from the 200–400 μm size fraction.

* Salinity (practical scale) is the mean value for each sediment trap/plankton tow; see Table S2 for salinity of individual trap/tow samples.

¹ Na/Ca is the mean value for each sediment trap/plankton tow/set of cultures; see Table S2 for Na/Ca of individual trap/tow/culture samples. Reported uncertainties are ±1σ sample variance.

² Na/Ca is the mean value for each sediment trap/plankton tow/set of cultures. Reported uncertainties are ±1σ population variance.

[†] Sample cleaned following solution protocol before analysis. n for this sample refers to the number of ablation pits in the homogenised foram standard, rather than number of foraminifera.

[‡] This LA data point was previously published (Evans et al., 2018).

were immediately picked from plankton concentrates to recovery dishes, the primary purpose of which was to identify specimens suitable for culturing (see Section 2.3). Those that did not fully recover were retained as a set of control specimens for both LA and solution ICP-MS analysis. Because specimens that did not recover were typically those that lost their spines during collection and did not re-grow them during recovery, these analyses represent *G. ruber* without spines (see supplementary materials). The sample locations are given in Table S1 and the hydrographic data are given in Table S2.

2.3. Core-top samples

A global suite of core-top samples were selected from the Atlantic, Pacific, and Indian Oceans, as well as the western Mediterranean Sea. The sample set spans a broad range of hydrographic conditions and is similar to that of Henehan et al. (2015). SST, SSS, and pre-industrial pH/CO₂[−] were calculated using the dataset of Takahashi et al. (2009) as described in detail in Henehan et al. (2015). Where possible, multiple size fractions and different morphotypes (*sensu stricto* versus *sensu lato*) were analysed from the same site; we find no systematic influence of size ($p > 0.7$) and a small but significant (0.3 ± 0.15 mmol, 95% CI) offset between the morphotypes, with values in *sensu lato* around 5% higher than *sensu stricto*. While these factors likely contribute to some of the apparent ‘noise’ in the coretop data (Fig. 2), they are not discussed further in the manuscript. The sample locations are given in Table S1 and the hydrographic data are given in Table S2.

2.4. Laser-solution ICP-MS comparison

A box-core was used in order to ascertain whether there is a substantial analytical artefact on Na/Ca measured by LA-ICP-MS as compared to solution ICP-MS. The purpose of the box-core material is to provide a homogenous cleaned foraminiferal ‘standard’ that we could measure by both techniques in order to test whether there is a substantial analytical offset between the two techniques resulting from differences in standardisation and/or matrix effects during mass spectrometry; by ruling out a substantial analytical bias due to the mass spectrometry, it follows that the differences observed between LA and solution analysis of recently living foraminifera must result from the different preparation of the samples, as this is the only other difference between the methods. We use a boxcore to provide sufficient material for this test, which requires a large number of individuals. Several hundred *G. ruber* from the upper 2 cm of box-core OCE205-50BC (26.23°N, 77.7°W, 817 m water depth; Gray et al., 2014) were first crushed and cleaned following the solution protocol outlined in Section 2.6. The cleaned sample was then divided into two aliquots; the first was analysed following the solution ICP-MS method outlined in Section 2.6.1. The second aliquot was set in Struers EpoFix epoxy resin, and analysed by laser ablation, as outlined in Section 2.7. Although the resin may have filled pores during mounting and thus contributed to the analysis, it has been previously shown that this resin is reasonably clean with respect to Na, with ablation of a pure resin end-member sample yielding Na counts close to the gas blank (Evans and Müller, 2013). The large sample size allowed us to make multiple determinations by both LA (n = 40 spots/depth

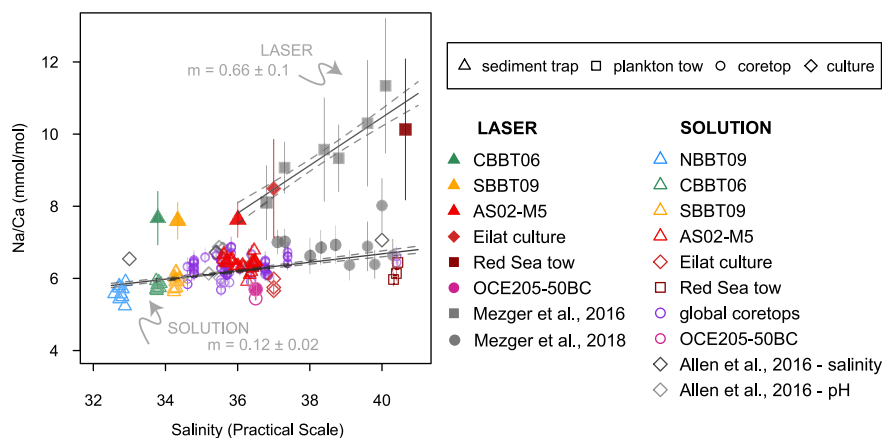


Fig. 2. Na/Ca in tests of *G. ruber* versus salinity, as measured by laser-ablation (filled symbols) and solution (open symbols) ICP-MS. Grey symbols are previously published; coloured symbols are from this study. Error bars show $\pm 1\sigma$ sample variability. Na/Ca measured by laser ablation shows a high sensitivity to salinity (above ~ 36 SU, slope = 0.66), whereas a much lower sensitivity to salinity is observed between Na/Ca measured by solution ICP-MS (slope = 0.12). Note that the coretop LA data (grey filled circles; Mezger et al., 2018) are not included in either of the regressions, but fall on the regression line of the solution data. The LA data of sample OCE205-50BC differs from the rest of the LA data reported here as this sample was first crushed and cleaned as per the solution ICP-MS method (see text for details), whereas the other samples were analysed as profiles through intact specimens. Note that the data of Allen et al. (2016) are for *G. ruber* (pink), all other data are for *G. ruber* (white). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

profiles, each integrating multiple fragments from multiple individuals) and solution ICP-MS ($n = 15$ aliquots of $\sim 100 \mu\text{g CaCO}_3$, each integrating multiple fragments from multiple individuals) to reduce analytical uncertainties and thus accurately determine any analytical bias due to the differences in mass spectrometry between the techniques. We determine the Na/Ca to be 5.44 ± 0.04 by solution ICP-MS and 5.70 ± 0.29 by LA-ICP-MS (see section 2.6 and 2.7 for analytical methods) indicating no significant analytical bias between the mass spectrometry techniques ($<5\%$ and within analytical uncertainty).

2.5. Culture experiments

To assess whether seawater carbonate chemistry exerts an effect on Na incorporation into *G. ruber* (white), foraminifera were cultured under a range of pH (for the primary objective of boron isotope analysis), as described in Henehan et al. (2013). Briefly, experimental seawater was prepared in large (≥ 5 l) batches to maintain consistency between culture flasks and stored in the dark in refrigerated air-tight containers. Seawater pH was modified by titration of either HCl or NaOH, such that pH, $[\text{CO}_3^{2-}]$, and alkalinity co-varied in these experiments. Seawater pH varied between 7.56 and 8.18 (total scale) and $[\text{CO}_3^{2-}]$ varied between 79 and 297 μM , covering much of the range of the modern surface ocean. In all cases, individual foraminifera were transferred to 120 ml glass (borosilicate) culture jars following recovery, sealed with ground-glass stoppers to prevent evaporation and gas exchange, and placed into simultaneously cooled and heated temperature-controlled circulating water baths. The baths were lit by metal halide lamps to give a light intensity of $\sim 200 \mu\text{mol photons m}^{-2} \text{s}^{-1}$ on a 13-hour light and 11-hour dark cycle. Foraminifera were fed a juvenile brine shrimp (*Artemia*) daily until gametogenesis took place, typically in 1–2 weeks. Following gametogenesis, foraminifera were rinsed in deionised water and dried. Mass balance calculations to determine the Na/Ca of CaCO_3 grown in culture follow Henehan et al. (2013, 2015).

2.6. Solution ICP-MS analysis

2.6.1. Sediment trap samples

Foraminifera were cleaned following a modified version of the method of Pak et al. (2004) which includes an extended oxidative

step (with 1% H_2O_2) to remove the additional organic matter associated with recently-living material; the oxidising solution was heated to 80 °C and samples were exposed to the reagents for 3x20 mins. Foraminiferal cleaning protocols typically use 0.1 M NaOH to buffer the hydrogen peroxide; instead, in this study we used 0.1 M NH_4OH (pH ~ 11) in order to avoid the potential of Na contamination from NaOH. Before dissolution samples were exposed to a weak acid leach using 50 μl of 0.001 M HNO_3 . Acidified samples were analysed using a magnetic-sector ICP-MS (Thermo Element XR) at Rutgers University. Na/Ca ratios were determined by comparison with matrix matched, gravimetrically spiked standard. Further details of the method are given in Gray et al. (2018). Method reproducibility, evaluated by repeated measurements of gravimetrically spiked consistency standards with a Na/Ca similar to *G. ruber* (w) was ~ 0.05 mmol/mol ($\sim 1\%$) (2σ) during the period of analysis. Six of the foraminiferal samples ($\sim 12\%$) were split into replicates and cleaned and analysed separately, with a typical reproducibility of 0.13 mmol/mol (2.0%) (2σ). The interlaboratory standardisation comparison of Stewart et al. (2020) shows interlaboratory variability of $\pm 4\%$ (1σ) for Na/Ca values in NIST standard RM 8301 (Foram), which we take as the uncertainty in solution Na/Ca when comparing values between labs. While the present analyses pre-dates the availability of this standard, we suggest future studies reporting solution analysis of foraminiferal Na/Ca (or any element/Ca) report values for this standard. All data are given in Table S2.

2.6.2. Core-top, plankton tow, and culture samples

Na/Ca was measured on an aliquot of solutions prepared from 1 to 3 mg of cleaned, dissolved planktic foraminifera for boron isotope analysis [published elsewhere; see Henehan et al. (2013, 2015)]. Sample cleaning was as described in these publications, and is based on the approach of Barker et al. (2003). Briefly, tests were crushed between two clean glass slides, ultrasonicated and rinsed at least five times with Milli-Q ultrapure water (18.2 M Ω) and oxidatively cleaned (1% H_2O_2 in 0.1 M NH_4OH in a water bath at 80 °C; 3×20 –30 min treatments of 250–400 μl for tow and culture material, 3×5 mins of 250 μl for core-top material). Samples were briefly leached in 0.0005 M HNO_3 and rinsed three further times with Milli-Q. Samples were then dissolved in 0.5 M HNO_3 and centrifuged, before an aliquot was taken for ICP-MS analysis using a Thermo Element 2 ICP-MS at the University of Southampton

(core-tops and sediment traps) or the Bristol Isotope Group (cultures and tows). Long-term reproducibility of Na/Ca measurements was better than 3% (2σ), based on repeat measurements of in-house consistency standards ranging from 5.3 to 15.9 mmol/mol. Analysis of the same consistency standards during these analytical runs ensured no analytical bias between these two laboratories, with an offset of <2%. All data are given in Table S2.

2.7. Laser ablation ICP-MS analysis

Sediment trap and plankton tow foraminifera were oxidatively cleaned to remove organic material on the outside of the test walls. Individual shells were ultrasonicated for one minute in 1% H_2O_2 and then retained in that solution until no visible organic material remained under a light microscope (~ 15 – 60 min). Subsequently, three further one-minute ultrasonication steps were performed in deionised water, which was replaced each time in order to ensure no Na contamination, followed by a final rinse.

LA-ICP-MS measurements were performed using the RESOLUTION M-50 prototype LA system at Royal Holloway University of London (Müller et al., 2009) coupled to an Agilent 8900 QQQ-ICP-MS. LA was performed via slow depth profiling (44 μm spot size, 2 Hz repetition rate) to maximise spatial resolution through the chamber wall. The laser energy was ~ 3 J cm^{-2} on both the samples and standards, and gas flow rates through the two-volume Laurin ablation cell were always 850 ml min^{-1} He and 8.5 ml min^{-1} H_2 . Primary standardisation was performed using NIST SRM612, except in the case of Mg/Ca (NIST610), with accuracy and precision assessed through analyses of either NIST SRM610 or the MACS-3 pressed powder carbonate. Data reduction was performed using an in-house Matlab script (Evans and Müller, 2018), which: (i) subtracts the mean of the adjacent gas blanks from each analysis, (ii) ratios all data to the internal standard (^{43}Ca), (iii) calculates synthetic (regression-based) down-hole element/Ca fractionation profiles using the mean of all NIST SRM61x analyses in a given sequence, and iv) standardises the sample data via line-by-line (line = ICP-MS sweep number) comparison of the raw ratios to these synthetic standard profiles. The data are given in Table S2.

Trace element data quality of this system is discussed in detail in Evans and Müller (2018). In that study, MACS-3 Na/Ca accuracy and long-term (~ 5 year) precision are 1.3% and 12.7% respectively ($n = 13$), whilst NIST SRM610 calibrated to NIST SRM612 yield an accuracy and precision of 0.8% and 2.5% respectively ($n = 372$). Because the original pressed powder version of MACS-3 is known to be heterogeneous with respect to many trace elements (Jochum et al., 2012; Evans and Müller, 2018), we additionally analysed the nanopellet version of MACS-3 (Garbe-Schönberg and Müller, 2014) in the same sessions as the foraminifera data reported here. Based on 26 repeat measurements and the MACS-3 reference values of Jochum et al. (2019), Na/Ca accuracy and precision were -4.4% and 3.7% respectively when using NIST SRM610 as the calibration standard and -5.6% and 3.7% when using NIST SRM612. This comparison strongly suggests that the relatively poor long-term reproducibility of the pressed powder version of MACS-3 (used by Evans and Müller, 2018) is driven by heterogeneity in the standard. The reproducibility of our measurements of MACS-3np conducted in the same sessions as the foraminifera is 3.7% , which we consider as representative of the analytical uncertainties. To represent the heterogeneity in each foraminiferal sample, we report the $\pm 1\sigma$ population variance.

Long-term (5-year) $^{25}\text{Mg/Ca}$ accuracy and precision determined in the same way (Evans & Müller, 2018) was 2.3% and 7.8% respectively when using NIST SRM610 as the calibration standard, based on the pressed powder version of MACS-3, the reference values of Jochum et al. (2019), and the NIST SRM610 [Mg] of Pearce et al. (1997), following Evans & Müller (2018). Based on the nanopellet

version of MACS-3 analysed in the same sessions as the foraminifera, $^{25}\text{Mg/Ca}$ NIST SRM610-standardised accuracy and precision were 9.1% and 2.5% , respectively.

3. Results

3.1. Foraminiferal Na/Ca data

The newly generated Na/Ca data of foraminifera collected by sediment trap, plankton tow, coretop, and grown in laboratory culture, measured both by solution and laser ablation ICP-MS are shown in Fig. 2. The data presented here are shown alongside the published laser ablation ICP-MS plankton tow data of Mezger et al. (2016), and the solution ICP-MS laboratory culture data of Allen et al. (2016). We find that the Na/Ca values measured by laser ablation are significantly higher ($p < 10^{-16}$) than those of the same samples measured by solution across the salinity range considered; this difference increases from ~ 2 mmol/mol ($\sim 30\%$) below salinities of ~ 36 to ~ 5 mmol/mol ($\sim 85\%$) at a salinity of ~ 40 , with the offset between solution and laser-ablation Na/Ca scaling with salinity above ~ 36 (Fig. 2.; Table 1). There is a strong correlation between Na/Ca and salinity in the laser ablation data at salinities above ~ 36 ($\text{Na/Ca} = 0.66 \pm 0.21 \times S_p - 16.07 \pm 8.11$; $R^2 = 0.85$, $\text{RSE} = 0.48$; $p < 0.001$, coefficient uncertainties are 2SE, where where S_p is salinity on the practical scale), but no significant relationship below salinities of 36. In contrast, we find only a weak relationship between Na/Ca and salinity in the solution ICP-MS data across the entire salinity range.

Pooling the sediment trap, plankton tow, culture, and coretop data analysed by solution ICP-MS together, yields the following relationship between Na/Ca and salinity:

$$\text{Na/Ca} = 0.12 \pm 0.03 \times S_p + 2.00 \pm 1.23 \quad (1)$$

$R^2 = 0.30$, $p < 0.001$, $\text{RSE} = 0.31$, coefficient uncertainties are 2SE.

Incorporating temperature and carbonate chemistry into a multiple linear least-squares regression model, yields the following equation, with a slightly lower salinity sensitivity than Eq. (1):

$$\text{Na/Ca} = 0.076 \pm 0.038 S_p - 0.029 \pm 0.018T + 0.0022 \pm 0.0013[\text{CO}_3^{2-}] + 3.68 \pm 1.50 \quad (2)$$

$R^2 = 0.38$, $\text{RSE} = 0.29$, where S_p is salinity on the practical scale, T is temperature in $^\circ\text{C}$, and $[\text{CO}_3^{2-}]$ is surface ocean carbonate ion concentration in $\mu\text{mol/kg}$. The terms for temperature ($p < 0.01$), salinity ($p < 0.001$), and carbonate ion ($p < 0.01$) are all significant in the regression. Using only our own sediment trap, plankton tow, and culture data we arrive at a very similar coefficient for salinity of 0.089 ± 0.042 ($p < 0.001$) as with the wider dataset, indicating the salinity sensitivity is not likely to be biased by any differences in cleaning methods between different solution ICP-MS studies (Bonnin et al. 2019), nor any effects of dissolution on coretop samples. Using only the data cultured under varying carbonate chemistry we find a similar sensitivity to $[\text{CO}_3^{2-}]$ as with the wider dataset (Fig. 3c), although this trend is not significant (likely due to the combination of a relatively low sensitivity and few number of datapoints).

To investigate the effects of post-depositional dissolution we use our coretop dataset. We regress the residual Na/Ca predicted from Eq. (2) (i.e. the portion of the coretop Na/Ca data that is unexplained by surface salinity, temperature, and $[\text{CO}_3^{2-}]$) against bottom water Ω_{calcite} . Following Tierney et al. (2019), we parameterise this as $\Omega_{\text{calcite}}^{-2}$ in the regression, such that Na/Ca becomes a linear function of Ω_{calcite} . Our results show a significant influence of bottom water Ω_{calcite} , with a sensitivity of -0.28 ± 0.17 mmol/mol given a one unit change in $\Omega_{\text{calcite}}^{-2}$ ($p < 0.01$; Fig. 3d). While significant, the sensitivity is weak, with the

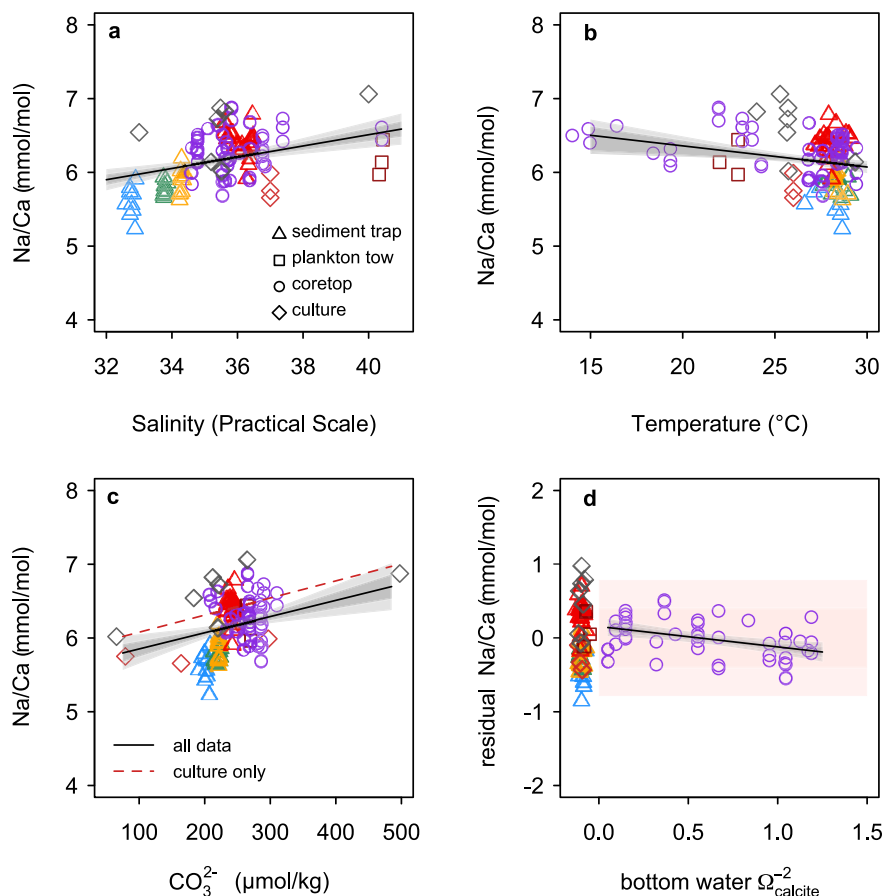


Fig. 3. *G. ruber* Na/Ca analysed by solution ICP-MS as a function of (a) salinity (b) temperature (c) CO_3^{2-} (d) residual Na/Ca versus bottom water $\Omega_{\text{calcite}}^{-2}$ (note the culture, plankton tow, and sediment trap data are not included in this regression). The solid line shows the best fit with the 95% CI represented by the shaded envelope. The regressions in a-c are for the entire dataset (cultures, plankton tows, sediment traps, coretops), except in the case of the red line in panel c, which shows regressions of the culture data only. In panel (d) the 1σ and 2σ variability of the 'pristine' (i.e. non-coretop) samples is shown by the pink shaded area. See Fig. 2 for complete symbol legend. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

predicted change in Na/Ca across the entire range in Ω_{calcite} within the coretop dataset (0.9–4.5) falling within the $\pm 1\sigma$ range of the 'pristine' sediment trap/plankton tow/culture samples (Fig. 3d). This result is consistent with the findings of Lorens et al. (1977) that post-deposition dissolution is not a dominant control on Na/Ca (see also Bertlich et al., 2018).

In Eqs. (1) and (2), the Na/Ca-salinity slope is substantially lower than in the laser ablation data. Overall, while we determine significant terms for salinity, temperature, carbonate chemistry, and bottom water saturation, none of these parameters has a strong effect on Na/Ca over the wide range of conditions studied (Fig. 3). Given that none of the environmental parameters investigated have a large influence on Na/Ca, we determine the mean Na/Ca in the primary foraminiferal calcite phase of *G. ruber* at modern seawater Na/Ca to be 6.17 ± 0.74 mmol/mol (2sd) across a wide range of salinity (33.9–40.7), carbonate chemistry (65–479 $\mu\text{mol/kg}$ [CO_3^{2-}]), temperature (15–30 °C), and Ω_{calcite} (0.9–4.5).

3.2. Methodological and cleaning effects: Laser versus solution ICP-MS comparison

The results of the experiment designed to facilitate direct comparison between LA and solution ICP-MS analyses on a homogenised foraminiferal 'standard' (Section 2.4) revealed no significant difference between techniques ($p > 0.1$; compare the

OCE205-50BC laser and solution data points on Fig. 2; Fig. 4); there is an offset of ~ 0.1 mmol/mol between the solution and laser analyses, which is within the precision of each of the techniques. This is additionally confirmed by the analysis of calcite standard MACS-3np by LA-ICP-MS (Section 2.7), which falls within the uncertainty of the reference value (Jochum et al. 2019). Therefore, both of these analytical tests demonstrate there is no substantial analytical offset between the techniques due to the mass-spectrometry, and thus the difference observed between the LA and solution ICP-MS measurements of the recently living samples (Fig. 2) is not an analytical artefact. We note that this test is only designed to assess if there is substantial analytical offset between the techniques relating to i.e. standardisation/matrix effects during the mass-spectrometry, and not to directly assess the impact of solution versus laser ablation cleaning protocols. The difference between the paired laser and solution analyses of the recently living foraminiferal samples is significantly higher than the analytical difference between the techniques ($p < 0.01$) (Fig. 4). Given the widespread application of the Mg/Ca palaeothermometer we also compare Mg/Ca measured on paired samples by laser and solution ICP-MS (Fig. 4). There is no significant offset between laser ablation and solution ICP-MS Mg/Ca measurements of recently living foraminifera ($p > 0.9$). Thus, Na/Ca appears to be an unusual case, and the discussion below does not imply any issues in comparing Mg/Ca of recently living foraminifera between techniques.

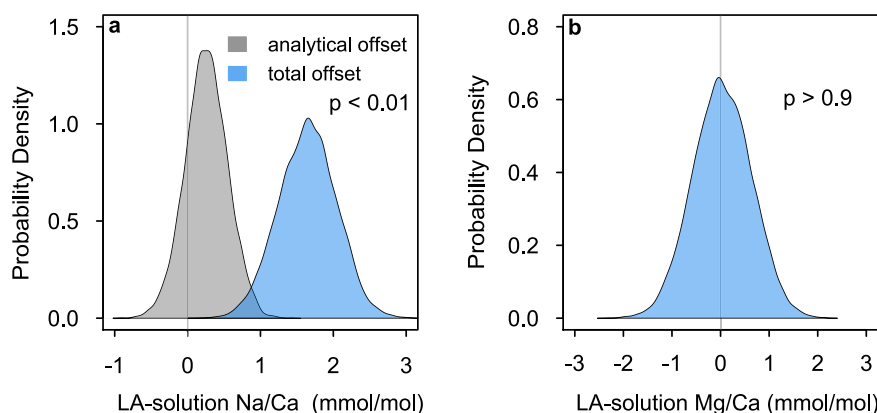


Fig. 4. (a) Probability density of Na/Ca offset between the paired samples of *G. ruber* measured by laser ablation ICP-MS and solution ICP-MS at salinities of <36 (blue), see Section 2.4 for methodological details. The total offset between the same specimens measured by these two different techniques is ~ 1.8 mmol/mol. A Monte-Carlo probability density of Na/Ca analytical offset between laser ablation ICP-MS and solution ICP-MS (grey) demonstrates that only ~ 0.2 mmol/mol of this offset can be explained by a possible analytical bias between the two techniques. The probabilities are based on multiple repeated measurements of the same crushed and cleaned foraminiferal calcite by laser ablation ($n = 40$) and solution ($n = 15$) ICP-MS, resampled 10,000 times to derive the probability density. A Student's T-test shows there is a significant difference (99% confidence interval) between recently living foraminiferal Na/Ca values measured by laser ablation ICP-MS and solution ICP-MS. (b) Monte-Carlo probability density of Mg/Ca difference between paired samples of *G. ruber* measured by laser ablation ICP-MS and solution ICP-MS. A Student's T-test shows there is no significant difference between foraminiferal Mg/Ca values measured by laser ablation ICP-MS and solution ICP-MS. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Discussion

4.1. Evidence for multiple Na-bearing phases in recently living foraminifera

The analytical comparison of a split of a coretop sample cleaned using the solution ICP-MS procedure and measured by both solution and laser-ablation ICP-MS (Section 2.4) produced indistinguishable Na/Ca (Table 1; Fig. 4). This result suggests that there is no resolvable analytical bias between the two analytical techniques resulting from differences in standardisation and standard matrix during mass spectrometry (confirmed by the LA-ICP-MS analysis of calcite standard MACS-3np). Therefore, the offset that we observe between solution and LA-ICP-MS measurements of the same recently living (sediment trap and plankton tow) samples (Table 1; Fig. 2) must stem from different preparation of the samples prior to analysis. Specifically, the higher Na/Ca values measured by LA-ICP-MS suggest an additional Na phase is measured by this technique, which would normally be removed at some stage during the cleaning procedure before solution ICP-MS analysis. This phase represents a substantial amount of Na, containing ~ 400 ppm at salinities of <36 and ~ 1200 ppm at a salinity of ~ 40 in *G. ruber*.

While the cleaning protocols for both LA and solution ICP-MS typically entail oxidative cleaning of the foraminiferal calcite, there are three important differences between the protocols (summarised in Table 2): Firstly, during cleaning for solution ICP-MS analysis foraminiferal tests are crushed into fragments before oxidation (while this may open up individual chambers and some sections of the chamber wall, these fragments are typically quite large), whereas foraminiferal tests are retained whole during cleaning for LA analysis; Secondly, during cleaning for solution ICP-MS analysis the oxidising agent is typically heated to 80–100 °C, whereas the oxidising agent is not heated during cleaning for LA analysis; Thirdly, during cleaning for solution ICP-MS analysis foraminiferal samples are typically leached in a small volume (50–100 μl) of weak acid (0.001 M HNO_3) prior to dissolution, whereas samples undergo no such leaching during cleaning for LA analysis. It follows, that the removal of the high-Na secondary phase in recently living foraminifera must occur due to the crushing of the sample and/or the heating of the oxidising agent and/or

Table 2

Summary of differences in typical cleaning protocols between solution and laser ablation ICP-MS.

Step	Solution ICP-MS ¹	Laser ICP-MS ²
Opening of foraminiferal chambers under glass plates	yes	no (shells retained whole)
Oxidative cleaning	1% H_2O_2 buffered in 0.1 M NaOH or NH_4OH heated to 80–100 °C*	2–5% NaOCl or 1% H_2O_2 buffered in 0.1 M NH_4OH no heating (room temperature)
Weak acid leach	50–100 μl of 0.0005/0.001 M HNO_3	no leach

* The oxidative step may be repeated up to 3 times in studies of recently living foraminifera. Occasionally, more concentrated H_2O_2 (15%) is used in studies of recently living foraminifera (e.g. Allen et al., 2016). The only study in the present compilation dataset to use more concentrated H_2O_2 is Allen et al (2016); the mean residual in the Allen et al (2016) data relative to the rest of the dataset is insignificant (0.36 ± 0.54 mmol/mol, 2σ), suggesting differences in oxidative cleaning protocol between different solution ICP-MS studies does not substantially impact Na/Ca.

¹ Barker et al. (2003) and Foster (2008).

² Evans et al. (2016)

the weak acid leach (which could potentially preferentially remove a more soluble phase).

Recently, Mezger et al. (2018) reported that Na/Ca measured in plankton tow samples are elevated relative to those of core-top samples recovered along a similar transect in the Red Sea (all measured by LA-ICP-MS). The plankton tow samples displayed a steep Na/Ca-salinity relationship and with elevated absolute values relative to the data measured by solution ICP-MS (Fig. 2). In contrast, the core top samples show no such relationship and have absolute values broadly similar to data measured by solution ICP-MS (Fig. 2), with an insignificant difference between the coretop values measured by LA-ICP-MS and those predicted by the regression between Na/Ca measured by solution ICP-MS and salinity (Fig. 2; $p > 0.3$). By extension, we posit that the previously reported offset between plankton tow and coretop data from the Red Sea (Mezger et al., 2018) can be explained by invoking early diagenesis that removes/decomposes this loosely-bound (or easily dissolved) Na-rich phase, in effect similar to the effect of the crushing/heating

oxidative cleaning/leaching procedure performed on specimens prior to solution ICP-MS analysis.

4.2. Identification of the secondary Na phase(s)

We show that a substantial portion of the Na present in the shells of planktonic foraminifera is present in a readily lost form that is not preserved in core-top samples or recently living (plankton tow/sediment trap) specimens that are cleaned using a typical solution ICP-MS procedure. However, our results in themselves cannot constrain the form of this Na phase and so we explore possible options here using mass-balance constraints. A simple mass-balance model based on the difference between the solution and LA ICP-MS data (Fig. 5) demonstrates that the secondary phase is either very rich in Na (>~2 wt%), very abundant in the shells of foraminifera (>~2 wt% of the shell), or both. Assuming a reasonable upper bound for the proportion of the secondary phase in the shell wall of 10 wt%, and given that organics and fluid inclusions generally do not make up more than a few percent of biogenic carbonates (Lecuyer & Neil, 1994; Weiner & Erez, 1984), we can constrain the concentration of sodium in the secondary phase to at least ~1 wt% at a salinity of 40 (i.e. the minimum x-axis value of the solid black and grey lines in Fig. 5). In addition, the mass balance constraints require that there is either a relatively large salinity-responsive shift in the amount of Na in the secondary phase and/or the proportion of this phase within the shell wall. Specifically, if only one of these factors responds to salinity then that factor must vary by at least ~1% in absolute terms. For instance, if the secondary phase always makes up 4 wt% of the shell wall irrespective of salinity, then the proportion of Na in this phase must increase from 1.4 to 2.1 wt% between salinities of 36–40.

Whilst our data clearly indicate the presence of a secondary Na-rich phase in foraminiferal calcite, identifying this phase is challenging. One constraint is that it must be in a form that is easily removed once the foraminifera tests are crushed/heated/leached,

given that these are the only significant difference between the LA and solution ICP-MS cleaning procedures, or during early diagenesis, given that core top samples measured by both techniques have low Na/Ca compared to plankton tow/cultured samples measured by LA. Some information on the nature of the secondary phase comes from the observations that (i) laser ablation profiles through the chamber walls lack any discernible structure (Fig. 6a–d), and (ii) the relative standard deviation of Na/Ca measured by laser-ablation ICP-MS increases as a function of Na/Ca (Fig. 6e). Given that this additional variability at high-Na/Ca values is driven by inter- rather than intra-individual variability, together, this demonstrates that the additional phase must be incorporated at a scale smaller than the effective spatial resolution of our LA measurements. In this study, the spatial resolution is equivalent to 44 μm horizontally and ~0.5 μm vertically, where the vertical resolution is in broadly the same direction as the growth axis of the foraminifera, given that the measurements were made via slow depth profiling through the chamber walls. Furthermore, the agreement between Mg/Ca of recently living foraminifera measured by laser ablation and solution (Fig. 4b), provides an additional constraint on the secondary phase. Specifically, it cannot contain a substantial amount of Mg, as the loss of this phase, as determined by the reduction in shell Na/Ca following the solution ICP-MS cleaning procedure (Fig. 4a) is not also associated with a resolvable change in Mg/Ca.

Below we consider the following non mutually-exclusive possibilities in turn: (i) the presence of remnant amorphous calcium carbonate [ACC], (ii) spines and spine bases, (iii) the presence of seawater inclusions in calcite, (iv) a Na-rich organic component that is more easily removed through oxidative cleaning when the shells are crushed/heated, and v) Na being present in more than one site in calcite.

Amorphous calcium carbonate [ACC]: While amorphous or metastable precursor phases have been suggested to be involved in foraminifera calcification (Jacob et al., 2017), we rule out

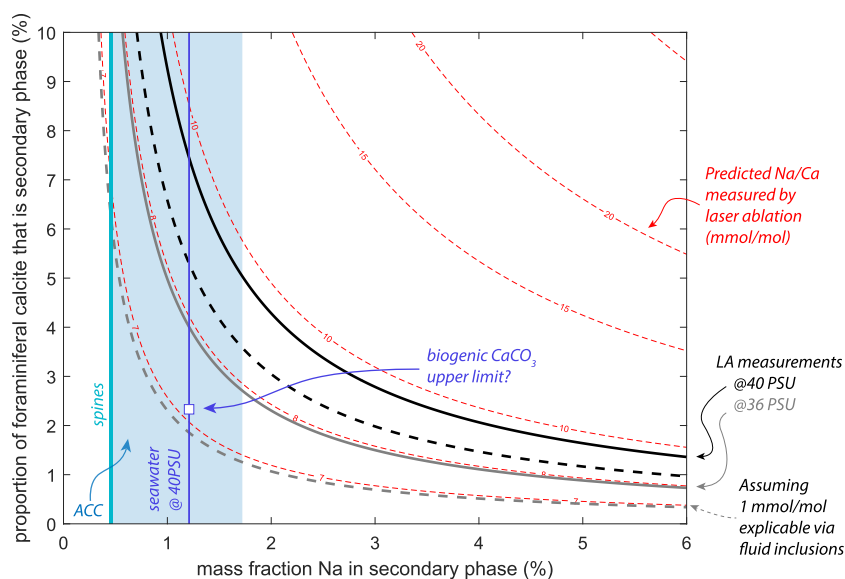


Fig. 5. Mass balance calculation of the proportion and Na content of the secondary phase necessary to explain the laser ablation (LA) ICP-MS Na/Ca data. Contours depict predicted LA-ICP-MS Na/Ca measurements assuming that an additional phase to that measured by solution ICP-MS is present. The thick grey and black lines depict the location of the LA-ICP-MS data shown in Fig. 2 at salinities of ~36 and 40. The possible contribution to bulk Na/Ca measurements resulting from spines/spine bases, fluid inclusions in calcite, and possible remnant amorphous calcium carbonate are shown (the uppermost biogenic fluid inclusion data point is from Lecuyer and Neil (1994), the range of Amorphous Calcium Carbonate Na/Ca is from Evans et al. (2020), and the spine Na/Ca value is from (Mezger et al., 2019)). The dashed lines show the LA-ICP-MS data adjusted to account for the presence of fluid inclusions, i.e. assuming that both fluid inclusions and a further secondary phase are present in foraminiferal calcite. The model demonstrates that i) the secondary phase must contain Na at a relatively high concentration (>~1 wt%) or represent a high proportion of the 'secondary' phase, and ii) that fluid inclusions or the presence of spine bases alone cannot explain the offset between solution and laser ablation measurement techniques. For example, spine bases would need to make between 14% and 25% of the mass of foraminiferal shells.

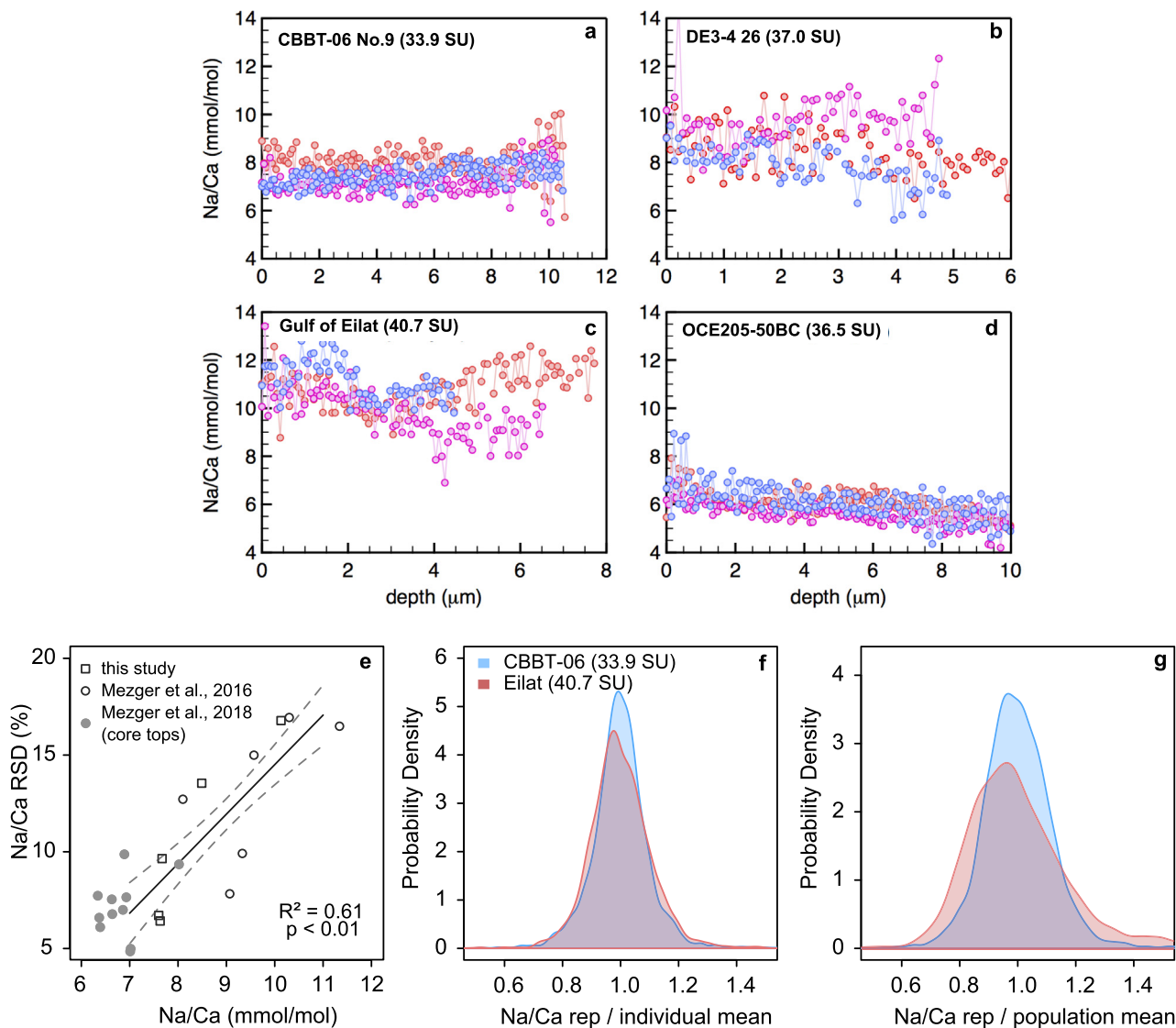


Fig. 6. (a–d) Representative LA-ICP-MS-derived Na/Ca profiles through the chamber wall of *G. ruber*. Panels a–c show individual chamber analyses from samples that were analysed as whole shells, whereas the sample shown in panel d was crushed and cleaned using the solution ICP-MS procedure (Section 2.4) and then analysed as fragments. Three examples are shown in each case from three different specimens, with each specimen represented by a different colour. (e) Relative standard deviation (RSD) of Na/Ca measurements from multiple individuals within a population versus Na/Ca measured by LA-ICP-MS. Note, the coretop data are not included in the regression. (f) Variance of individual Na/Ca replicates within individual LA-ICP-MS profiles relative to the profile mean of two samples at low and high salinities (g) Variance of individual Na/Ca replicates within individual LA-ICP-MS profiles relative to the sample mean of two samples at salinities of 33.9 and 40.7. The increase in scatter with increasing Na/Ca values measured by LA-ICP-MS is driven by greater variability between individuals, rather than greater variability within individuals.

remnant ACC as a likely explanation for the secondary Na-bearing phase. While the Na partition coefficient into ACC (D_{Na}) is ~ 1 order of magnitude higher than calcite (Evans et al., 2020) and therefore remnant ACC would lead to elevated measured Na/Ca, an unfeasible amount of ACC remaining in the shell wall would be required to explain the Na/Ca of plankton tow and cultured foraminifera measured by laser ablation (~ 4 – 10% ; Fig. 5). Furthermore, while Jacob et al. (2017) found $< 5\%$ vaterite in recently living foraminifera, no remnant ACC was detected. In addition, both ACC and vaterite have elevated Mg partition coefficients compared to calcite (Evans et al., 2020; Zhou et al., 2021), such that a substantial presence of these phases would lead to an offset between Mg/Ca measured by laser and solution, which is not observed (Fig. 4b).

Spines/spine bases: Demonstrating that foraminiferal spines have a high Na/Ca (~ 20 mmol/mol), Mezger et al. (2018) suggest that the difference between plankton tow and core top samples

could be due to the loss of the foraminifer's spines in the latter (this explanation would presumably imply no relationship between chamber wall Na/Ca and salinity). However, none of our sediment trap, plankton tow, or core-top specimens retained their spines (see the supplementary material). Mezger et al. (2018) also demonstrated that spine bases were elevated in Na/Ca; however, given spines typically contain $< 0.5\%$ Na (Na/Ca ~ 20 mmol/mol), spine bases would need to account for ~ 13.5 – 25% of the total mass of the shell to account for the measured offset at salinities of 36 and 40, respectively. Furthermore, as Mezger et al. (2018) found that neither spine Na/Ca nor the number of spines increased as a function of salinity, the presence of spine bases cannot explain the high sensitivity between Na/Ca and salinity observed in recently living foraminifera measured by laser ablation ICP-MS. Finally, given spine bases are not evenly distributed through the shell wall (with a preferential distribution towards the outer edge

of the shell), the homogenous (but elevated) laser ablation Na/Ca profiles require an additional Na bearing phase. Thus, while the presence of spine bases may lead to some elevation of Na/Ca values, spine bases cannot be the sole explanation for the difference we observe between foraminifera analysed by laser ablation and solution ICP-MS.

Fluid inclusions: To our knowledge, there are no direct measurements of the water content of foraminiferal calcite. As such, we alternatively utilise the range of published water content data for abiogenic and biogenic CaCO₃ to evaluate whether fluid inclusions may account for the Na that is lost during cleaning for solution ICP-MS analysis and upon early diagenesis of core top samples. Fluid inclusions have been reported in a wide range of biogenic and abiogenic carbonates, including speleothems (Schwarcz et al., 1976), cements (Goldstein, 1986), and a number of marine organisms including mussels, corals, gastropods, and bivalve molluscs (e.g. Gaffey, 1988; Lecuyer and Neil, 1994). Given their almost ubiquitous nature in other marine carbonates, it seems reasonable to explore the possibility that they are also a feature of foraminiferal calcite.

Assuming that all of the water in fluid inclusions in biogenic carbonates is seawater, this would increase the Na/Ca by up to 1.0 mmol/mol (using the uppermost reported value for the amount of water in marine CaCO₃). Thus, even in this extreme ‘watery end-member’ case, the amount of Na incorporated as seawater inclusions is insufficient to explain all of the offset (2–5 mmol/mol) between laser ablation and solution ICP-MS. Although fluid inclusions may provide an explanation for a substantial portion of the observed difference between laser ablation and solution ICP-MS measurements of plankton-tow or cultured foraminifera, the fluid inclusions would need to be large enough that they would be easily cracked open and cleaned during the solution ICP-MS pre-analysis cleaning; yet, the homogenous LA profiles suggest the secondary Na phase is homogeneously distributed at a spatial scale of <44 μm horizontally and ~0.5 μm vertically. Overall, seawater inclusions alone cannot be the sole explanation for the secondary Na phase, and unless the proportion of fluid inclusions in foraminiferal calcite changes as a function of salinity, they also cannot account for the steep slope between Na/Ca and salinity observed in recently living foraminifera measured by laser ablation ICP-MS.

Na associated with organics: We explore whether Na bound to organic matter within the calcite may constitute the secondary Na-bearing phase. At least some of the shell-associated organic material is readily removed during the crushing/oxidative cleaning procedure in the preparation of samples for solution ICP-MS analysis, whereas this may not be the case when specimens are retained whole for laser ablation.

Branson et al. (2016) and Bonnin et al. (2019) reported elevated Na (and Mg) concentrations associated with the primary organic sheet (POS) within three species of planktonic foraminifera, highlighting the importance of considering intra-chamber organics as an additional source of (trace) elements in the shells of foraminifera. In the study by Branson et al. (2016), Mg and Na were present in the organic template in a ratio of ~1.5 mol/mol. In contrast, we see no significant difference ($p > 0.9$) between Mg/Ca values measured by laser-ablation ICP-MS and solution ICP-MS in our dataset (Fig. 4b). This suggests that if organics are responsible for the secondary Na phase, the phenomenon cannot be attributed to the POS alone, which is probably too small in terms of the overall shell mass to represent a significant source of bias when measuring shell trace element ratios. However, if this finding is applicable to other organic components then sufficient organic bound Na could be present to bias Na/Ca measured by laser ablation. Indeed, around 40–90% of the potassium present in coral aragonite has been shown to be associated with organics (Li et al., 2022). If this is similarly true for the foraminifera, and for other alkali elements, then organic-

associated Na may be a good explanation for the laser ablation-solution ICP-MS offset (Fig. 2), although we note that following similar mass balance constraints explored above (Fig. 5), this would require >10 wt% Na in the organic phase given the organic proportion of the mass of foraminifera shells (Weiner & Erez, 1984).

Sodium in interstitial sites: The location of Na in the lattice of calcite is a matter of ongoing research. Earlier work based on Na partitioning between the solid and fluid phase suggested an interstitial site (White, 1978; Ragland et al., 1979; Ishikawa and Ichikuni, 1984), whereas a more recent spectroscopic study has argued for altrivalent substitution for Ca, with the charge imbalance accommodated via CO₃ vacancies (Yoshimura et al., 2017). An alternative possibility may be that Na is incorporated into both positions, with Na in the interstitial sites being far more sensitive to laboratory cleaning procedures and dissolution at the sea floor. Mezger et al. (2018) report data analysed on *T. sacculifer* and *G. ruber* plankton tow samples collected through the upper 500 m of the water column. These data show that in the Red Sea, the additional Na phase is largely lost before the sinking foraminifera reach the sea floor. However, selective removal of ions in interstitial sites seems unlikely given the oversaturated (with respect to calcite) conditions in the water column of the Red Sea. In addition, although samples are crushed gently prior to oxidative cleaning for solution ICP-MS measurements this is typically done between glass slides to remove (e.g.) silicate minerals trapped inside the shell, which does not pulverise the calcite. It is therefore highly unlikely that the necessary grain size reduction required to selectively remove ions in interstitial sites from all crystals takes place.

More than one secondary phase? Many of the possibilities listed above can be immediately ruled out as the sole explanation on the basis that none of these phases (ACC, fluid inclusions, spine bases) are present to a great enough degree to fulfil the necessary mass balance constraints to explain the offset between plankton tow and laboratory culture laser ablation and solution ICP-MS data (Fig. 5). However, it is possible that more than one secondary Na phase exists within foraminiferal tests. Given the ubiquitous nature of fluid inclusions in biogenic carbonates (Lecuyer and Neil, 1994), and the elevated Na content of organics (Branson et al., 2016; Bonnin et al., 2019), a combination of fluid inclusions, spine bases, meta-stable CaCO₃ phases, and organics may be the most likely explanation. To explore this, the dashed black and grey lines in Fig. 5 show a mass balance model revised to include the assumption that all foraminifera shells contain fluid inclusions at the upper limit of the proportion found in other marine organisms (2.3%; Lecuyer and Neil, 1994). Whilst this can account for a significant amount of the Na removed during the solution ICP-MS cleaning procedure as described above, the overall results of the exercise remain broadly unchanged; the additional secondary phase must be present in large quantities or contain a very large Na mass fraction. For example, 14% of the chamber wall would need to be composed of spine bases at a salinity of 40 to explain the total offset between the solution and laser ablation measurements (Figs. 2 and 5).

4.3. A Sodundrum

How can the relationship between laser ablation Na/Ca and salinity above a salinity of ~36 be explained? Given that the proportion of the shell consisting of fluid inclusions or spine bases cannot, alone, provide the full explanation of the origin of the secondary Na phase, we explore the constraints that need to be fulfilled using Na rich organics, as an example test-case. Given a hypothetical foraminifera shell with 2 wt% organics, plus a constant contribution from fluid inclusions/spine bases of 2.3 wt%, the organic Na concentration phase would need to increase from

0.9 to 2.0 wt% between salinities of 36–40 in order to explain the trend in the laser ablation data with salinity (Fig. 2), thus proportionally increasing by nearly one order of magnitude more in relative terms than the free Na activity over the same salinity range (Wit et al., 2013). While our data cannot constrain the range of possibilities further, we hypothesise that it is more likely that the proportion of the secondary phase is responsive to salinity rather than the amount of Na in this phase. For example, an organic component with 1.5 wt% Na would need to increase from ~1.5 to 3% of the shell mass to explain the LA Na/Ca-salinity relationship.

It nonetheless remains the case that unless foraminiferal tests are characterised by a relatively high organic component (>5 wt %, cf. e.g. Weiner & Erez, 1984, who report ~0.1–0.2 wt% in *Heterostegina depressa*), the organic phase must be characterised by a Na concentration in excess of seawater (Fig. 5). If present, organic matter with such high Na concentrations may be the result of active pumping by Na,K-ATPase pumps, which are ubiquitous in cells (Skou, 1957; Clausen et al., 2017), and possibly relate to biomineralisation or some other physiological process pertaining to cell regulation. To our knowledge there are few measurements of the organic component of skeletal carbonates with which to compare. Amiel et al. (1973) found that Na is present in coral organics at a higher concentration than Mg, Sr, or K, whilst Li et al. (2022) show that 40–90% of the K in coral aragonite is present in organics. However, in both cases it is probably infeasible to reconcile these observations with simple mass balance constraints (Fig. 5) if organic-associated Na is to be the sole explanation for the secondary phase. Amiel et al. (1973) report ~600 ppm Na in coral organics, a concentration much lower than required by the above mass balance model (>10 wt% given an organic mass fraction of <1% in foraminifera). Either foraminifera differ greatly from corals in this respect, or an alternative explanation is required.

4.4. Comparison to *Trilobatus sacculifer*

Comparison of published *T. sacculifer* Na/Ca data from pristine cultured and plankton tow samples measured by both solution and laser-ablation ICP-MS reveals a very similar pattern to *G. ruber* (Allen et al., 2016; Mezger et al., 2016; Bertlich et al., 2018; Watkins et al., 2021; Fig. 7). The LA-ICP-MS Na/Ca data of Mezger et al. (2016) are characterised by a relatively steep slope with salinity ($m = 0.62 \pm 0.06$), and absolute Na/Ca of ~8–10 mmol/mol. In contrast, the solution ICP-MS data of Allen et al. (2016) show no relationship between Na/Ca and salinity and Na/Ca values ~2–4 mmol/mol lower than the LA data. While Watkins et al. (2021) do report a relatively steep relationship between Na/Ca and salinity with a slope similar to that of the laser ablation data of Mezger et al. (2016), the relatively narrow salinity range and small sample size ($n = 8$) means that this finding could be coincidental given that the degree of variation from the mean of all data in that study is similar to the variance in the compiled solution data (Fig. 7). Moreover, the solution ICP-MS data of Watkins et al. (2021) are characterised by absolute values ~4 mmol/mol lower than the plankton tow laser ablation data of Mezger et al. (2016). Together, this suggests that the secondary Na-rich phase discussed above with respect to *G. ruber* is similarly present in other planktonic foraminifera.

Bertlich et al. (2018) report EPMA data from cultured *T. sacculifer*, wherein samples were polished and carbon coated for analysis, but not otherwise (i.e. oxidatively) cleaned. These data are overall characterised by a significant ($p < 0.01$) Na/Ca-salinity relationship with a slope of 0.071 ± 0.036 mmol/mol/salinity unit (Fig. 7), or 0.097 when gametogenic calcite is excluded from the regression (Bertlich et al., 2018), substantially shallower than that of Mezger et al. (2016). Given the data described above, this suggests that the secondary phase measured by LA-ICP-MS is not present, or

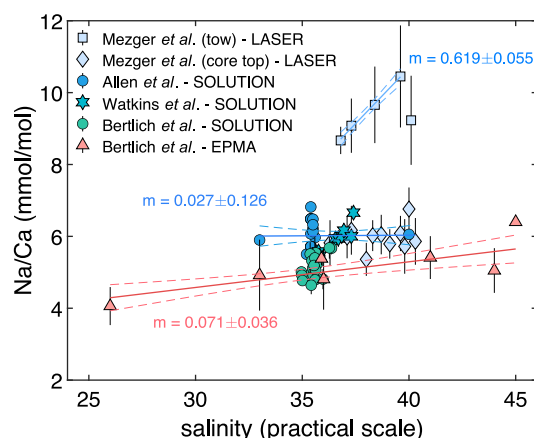


Fig. 7. Comparison of culture, plankton tow, and core-top *T. sacculifer* Na/Ca measured by LA-ICP-MS (Mezger et al., 2016 (plankton tow) and Mezger et al., 2018 (core top)), solution ICP-MS/OES (Allen et al., 2016; Bertlich et al., 2018; Watkins et al., 2021), and Electron Probe Microanalyzer (EPMA; Bertlich et al., 2018). As is the case for *G. ruber*, plankton-tow specimens are characterised by a steep Na/Ca salinity relationship when measured by LA-ICP-MS, whereas no such relationship exists for core-top and laboratory cultured samples measured by either laser-ablation or solution ICP-MS. Error bars are $\pm 2\sigma$. The core-top/cultured sample regression does not use the core-top laser ablation data of Mezger et al. (2018) to avoid potential bias introduced by considering samples measured by more than one analytical technique, although including these data in the regression would not substantially alter the regression (including all core-top and cultured sample data irrespective of analytical technique results in $m = 0.003 \pm 0.070$).

was not measured, in these samples. In addition, the absolute Na/Ca reported by Bertlich et al. (2018) fall below those of Allen et al. (2016), the latter offset to values ~1 mmol/mol higher at 35 SU. At face value, this is contrary to expectation given that these samples were not further cleaned after polishing, such that the secondary phase(s) discussed above should remain in the foraminifera shell walls. Given that we do not present new EPMA data, it is beyond the scope of this study to examine this difference in detail, although we note that the analytical comparability between EPMA and ICP-MS techniques remains to be established for calcite Na/Ca data; a coral standard material analysed by Bertlich et al. (2018) was characterised by an accuracy of -25.8% , similar to the offset between solution ICP-MS and EPMA shown in Fig. 7. Additional explanations for this offset may be that: (i) pixels with a [Ca] deviating from that of calcite were excluded from the data analysis of Bertlich et al. (2018), and (ii) Bertlich et al. (2018) avoid spines and spine bases in their analyses. However, the EPMA data of cultured specimens and the ICP-OES data of core-top samples from Bertlich et al. (2018) are in good agreement with each other (Fig. 7), which indicates that other factors are likely to be important [e.g. Na loss in the primary phase due to dissolution (Bertlich et al., 2018; Zhou et al., 2021)] which does not affect cultured or towed foraminifera.

4.5. Na/Ca of core-top samples and outlook for proxy reconstructions based on Na/Ca

In Sections 4.1 and 4.2 we showed that the relatively steep Na/Ca-salinity slope characteristic of laser ablation ICP-MS measurements is not present in samples analysed by solution ICP-MS. This observation, coupled with the results of Mezger et al. (2018) that demonstrate the Na/Ca-relationship of pristine (i.e. recently living) samples is lost as the foraminifera sink through the water column and is not present in LA analyses of core top samples (Fig. 1), suggests that the Na-bearing phase with a high-salinity sensitivity is unlikely to be recoverable in down-core sediments.

The question is then whether the Na/Ca in the primary calcite phase (i.e. as measured in coretops or in recently living foraminifera by solution ICP-MS), can yield useful salinity reconstructions downcore. The multiple linear regression of the culture, sediment trap, plankton tow, and coretop Na/Ca data analysed by solution ICP-MS shows a weak but significant relationship between Na/Ca and salinity (Eq. (2)). Given the slope of 0.076 ± 0.038 mmol/mol/salinity unit and the RSE of 0.29 in Eq. (2), salinity changes of less than ~ 4 salinity units are not likely to be resolvable. Furthermore, we find weak but significant influences of temperature, CO_3^{2-} , and bottom water Ω_{calcite} on Na/Ca; these parameters would therefore also need to be accounted for in any downcore reconstruction of salinity using Na/Ca. As such, we suggest Na/Ca is unlikely to find widespread utility as a salinity proxy.

Due to the long residence time of Na in the ocean, the Na/Ca of foraminiferal calcite has been suggested as a proxy for past changes in the ocean Ca^{2+} concentration on longer (i.e. geologic) timescales (Hauzer et al., 2018; Zhou et al., 2021). The consistent Na/Ca we observe in the primary calcite phase across a wide range of sample types (culture, sediment trap, plankton tow) and environmental conditions, indicates that this proxy is robust to changes in other environmental parameters when applied to fossil samples. Whereas we do observe a significant relationship between Na/Ca and both temperature and CO_3^{2-} , the sensitivity of Na/Ca to these parameters is too low to warrant concern given the uncertainties with which we can reconstruct these within the Cenozoic. For example, given the temperature sensitivity of -0.037 mmol/mol/ $^\circ\text{C}$ (Eq. (2)), a 5 $^\circ\text{C}$ temperature uncertainty would only result in a bias of ~ 0.19 mmol/mol, considerably smaller than the ~ 2 mmol/mol change in Na/Ca from changing seawater [Ca] expected over the Cenozoic (Hauzer et al., 2018; Zhou et al., 2021).

5. Summary and conclusions

Using spatially resolved analyses (mostly laser-ablation) of pristine culture or plankton tow samples, a number of previous studies have suggested that the Na/Ca of foraminiferal calcite may be a potential proxy for salinity. We find that despite the relationship between Na/Ca and salinity present in pristine sediment trap/plankton tow samples measured by LA-ICP-MS, solution ICP-MS measurements of sample splits of the same samples yield a far shallower Na/Ca-salinity slope, and are ~ 2 – 5 mmol/mol lower (depending on salinity). By analysing a cleaned/homogenised 'foraminiferal standard' by both solution and LA ICP-MS we show that this offset is not an analytical artefact relating to i.e. standardisation/matrix effects, and instead must relate to the removal of a secondary Na-bearing phase when samples are crushed/heated during oxidative cleaning/leached for solution analysis, but retained when shells are analysed whole by laser ablation. Possible candidates for this secondary phase are, remnant amorphous calcium carbonate, spine bases, fluid inclusions, organic material, and Na in interstitial sites (as opposed to that which may substitute for Ca^{2+}). Based on a simple mass balance model, amorphous calcium carbonate, fluid inclusions, and spine bases alone cannot explain the solution-laser ablation discrepancy, whilst the rate at which this Na is lost from samples settling through the water column (Mezger et al., 2018) argues against a loss from interstitial ions. The most likely explanation, therefore, is that planktonic foraminifera contain multiple Na bearing secondary phases and that either (i) the amount of one of these phases (most likely), or (ii) the amount of Na in one of these phases (less likely), varies with salinity. The rapid loss of the high Na secondary phase as foraminifera settle through the water column, and agreement between coretop samples analysed by LA-ICP-MS (Mezger et al., 2018) and the solution ICP-MS data (Fig. 2) suggests that this Na-rich phase

with a high-salinity sensitivity is unlikely to be recoverable in down-core sediments.

Na/Ca in the primary calcite phase (i.e. as determined by solution ICP-MS), shows only a weak relationship with salinity and is also weakly sensitive to temperature, carbonate ion concentration, and bottom water Ω_{calcite} . Hence, Na/Ca in planktonic foraminifera is unlikely to find widespread utility as a salinity proxy. However, given that Na/Ca in the primary calcite phase shows only a weak response to salinity, temperature, carbonate chemistry, and bottom water saturation state, these factors are unlikely to pose a major complication to seawater [Ca] reconstructions based on Na/Ca (Hauzer et al., 2018; Zhou et al., 2021), providing a potential tool to track the major ion chemistry of seawater in the geological past.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

There are three supplementary files associated with this manuscript. Table S1 contains the location (lat, lon, water depth) of the sediment trap, plankton tow, and coretop samples analysed in this study. Table S2 contains the *G. ruber* Na/Ca data generated in this study and compiled from previous studies, reported with the 1sd of any replicate measurements of the sample, along with the sample type (sediment trap/plankton tow/coretop), the analytical method used (solution/laser), the reference study for the data, the size fraction and morphotype of foraminifera analysed, the water depth of the sample, and estimates of bottom water Ω_{calcite} , surface temperature, salinity, pH, and CO_3^{2-} . The supplementary PDF file contains images of the *G. ruber* analysed by laser ablation in this study. Supplementary material to this article can be found online at <https://doi.org/10.1016/j.gca.2023.03.011>.

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