Biogeosciences Discuss., 10, 6039–6063, 2013
www.biogeosciences-discuss.net/10/6039/2013/
doi:10.5194/bgd-10-6039-2013

Biogeosciences
Discussions
Open Access

A novel salinity proxy based on Na incorporation into foraminiferal calcite

J. C. Wit[1], L. J. de Nooijer[2], M. Wolthers[1,3], and G. J. Reichart[1,2]

[1]Department of Geochemistry, Utrecht University, Budapestlaan 4, 3584 CD, Utrecht, the Netherlands
[2]Department of Marine Geology, Royal Netherlands Institute for Sea Research, Lansdiep 4, 1797 SZ, t' Horntje Texel, the Netherlands
[3]Department of Chemistry, University College London, 20 Gordon Street, London WC1 H0AJ, UK

Received: 14 March 2013 – Accepted: 20 March 2013 – Published: 28 March 2013

Correspondence to: J. C. Wit (j.c.wit@uu.nl)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Salinity and temperature determine seawater density and differences in both thereby control global themohaline circulation. Whereas numerous proxies have been calibrated and applied to reconstruct temperature, a direct and independent proxy for salinity is still missing. Ideally, a new proxy for salinity should target one of the direct constituents of dissolved salt, such as [Na^+] or [Cl^-]. This study investigates the impact of salinity on foraminiferal Na/Ca values by laser ablation ICP-MS analyzes of specimens of the benthic foraminifer *Ammonia tepida* cultured at a range of salinities (30.0–38.6).

Foraminifera at lower salinities (30.0 and 32.5) added more chambers (10–11) to their test over the course of the experiment than foraminifera cultured under higher salinity (36.1, 7–8 chambers, and 38.6, 6–7 chambers), suggesting that lower salinity promotes growth rates in this species. The Na/Ca of cultured specimens correlates significantly with seawater salinity ($\mathrm{Na/Ca} = 0.22S - 0.75$, $R^2 = 0.96$, $p < 0.01$) and size. Values for Na/Ca and D_{Na} vary between 5.17 and 9.29 mmol mol^{-1} and 0.12–0.16×10^{-3}, which is similar to inorganic precipitated calcite. The significant correlation between test size and Na/Ca results from co-variation with salinity. This implies that foraminiferal Na/Ca may well be a robust and independent proxy for salinity, enabling independent salinity reconstruction. The quantified effect of salinity on Mg/Ca in our culture experiment, furthermore allows a direct correction for the bias in Mg/Ca based temperature reconstructions caused by differences in salinity.

1 Introduction

Temperature and salinity are among the most relevant parameters when studying past ocean circulation, as they together control ocean water density and thus thermohaline circulation. A large number of proxies for reconstructing seawater temperature have been developed (e.g. carbonate δ^{18}O and Mg/Ca), some of which are now well

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
|◀ | ▶|
◀ | ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

established and widely applied (e.g. Epstein et al., 1953; O'Neil et al., 1969; Shackleton, 1974; Prahl and Wakeham, 1987; Nürnberg et al., 1996; Bemis et al., 1998; Hastings et al., 1998; Elderfield and Ganssen, 2000; Lear et al., 2000; Anand et al., 2003). Independent quantitative tools for the reconstruction of past salinities are, however, lacking. Until now salinity can be reconstructed using dinoflagellate and diatom species composition (Zonneveld et al., 2001), process length of dinoflagellates (Mertens et al., 2009), under some conditions using the bivalve strontium isotope composition (Israelson and Buchardt, 1999) and Ba concentration of foraminiferal calcite (Weldeab et al., 2007). These proxies, however, are either indirect, through changes in ecology, or strongly dependent on regional oceanography (i.e. river water input). Other indirect approaches involve using the correlation between seawater oxygen and hydrogen isotope composition and salinity (Gat, 1996). Foraminiferal δ^{18}O (after correcting for the effect of temperature using Mg/Ca or $U_{37}^{k'}$) or hydrogen isotope composition (δD) of alkenones can be used to infer salinity (Elderfield and Ganssen, 2000; Schouten et al., 2006; Van der Meer et al., 2007). Spatial and temporal variations in the relationship between water stable isotopes and salinity, however, limit the accuracy of this approach. At best, the relation between salinity and seawater isotope composition can be modeled, involving assumptions on precipitation, evaporation and/or river runoff, introducing relatively large uncertainties in reconstructed salinities (Rohling and Bigg, 1998).

Ideally, a new proxy for seawater salinity should target one of the major constituents of sea salt, rather than using indirect relations between the isotopic composition of seawater and salinity. By far the largest components of seawater salinity are Na^+ and Cl^-. Incorporation of sodium into calcium carbonate has been shown to vary with salinity in the Atlantic Oyster (*Crassastrea virginica*: Rucker and Valentine, 1961), barnacle shells (Gordon et al., 1970), and inorganically precipitated calcium carbonate (Kitano et al., 1975; Ishikawa and Ichikuni, 1984). Application in paleoceanographic reconstructions requires, however a more general proxy signal carrier. Here, we investigate the impact of salinity on foraminiferal Na incorporation by laser ablation ICP-MS analyses of specimens of the benthic foraminifer *Ammonia tepida* cultured at controlled conditions at different salinities (30.0–38.6). Since seawater pH, alkalinity and total dissolved inorganic carbon (DIC) were kept constant to avoid a possible impact by inorganic carbon chemistry (as observed for, e.g. Mg; Nürnberg et al., 1996; Kisakürek et al., 2008; Dueñas-Bohórquez et al., 2009), changes can be interpreted in terms of salinity only.

2 Methods

The benthic, cosmopolitan foraminifer *Ammonia tepida* inhabits a wide range of environments, and is one of the few species found in habitats with highly variable temperatures and salinities (Murray, 1968; Hayward et al., 2004). This adaptation makes it a suitable species to culture at a wide range of conditions (e.g. De Nooijer et al., 2007; Dissard et al., 2010; Dueñas-Bohórquez et al., 2011a). Surface (0–2 cm) sediments were collected from an intertidal mudflat at the Wadden Sea near Den Oever, the Netherlands. Upon return in the laboratory, individual specimens were isolated from this material and placed in filtered seawater with a salinity of 35, at 20 °C. These specimens were subsequently monitored for reproduction. Shortly after an asexual reproduction event, megalospheric juvenile specimens consisting of 2–3 chambers were handpicked and transferred to the culture set up.

Culture media consisted for 50 % of artificially prepared and 50 % natural seawater (Mediterranean Sea, filtered and diluted to a salinity of 35) using the recipe of Kester et al. (1967). Culture media with different salinities were obtained by varying the amount of salts added to each solution (Table 1). Amounts of added $NaHCO_3$ and $B(OH)_3$ were kept constant for each batch of culture media in order to obtain media with similar alkalinity and dissolved inorganic carbon (DIC) concentration. Subsequently, all prepared artificial seawater batches were mixed with equal amounts of natural seawater with a salinity of 35. The resulting media thus had salinities of 30.0, 32.5, 36.1 and 38.6, covering a large part of the range in salinities found in the open ocean. Temperature, salinity, alkalinity and DIC were monitored over the course of each experiment (Table 2).

Element composition of the culture media was determined by ICP-OES (Spectro Arcos). Measured alkalinity and DIC were used to calculate the other parameters of the inorganic carbon system of the culture media, using CO2SYS (Lewis and Wallace, 1998) (Table 2). Speciation and activities of free elements in the culturing experiments was modeled using PHREEQC (LLNL database, Parkhurst and Appelo, 1999).

Experiments ran for 6–8 weeks to ensure that sufficient foraminiferal chambers were added for elemental analysis. Specimens were harvested and sieved over a screen with a 125 µm mesh size. Size of individual foraminifera was determined using a calibrated microscope camera and computer software. Since the spiral growth mode of *A. tepida* produces outlines that are not perfectly circular, diameter of every individual foraminifer was measured 4 times to calculate average diameter (Tables 3 and 4).

Foraminiferal Na/Ca and Mg/Ca were determined using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS), performed at Utrecht University. Single chamber element composition was determined using ^{23}Na, ^{24}Mg, ^{26}Mg, ^{27}Al, ^{43}Ca, ^{44}Ca, ^{55}Mn and ^{88}Sr and their relative natural abundances (Reichart et al., 2003; Wit et al., 2010). All laser spots were 80 µm in diameter, repetition rate was 7 Hz and laser energy density was set at $\sim 1\,\mathrm{J\,cm^{-2}}$. Time resolved signals were selected for integration, background subtracted, internally standardized to ^{43}Ca, and calibrated against a glass standard (NIST SRM610; elemental concentrations from Jochum et al., 2011) that was ablated at a higher energy density ($\sim 5\,\mathrm{J\,cm^{2}}$). Using different ablation energies for glass and calcite was previously shown not to affect the analyses (Wit et al., 2010; Dueñas-Bohórquez et al., 2011). Integration windows that separate the calcitic signal from background and detection of any contaminants at the test surface was done using designated software (Glitter). Elemental ratios with respect to Ca were based on the average of each ablation profile.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

3 Results

Culture solution parameters were stable, for each of the four experimental conditions and, with the exception of salinity, similar between experiments. Seawater Mg/Ca values increased slightly with salinity (Table 2). *Ammonia tepida* at lower salinities (30.0 and 32.5) added more chambers (10–11) to their test over the course of the experiment than foraminifera cultured under higher salinity (36.1, 7–8 chambers, and 38.6, 6–7 chambers), implying somewhat higher growth rates at lower salinities. Foraminiferal survival rates were similar across experiments (44–47 %), while test size significantly increased with salinity ($R^2 = 0.97$, $p < 0.01$) (Table 3, Fig. 1).

The Na/Ca of cultured specimens correlated significantly ($p < 0.01$) with seawater salinity (Fig. 2) and size ($R^2 = 0.96$, $p < 0.01$, Fig. 1). Foraminiferal Na/Ca values ranged from 5.17 to 9.29 mmol mol^{-1} over all experiments. Inter-individual variability within each experiment was between 9 and 17 % (Table 3) and of the same order in single chamber ablation profiles. Values for Mg/Ca measured on the calcite test correlated positively with salinity ($R^2 = 0.99$, $p < 0.01$) (Table 4, Fig. 2). Foraminiferal Mg/Ca ranged from 0.98 to 2.57 mmol mol^{-1} over all experiments. Inter-individual variability in Mg/Ca within each salinity treatment varied between 13–16 % (relative standard deviation) and was similar between the different experiments.

4 Discussion

4.1 Na/Ca and salinity

Results indicated a significant ($p < 0.01$), positive correlation between seawater salinity and calcite Na/Ca (Fig. 2). Inter-individual variability for Na/Ca values (relative standard deviation of 9–17 %) was similar as previously recorded for some other elements (e.g. Mg) measured on single chambers (Sadekov et al., 2008; Wit et al., 2010, 2012; Dueñas-Bohórquez et al., 2011b). Both Mg and Na showed distinct banding in the test carbonate of some species (Erez, 2003) and changes in the relative contributions of high and low Na and Mg bands could explain the observed inter chamber variability.

To facilitate comparison of our foraminiferal Na/Ca values to ratios obtained in other studies, calcitic Na/Ca values are henceforth expressed as partition coefficients (D_{Na}). The D_{Na} is the ratio of sodium over calcium in foraminiferal calcite divided by the ratio of these elements in the culture medium. The D_{Na} for foraminifera reported here (0.12–0.16×10^{-3}) is similar to that found in inorganically precipitated calcites (0.07–0.20×10^{-3}; Kitano et al., 1975; Ishikawa and Ichikuni, 1984). This similarity suggests that the general biological control on Na incorporation in *A. tepida* is likely to be minor. Moreover, D_{Na} for planktonic foraminiferal species is within the same range (0.11–0.17×10^{-3}) (Delaney et al., 1985; Lea et al., 1999), suggesting that incorporation of Na is similar across Rotaliid foraminifera. Still, the observed Na banding (Erez, 2003) indicates that some biological control must exist.

Previous studies reporting partition coefficients for Na in biogenic and inorganically precipitated calcium carbonates could not distinguish between lattice-bound Na and that present in microscopic seawater inclusions (Rucker and Valentine, 1961; Gordon et al., 1970, Kitano et al., 1975; Ishikawa and Ichikuni, 1984). Although chloride is also incorporated in calcium carbonate, this occurs at 20–40 times lower concentrations than Na (Kitano et al., 1975). The much lower Cl concentration excludes primary incorporation of Na in fluid inclusions and hence suggests that Na is structurally bound in the calcite lattice. This is supported by the lack of so-called hotspots in the Na profiles.

Some cations (e.g. Mg^{2+} and Sr^{2+}) are incorporated into calcite by substituting for calcium ions (Morse et al., 2007). For these elements, seawater element/Ca values impact calcitic element/Ca values (e.g. De Nooijer et al., 2007; Segev and Erez, 2006). Since Na^{+} is not directly substituting for Ca^{2+}, due the charge difference, incorporation of Na in inorganically precipitated calcium carbonate does not depend on seawater Ca^{2+} concentration and is therefore not necessarily impacted by seawater Na/Ca (Ishikawa and Ichikuni, 1984). Instead, Na incorporation depends primarily on the activity of Na in seawater, which is a function of its concentration and, to a lesser extent, its activity coefficient (Ishikawa and Ichikuni, 1984). Increasing salinity (and hence [Na^+]) increases the activity of Na, while the associated decrease in its activity coefficient, because of the higher salinity, might explain the offset from a 1 : 1 relation between (foraminiferal) Na/Ca and salinity (Fig. 2) (Zeebe and Wolf-Gladrow, 2001). Since the activity coefficient of Na in seawater is only slightly affected by temperature over the relevant range, the effect of temperature on Na incorporation is negligible (Ishikawa and Ichikuni, 1984; Delaney et al., 1985; Lea et al., 1999; Zeebe and Wolf-Gladrow, 2001). This implies that foraminiferal Na/Ca may thus primarily reflect seawater [Na^+] and can thus be used to directly reflect seawater salinity

Incorporation of certain elements into the calcite of some foraminiferal species is correlated to ontogeny, i.e. depends on test size (Nürnberg et al., 1996; Wit et al., 2010; Dueñas-Bohórquez et al., 2011b). Since test size of the cultured foraminifera varied between salinities (Fig. 1, Table 3), the relation between foraminiferal Na/Ca and salinity may potentially have been affected by differences in test sizes. To test the potential impact of test size on the relation between Na/Ca and salinity, results for the four salinity treatments were analyzed separately. Foraminifera from experiments at salinities 30.0, 32.5, 36.1 and 38.6 show a significant correlation between size and Na/Ca ($R^2 = 0.33$, $p < 0.05$, $R^2 = 0.23$, $p < 0.05$, $R^2 = 0.59$, $p < 0.01$ and $R^2 = 0.29$, $p < 0.05$, respectively Fig. 3), indicating a potential ontogenetic effect. However, if the relation between salinity and foraminiferal Na/Ca would be exclusively caused by ontogeny, no relation between foraminiferal Na/Ca of a single chamber number (whorl position) and salinity would be expected. Chambers 3 through 11 (Fig. 4) all showed a positive correlation between Na/Ca and salinity. The correlation between foraminiferal Na/Ca and test size is, therefore, primarily caused by co-variation of both parameters with salinity. Still, a small size effect may be present due to variability in the relation between salinity and single chamber Na/Ca (Fig. 3). However, this does not effect the calibration significantly when measuring multiple chambers per individual, as done here.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀◀ ▶▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

4.2 Correcting Mg/Ca based temperatures for salinity

The incorporation of Mg in foraminiferal test carbonate is known to be affected by salinity (Nürnberg et al., 1996; Kisakürek et al., 2008; Dueñas-Bohórquez et al., 2009; Dissard et al., 2010) in addition to temperature and paired Mg/Ca and Na/Ca ratios, measured on the same individuals, now offer the opportunity to correct for such a salinity effect. The D_{Mg} of the cultured *A. tepida* correlated positively with salinity ($R^2 = 0.99$, $p < 0.01$) (Table 4, Fig. 1), indicating that the effect of seawater Mg/Ca on foraminiferal Mg/Ca did not influence our results. Within previous experiments (Kisakürek et al., 2008; Dueñas-Bohórquez et al., 2009; Dissard et al., 2010), saturation state of the seawater (Ω) was kept constant, but alkalinity and DIC varied with salinity. Assuming limited differences between species in their calcification pathways, the similarity in response of Mg/Ca with salinity (where alkalinity and DIC were kept constant) indicates that alkalinity and DIC have a minor effect on foraminiferal Mg/Ca over this range. The similarity between the relation between Mg/Ca and salinity, for such a variety of independent culture experiments, analytical approaches and species, furthermore hints at a general control of salinity on the incorporation of Mg into foraminiferal calcite. The relation between salinity and foraminiferal Mg/Ca could, therefore, be related purely to a-biotic differences in element speciation. This hypothesis was tested by modeling the speciation and activities of (free) elements in the culture media using PHREEQC (Parkhurst and Appelo, 1999).

Model results showed that the activities of free Mg and Ca increase linearly with salinity, and are an order of magnitude higher for free Mg^{2+} than for free Ca^{2+} (Fig. 6). So, despite the fact that we kept the Mg/Ca concentration ratio constant with salinity, the free Mg to free Ca activity ratios of the culture media increased with increasing salinity, providing a mechanistic link between salinity and foraminiferal Mg/Ca.

Incorporation of Mg might also be affected by ontogeny, since test size of the cultured foraminifera varies significantly with salinity (Fig. 1, Table 4). Foraminifera from experiments at salinities 30.0 and 32.5 do not show a significant correlation between size and Mg/Ca ($R^2 = 0.02$, $p > 0.10$ and $R^2 = 0.03$, $p > 0.10$ respectively, Fig. 3). At higher salinities (36.1 and 38.6), however, a small but significant effect of size on foraminiferal Mg/Ca is present ($R^2 = 0.22$, $p < 0.05$ and $R^2 = 0.45$, $p < 0.01$ respectively). Chambers 3 through 14 (Fig. 5) all show a positive correlation between Mg/Ca and salinity, indicating that a minor ontogenetic effect is to be expected, if multiple chambers per individual foraminifer are measured, following the same reasoning as for the Na/Ca.

The impact of salinity on foraminiferal Mg/Ca as measured here may impact reconstructed temperatures by 0.25–1.5 °C per salinity unit, depending on the sensitivity of Mg incorporation to temperature (Nürnberg et al., 1996; Kisakürek et al., 2008; Dueñas-Bohórquez et al., 2009; Dissard et al., 2010; Wit et al., 2012). However, in addition to independent and direct reconstructions of seawater salinity, foraminiferal Na/Ca values can also be used to correct the effect of salinity on Mg/Ca-temperature reconstructions. As an example, the relation established between *Ammonia tepida* Mg/Ca values and salinity was combined with the relation between temperature and Mg/Ca for *Ammonia beccarii* (Toyofuku et al., 2011). A multiple regression combining the response of Mg/Ca as a function of salinity (Fig. 2) and temperature (Toyofuku et al., 2011) resulted in Eq. (1), in which foraminiferal Mg/Ca is depending on both temperature (T) and salinity (S).

$$\mathrm{Mg/Ca}{=}0.21 \cdot e^{(0.07 \cdot T)} \cdot (0.05 \cdot S + 0.24) \tag{1}$$

Within Eq. (1), Mg/Ca is now depending on both temperature and salinity. Since salinity can now be independently reconstructed using foraminiferal Na/Ca values (Fig. 2), paired analyses of Na/Ca and Mg/Ca allows correcting Mg/Ca-based temperatures for changes in salinity.

5 Conclusions

Foraminiferal Na/Ca and Mg/Ca as measured on cultured benthic foraminifer *A. tepida* correlate significantly with salinity. This positive correlation is related to the increase in the activity of free Mg/Ca and free Na^+ with increasing salinity. Although size effects might play a role in these calibrations, their effect is insignificant compared to the effect of salinity, and negligible (within the experimental error) when multiple chambers in different individuals are analyzed. Foraminiferal Na/Ca appears to be a robust and independent proxy for salinity, one of the most sought after paleoceanographic proxies, enabling a whole new range of independent salinity reconstructions. Furthermore, in combination with foraminiferal Mg/Ca, it allows a direct correction for one of the most used paleo-thermometers (i.e. Mg/Ca).

Acknowledgements. This research is supported by the Utrecht University, the Darwin Centre for Geobiology projects "Biological validation of proxies for temperature, salinity, oxygenation and pCO_2 based on experimental evidence using benthic foraminiferal cultures" and Natural Environment Research Council fellowship #NE/J018856/1 to MW.

References

Anand, P., Elderfield, H., and Conte, M. H.: Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap series, Paleoceanography, 18, 1050–1064, 2003.

Bemis, B. E., Spero, H. J., Bijma, J., and Lea, D. W.: Reevaluation of the oxygen isotopic composition of planktonic foraminifera: experimental results and revised paleotemperature equations, Paleoceanography, 13, 150–160, 1998.

Delaney, M. L., Bé, A. W. H., and Boyle, E. A.: Li, Sr, Mg and Na in foraminiferal calcite shells from laboratory culture, sediment traps, and sediment cores, Geochim. Cosmochim. Ac., 49, 1327–1341, 1985.

de Nooijer, L. J., Reichart, G. J., Dueñas-Bohórquez, A., Wolthers, M., Ernst, S. R., Mason, P. R. D., and van der Zwaan, G. J.: Copper incorporation in foraminiferal calcite: results from culturing experiments, Biogeosciences, 4, 493–504, doi:10.5194/bg-4-493-2007, 2007.

Dissard, D., Nehrke, G., Reichart, G. J., and Bijma, J.: The impact of salintiy on the Mg/Ca and Sr/Ca ratio in the benthic foraminifera *Ammonia tepida*: results from culture experiments, Geochim. Cosmochim. Ac., 74, 928–940, 2010.

Dueñas-Bohórquez, A., da Rocha, R. E., Kuroyanagi, A., Bijma, J., and Reichart, G. J.: Effect of salinity and seawater calcite saturation state on Mg and Sr incorporation in cultured planktonic foraminifera, Mar. Micropal., 73, 178–189, 2009.

Dueñas-Bohórquez, A., Raitzsch, M., De Nooijer, L. J., and Reichart, G. J.: Independent impacts of calcium and carbonate ion concentration on Mg and Sr incorporation in cultured benthic foraminifera, Mar. Micropal., 81, 122–130, 2011a.

Dueñas-Bohórquez, A., da Rocha, R. E., Kuroyanagi, A., De Nooijer, L. J., Bijma, J., and Reichart, G. J.: Interindividual variability and ontogenetic effects on Mg and Sr incorporation in the planktonic foraminifer *Globigerinoides sacculifer*, Geochim. Cosmochim. Ac. 75, 520–532, 2011b.

Elderfield, H. and Ganssen, G. M.: Past temperatures and δ^{18}O of surface waters inferred from foraminiferal Mg/Ca ratios, Nature, 405, 442–445, 2000.

Epstein, S., Buchsbaum, R., Lowenstam, and Urey, H. C.: Revised carbonate-water isotopic temperature scale, Geol. Soc. Am. Bull., 64, 1315–1325, 1953.

Erez, J.: The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies, Rev. Miner. Geochem., 54, 115–149, 2003.

Gat, J. R.: Oxygen and hydrogen isotopes in the hydrologic cycle, Ann. Rev. Earth Planet. Sci., 24, 225–262, 1996.

Gordon, C. M., Carr, R. A., and Larson, R. E.: The influence of environmental factors on the sodium and manganese content of barnacle shells, Limnol. Ocean., 15, 461–466, 1970.

Hastings, D. W., Russell, A. D., and Emerson, S. R.: Foraminiferal magnesium in *Globigerinoides sacculifer* as a paleotemperature proxy, Paleoceanography, 13, 161–169, 1998.

Hayward, B. W., Holzmann, M., Grenfell, H. R., Pawlowski, J., and Triggs, C. M.: Morphological distinction of molecular types in Ammonia – towards a taxonomic revision of the world's most commonly misidentified foraminifera, Mar. Micropal., 50, 237–271, 2004.

Ishikawa, M. and Ichikuni, M.: Uptake of sodium and potassium by calcite, Chem. Geol., 42, 137–146, 1984.

Israelson, C. and Buchardt, B.: Strontium and oxygen isotopic composition of East Greenland rivers and surface waters: implication for palaeoenvironmental interpretation, Palaeogeogr. Palaeoclimatol. Palaeoecol., 153, 93–104, 1999.

Jochum, K. P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D. E., Stracke, A., Birbaum, K., Frick, D. A., Günther, G., and Enzweiler, J.: Determination of Reference Values for NIST SRM 610–617 Glasses Following ISO Guidelines, Geostand. Geoanal. Res., 35, 397–429, 2011.

Kester, D. R., Duedall, I. W., Connors, D. N., and Pytkowicz, R. M.: Preperation of artificial seawater, Limonol. Oceangr., 12, 176–179, 1967.

Kisakürek, B., Eisenhauer, A., Böhm, F., Garbe-Schönberg, D., and Erez, J.: Controls on Shell Mg/Ca and Sr/Ca in cultured planktonic foraminiferan, *Globigerinoides ruber* (white), Earth Planet. Sci. Lett., 273, 260–269, 2008.

Kitano, Y., Okumura, M., and Idogaki: M. Incorporation of sodium, chloride and sulfate with calcium carbonate, Geochem. J., 9, 75–84, 1975.

Lea, D. W., Mashiotta, T. A., and Spero, H. J.: Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing, Geochim. Cosmochim. Ac., 63, 2369–2379, 1999.

Lear, C. H., Elderfield, H., and Wilson, P. A.: Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite, Science, 287, 269–272, 2000.

Lewis, E. and Wallace, D.: Program developed for CO_2 system calculations, edited by: Allison, L. J., Carbon Dioxide Information System, Oak Ridge National Laboratory, Oak Ridge, 38 pp., 1998.

Mertens, K. N., Ribeiro, S., Bouimearhan, I., Caner, H., Combourieu-Nebout, N., Dale, B., De Vernal, A., Ellegaard, M., Filipova, M., Godhe, A., Goubert, E., Grøsfjeld, K., Holzwarth, U., Kotthoff, U., Leroy, S. A. G., Londeix, L., Marret, F., Matsuoka, K., Mudie, P. J., Naudts, L., Pena-Manjarrez, J. L., Persson, A., Popescu, S. M., Pospelova, V., Sangiorgi, F., van der Meer, M. T. J., Vink, A., Zonneveld, K. A. F., Vercauteren, D., Vlassenbroeck, J., and Louwye, S.: Process length variation in cysts of a dinoflagellate, *Lingulodium machaerophorum*, in surface sediments: investigating its potential as salinity proxy, Mar. Micropaleo., 70, 54–69, 2009.

Morse, J. W., Arvidson, R. S., and Lüttge, A.: Calcium carbonate formation and dissolution, Chem. Rev., 107, 342–381, 2007.

Murray, J. W.: Living foraminifers of lagoons and estuaries, Micropaleontology, 14, 435–455, 1968.

Nürnberg, D., Bijma, J., Hemleben, C.: Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperature, Geochim. Cosmochim. Ac., 60, 803–814, 1996.

O'Neil, J. R., Clayton, R. N., Mayeda, T. K.: Oxygen isotope fractionation in divalent metal carbonates, J. Chem. Phys., 51, 5547–5558, 1969.

Parkhurst, D. L. and Appelo, C. A. J.: User's Guide to PHREEQC, US Geological Survey, 1999.

Prahl, F. G. and Wakeham, S. G.: Calibration of unsaturation patterns in long-chain ketone composition for palaeotemperature assessment, Nature 330, 367–369, 1987.

Reichart, G. J., Jorissen, F., Anschutz, P., and Mason, P. R. D.: Single foraminiferal test chemistry records the marine environment, Geology 31, 355–358, 2003.

Rohling, E. J. and Bigg, G. R.: Paleosalinity and δ^{18}O: a critical assessment, J. Geophys. Res., 103, 1307–1318, 1998.

Rucker, J. B. and Valentine, J. W.: Salinity response of trace elements concentration in *Crassostrea virginica*, Nature, 190, 1099–1100, 1961.

Sadekov, A., Eggins, S., De Deckker, P., and Kroon, D.: Uncertainties in seawater thermometry deriving from intratest and intertest Mg/Ca variability in *Globigerinoides ruber*, Paleoceanography, 23, 1–12, 2008.

Shackleton, N. J.: Attainment of isotopic equilibrium between ocean water and benthonic foraminifera genus Uvigerina: isotopic changes in the oceans during the last glacial, Cent. Natl. Rech. Sci. Colloq. Int., 219, 203–210, 1974.

Schouten, S., Ossebaar, J., Schreiber, K., Kienhuis, M. V. M., Langer, G., Benthien, A., and Bijma, J.: The effect of temperature, salinity and growth rate on the stable hydrogen isotopic composition of long chain alkenones produced by *Emiliania huxleyi* and *Gephyrocapsa oceanica*, Biogeosciences, 3, 113–119, doi:10.5194/bg-3-113-2006, 2006.

Segev, E. and Erez, J.: Effect of Mg/Ca ratio in seawater on shell composition in shallow benthic foraminifera, Geochem. Geophys. Geosys., 7, 1–8, 2006.

Toyofuku, T., Suzuki, M., Sug, H., Sakai, S., Suzuki, A., Ishikawa, T., De Nooijer, L. J., Schiebel, R., Kawahata, H., and Kitazato, H.: Mg/Ca and δ^{18}O in the brackish shallow-water benthic foraminifer *Ammonia "beccarii"*, Mar. Micropaleo., 78, 113–120, 2011.

Van der Meer, M. T. J., Baas, M., Rijpstra, W. I. C., Marino, G., Rohling, E. J., Sinninghe Damsté, J. S., and Schouten, S.: Hydrogen isotopic compositions of long-chain alkenones record freshwater flooding of the Eastern Mediterranean at the onset of sapropel deposition, Earth Planet. Sci. Lett., 262, 594–600, 2007.

Weldeab, S., Lea, D. W., Schneider, R. R., and Andersen, N.: Centennial scale climate instabilities in a wet early Holocene West African monsoon, Geophys. Res. Lett., 34, 1–6, 2007.

Wit, J. C., Reichart, G. J., Jung, S. J. A., and Kroon, D.: Approaches to unravel seasonality in sea surface temperatures using paired single-specimen foraminiferal δ^{18}O and Mg/Ca analyses, Paleoceanography 25, 1–15, 2010.

Wit, J. C., de Nooijer, L. J., Barras, C., Jorissen, F. J., and Reichart, G. J.: A reappraisal of the vital effect in cultured benthic foraminifer *Bulimina marginata* on Mg/Ca values: assessing temperature uncertainty relationships, Biogeosciences, 9, 3693–3704, doi:10.5194/bg-9-3693-2012, 2012.

Zeebe, R. E. and Wolf-Gladrow, D.: CO_2 in Seawater: Equilibrium, Kinetics, Isotopes, Elsevier Oceanography Series 65, edited by: Halpern, D., Elsevier, Amsterdam, 346 pp., 2001.

Zonneveld, K. A. F., Hoek, R. P., Brinkhuis, H., and Willems, H.: Geographical distributions of organic-walled dinoflagellate cysts un surficial sediments of the Benguela upwelling region and their relationship to upper ocean conditions, Prog. Oceanogr., 48, 25–72, 2001.

Table 1. Amounts of salt used for 1 L of artificial seawater following the recipe of Kester et al. (1967). Artificial seawater is mixed with one liter of natural seawater at salinity of 35.

Salinity	30.0	32.5	36.1	38.6
NaCl (g)	17.0509	20.4611	25.2353	28.6455
Na_2SO_4 (g)	2.8563	3.4276	4.2273	4.7986
KCl (g)	0.4825	0.5790	0.7140	0.8105
$NaHCO_3$ (g)	0.1960	0.1960	0.1960	0.1960
KBr (g)	0.0698	0.0838	0.1034	0.1173
$B(OH)_3$ (g)	0.0260	0.0260	0.0260	0.0260
NaF (g)	0.0021	0.0026	0.0032	0.0036
1M $MgCl_2$ (mL)	37.6280	45.1536	55.6894	63.2150
1M $CaCl_2$ (mL)	7.3403	8.8084	10.864	12.332
1M $SrCl_2$ (mL)	0.0713	0.0855	0.106	0.120

Table 2. Experiment culture media data. Carbonate ion concentration and $\Omega_{calcite}$ are calculated using CO2SYS and alkalinity and DIC as system parameters (Lewis and Wallace, 1998). Standard deviations are based on all measurements over the course of each experiment.

Experiment	Salinity	Temperature (°C)	DIC ($\mu mol\,kg^{-1}$)	Alkalinity ($\mu mol\,kg^{-1}$)	CO_3^{2-} ($\mu mol\,kg^{-1}$)	$\Omega_{Calcite}$	Mg/Ca ($mol\,mol^{-1}$)
S 30.0	30.0 ± 0.1	20.1 ± 0.3	2131 ± 17	2462 ± 32	246 ± 15	6.10 ± 0.4	4.98 ± 0.02
S 32.5	32.5 ± 0.2	20.0 ± 0.2	2222 ± 25	2543 ± 46	238 ± 50	5.81 ± 1.2	5.08 ± 0.03
S 36.1	36.1 ± 0.2	19.9 ± 0.1	2188 ± 24	2526 ± 23	244 ± 32	5.80 ± 0.8	5.15 ± 0.04
S 38.6	38.6 ± 0.1	20.0 ± 0.2	2126 ± 7	2493 ± 21	258 ± 40	6.01 ± 0.4	5.19 ± 0.04
μ	34.3	20.0	2161	2502	248	5.97	5.10
σ	3.8	0.4	41	40	13	0.44	0.09

Table 3. Individual Na/Ca values for cultured benthic foraminifer *A. tepida*. The uncertainty (±) in the individual measurements and the average (bold) are based on the standard error of the mean ($\sigma/\sqrt{n}$). Na/Ca values of individual foraminifers are based on the ablation profiles of 2–4 chambers.

Salinity	Size (μm)	Na/Ca (mmol mol^{-1})	Average (mmol mol^{-1})	Salinity	Size (μm)	Na/Ca (mmol mol^{-1})	Average (mmol mol^{-1})
30.0	186	6.73 ± 0.96	5.83 ± 0.17	36.1	128	6.39 ± 0.16	6.87 ± 0.41
30.0	165	6.52 ± 0.78		36.1	117	8.65 ± 0.67	
30.0	187	5.95 ± 0.31		36.1	134	8.61 ± 1.21	
30.0	189	5.78 ± 0.26		36.1	146	7.00 ± 0.88	
30.0	178	5.44 ± 0.34		36.1	173	6.21 ± 0.33	
30.0	192	5.52 ± 0.27		36.1	179	6.28 ± 0.21	
30.0	216	5.79 ± 0.34		36.1	176	5.48 ± 0.32	
30.0	228	5.17 ± 0.27		36.1	181	6.31 ± 0.45	
30.0	233	5.60 ± 0.31		38.6	133	6.94 ± 0.76	7.69 ± 0.30
32.5	188	6.57 ± 0.73	6.12 ± 0.33	38.6	128	9.29 ± 1.82	
32.5	184	5.44 ± 0.64		38.6	131	7.70 ± 1.89	
32.5	159	6.31 ± 0.58		38.6	116	8.34 ± 0.13	
32.5	156	7.24 ± 1.12		38.6	154	8.45 ± 0.34	
32.5	180	7.77 ± 1.32		38.6	150	7.00 ± 0.67	
32.5	215	5.95 ± 0.54		38.6	159	6.55 ± 0.17	
32.5	197	6.83 ± 0.32		38.6	139	8.02 ± 0.65	
32.5	191	5.66 ± 0.15		38.6	149	6.93 ± 0.45	
32.5	206	4.97 ± 0.50					
32.5	196	4.43 ± 0.30					

Table 4. Mg/Ca and size data for the individual foraminifera of each salinity experiment. The uncertainty (±) in the individual measurements and the average (bold) are based on the standard error of the mean ($\sigma/\sqrt{n}$). Mg/Ca values of individual foraminifers are based on the ablation profiles of 2–4 chambers.

Sample	Experiment	Size (µm)	Mg/Ca (mmol/mol)	Average Mg/Ca	Sample	Experiment	Size (µm)	Mg/Ca (mmol/mol)	Average Mg/Ca
1	S 30.0	192	1.74 ± 0.19	1.48 ± 0.05	39	S 36.1	208	2.05 ± 0.27	
2	S 30.0	198	1.45 ± 0.16		40	S 36.1	207	1.82 ± 0.17	
3	S 30.0	216	1.79 ± 0.88		41	S 36.1	193	1.66 ± 0.38	
4	S 30.0	220	1.72 ± 0.08		42	S 36.1	194	1.72 ± 0.28	
5	S 30.0	217	1.40 ± 0.28		43	S 36.1	173	2.46 ± 0.34	
6	S 30.0	237	1.33 ± 0.21		44	S 36.1	179	1.69 ± 0.02	
7	S 30.0	289	1.29 ± 0.32		45	S 36.1	175	2.07 ± 0.30	
8	S 30.0	198	1.56 ± 0.26		46	S 36.1	176	1.97 ± 0.29	
9	S 30.0	206	1.82 ± 0.40		47	S 36.1	181	2.12 ± 0.26	
10	S 30.0	172	1.29 ± 0.28		48	S 36.1	147	1.88 ± 0.29	
11	S 30.0	185	1.41 ± 0.20		49	S 36.1	174	1.91 ± 0.26	
12	S 30.0	186	1.40 ± 0.27		50	S 36.1	153	1.81 ± 0.12	
13	S 30.0	165	1.61 ± 0.16		51	S 36.1	147	2.74 ± 1.08	
14	S 30.0	187	0.98 ± 0.07		52	S 36.1	140	1.88 ± 0.31	
15	S 30.0	189	1.40 ± 0.11		53	S 36.1	128	1.98 ± 0.14	
16	S 30.0	178	1.59 ± 0.16		54	S 36.1	117	2.09 ± 0.41	
17	S 30.0	221	1.43 ± 0.19		55	S 36.1	134	1.66 ± 0.31	
18	S 32.5	215	2.18 ± 0.45	1.70 ± 0.05	56	S 36.1	146	1.86 ± 0.19	
19	S 32.5	197	1.50 ± 0.14		57	S 38.6	190	1.75 ± 0.11	2.21 ± 0.08
20	S 32.5	191	1.65 ± 0.37		58	S 38.6	182	1.55 ± 0.18	
21	S 32.5	206	1.63 ± 0.60		59	S 38.6	179	1.93 ± 0.23	
22	S 32.5	196	1.55 ± 0.24		60	S 38.6	180	2.22 ± 0.24	
23	S 32.5	225	1.53 ± 0.26		61	S 38.6	169	1.94 ± 0.17	
24	S 32.5	222	1.41 ± 0.24		62	S 38.6	154	2.10 ± 0.25	
25	S 32.5	219	1.56 ± 0.08		63	S 38.6	150	2.46 ± 0.33	
26	S 32.5	226	1.87 ± 0.24		64	S 38.6	159	2.03 ± 0.26	
27	S 32.5	207	1.96 ± 0.22		65	S 38.6	139	2.90 ± 0.31	
28	S 32.5	222	1.85 ± 0.47		66	S 38.6	149	2.07 ± 0.19	
29	S 32.5	185	1.76 ± 0.29		67	S 38.6	129	2.32 ± 0.14	
30	S 32.5	197	1.93 ± 0.51		68	S 38.6	149	1.87 ± 0.51	
31	S 32.5	171	1.69 ± 0.42		69	S 38.6	143	2.01 ± 0.54	
32	S 32.5	236	1.30 ± 0.21		70	S 38.6	116	2.86 ± 0.65	
33	S 32.5	188	1.47 ± 0.05		71	S 38.6	120	2.13 ± 0.10	
34	S 32.5	184	1.67 ± 0.12		72	S 38.6	133	2.57 ± 0.39	
35	S 32.5	159	1.83 ± 0.29		73	S 38.6	128	2.66 ± 0.11	
36	S 32.5	156	1.63 ± 0.25		74	S 38.6	131	1.93 ± 0.67	
37	S 32.5	180	1.97 ± 0.20		75	S 38.6	122	2.41 ± 0.32	
38	S 36.1	236	1.44 ± 0.30	1.94 ± 0.07	76	S 38.6	116	2.57 ± 0.22	

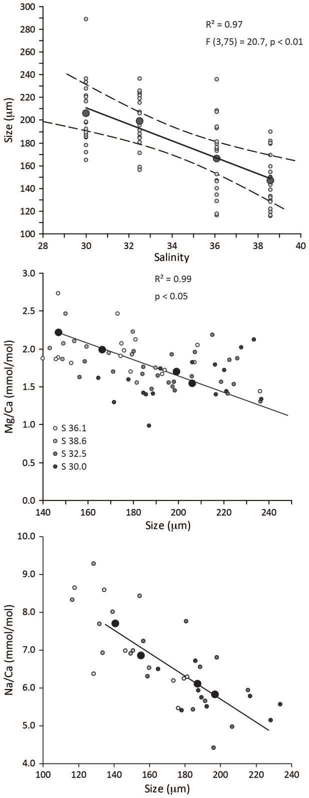

Fig. 1. Individual size (upper panel), foraminiferal Mg/Ca values (middle panel) and Na/Ca values (lower panel) as measured on *A. tepida* versus the salinity of the culture solutions. Correlation coefficients are based on the averaged values. A one-way analyses of variance (ANOVA) was performed with all data points to test the experimental effect of salinity for its significance.

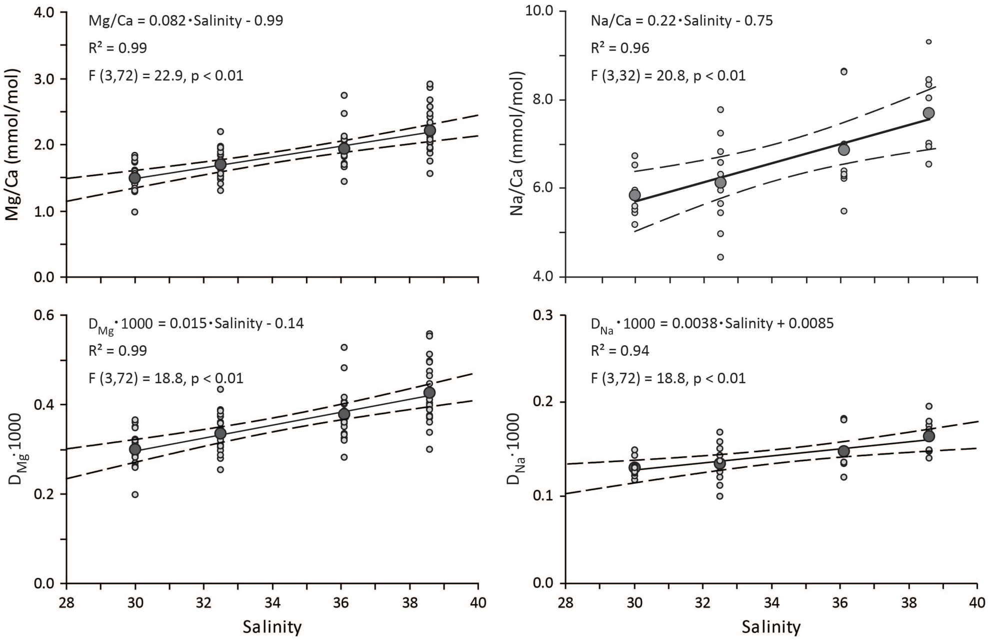

Fig. 2. Foraminiferal Mg/Ca and Na/Ca values (upper panels) or D_{Mg} and D_{Na} (lower panels) as measured on *A. tepida* versus the salinity of the culture solutions. Correlation coefficients are based on the averaged values. A one-way analysis of variance (ANOVA) was performed with all data points to test the experimental effect of salinity for its significance.

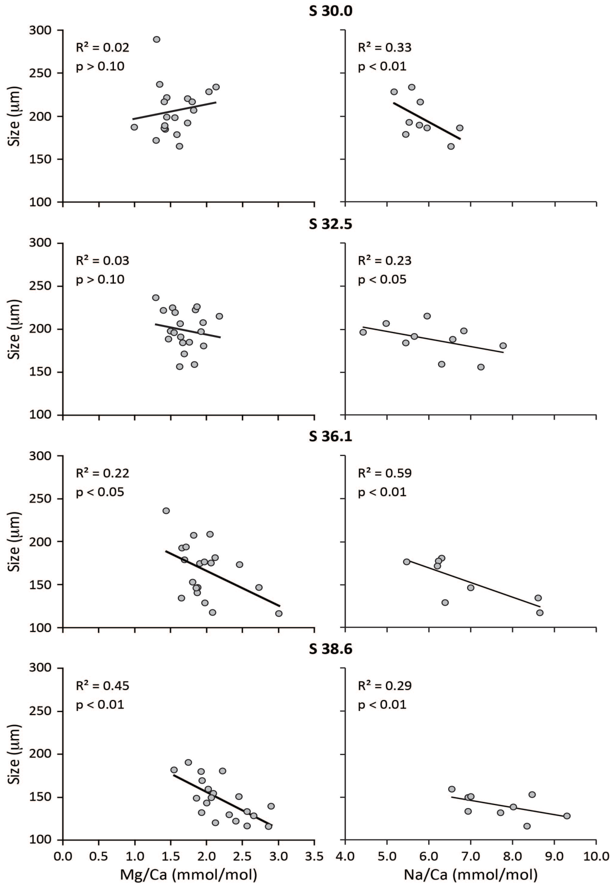

Fig. 3. Measured Mg/Ca and Na/Ca values of individual foraminifera versus size for the all salinity experiments. All relations are tested for significance with a one-way ANOVA.

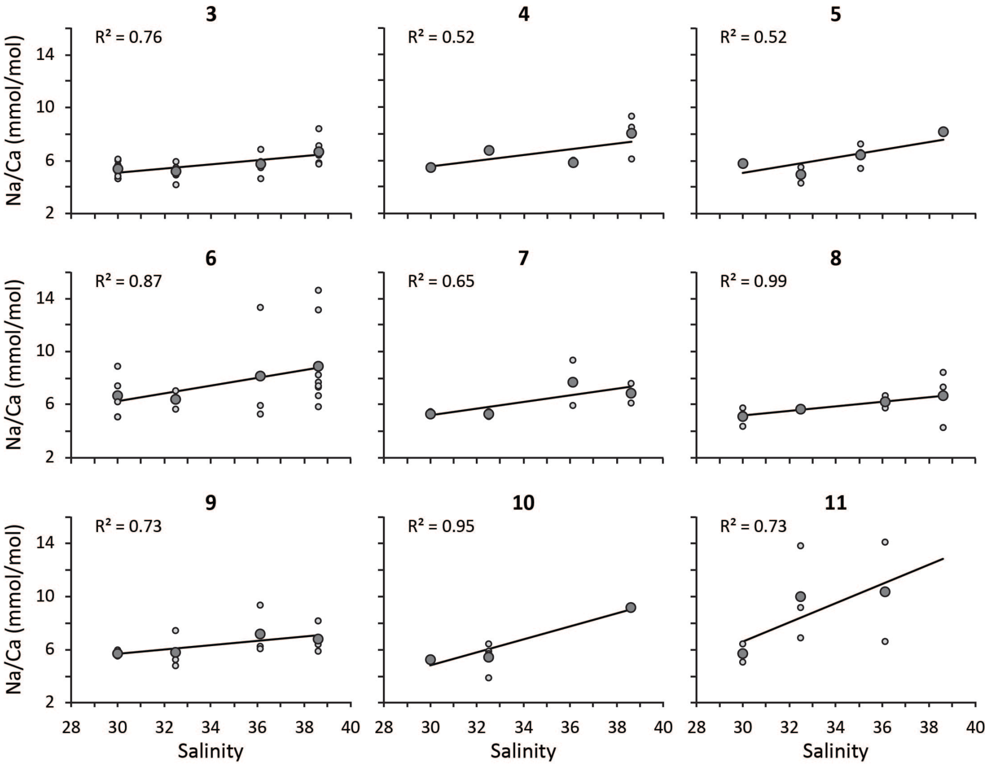

Fig. 4. Salinity versus individual Mg/Ca values for each individual chamber. Chamber position is determined by counting the chambers in the whirl, starting at the youngest chambers. Correlation coefficients are determined on the averaged values per experiment.

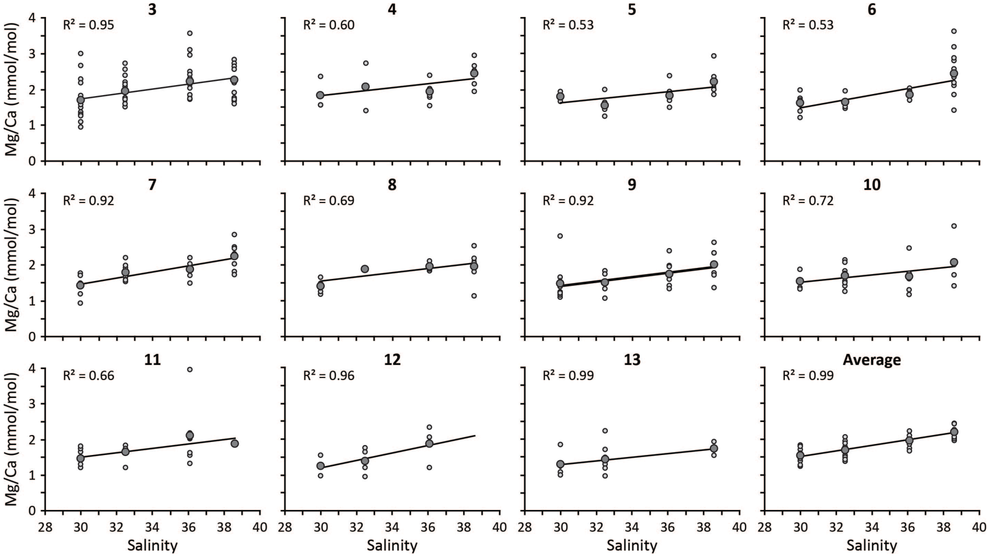

Fig. 5. Salinity versus individual Na/Ca values for each individual chamber. Chamber position is determined by counting the chambers in the whorl, starting at the youngest chambers. Correlation coefficients are determined on the averaged values per experiment.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
I◀
▶I
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

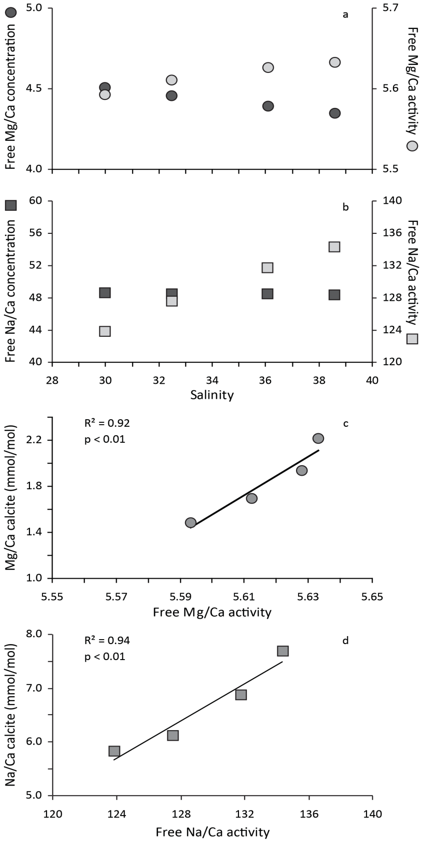

Fig. 6. Experiment salinity versus modeled concentration and activity of free Mg/Ca **(a)** and Na/Ca values **(b)** and measured foraminiferal Mg/Ca **(c)** and Na/Ca **(d)** versus the free Mg/Ca and Na/Ca activity. Parameters were modeled using PHREEQC (LLNL database, Parkurst and Appelo, 1999).