



A novel salinity proxy based on Na incorporation into foraminiferal calcite

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Abstract. Salinity and temperature determine seawater density, and differences in both thereby control global thermohaline 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 $[\text{Na}^+]$ or $[\text{Cl}^-]$. This study investigates the impact of salinity on foraminiferal Na/Ca values by laser ablation ICP-MS analyses 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 culturing experiment than those maintained at higher salinities (36.1, 7–8 chambers, and 38.6, 6–7 chambers), suggesting that growth rates in this species are promoted by lower salinities. The Na/Ca of cultured specimens correlates significantly with seawater salinity ($\text{Na}/\text{Ca} = 0.22S - 0.75$, $R^2 = 0.96$, $p < 0.01$) and size. Values for Na/Ca and D_{Na} vary between 5.17 and 9.29 mmol mol^{-1} and $0.12 - 0.16 \times 10^{-3}$, which are similar to values from inorganic precipitation experiments. The significant correlation between test size and Na/Ca results from co-variation with salinity. This implies that foraminiferal Na/Ca could serve as a robust and independent proxy for salinity, enabling salinity reconstructions independent of calcitic $\delta^{18}\text{O}$.

1 Introduction

Temperature and salinity are among the most relevant parameters in studying past ocean circulation, since together they control ocean water density and thereby thermohaline circulation. A large number of proxies for reconstructing seawater temperature have been developed (e.g., carbonate $\delta^{18}\text{O}$ and Mg/Ca), some of which are now well 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. Currently, salinity is reconstructed using dinoflagellate and diatom species composition (Zonneveld et al., 2001), process length of dinoflagellates (Mertens et al., 2009), bivalve strontium isotope composition (Israelson and Buchardt, 1999), Ba/Ca of foraminiferal calcite (Weldeab et al., 2007) and the morphology and size of *Emiliania huxleyi* placoliths (Bollmann et al., 2009). These proxies, however, are either inferred from indirect changes in ecology or strongly dependent on regional oceanography (i.e., river water input). Other indirect approaches rely on the correlation between seawater oxygen and hydrogen isotope composition and salinity (Gat, 1996). Foraminiferal $\delta^{18}\text{O}$ (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;

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 1 L of natural seawater at a salinity of 35.

Salinity	30.0	32.5	36.1	38.6
NaCl (g)	17.0509	20.4611	25.2353	28.6455
Na ₂ SO 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

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 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 (*Crassostrea virginica*) as reported by Rucker and Valentine (1961), barnacle shells (Gordon et al., 1970), and inorganically precipitated calcium carbonate (Kitano et al., 1975; Ishikawa and Ichikuni, 1984; Okukura and Kitano, 1986). Application in paleoceanographic reconstructions requires, however, a more widely distributed 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, for example, Mg; Nürnberg et al., 1996; Kisakürek et al., 2008; Dueñas-Bohórquez et al., 2009), changes in Na/Ca can be interpreted in terms of salinity only.

2 Methods

The benthic, cosmopolitan foraminifer *Ammonia tepida* inhabits a wide range of environments, and is found in habitats with highly variable temperatures and salinities (Murray, 1968; Hayward et al., 2004). This adaptation makes it a suit-

able 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, living specimens were isolated from the sediment and placed in filtered (0.2 µm) seawater with a salinity of 35, at 20 °C. Vitality of specimens was assessed by checking for algal content (*Dunaliella salina*) in the last three chambers, movement within Petri dish and presence of active pseudopodia emerging from the aperture. 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 setup. This consisted of a closed-system in order to minimize changes to the set salinities. Flasks contained 250 mL of culture media, which was refreshed once every three weeks. All salinity treatments were placed in an incubator set at 20 ± 0.1 °C.

Culture media consisted of 50 % 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 NaHCO₃ 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). Alkalinity was determined by automated titration of 50 mL of sample water with a weak acid solution (0.1 M HCl). Subsamples (10 mL) for DIC were filtered over a 0.2 µm mesh and measured on an automated Shimadzu TOC 5050 (TIC method, ±2 µmol L⁻¹, Utrecht University). Element composition of the culture media was determined by ICP-OES (Spectro Arcos). Samples from the stock solution and experiments for elemental composition, DIC and alkalinity were taken at the beginning and end of the experiment and twice during the experiment itself. 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 were 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. Diameter of individual Foraminifera was determined using a microscope camera (Nikon Digital Sight DS-Fi1), calibrated at the micrometer scale (Ernst

Table 2. Experiment culture media data: carbonate ion concentration and Ω_{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. Low Sr/Ca values at a salinity of 30 are due to an error in culture media preparation and do fall in line with the other experiments when corrected for (D_{Sr} , Fig. 3).

Experiment	Salinity	Temperature (°C)	DIC ($\mu\text{mol kg}^{-1}$)	Alkalinity ($\mu\text{mol kg}^{-1}$)	CO_3^{2-} ($\mu\text{mol kg}^{-1}$)	Ω_{Calcite}	Mg/Ca (mol mol^{-1})	Na/Ca (mol mol^{-1})	Sr/Ca (mmol 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	46.97 ± 0.48	5.01 ± 0.08
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	47.82 ± 0.69	9.27 ± 0.15
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	48.76 ± 0.89	9.38 ± 0.15
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	48.95 ± 0.44	9.55 ± 0.15
μ		20.0	2161	2502	248	5.97	5.10	48.12	8.30
σ		0.4	41	40	13	0.44	0.09	0.91	2.20

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

Salinity	Size (μm)	Chambers	Na/Ca (mmol mol^{-1})	Average (mmol mol^{-1})	Salinity	Size (μm)	Chambers	Na/Ca (mmol mol^{-1})	Average (mmol mol^{-1})
30.0	186	13	6.73 ± 0.96	5.83 ± 0.17	36.1	128	12	6.39 ± 0.16	6.87 ± 0.41
30.0	165	11	6.52 ± 0.78		36.1	117	9	8.65 ± 0.67	
30.0	187	14	5.95 ± 0.31		36.1	134	11	8.61 ± 1.21	
30.0	189	13	5.78 ± 0.26		36.1	146	8	7.00 ± 0.88	
30.0	178	13	5.44 ± 0.34		36.1	173	9	6.21 ± 0.33	
30.0	192	12	5.52 ± 0.27		36.1	179	9	6.28 ± 0.21	
30.0	216	14	5.79 ± 0.34		36.1	176	10	5.48 ± 0.32	
30.0	228	10	5.17 ± 0.27		36.1	181	10	6.31 ± 0.45	
30.0	233	12	5.60 ± 0.31		38.6	133	7	6.94 ± 0.76	7.69 ± 0.30
32.5	188	17	6.57 ± 0.73	6.12 ± 0.33	38.6	128	9	9.29 ± 1.82	
32.5	184	17	5.44 ± 0.64		38.6	131	11	7.70 ± 1.89	
32.5	159	15	6.31 ± 0.58		38.6	116	8	8.34 ± 0.13	
32.5	156	13	7.24 ± 1.12		38.6	154	6	8.45 ± 0.34	
32.5	180	15	7.77 ± 1.32		38.6	150	10	7.00 ± 0.67	
32.5	215	10	5.95 ± 0.54		38.6	159	9	6.55 ± 0.17	
32.5	197	11	6.83 ± 0.32		38.6	139	8	8.02 ± 0.65	
32.5	191	11	5.66 ± 0.15		38.6	149	7	6.93 ± 0.45	
32.5	206	10	4.97 ± 0.50						
32.5	196	10	4.43 ± 0.30						

Leitz GmbH, Wetzlar) and computer software (Nikon Imaging SOFT NIS-Elements BR). 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).

Calcitic Na/Ca, Sr/Ca and Mg/Ca were determined using deep ultraviolet wavelength (193 nm) laser ablation (LA) (Geolas 200Q Excimer) coupled to a sector field inductively coupled plasma mass spectrometer (ICP-MS) (Element 2, Thermo Scientific), at Utrecht University. Prior to LA-ICP-MS measurements, foraminiferal tests were cleaned in pH buffered 5 % sodium hypochloride (NaOCl) for 10 min to remove organic material and rinsed twice in ultra pure (Milli-Q) water. Individual Foraminifera were subsequently rinsed in 0.5 mL Eppendorf cups with ultra pure water (Milli-Q)

(3 times), methanol (2 times), ultra pure water (Milli-Q) (3 times) with a sonication step between each rinse and dried before laser ablation analyses. 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 $\sim 1 \text{ J cm}^{-2}$. 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 ($\sim 5 \text{ J cm}^{-2}$). Using different ablation energies for glass and calcite was previously shown not to affect the analyses (Hathorne et al., 2008; Wit et al., 2010; Dueñas-Bohórquez

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

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

et al., 2011b). It has furthermore been shown that there is no difference in element/Ca ratios between laser ablation and solution-based ICP-MS when measuring foraminiferal calcite (e.g., Eggins et al., 2003; Sadekov et al., 2008; Disard et al., 2010; Wit et al., 2010; Dueñas-Bohórquez et al., 2011b). Sodium concentrations in the NIST610 are notably higher than those in foraminiferal calcite, which might influence determined foraminiferal Na/Ca values through introduction of contamination after ablating the glass standard. Therefore, sodium background values were monitored (30–60 s) before measuring individual Na/Ca on Foraminifera as well as the overall increase over one measuring sequence. Recorded background for ^{23}Na before and after ablation of the NIST610 did not change notably (200–400 000 cps), nor did it change over the course of a day. Integration windows that separate the calcitic signal from background and detection of any contaminants at the test surface were done us-

ing designated software (Glitter) (Dueñas-Bohórquez et al., 2009; Wit et al., 2012). Elemental ratios with respect to Ca were based on the average of each ablation profile (Fig. 1).

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 the mean

Table 5. Sr/Ca and size data for the individual Foraminifera of each salinity experiment: the uncertainty (\pm) in the individual measurements and the average (bold) are based on the standard error of the mean (σ/\sqrt{n}). Mg/Ca values of individual foraminifers are based on the ablation profiles of 2–4 chambers.

Sample	Experiment	Size (μm)	Chambers	Sr/Ca (mmol mol^{-1})	Average Sr/Ca	Sample	Experiment	Size (μm)	Chambers	Sr/Ca (mmol mol^{-1})	Average Sr/Ca
1	S 30.0	192	12	0.86 ± 0.06	0.91 ± 0.01	39	S 36.1	208	14	1.79 ± 0.12	1.90 ± 0.03
2	S 30.0	198	15	0.95 ± 0.08		40	S 36.1	207	12	1.85 ± 0.19	
3	S 30.0	216	12	0.90 ± 0.12		41	S 36.1	193	10	1.90 ± 0.23	
4	S 30.0	220	15	0.84 ± 0.04		42	S 36.1	194	10	1.93 ± 0.26	
5	S 30.0	217	12	0.95 ± 0.12		43	S 36.1	173	9	1.87 ± 0.17	
6	S 30.0	237	12	0.90 ± 0.11		44	S 36.1	179	9	1.71 ± 0.06	
7	S 30.0	289	14	0.97 ± 0.17		45	S 36.1	175	11	1.76 ± 0.23	
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9	S 30.0	206	12	0.99 ± 0.19		47	S 36.1	181	10	2.05 ± 0.26	
10	S 30.0	172	15	0.96 ± 0.17		48	S 36.1	147	11	1.82 ± 0.23	
11	S 30.0	185	18	0.93 ± 0.08		49	S 36.1	174	13	1.69 ± 0.12	
12	S 30.0	186	13	0.84 ± 0.19		50	S 36.1	153	9	2.02 ± 0.24	
13	S 30.0	165	11	0.92 ± 0.16		51	S 36.1	147	9	1.66 ± 0.32	
14	S 30.0	187	10	0.92 ± 0.07		52	S 36.1	140	9	1.21 ± 0.16	
15	S 30.0	189	13	0.92 ± 0.11		53	S 36.1	128	12	1.75 ± 0.16	
16	S 30.0	178	13	0.81 ± 0.06		54	S 36.1	117	9	1.86 ± 0.21	
17	S 30.0	221	14	0.98 ± 0.09		55	S 36.1	134	11	1.74 ± 0.17	
18	S 32.5	215	10	1.69 ± 0.21	1.70 ± 0.03	56	S 36.1	146	8	1.86 ± 0.15	
19	S 32.5	197	11	1.80 ± 0.10		57	S 38.6	190	9	1.99 ± 0.09	
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23	S 32.5	225	10	1.80 ± 0.11		61	S 38.6	169	7	2.08 ± 0.08	
24	S 32.5	222	10	1.74 ± 0.24		62	S 38.6	154	6	1.77 ± 0.28	
25	S 32.5	219	10	1.78 ± 0.11		63	S 38.6	150	10	1.64 ± 0.23	
26	S 32.5	226	10	1.95 ± 0.24		64	S 38.6	159	9	1.96 ± 0.15	
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34	S 32.5	184	17	1.72 ± 0.09		72	S 38.6	133	7	1.80 ± 0.19	
35	S 32.5	159	15	1.62 ± 0.21	73	S 38.6	128	9	2.04 ± 0.16		
36	S 32.5	156	13	1.86 ± 0.27	74	S 38.6	131	11	1.84 ± 0.32		
37	S 32.5	180	15	1.48 ± 0.09	75	S 38.6	122	10	1.90 ± 0.42		
38	S 36.1	236	13	1.90 ± 0.13	1.79 ± 0.05	76	S 38.6	116	8	1.85 ± 0.12	

value of test diameter significantly decreased with salinity ($R^2 = 0.97$, $p < 0.01$) (Table 3, Fig. 2).

The Na/Ca of cultured specimens correlated significantly ($p < 0.01$) with seawater salinity (Fig. 3) and size ($R^2 = 0.96$, $p < 0.01$, Fig. 2). Foraminiferal Na/Ca values ranged from 5.17 to 9.29 mmol mol^{-1} over all experiments. Inter-individual variability in Na/Ca 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. 3). 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 and 16 % (relative standard deviation) and was similar between the different experiments. Measured values for Sr/Ca varied between 0.81 and 2.07 mmol mol^{-1} , with a inter-individual variability of

6–10 % per experiment (Table 5). Salinity is positively correlated to foraminiferal Sr/Ca ($R^2 = 0.96$, $p < 0.01$). Values for Sr/Ca at the experiment at a salinity of 30 are much lower (Fig. 3, Table 5). Average Sr/Ca values (with the exception of experiment S30) decreased with increasing size. However, no correlation between test size and Sr/Ca was observed for the individual experiments (Figs. 2 and 4).

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. 3). 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

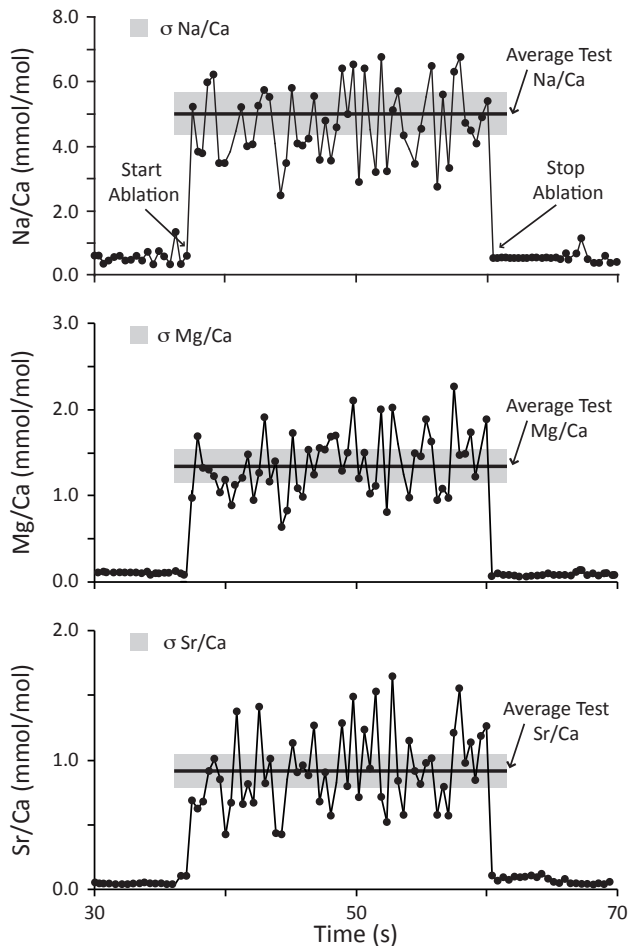


Fig. 1. Ablation profile for Na/Ca, Mg/Ca and Sr/Ca as measured on a cultured specimen of *Ammonia tepida* from S30 experiment.

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. The source of these bands has been attributed to vertical movements of individual Foraminifera, although the magnitude of the variability and its presence in planktonic as well as benthic species renders this unlikely due to the small in-sediment temperature variability (Sadekov et al., 2008; Wit et al., 2010). Another potential source of these bandings is the periodical change in the carbonate ion concentration. Light–dark cycles have been reported to influence the activity of photosynthetic symbionts in planktonic Foraminifera, which in turn affects the carbonate ion concentration of its micro-environment and thereby the incorporation of Mg (Eggins et al., 2004). These same variations have been observed in benthic Foraminifera as a result of carbonate ion concentration changes within sediment habitat depth of the Foraminifera (Elderfield et al.,

2006; Rathmann and Kuhnert, 2008). Alternatively, such banding has been ascribed to variable element adsorption to organic linings and elemental differences between primary and secondary calcite (Erez, 2003). This variability potentially hinders the accuracy of proxies based on the Na/Ca and Mg/Ca values of foraminiferal calcite, but does not impact their applicability in paleoceanography when sufficient specimens are combined to determine element/Ca values to account for the inter- and intra-individual variability in element/Ca ratios (Sadekov et al., 2008; Wit et al., 2012). 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 ($0.12\text{--}0.16 \times 10^{-3}$) is similar to that found in inorganically precipitated calcites ($0.07\text{--}0.20 \times 10^{-3}$; Kitano et al., 1975; Ishikawa and Ichikuni, 1984; Okukura and Kitano, 1986). This similarity suggests that the general biological control on Na incorporation in *A. tepida* is minor. Moreover, D_{Na} for planktonic foraminiferal species is within the same range ($0.11\text{--}0.17 \times 10^{-3}$) (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 might exist, at least in some species.

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; Okukura and Kitano, 1986). 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 (Fig. 1).

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+} during calcite precipitation due to the charge difference, incorporation of Na in inorganically precipitated calcite does not depend on seawater Ca^{2+} concentration and therefore is 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 $[\text{Na}^+]$) increases the activity of Na, while the associated decrease in its activity coefficient, because

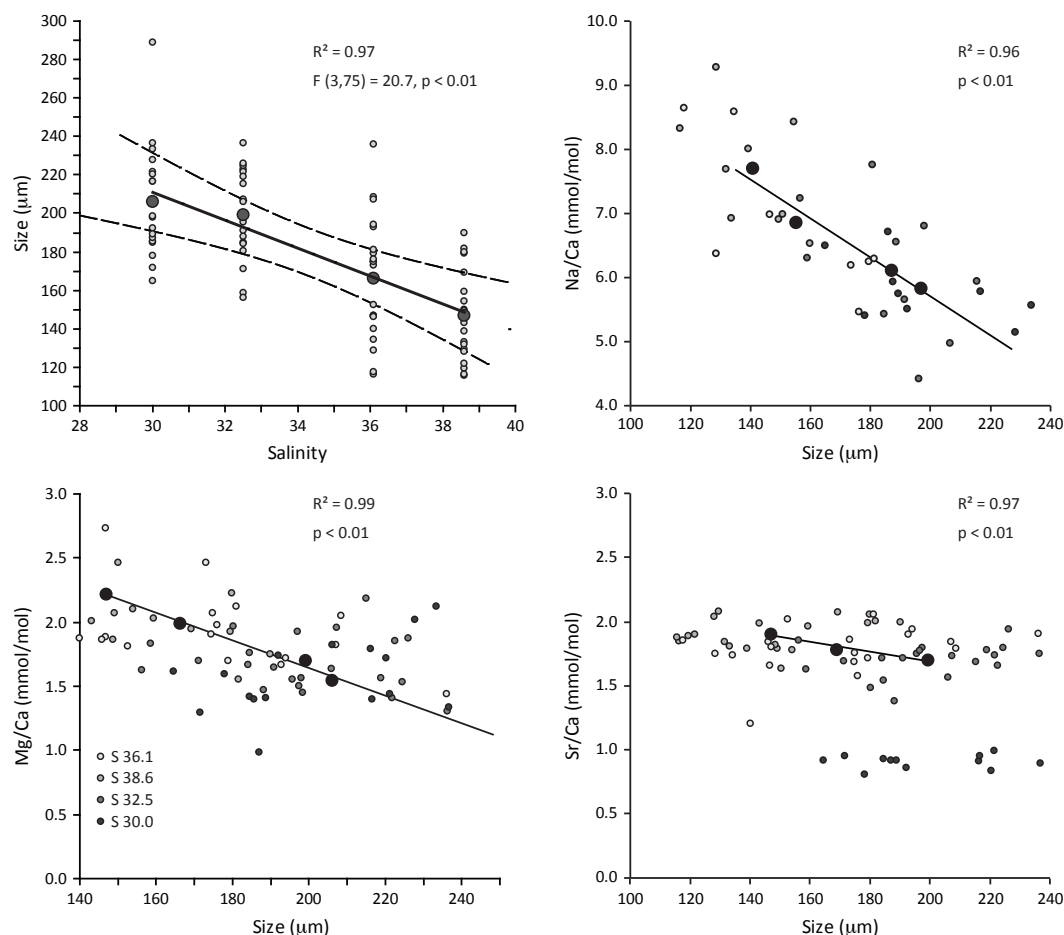


Fig. 2. Individual size, foraminiferal Mg/Ca, Na/Ca and Sr/Ca as measured on *A. tepida* versus the salinity of the culture solutions: correlation coefficients are based on the averaged values. A one-way analysis of variance (ANOVA) was performed with all data points to test the experimental effect of salinity for its significance.

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 $[\text{Na}^+]$ and can thus be used to reflect seawater salinity directly.

Incorporation of certain elements into the calcite of some foraminiferal species is correlated to ontogeny, i.e., depending 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. Incorporation of Sr into foraminiferal calcite has previously been linked to changes in growth rates and size in both inorganic calcite precipitation experiments (Lorens, 1981; Mucci

and Morse, 1983; Nehrke et al., 2007) and foraminiferal culture and core top studies (Elderfield et al., 2002; Kisakurek et al., 2008; Dissard et al., 2010) and can therefore be used to unravel size effects from salinity control on Na incorporation. Average Sr/Ca values decrease slightly as size increases (Fig. 2) and salinity decreases (Fig. 3). To determine whether size affected Sr/Ca, we analyzed the relation between size and Sr/Ca within each experiment (i.e., at constant salinity, Fig. 4). No significant correlation between size and Sr/Ca was found within individual experiments. We, therefore conclude that, despite the variation in foraminiferal size, calcite precipitation rates (i.e., the rate at which CaCO_3 precipitates during chamber formation) were similar and hence did not affect our Na/Ca-salinity calibration. 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. 4), indicating a potential ontogenetic effect. However, if the relation between salinity and foraminiferal Na/Ca

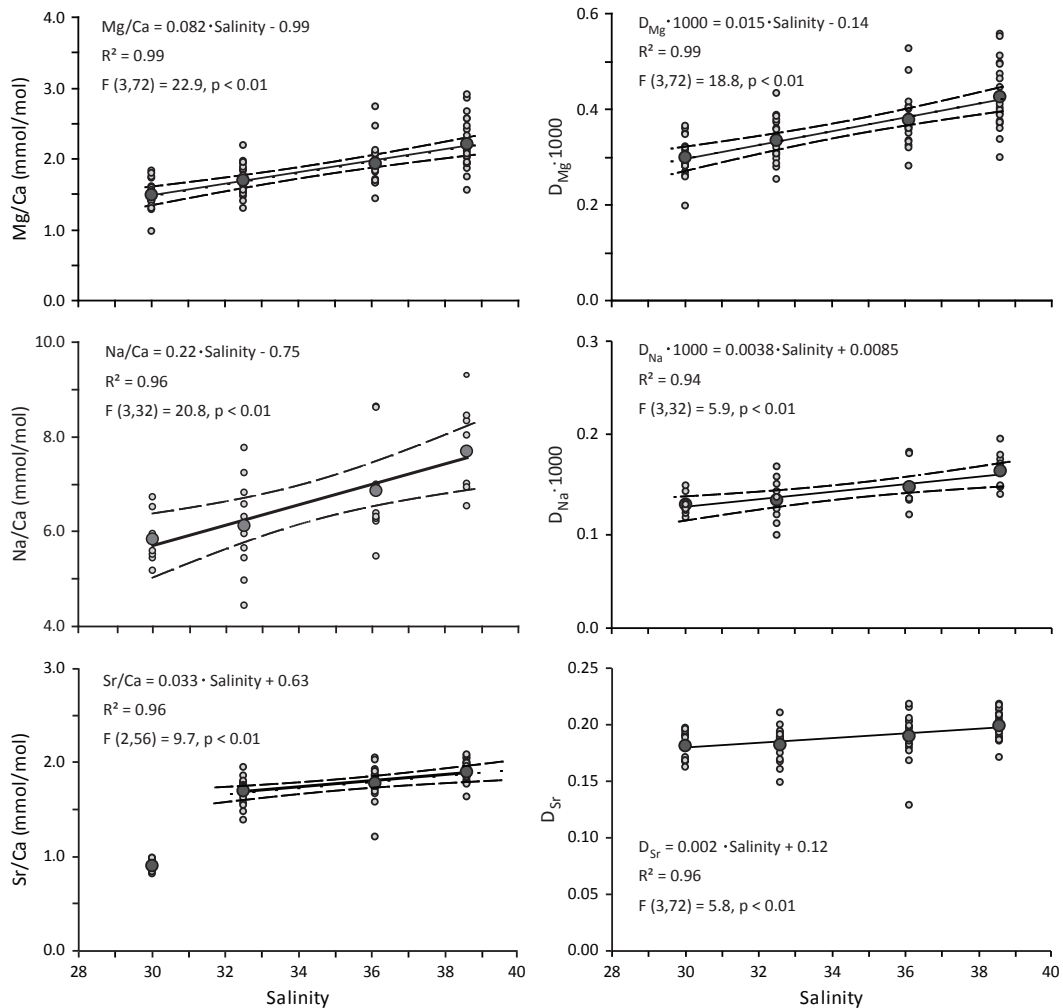


Fig. 3. Foraminiferal Mg/Ca, Na/Ca values and Sr/Ca (left panels) or D_{Mg} , D_{Na} and D_{Sr} (right panels) as measured on *A. tepida* versus the salinity of the culture solutions: correlation coefficients are based on the averaged values. A one-way analysis of variance (ANOVA) was performed with all data points to test the experimental effect of salinity for its significance. Low Sr/Ca values at a salinity of 30 are due to an error in culture media preparation and do fall in line with the other experiments when corrected for (D_{Sr}).

were 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. 5) all showed a positive correlation between Na/Ca and salinity. The correlation between foraminiferal Na/Ca and test size is primarily caused by co-variation of both parameters with salinity, based on the Sr/Ca versus size per experiment and the apparent chamber-specific Na/Ca-salinity relationships. Still, a small size effect cannot entirely be excluded due to variability in the relation between salinity and single chamber Na/Ca (Fig. 5). This does, however, not affect the calibration significantly when measuring multiple chambers per individual, as done here.

Furthermore, the smaller test sizes at the higher salinities could indicate that the calcification process is influenced, since these experiments are at the upper limit of the salinity tolerance of *Ammonia tepida* (Bradshaw, 1957). However,

none of the individuals from the higher salinity experiments (36.1 and 38.6) showed any signs of dissolution, more transparent tests or abnormal chamber formation.

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. Paired Mg/Ca and Na/Ca ratios, measured on the same individuals, therefore offer the opportunity to correct for the effect of salinity on Mg/Ca. The D_{Mg} of the cultured *A. tepida* correlated positively with salinity ($R^2 = 0.99$, $p < 0.01$) (Table 4, Fig. 2), indicating that the effect of seawater Mg/Ca on foraminiferal Mg/Ca did not influence our results. Within previous experiments (Kisakürek et al.,

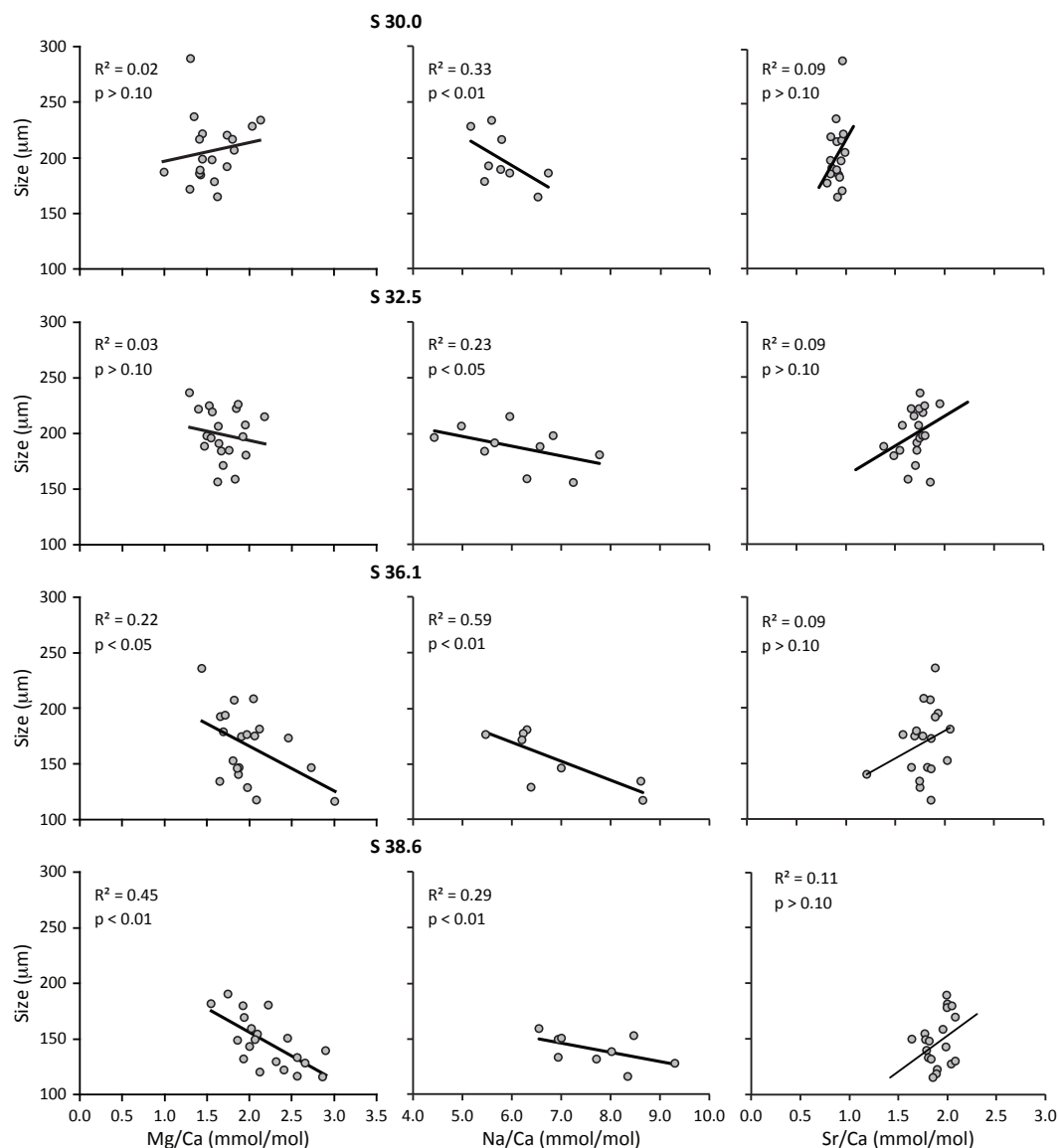


Fig. 4. Measured Mg/Ca, Na/Ca and Sr/Ca values of individual Foraminifera versus size for the all salinity experiments: all relations are tested for significance with a one-way ANOVA.

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, similarity in response of Mg/Ca to 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 in observed relations between Mg/Ca and salinity for such a variety of culture experiments, analytical approaches and investigated species 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 abiotic 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. 7). 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. 2, Table 4). Similar to Na and Sr, Foraminifera from experiments at salinities 30.0 and 32.5 do

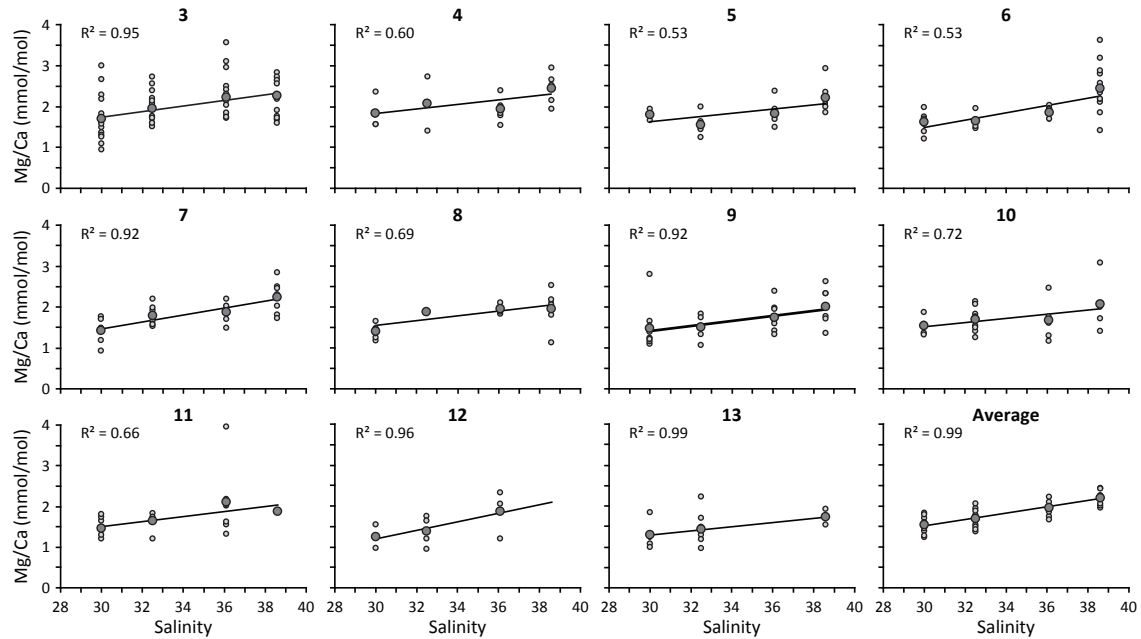


Fig. 5. Salinity versus individual Mg/Ca values for each individual chamber: chamber position is determined by counting the chambers in the whirl, starting at the youngest chambers. Correlation coefficients are determined on the averaged values per experiment.

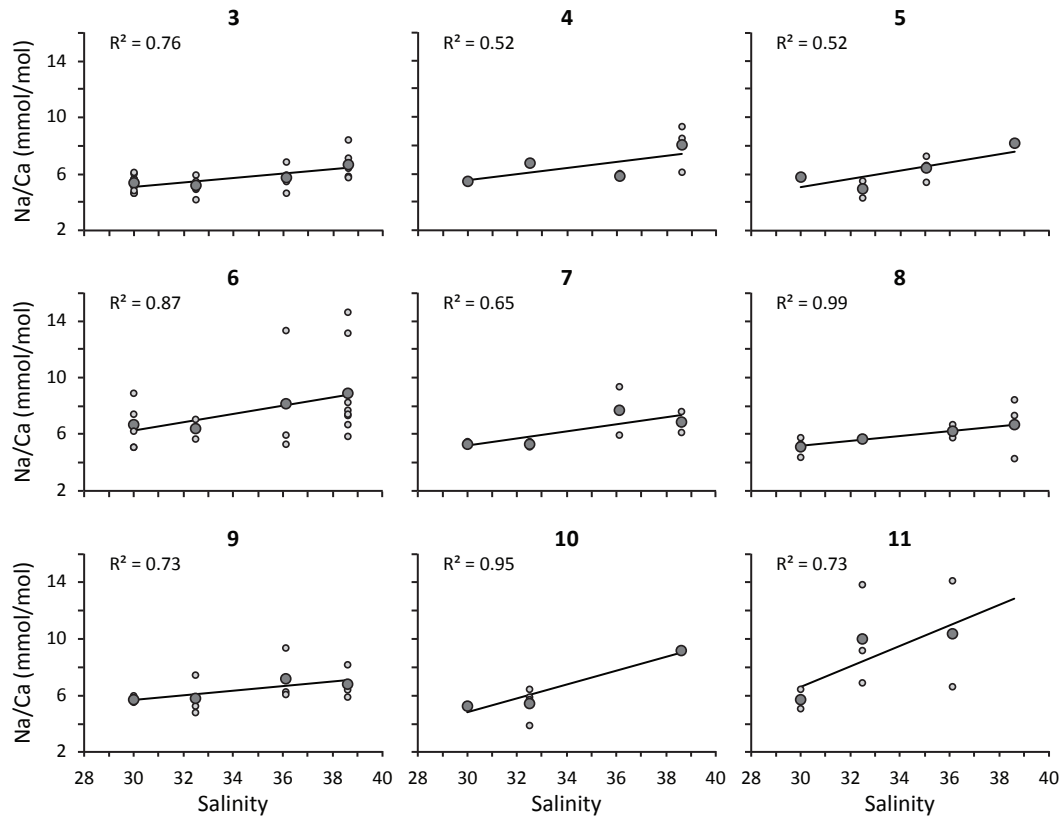


Fig. 6. Salinity versus individual Na/Ca values for each individual chamber: chamber position is determined by counting the chambers in the whorl, starting at the youngest chambers. Correlation coefficients are determined on the averaged values per experiment.

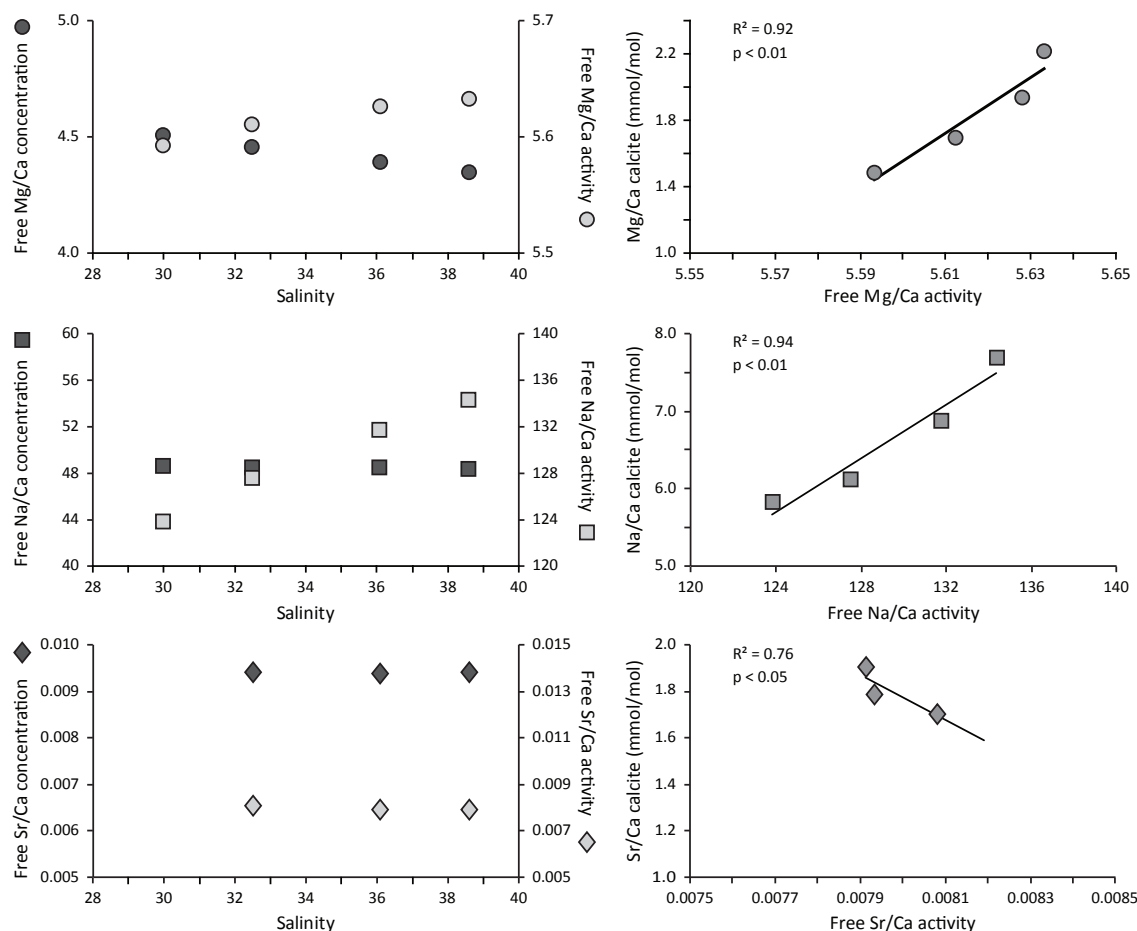


Fig. 7. Experiment salinity versus modeled concentration and activity of free Mg/Ca, Na/Ca and Sr/Ca values and measured foraminiferal Mg/Ca, Na/Ca and Sr/Ca versus the free Mg/Ca and Na/Ca activity: parameters were modeled using PHREEQC (LLNL database, Parkurst and Appelo, 1999).

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. 4). 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. 6) 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.

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 er-

ror) 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 often used paleothermometers (i.e., Mg/Ca).

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