Biogeosciences

Impact of seawater $p\mathrm{CO_2}$ on calcification and Mg/Ca and Sr/Ca ratios in benthic foraminifera calcite: results from culturing experiments with *Ammonia tepida*

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Abstract. Evidence of increasing concentrations of dissolved carbon dioxide, especially in the surface ocean and its associated impacts on calcifying organisms, is accumulating. Among these organisms, benthic and planktonic foraminifera are responsible for a large amount of the globally precipitated calcium carbonate. Hence, their response to an acidifying ocean may have important consequences for future inorganic carbon cycling. To assess the sensitivity of benthic foraminifera to changing carbon dioxide levels and subsequent alteration in seawater carbonate chemistry, we cultured specimens of the shallow water species *Ammonia tepida* at two concentrations of atmospheric CO_2 (230 and 1900 ppmv) and two temperatures (10 °C and 15 °C). Shell weights and elemental compositions were determined. Impact of high and low $p\mathrm{CO_2}$ on elemental composition are compared with results of a previous experiment were specimens were grown under ambient conditions (380 ppvm, no shell weight measurements of specimen grown under ambient conditions are, however, available). Results indicate that shell weights decrease with decreasing $[CO_3^{2-}]$, although calcification was observed even in the presence of calcium carbonate under-saturation, and also decrease with increasing temperature. Thus both warming and ocean acidification may act to decrease shell weights in the future. Changes in $[CO_3^{2-}]$ or total dissolved inorganic carbon do not affect the Mg distribution coefficient. On the contrary, Sr incorporation is enhanced under increasing $[CO_3^{2-}]$. Implications of these results for the paleoceanographic application of foraminifera are discussed.

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1 Introduction

Since the mid 19th century, utilization of fossil fuels and land use change have impacted biogeochemical carbon cycling, leading to global environmental perturbations (see e.g. IPCC report, 2001, 2007). Increased levels of atmospheric CO_2 resulted in increased concentrations of dissolved CO_2 ($CO_{2(aq)}$) especially in the surface ocean (Caldeira and Wickett, 2003). It has been estimated that the oceans have taken up approximately 30% of the CO_2 emitted (Sabine et al., 2004) and thereby mitigated human induced global warming. In addition, this also resulted in surface ocean acidification. Increasing atmospheric CO_2 concentrations from 280 (pre-industrial value) to 380 ppmv (current value) decreased oceanic pH by approximately 0.1 unit (Orr et al., 2005). Estimates of future atmospheric $p\mathrm{CO_2}$ suggest values reaching 800–1000 ppmv by the end of this century (IPCC, 2001), equivalent to another 0.3 unit decrease in ocean pH (Caldeira and Wickett, 2005).

Since marine calcifying organisms build their calcareous skeletons according to the simplified reaction $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$, an impact of CO_2 on biocalcification is expected. Indeed, an increasing number of field and laboratory studies demonstrate the impact of increased seawater $[CO_{2(aq)}]$ and related changes in carbonate chemistry on both planktonic and benthic marine calcifying organisms, such as coccolithophores, corals, shellfish and foraminifera (e.g. Bijma et al., 1999; Kleypas et al., 1999; Leclercq et al., 2000; Riebesell et al., 2000; Zondervan et al., 2001; Delille et al., 2005; Gazeau et al., 2007). In turn, a decrease in calcification of marine calcifiers may act as a negative feedback on atmospheric CO_2 levels (assuming the organic pump remains constant) (Riebesell et al., 2000; Zondervan et al., 2001; Ridgwell, 2007). Establishing an

accurate relationship between pCO$_2$ and calcification is crucial for assessing the impact of such a feedback in the future.

During calcification, elements such as Sr and Mg are incorporated into biogenic calcium carbonate. The ratio of these elements to Ca depends on the physical and chemical conditions in the calcification environment. Therefore, elemental compositions of foraminiferal shells have become an important tool to estimate past oceanic conditions. (e.g., Boyle 1981; Marchitto et al., 1998; Martin et al., 1999; Rickaby and Elderfield, 1999; Russell et al., 2004; Hall and Chan, 2004, 2005). Magnesium occurred in seawater with nearly constant ratios to calcium (for the last 1Myr, Broecker and Peng, 1982), and variations in Mg/Ca in benthic foraminiferal shells on shorter timescale are shown to be mainly related to changes in temperature (Nürnberg et al., 1996; Rathburn and DeDeckker, 1997; Rosenthal et al., 1997; Hastings et al., 1998; Lea et al., 1999; Toyofuku et al., 2000; Lear et al., 2002; Reichart et al., 2003; Anand et al., 2003; Barker et al., 2004). However, other environmental parameters like salinity, pH or [CO$_3^{-2}$], may influence Mg incorporation as well. Abrupt changes in the elemental compositions of benthic foraminiferal shells with water depth have been related to changes in the local carbonate ion concentration (McCorkle et al., 1995; Elderfield et al., 1996; Marchitto et al., 2000). However, contradictory responses to variations in pH or [CO$_3^{2}$], on Mg incorporation into foraminiferal calcite, have been observed in recent field and culture studies (Lea et al., 1999; Russell et al., 2004; Elderfield et al., 2006; Rosenthal et al., 2006; Rathmann and Kuhnert, 2008). The application of calcitic Sr/Ca ratios in paleoceanography is less straightforward, although it appears to be marginally influenced by temperature (Rathburn and DeDeckker, 1997; Mortyn et al., 2005). Recent studies have shown that variations in [CO$_3^{2-}$] and consequently in the calcite saturation state (Ω) may determine Sr incorporation (Lea et al., 1999; Russell et al., 2004; Mortyn et al., 2005; Rosenthal et al., 2006; Rathmann and Kuhnert, 2008).

In order to quantify the effect of ocean acidification on foraminiferal calcification and to improve the robustness of proxy based reconstructions, we cultured foraminifera under controlled physico-chemical conditions. We combined shell weight and size measurements with Mg/Ca and Sr/Ca analyses of specimens of the symbiont barren, shallow water species *Ammonia tepida*, grown under different pCO$_2$ conditions (230 and 1900 ppmv) two temperatures (10 and 15 °C) and two salinities (24 and 33).

2 Material and methods

2.1 Collecting and culturing foraminifera

The symbiont-barren species *Ammonia tepida* is characterized by the broad range of temperatures (5 to 40 °C, Pascal et al., 2008), salinities (12 to 40; Brasier, 1981; Mur-

ray, 1991; Pascual et al., 2002) and seasonal regimes (Bradshaw, 1961; Walton and Sloan, 1990) under which it can survive. This robustness makes *A. tepida* a particularly suitable species for experimentation. In 2006, live specimens of *A. tepida* (referred to as molecular type T6E by Hayward et al., 2004, further referred to as *A. tepida*) were collected at an intertidal flat in the German Wadden Sea (near Dorum). Sediments were sieved over a 630 μm mesh to remove larger meiofauna, keeping the finer fraction with the foraminifera in stock-cultures. Less than two weeks after collection, living individuals of *Ammonia* were picked from the stock cultures. They were screened under an inverted microscope (Zeiss Axiovert 200M) for pseudopodial activity (a sign for vitality) and subsequently transferred to one of eight semi-closed aquaria. Aquaria contained filtered seawater (0.2 μm) of salinity 33 (natural seawater from the North Sea, near Helgoland) or salinity 24 (natural seawater diluted with deionised water, to mimic salinity near the collection site) (Table 1). Two gas mixing pumps (DIGAMIX, H. Wösthoff Meßtechnik GmbH) were used to adjust the pCO$_2$ of the culture water. To prevent evaporation, the water was bubbled with air pre-saturated with water. The pCO$_2$ of the water was adjusted to 230 ppmv (pH=8.4) and 1900 ppmv (pH=7.5), respectively. The duration of the experiment was one and a half months. Salinity and pH (NBS) levels were verified every second day (WTW conductivity meter 330i with TetraCon 325 electrode; WTW pH 3000 with Schott BlueLine Electrodes calibrated with NIST buffers) (Table 1). To minimize bacterial growth and changes in salinity (due to evaporation), growth media were replaced every two weeks. Samples were taken at the start and end of each replacement for dissolved inorganic carbon (DIC), total alkalinity (TA), and elemental composition (ICP-OES) measurements. Dissolved inorganic carbon samples were sterile-filtered (0.2 μm) and stored in 13 mL-borosilicate flasks free of air-bubbles at 4 °C until they were measured photometrically with an autoanalyzer (Technicon TRAACS 800, Bran&Lübbe, Norderstedt, Germany) with an average precision of 10 μmol kg^{-1} based on triplicate analyses. Alkalinity samples were stored in 300 mL borosilicate flasks at 4 °C and measured in triplicate by potentiometric titration with an average precision of 8 μEq kg^{-1} (Brewer et al. 1986). Total alkalinity was calculated from linear Gran Plots (Gran, 1952). The carbonate chemistry was kept constant during the experiments (Table 1). Foraminifera were fed with a mixture of dried algae (*Phaeodactylum triconortum*, *Dunaliella salina* and *Isochrisis galbana*) at the beginning of the experiment and every second week when growth media were changed. To each growth medium, 5 mg/L of the fluorescent compound calcein was added. This fluorescent-labelling technique was used as a means to distinguish newly grown calcite (fluorescent) from pre-existing calcite (non fluorescent) after termination of the experiments (Bernhard et al., 2004; Dissard et al., 2009a) (Fig. 1). Only chambers labelled with calcein were measured by LA-ICP-MS. The Mg and Sr distribution

Table 1. Carbonate chemistry of the culture media. Experiments ran for one and a half months. Alkalinity and DIC were analysed every two weeks, salinity and pH every second day. Numbers represent average values of Alkalinity, DIC, salinity and pH measured for each experimental condition. Ω, [HCO$_3^-$], [CO$_3^{2-}$], pH cal., and pCO$_2$cal. were calculated with the CO$_2$ Sys program (Lewis and Wallace, 1998) from measured alkalinity, DIC, temperature and salinity.

Experimental Conditions	T ALK (µeq kg^{-1})	DIC (µmol kg^{-1})	Average Salinity	pH meas. (NBS)	pH cal. (NBS)	Ω	[HCO$_3^-$] (µmol kg^{-1})	[CO$_3^{2-}$] (µmol kg^{-1})	pCO$_2$cal (ppmv)
Sal 24, 10 °C, 230 ppmv	1868 ($\pm$26)	1703 ($\pm$14)	24.7 ($\pm$0.4)	8.31 ($\pm$0.07)	8.33	3.0	1573	119	232
Sal 24, 10 °C, 1900 ppmv	1916 ($\pm$67)	1981 ($\pm$61)	24.8 ($\pm$0.5)	7.49 ($\pm$0.04)	7.46	0.5	1868	19	2017
Sal 24, 15 °C, 230 ppmv	1891 ($\pm$33)	1696 ($\pm$27)	24.7 ($\pm$0.4)	8.39 ($\pm$0.06)	8.33	3.6	1546	141	239
Sal 24, 15 °C, 1900 ppmv	1931 ($\pm$47)	1971 ($\pm$83)	24.6 ($\pm$0.4)	7.53 ($\pm$0.05)	7.50	0.6	1869	25	1940
Sal 33, 10 °C, 230 ppmv	2558 ($\pm$15)	2232 ($\pm$59)	33.2 ($\pm$0.5)	8.36 ($\pm$0.09)	8.41	5.7	1987	236	223
Sal 33, 10 °C, 1900 ppmv	2507 ($\pm$44)	2526 ($\pm$36)	32.8 ($\pm$0.5)	7.52 ($\pm$0.03)	7.59	1.0	2404	42	1803
Sal 33, 15 °C, 230 ppmv	2537 ($\pm$54)	2175 ($\pm$81)	32.7 ($\pm$0.5)	8.39 ($\pm$0.11)	8.41	3.4	1904	263	229
Sal 33, 15 °C, 1900 ppmv	2506 ($\pm$17)	2504 ($\pm$41)	33.1 ($\pm$0.6)	7.61 ($\pm$0.03)	7.59	1.2	2383	51	1868

coefficients D(E)=(E/Ca)ca/(E/Ca)sw, representing the distribution of the element (E), between calcite (ca) and the aqueous phase (sw) from which the minerals form, were calculated for all experimental conditions. The culture experiments were conducted in two parallel series at 10 and 15 °C (maximum temperature deviation during the experiment was 0.5 °C).

2.2 Measurements with Laser Ablation-ICP-MS

2.2.1 Cleaning procedures

Since the foraminifera were cultured without sediment, a rigorous cleaning procedure as required for specimens collected from sediment cores, was not necessary. Instead, a modified cleaning procedure was adopted, in which organic matter is removed by soaking for 30 min in a 3–7% NaOCl solution before analysis (Gaffey and Brönniman, 1993). A stereomicroscope was used during cleaning and specimens were removed from the reagent directly after complete bleaching. The samples were immediately and thoroughly rinsed with deionised water to ensure complete removal of the reagent. After cleaning, specimens were checked with scanning electron microscopy and showed no visible signs of dissolution.

2.2.2 Laser Ablation-ICP-MS

Newly formed chambers were ablated using an Excimer laser (Lambda Physik) with GeoLas 200Q optics inside an ablation chamber flushed with helium (Reichart et al. 2003). Pulse repetition rate was set at 6 Hz, with an energy density at the sample surface of 4 J/cm^2. Ablation craters were 80 µm in diameter (Fig. 2) and ablated material was analyzed with respect to time (and hence depth) using a quadrupole ICP-MS instrument (Micromass Platform ICP-MS). Analyses were calibrated against NIST SRM 610 glass, using concentration data of Pearce et al. (1997) with Ca as an internal standard. Calcium is ideal, because the concentration is
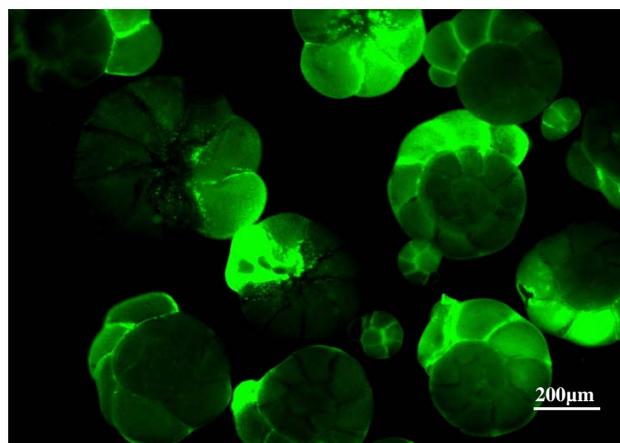

Fig. 1. Newly formed chambers are visible under fluorescent light as a result of the incorporation of calcein.

constant at 40 wt % in all foraminiferal shells, and because it allows direct comparisons with element to Ca ratios from wet-chemical studies. Concentrations of Mg and Sr were calculated using ^{24}Mg and ^{88}Sr. An in-house matrix matched carbonate standard was used to verify potentially different ablation behaviour for glass and carbonate. Simultaneous monitoring of Al and Mn allowed us to discard profiles contaminated, or part of the profiles, from further calculations of elemental concentrations.

2.3 Size/weight measurements

Sizes of the foraminiferal shells were measured (maximum diameter) with a stereomicroscope (ZEISS Stemi SV 11). They were subsequently washed with deionised water, dried in an oven at 50 °C for 3 h, and transferred to a desiccator. The following day, foraminifera were weighed using a Micro Analytical Lab Balance (Mettler Toledo UMX2) with a
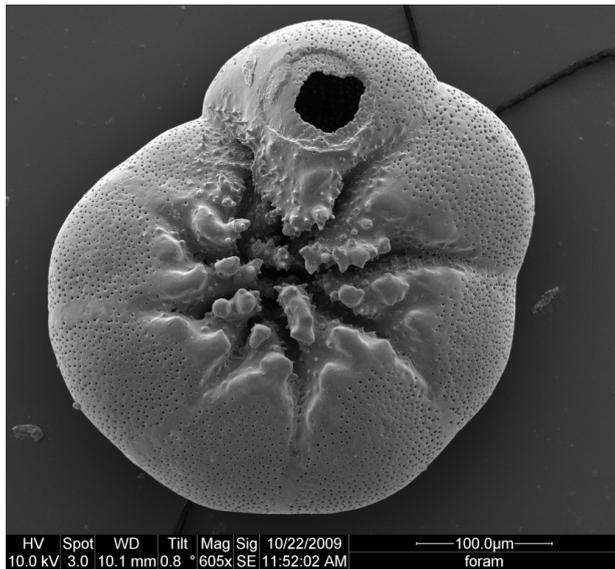
Fig. 2. Scanning electron microscope image of laser ablation crater in *Ammonia tepida*.

precision of 0.1 µg. Shell weight versus shell size is plotted for each experimental condition (Figs. 3 and 4). Shells were weighed after laser ablation. Although some material is removed during ablation, the amount can be neglected since only a small part of the last chamber (from an average of about 20 chambers per individuals) was removed. Moreover, since a similar amount of material was removed from each shell, inter experimental differences are not affected. Different experimental conditions (carbonate ion concentration and temperature) may influence the number of new chambers grown during the experiment. To avoid systematic offsets caused by the contrasting experimental conditions only specimens (size range 350–500 µm) that added two or three new chambers during the experiment were used for weight analyses.

2.4 Carbonate system

The semi-enclosed culture system allowed us to bubble the growth medium with air with different preset pCO$_2$. Differences in pCO$_2$ result in differences in [CO$_2$(aq)], pH and DIC (DIC=[CO$_3^{2-}$]+[HCO$_3^-$]+[CO$_2$(aq)]), while TA (TA$\approx$[HCO$_3^2$]+2[CO$_3^{2-}$]+[B(OH)$_4^-$]+[OH$^-$]+[H$^+$]) remains constant. Laboratory experiments can be a powerful tool to elucidate natural processes. To reveal the underlying mechanisms, however, it is often necessary to alter the physicochemical conditions beyond the range typically observed in nature. Therefore, two extreme values for CO$_2$ (1900 and 230 ppmv) were selected. Dissolved inorganic carbon, pH and TA of the growth media bubbled with a pCO$_2$ of 1900 ppmv are given in Table 1. A pCO$_2$ of 1900 drives the system to lower [CO$_3^{2-}$] (Bjerrum, 1914) and, therefore, de-

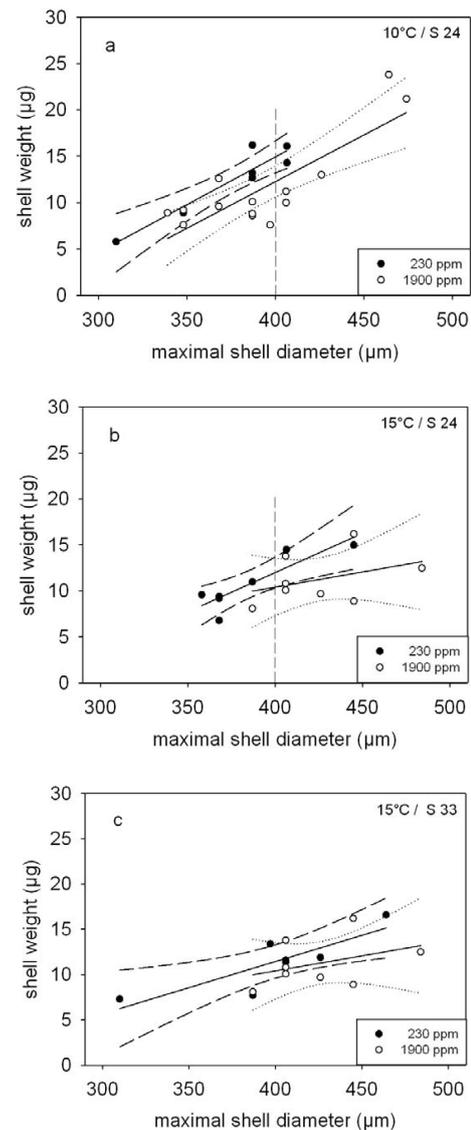**Fig. 3.** Weight (µg) versus size (µm) of foraminifera grown under 230 ppmv (closed circles) and 1900 ppmv (open circles), at 10 °C, salinity 24 **(a)**, at 15 °C, salinity 24 **(b)**, and at 15 °C, salinity 33 **(c)**. Data for 10 °C and salinity 33 not available. Full lines represent linear regression for each experimental condition. Dashed lines indicate the corresponding 95% confidence interval for the regression.

creases the calcite saturation state Ω (Ω=Ion Activity Product (IAP)/Ksp, where Ksp represents the solubility product of calcite) below saturation (less than 1). On the other hand, bubbling with a low concentration of CO$_2$ (230 ppmv) allows us to mimic the impact of extremely low atmospheric pCO$_2$ on the carbonate chemistry of the seawater, with a significant decrease in DIC and an increase in pH (Table 1). This results in a significant increase of the calcite saturation state Ω. As CO$_2$ is more soluble in cold water, pH and Ω are lower at 10 °C compared to 15 °C. A decrease in salinity from 33 to
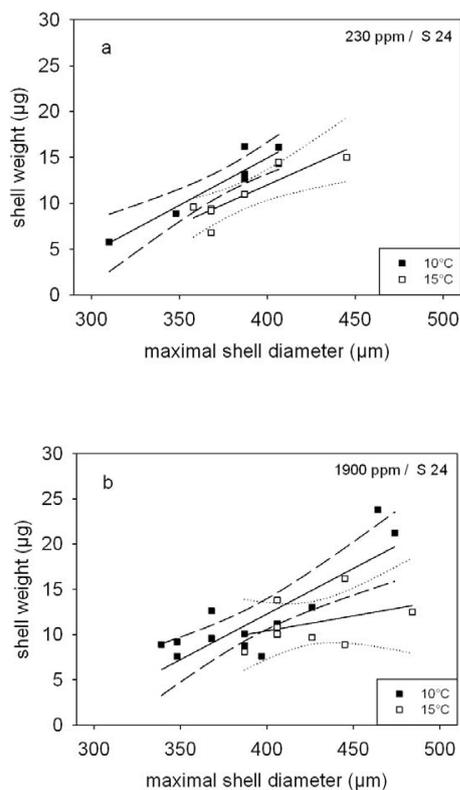
Fig. 4. Weight (µg) versus size (µm) of foraminifera grown at salinity 24, under 230 ppmv **(a)** and 1900 ppmv **(b)**. Closed squares represent foraminifera grown at 10 °C and open squares foraminifera grown at 15 °C. Full lines represent linear regression for each experimental condition. Dashed lines indicate the corresponding 95% confidence interval for the regression.

24 decreases both [Ca^{2+}] and [CO$_3^{2-}$]. As a result, TA decreases by approximately 25% and Ω by 50%. The carbonate system was calculated from TA, DIC, temperature, and salinity using the CO$_2$ Sys program (Lewis and Wallace 1998) (equilibrium constants of Mehrbach et al. (1973), as refitted by Dickson and Millero (1987), were chosen). Omega values are presented in Table 1. In order to cross-check analyses, pH values calculated with the CO$_2$ Sys program (pH calculated), based on DIC and TA measurements, and measured pH values during the experiment (pH measured) are compared in Table 1.

3 Results

3.1 Calcite added and survival rate

In all experiments at least 50% of the specimens added new chambers (Fig. 1), regardless of variation in pCO$_2$ (Table 2). Even at undersaturated conditions ($\Omega < 1$) most specimens survived and calcified, no dissolution was observed. At salinity 24, which is closer to their natural environment, the num-

ber of new chambers per specimen was higher than at salinity 33. The results of the LA-ICP-MS measurements are shown in Table 2. The limited size (<100 µm) of chambers did not allow multiple analyses of single chambers. To avoid an impact of ontogeny only measurements from specimens between 350 µm to 500 µm were taken into account. None of the newly added chambers showed abnormalities.

3.2 Weight measurements

Specimens grown at a pCO$_2$ of 1900 ppmv, when cultured under the same temperature and salinity conditions, are generally lighter than those grown at a pCO$_2$ of 230 ppmv (Fig. 3). Specimens grown at 15 °C, when grown under the same pCO$_2$ and salinity conditions, are lighter compared to the specimens grown at 10 °C (Fig. 4a and b). Only the newly grown chambers are responsible for the observed differences, since the initial parts of the shells were grown under natural conditions. The observed differences between the different experiments will, therefore, underestimate the impact of the different variables.

3.3 Elemental concentration

The Mg/Ca of *A. tepida* is low (between 0.4 and 0.8 mmol/mol; Table 4) compared to other species (Bentov and Erez, 2006). Overall values of Sr/Ca ratios vary between 1.25 and 1.50 mmol/mol (Table 4). The Mg and Sr distribution coefficients are calculated for each experiment and plotted against [CO$_3^{2-}$] (Figs. 5 and 6). At salinity 33, D(Mg) increases strongly with temperature. The increase in D(Mg) with increasing temperature is much less obvious at salinity 24. At 15 °C D(Mg) increases with increasing salinity, which is not observed at 10 °C. Due to loss of specimens during sample handling, elemental concentrations of the 10 °C and salinity 33 experiment are based on a small number of foraminifera (Table 2), increasing their error. A larger uncertainty could result in an underestimation of the D(Mg) of the experiment at salinity 33, 10 °C, explaining the lack in correlation. No appreciable change in D(Mg) with [CO$_3^{2-}$] was observed in our experiments (Fig. 5a). Due to technical limitations no control experiments (pCO$_2$=380 ppmv) could be run during this series experiment. However, an additional set of data obtained on specimens grown in different culture experiments (investigating the impact of salinity on Mg incorporation) is presented for comparison Figs. 5b and 6. These experiments were performed following the same protocol as described in Sect. 2.1, but under different salinity (20, 33 and 40) and pCO$_2$ conditions (380 ppmv) (for detailed information see Dissard et al., 2009b). Under similar salinity and temperature conditions, a slight increase in DMg is observed for specimen grown under ambient pCO$_2$ (380 ppmv), relative to specimen grown under either low (230 ppmv) or elevated (1900 ppmv) pCO$_2$. However these variations remain too small to be statistically significant (Fig. 5b). For Sr, a
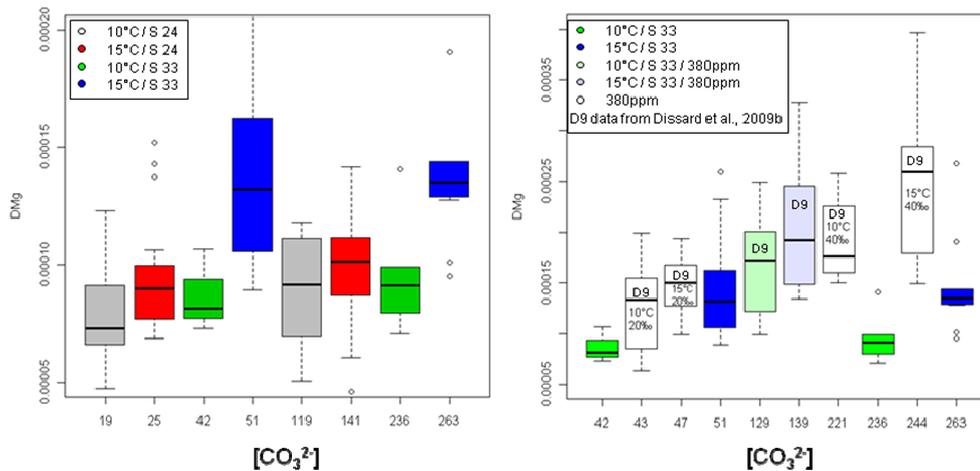
Fig. 5. Mg distribution coefficient (D(Mg)) versus [CO$_3^{2-}$] (μmol kg^{-1}) at 10 °C, salinity 24 (grey); 15 °C, salinity 24 (red); 10 °C, salinity 33 (green); and 15 °C, salinity 33 (blue) **(a)**; and at 10 °C, salinity 33 (green); 15 °C, salinity 33 (blue); 10 °C, salinity 33, 380 ppmv (pale green); 15 °C, salinity 33, 380 ppmv (pale blue); 10 °C, salinity 20, 380 ppmv; 15 °C salinity 20, 380 ppmv; 10 °C, salinity 40, 380 ppmv, and 15 °C salinity 40, 380 ppmv (white) **(b)**. Data for ambient atmospheric conditions (380 ppmv, labelled D9) are from Dissard et al. (2009b). The first to third quartile (box), range (dotted line) and median (thick line) are shown for each experiment.

Table 2. Number of individuals at the start of the experiments, number of specimens that added new chambers, total number of added chambers, number of LA-ICP-MS measurements used for elemental concentration calculations.

Experimental Conditions	Number of specimens at the beginning of the experiment	Number of specimens presenting new chambers at the end of the experiment	Number of new chambers added	Number of LA-ICP-MS measurements used for elemental concentrations
Sal 24, 10 °C, 230 ppmv	50	31	64	10
Sal 24, 10 °C, 1900 ppmv	50	41	86	19
Sal 24, 15 °C, 230 ppmv	50	29	82	15
Sal 24, 15 °C, 1900 ppmv	50	33	83	17
Sal 33, 10 °C, 230 ppmv	50	30	67	5
Sal 33, 10 °C, 1900 ppmv	50	30	63	3
Sal 33, 15 °C, 230 ppmv	50	29	47	11
Sal 33, 15 °C, 1900 ppmv	50	31	65	12

progressive DSr increase is observed with increasing [CO$_3^{2-}$] (Fig. 6).

4 Discussion

4.1 Temperature and [CO$_3^{2-}$] impact on shell weight

Shell weights were higher in the low pCO$_2$, high calcite saturation state, experiments (Fig. 3), although this difference was not as strong in the higher salinity (33 versus 24) cultures (Fig. 3). Unfortunately, due to technical limitations no control experiments (pCO$_2$=380 ppmv) could be run for this series of experiments. No shell weight measurements are available for the specimen grown under ambient pCO$_2$ condition as this additional data set was obtained from a different set of culture experiments (see Sect. 3.3). The overall positive correlation between shell weight and carbonate ion

concentration agrees well with previous publications focusing on other calcifying organisms. Indeed, although some coccolithophores show species specific (Langer et al., 2006), and even strain specific (Langer et al., 2009) responses, most studies indicate a decrease in calcification at higher [CO$_2$] (e.g. Gattuso et al., 1998; Kleypas, 1999; Bijma et al., 1999; Gattuso and Buddemeier, 2000; Riebesell et al., 2000; Zondervan et al., 2001). Culture studies on two planktonic foraminifera, *Orbulina Universa* and *Globigerinoides sacculifer,* (Russell et al., 2004; Bijma et al., 1999, 2002) report that [CO$_3^{2-}$] primarily controls shell thickness and, by extension, shell weight. Recently, Moy et al. (2009) report that modern planktonic foraminifera shell weights (*Globigerina bulloides*) collected from sediment traps in the Southern Ocean, are 30–35% lower than those preserved in the underlying Holocene sediments, consistent with reduced calcification as a consequence of ocean acidification. These
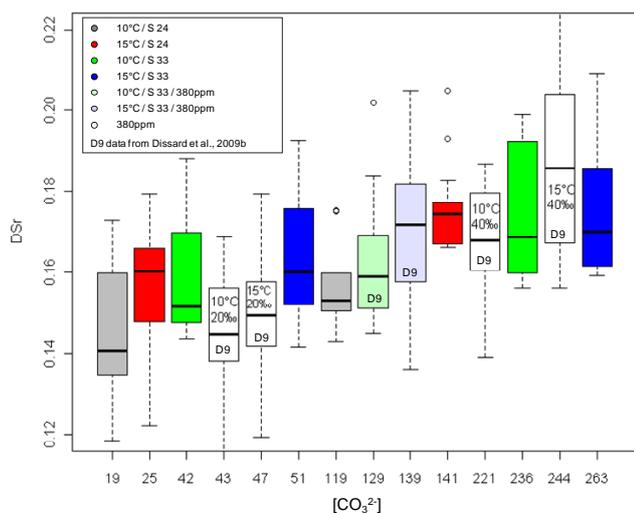
Fig. 6. Sr distribution coefficient (D(Sr)) versus [CO$_3^{2-}$] (µmol kg^{-1}) at 10 °C, salinity 24 (grey); 15 °C, salinity 24 (red); 10 °C, salinity 33 (green); and 15 °C, salinity 33 (blue); at 10 °C, salinity 33, 380 ppmv (pale green); 15 °C, salinity 33, 380 ppmv (pale blue); 10 °C, salinity 20, 380 ppmv; 15 °C salinity 20, 380 ppmv; 10 °C, salinity 40, 380 ppmv, and 15 °C salinity 40, 380 ppmv (white). Data for ambient atmospheric conditions (380 ppmv, labelled D9) are from Dissard et al. (2009b). The first to third quartile (box), range (dotted line) and median (thick line) are shown for each experiment.

observations are in good agreement with the study of de Moel et al. (2009) who also report a good correlation between decrease in planktonic foraminifera shell weight (*Globigerinoides ruber* from the werstern Arabian sea) and anthropogenically induced ocean acidification, suggesting strong control by [CO$_3^{2-}$]. On the other hand, it has been suggested that shell thickness is closely related to temperature (Barker and Elderfield, 2002). However, the latter is also related to changes in carbonate chemistry as CO$_2$ solubility in seawater depends on the temperature (see Sect. 2.4.). Subsequent dissociation of CO$_{2(aq)}$ into HCO$_3^-$ and CO$_3^{2-}$, induce a temperature dependence of the open ocean water [CO$_3^{2-}$]. Planktonic foraminifera shell weight have been shown to increase with increasing temperature (Barker and Elderfield, 2002), therefore, the co-variation of these two parameters made it difficult to deconvolve their respective impact on shell weight. In sediment cores from the North Atlantic, Barker and Elderfield (2002) observed a decrease in *G. bulloides* shell weight from the last termination towards the Holocene. Considering that [CO$_3^{2-}$] decreases while temperature increases during the deglaciation, this suggests that [CO$_3^{2-}$] is the primary control of foraminiferal shells weight. In our experiment, even though shells weight increases with increasing [CO$_3^{2-}$] (Fig. 3), they are also observed to decrease with increasing temperature (and therefore increasing [CO$_3^{2-}$]) (Fig. 4a and b), suggesting that tem-

perature and [CO$_3^{2-}$] both influence significantly *Ammonia tepida* shell weight. Nevertheless, the small temperature range applied in our experiments (10 to 15 °C) do not allow us to determine if temperature or [CO$_3^{2-}$] primarily control the shell weight of *Ammonia tepida*. Many possible parameters may lead to the different response of *Ammonia tepida* shell weight to changes in temperature, when compared to planktonic foraminifera, like lower optimal growth temperatures, or variations in symbiotic activity for planktonic symbiont-bearing species (e.g. *G. sacculifer*, Bé et al., 1982).

4.2 [CO$_3^{2-}$] impact on Mg/Ca

Incorporation of Mg in *A. tepida* shells is independent of changes in the carbonate ion concentration of the culture medium (Fig. 5a). Even though a slight increase in DMg is observed for specimen grown under ambient pCO$_2$ (380 ppmv) relative to specimen grown under similar salinity and temperature conditions and either low (230 ppmv) or elevated (1900 ppmv) pCO$_2$, these variations remain too small to be statistically significant (Fig. 5b). Interestingly, specimen grown in experiments in which [CO$_3^{2-}$] was increased by increasing the salinity (40) of the culture medium, present a significant rise in DMg when compared to the specimen grown in experiments in which the [CO$_3^{2-}$] was increased by bubbling of the culture medium with low concentrations of pCO$_2$ (230 ppmv) (Fig. 5b). These observations indicate that salinity of the culture medium impact significantly the Mg incorporation, while the [CO$_3^{2-}$] seem to play a minor role on the elemental composition of the calcitic shells of *A. tepida*. To our knowledge, only two culture studies previously investigated the effect of [CO$_3^{2-}$] (or pH) on Mg incorporation into foraminiferal shell carbonate. Lea et al. (1999) measured the Mg concentration of the symbiont bearing species *O. universa* and symbiont barren species *G. bulloides* grown under different pH conditions. They observed for both species a decrease in Mg/Ca ratios of about 6% per 0.1 pH unit increase. Russell et al. (2004) report for the same species a similar Mg/Ca decrease of about 7% (*O. universa*) and 16% (*G. bulloides*) respectively per 0.1 unit increase below ambient pH (8.2). No significant changes in Mg incorporation were observed in the same study above ambient pH. Both Lea et al. (1999) and Russell et al. (2004) modified seawater by adding NaOH and HCl (constant DIC, varying TA), whereas in our experiments carbonate chemistry was modified through bubbling with air with different preset pCO$_2$ (varying DIC, constant TA). This fundamental difference in adjusting pCO$_2$ could potentially affect trace element incorporation differently. When studying the impact of carbonate chemistry on isotopic fractionation, Bijma et al. (1999) tested this by culturing planktonic foraminifera under (1) constant TA, and varying DIC, and (2) constant DIC, and varying TA. For both experimental approaches *Orbulina universa* shell δ^{18}O and δ^{13}C decreased as [CO$_3^{2-}$] increased with similar slopes.

Table 3. Measured [Mg^{2+}], [Sr^{2+}], [Ca^{2+}] (mg/kg), Mg/Ca and Sr/Ca (mmol/mol) of the growth media. The experiment ran for one and a half months. Growth media were changed every two weeks. The numbers indicated represent average values of [Mg^{2+}], [Sr^{2+}], [Ca^{2+}], Mg/Ca and Sr/Ca for each experimental condition.

Experimental conditions	Average [Mg^{2+}] in mg/kg	Average [Sr^{2+}] in mg/kg	Average [Ca^{2+}] in mg/kg	Average Mg/Ca in mmol/mol	Average Sr/Ca in mmol/mol
Sal 24, 10 °C, 230 ppmv	775 (±21)	4.5 (±0.1)	242 (±5)	5297 (±51)	8.54 (±0.03)
Sal 24, 10 °C, 1900 ppmv	782 (±28)	4.6 (±0.2)	245 (±8)	5270 (±53)	8.52 (±0.04)
Sal 24, 15 °C, 230 ppmv	777 (±22)	4.5 (±0.1)	242 (±6)	5286 (±37)	8.55 (±0.04)
Sal 24, 15 °C, 1900 ppmv	782 (±28)	4.5 (±0.1)	244 (±7)	5279 (±30)	8.50 (±0.03)
Sal 33, 10 °C, 230 ppmv	1083 (±37)	6.0 (±0.2)	331 (±8)	5392 (±81)	8.40 (±0.08)
Sal 33, 10 °C, 1900 ppmv	1024 (±27)	6.0 (±0.1)	329 (±6)	5390 (±68)	8.37 (±0.06)
Sal 33, 15 °C, 230 ppmv	1085 (±39)	6.1 (±0.2)	332 (±9)	5391 (±69)	8.38 (±0.06)
Sal 33, 15 °C, 1900 ppmv	1073 (±25)	6.1 (±0.2)	331 (±8)	5344 (±74)	8.38 (±0.06)

Table 4. Measured Mg/Ca and Sr/Ca ratios in foraminiferal calcite in mmol/mol and calculated distribution coefficient $D_{(Mg)}$ and $D_{(Sr)}$ for each experimental condition. Uncertainties (standard deviation (one sigma) calculated per experimental condition) are presented in brackets.

Experimental Conditions	Average Mg/Ca in mmol/mol	Average Sr/Ca in mmol/mol	D(Mg)= ((Mg/Ca)ca/(Mg/Ca)sw) x10^{-5}	D(Sr)= ((Sr/Ca)ca/(Sr/Ca)sw)
Sal 24, 10 °C, 230ppmv	0.47 (±0.12)	1.33 (±0.10)	8.8 (± 2.3)	0.156 (±0.011)
Sal 24, 10 °C, 1900ppv	0.44 (±0.19)	1.25 (±0.17)	8.4 (± 3.6)	0.147 (±0.020)
Sal 24, 15 °C, 230ppmv	0.52 (±0.13)	1.50 (±0.09)	9.8 (± 2.5)	0.176 (±0.011)
Sal 24, 15 °C, 1900ppv	0.51 (±0.13)	1.34 (±0.13)	9.6 (± 2.5)	0.157 (±0.016)
Sal 33, 10 °C, 230ppmv	0.52 (±0.15)	1.47 (±0.16)	9.6 (± 2.7)	0.175 (±0.019)
Sal 33, 10 °C,1900ppmv	0.47 (±0.09)	1.35 (±0.20)	8.7 (± 1.7)	0.161 (±0.024)
Sal 33, 15 °C, 230ppmv	0.79 (±0.25)	1.48 (±0.13)	15.6 (± 4.7)	0.176 (±0.016)
Sal 33, 15 °C,1900ppmv	0.77 (±0.28)	1.38 (±0.14)	14.5 (± 5.3)	0.165 (±0.017)

To our knowledge no others culture studies have been carried out to investigate Mg incorporation as a function of [CO$_3^{2-}$] in benthic foraminifera. In the natural environment Martin et al. (2002), Lear et al. (2004), and Elderfield et al. (2006) observed lowered Mg/Ca ratios in the foraminiferal calcite of *Cibicidoides* species, at temperature below ∼3 °C, coinciding with a steep increase in the oceanic [CO$_3^{2-}$] gradient. Also, Rosenthal et al. (2006) report a decrease of Mg/Ca ratio in the shells of the aragonitic species *Hoeglundina elegans* below the aragonite saturation level (15 µmol/kg). Therefore, Elderfield et al. (2006) suggested that below a certain Δ[CO$_3^{2-}$] threshold value, D(Mg) is lowered by a linear carbonate ion effect. In order to compare our values with these studies we calculated the calcite saturation level Δ[CO$_3^{2-}$], using the equation from Broecker and Peng (1982), where Δ[CO$_3^{2-}$]=[CO$_3^{2-}$]$_{insitu}$ - [CO$_3^{2-}$]$_{saturation}$. Calcite [CO$_3^{2-}$]$_{saturation}$=Ksp/[Ca^{2+}] (Ksp was calculated following Millero (1995), and [Ca^{2+}] is based on measured concentrations in our growth media) (Table 3). The range of Δ[CO$_3^{2-}$] calculated for our experiments varies from −26 µmol/kg to 213 µmol/kg. These values include the Δ[CO$_3^{2-}$] range below which D(Mg) should be reduced by a linear carbonate ion effect. However, we do not observe any significant variation in Mg incorporation as a function of

Δ[CO$_3^{2-}$]. Still, in our experimental setup, Δ[CO$_3^{2-}$] is manipulated by bubbling with preset pCO$_2$ air. In the abyssal ocean, [CO$_3^{2-}$]$_{saturation}$ increases mainly with water depth as a result of increasing pressure. In that case a potential effect of pressure on the distribution coefficient D(Mg), instead of carbonate ion concentration, can not be excluded. Also Rathburn and DeDecker (1997) did not observe any departure from the established Mg/Ca versus T °C calibration below 3 °C for *Cibicidoides* sp., whereas Rathmann and Kuhnert (2008), observe only little resemblance between temperature corrected Mg/Ca ratios (*Oridorsalis umbonatus)* and [CO$_3^{2-}$].

In a recent study Raitzsch et al. (2008) report that variations in DIC affect temperature corrected Mg/Ca values of *C. wuellerstorfi*. In our experiments, Mg distribution coefficients in *A. tepida* calcite do not respond to changes in DIC. The variations in D(Mg) observed between experimental conditions (Fig. 5a), are explained by changes in temperature and salinity alone.

4.3 [CO$_3^{2-}$] impact on Sr/Ca

The incorporation of Sr increases with increasing [CO$_3^{2-}$] (increasing pH) (Fig. 6). To test for significance, statistic tests performed with the statistic program R (R Development

Table 5. Statistical test (Shapiro-test, F-test, and t-test) applied to DSr values, using statistic program R (R Development Core Team (2005); http://www.r-project.org).

Normality test		
Experimental conditions	p-value Shapiro-test	$[CO_3^{2-}]$
		(μmol kg^{-1})
Sal 24, 10°C, 230ppmv	0.12	19
Sal 24, 10°C, 1900ppmv	0.14	119
Sal 24, 15°C, 230ppmv	0.73	25
Sal 24, 15°C, 1900ppmv	**0.005** significant deviation from normality	141
Sal 33, 10°C, 230ppmv	0.32	42
Sal 33, 10°C, 1900ppmv	0.30	236
Sal 33, 15°C, 230ppmv	0.42	51
Sal 33, 15°C, 1900ppmv	0.10	263
Variance test (F-test)		
Experimental conditions	p-pvalue	variances between
		the 2 pCO$_2$ traitments
Sal 24, 10°C	0.076	non sign.
Sal 24, 15°C	0.178	non sign.
Sal 33, 10°C	0.636	non sign.
Sal 33, 15°C	0.898	non sign.
t-test of means one sided, to test whether lower $[CO_3^{2-}]$ show a lower mean D$_{(Sr)}$		
Experimental conditions the 2 pCO$_2$ traitments	p-pvalue	t-statistic
Sal 24, 10°C	0.0590	-1.62	almost sign. Alpha=6 %
Sal 24, 15°C	0.0003	-3.85	significant
Sal 33, 10°C	0.2187	-0.87	excluded
Sal 33, 15°C	0.0622	-1.60	almost sign. Alpha=7 %

Core Team (2005); http://www.r-project.org) were applied to the data (Table 5). First, normalities were checked by the means of a Shapiro test. Only one experimental condition (S=24, 15 °C, 230 ppmv) appears to deviate significantly from normality. Subsequently, a F-test was applied to look at the variance to the mean value of the experiments run at same salinity and temperature, but varying pCO$_2$ con-

ditions. None of them appeared to be significantly different. Finally, a F-test (one sided) was made in order to test whether lower $[CO_3^{2-}]$ resulted in lower mean DSr at constant temperature and salinity conditions. " When considering alpha=7% (alpha representing the probability level at which to reject the null hypothesis), mean DSr values measured at enhanced $[CO_3^{2-}]$, are significantly higher compared

to mean DSr measured at lower [CO$_3^{2-}$], for three of the four experimental conditions (24‰, 10 °C; 24‰, 15 °C; 33‰, 15 °C). For these three conditions, the incorporation of Sr can be considered to increase significantly with increased [CO$_3^{2-}$]. At salinity 24, Sr/Ca ratios increased from 1.25 to 1.33, and from 1.34 to 1.50, for an increase of 0.8 unit pH, at 10 and 15 °C, respectively. At salinity 33, Sr/Ca ratios increased from 1.35 to 1.47 and from 1.38 to 1.48, for the same pH increase of 0.8 unit, at 10 °C and 15 °C, respectively. These results are in good agreement with previous observations made by Lea et al. (1999) (1.1±0.5% increase per 0.1 pH unit) and Russell et al. (2004) (1.6±0.4% increase per 0.1 pH unit) for *O. universa* (Fig. 7). However, these two studies also show insensitivity of Sr/Ca to pH in another planktonic foraminiferal species, *G. bulloides*. To explain this species-specific response, Russell et al. (2004) proposed that changes in ambient pH impact photosynthetic activity of the symbionts and hence calcification rate in *O. universa*. Strontium in turn is affected by the calcification rate in inorganic calcite precipitation (Nehrke et al., 2007). Since *G. bulloides* has no symbionts, no impact of pH was observed. *Ammonia tepida*, like *G. bulloides*, is a symbiont barren species; therefore changes in pH (or [CO$_3^{2-}$]) do not (only) affect Sr incorporation via an impact on symbiont activity.

A control of [CO$_3^{2-}$] on the Sr/Ca in the shell of benthic foraminifera was first suggested by Elderfield et al. (1996). However, the positive correlation of [CO$_3^{2-}$] with other environmental parameters such as temperature (see Sect. 4.1.) or salinity (Zeebe and Wolf Gladrow, 2001) observed in the natural environment makes the interpretation of the Sr incorporation into foraminifera as a function of changes in [CO$_3^{2-}$], difficult. Rosenthal et al. (2006) support the observation that higher [CO$_3^{2-}$] increased the Sr incorporation in the aragonitic benthic foraminifer *Hoeglundina elegans* in waters undersaturated with respect to aragonite. On the other hand, Rathman and Kuhnert (2007), observed an increase of the Sr incorporation of the endobenthic species *O. umbonatus* with decreasing [CO$_3^{2-}$] of the pore-water.

In our experiments, the Sr concentration of *A. tepida* increases with increasing temperature and salinity (Table 4, Fig. 6). As explained in Sect. 2.4., CO$_2$ is more soluble in cold water. Hence an increase in temperature leads to a decrease in [CO$_2$(aq)], and a subsequent increase in [CO$_3^{2-}$]. On the other hand, an increase in salinity by evaporation increases both [Ca^{2+}] and [CO$_3^{2-}$]. In contrast to Mg, D(Sr) increases with increasing [CO$_3^{2-}$] independently whether the [CO$_3^{2-}$] increase of the culture medium is due to increased salinity or to bubbling with low pCO$_2$ concentrations (230 ppmv), (Fig. 6). Therewith it appears that [CO$_3^{2-}$] is the main parameter controlling Sr incorporation. Inorganic precipitation experiments suggest that higher Sr/Ca is associated with higher calcification rates (Lorens, 1981; Tesoriero and Pankow, 1996). In our experiments we observed that, at
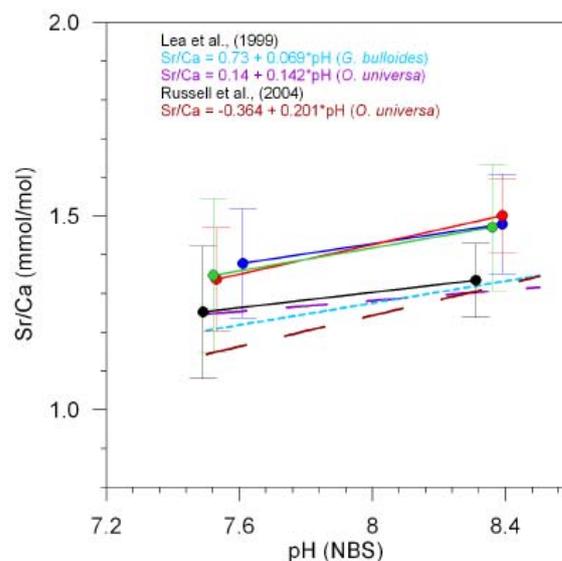

Fig. 7. Sr/Ca ratios in *Ammonia tepida* (solid lines -this study-, average of the Sr/Ca ratios calculated per experimental condition, same color code used as in Fig. 6), in *Orbulina universa* (dashed lines, Lea et al., 1999 and Russell et al., 2004) and in *Globigerinoides bulloides* (doted lines, Lea et al., 1999), versus pH (NBS).

equal temperature and salinity, increasing [CO$_3^{2-}$] induced increasing shells weight (see Sect. 4.1). Hence, it seems likely that higher [CO$_3^{2-}$] induces an increase of the Sr incorporation via increasing calcification rate.

5 Conclusions

Ammonia tepida shell weight increases with increasing [CO$_3^{2-}$], and decreases with increasing temperature. Changes in [CO$_3^{2-}$] or DIC do not affect significantly the Mg distribution coefficient of *A. tepida*, but D(Sr) increases with increasing [CO$_3^{2-}$] (increasing pH). Furthermore it is shown that *A. tepida* is able to calcify at undersaturated conditions ($\Omega \sim 0.5$), without showing signs of dissolution.

Edited by: T. Trull

References

Anand, P., Elderfield, H., and Conte, M. H.: Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series, *Paleoceanography*, 18(15), 28.1–28.15, 2003.

Barker, S. and Elderfield, H.: Foraminiferal calcification response to glacial-interglacial changes in atmospheric CO$_2$, Science, 297, 833–836, 2002.

Barker, S., Kiefer, T., and Elderfield, H.: Temporal changes in North Atlantic circulation constrained by planktonic foraminiferal shell weights, Paleoceanography, 19, PA3008, doi:10.1029/2004PA001004, 2004.

Bé, A. W. H., Spero, H. J., and Anderson, O. R.: Effects of Symbiont Elimination and Reinfection on the Life Processes of the Planktonic Foraminifer Globigerinoides sacculifre, Mar. Biol., 73–86, 1082.

Bentov, S. and Erez, J.: Impact of biomineralization processes on the Mg content of foraminiferal shells: A biological perspective, Geochem. Geophy. Geosy., 7, Q01P08, doi:10.1029/2005GC001015, 2006.

Bernhard, J. M., Blanks, J. K., Hintz, C. J., and Chandler, G. T.: Use of the fluorescent calcite marker calcein to label foraminiferal tests, J. Foramin. Res., 34, 96–101, 2004.

Bijma, J., Spero, H. J., and Lea, D. W.: Reassessing Foraminiferal Stable Isotope Geochemistry: Impact of the Oceanic Carbonate System (Experiemental Results), in: Use of Proxies in Paleoceanography: Examples from the South Atlantic., edited by: Fischer, G. and Wefer, G., 489–512, Springer-Verlag, Heidelberg, 1999.

Bijma, J., Honisch, B., and Zeebe, R. E.: Impact of the ocean carbonate chemistry on living foraminiferal shell weight: Comment on "Carbonate ion concentration in glacial-age deep waters of the Caribbean Sea" by W. S. Broecker and E. Clark, Geochem. Geophy. Geosy., 3, 1064, doi:10.1029/2002GC000388, 2002.

Bjerrum, N.: Die theorie der alkalischen und azidemetrischen Titrierung, Sammlung chemischer und chem-technischer Vorträge, 21, 1–128, 1914.

Boyle, E. A.: Cadmium, Zinc, Copper, and Barium in Foraminifera Tests, Earth Planet. Sci. Lett., 53, 11–35, 1981.

Bradshaw, J. S.: Laboratory experiments on the ecology of foraminifera. Contributions from the Cushman Foundation for Foraminiferal research, 12(3), 87–106, 1961.

Brasier, M. D.: Microfossil transport in the tidal Humber basin, in: Microfossils from recent and fossil shelf seas, edited by: Neale, J. W. and Brasier, M., Ellis Horwood Limited, Chichester, England, 314–322, 1981

Brewer, P. G., Bradshow, A. L., and Williams, R. T.: Measurement of total carbon dioxide and alkalinity in the North Atlantic Ocean in 1981, in: The Changing Carbon Cycle – A global Analysis, edited by: Trabalka, J. R. and Reichle, D. E., Springer-Verlag, New York, 358–381, 1986.

Broecker, W. S. and Peng, T.-H.: Tracers in the Sea, Eldigio Press ed., Lamont Doherty Geological observatory, Palisades NY, 690 pp., 1982.

Caldeira, K. and Wickett, M. E.: Anthropogenic carbon and ocean pH, Nature, 425, 365–365, 2003.

Caldeira, K. and Wickett, M. E.: Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean, J. Geophys. Res.-Ocean., 110, C09S04, doi:10.1029/2004JC002671, 2005.

Delille, B., Harlay, J., Zondervan, I., Jacquet, S., Chou, L., Wollast, R., Bellerby, R. G. J., Frankignoulle, M., Borges, A. V., Riebesell, U., and Gattuso, J. P.: Response of primary production and calcification to changes of pCO(2) during experimental blooms of the coccolithophorid Emiliania huxleyi, Global Biogeochemical Cycles, 19, GB2023, doi:10.1029/2004GB002318, 2005.

de Moel, H., Ganssen, G. M., Peeters, F. J. C., Jung, S. J. A., Kroon, D., Brummer, G. J. A., and Zeebe, R. E.: Planktic foraminiferal shell thinning in the Arabian Sea due to anthropogenic ocean acidification?, Biogeosciences, 6, 1917–1925, 2009, http://www.biogeosciences.net/6/1917/2009/.

Dickson, A. G. and Millero, F. J.: A comparison of the equilibrium constant s for the dissociation of carbonic acid in seawater media, Deep-Sea Res., 34, 1733–1743, 1987.

Dissard, D., Nehrke, G., Reichart, G. J., Nouet, J., and Bijma, J.: Effect of the fluorescent indicator calcein on Mg and Sr incorporation into foraminiferal calcite, Geochem. Geophy. Geosy., 10(1), Q11001, doi:10.1029/2009GC002417, 2009a.

Dissard, D., Nehrke, G., Reichart, G. J., and Bijma, J.: The impact of salinity on the Mg/Ca and Sr/Ca ratio in the benthic foraminifera Ammonia tepida: Results from culture experiments, Geochim. Cosmochim. Acta, 74(2010), 928–940 doi:10.1016/j.gca.2009.10.040, 2009b.

Elderfield, H., Bertram, C. J., and Erez, J.: Biomineralization model for the incorporation of trace elements into foraminiferal calcium carbonate, Earth Planet. Sci. Lett., 142, 409–423, 1996.

Elderfield, H., Yu, J., Anand, P., Kiefer, T., and Nyland, B.: Calibrations for benthic foraminiferal Mg/Ca paleothermometry and the carbonate ion hypothesis, Earth Planet. Sci. Lett., 250, 633–649, 2006.

Gaffey, S. J. and Bronnimann, C. E.: Effects of Bleaching on Organic and Mineral Phases in Biogenic Carbonates, J. Sediment. Petrol., 63, 752–754, 1993.

Gattuso, J. P., Frankignoulle, M., Bourge, I., Romaine, S., and Buddemeier, R. W.: Effect of calcium carbonate saturation of seawater on coral calcification, Global Planet. Change, 18, 37–46, 1998.

Gattuso, J. P. and Buddemeier, R. W.: Ocean biogeochemistry - Calcification and CO$_2$, Nature, 407, 311–313, 2000.

Gazeau, F., C. Quiblier, J. M. Jansen, J. P. Gattuso, J. J. Middelburg, and C. H. R. Heip (2007), Impact of elevated CO$_2$ on shellfish calcification, Geophysical Research Letters, 34, 5.

Gran, G.: Determination of the equivalence point in potentiometric titrations of seawater with hydrochloric acid, Oceanol. Acta, 5, 209–218, 1952.

Hall, J. M. and Chan, L. H.: Ba/Ca in Neogloboquadrina pachyderma as an indicator of deglacial meltwater discharge into the western Arctic Ocean, Paleoceanography, 19(9), PA1017, doi:10.1029/2003PA000910, 2004.

Hall, J. M., Chan, L. H., McDonough, W. F., and Turekian, K. K.: Determination of the lithium isotopic composition of planktic foraminifera and its application as a paleo-seawater proxy, Mar. Geol., 217, 255–265, 2005.

Hastings, D. W., Russell, A. D., and Emerson, S. R.: Foraminiferal magnesium in Globeriginoides 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. Micropaleontol., 50, 237–271, 2004.

IPCC Climate change 2001: The scientific basis. Intergovernmental Panel on Climate Change, edited by: Houghton, J. T., Ding, Y., Griggs, D., Noguer, M., Linden, P. J. V. d., Dai, X., Johnson, C. A., and Maskell, K., Cambridge University Press, Cambridge, UK, 2001.

IPCC Climate Change 2007: The physical science Basis. Contribution of Working Group I to the fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Av-

eryt, K. B., Tignor, M., and Miller, L. H., Cambridge University Press, Cambridge United Kingdom, 996 pp., 2007.

Kleypas, J. A., Buddemeier, R. W., Archer, D., Gattuso, J. P., Langdon, C., and Opdyke, B. N.: Geochemical consequences of increased atmospheric carbon dioxide on coral reefs, Science, 284, 118–120, 1999.

Langer, G., Geisen, M., Baumann, K. H., Klas, J., Riebesell, U., Thoms, S., and Young, J. R.: Species-specific responses of calcifying algae to changing seawater carbonate chemistry, Geochem. Geophy. Geosy., 7(12), Q09006, doi:10.1029/2005GC001227, 2006.

Langer, G., Nehrke, G., Probert, I., Ly, J., and Ziveri, P.: Strain-specific responses of *Emiliania huxleyi* to changing seawater carbonate chemistry, Biogeosciences Discuss., 6, 4361–4383, 2009, http://www.biogeosciences-discuss.net/6/4361/2009/.

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. Acta, 63, 2369–2379, 1999.

Lear, C. H., Rosenthal, Y., and Slowey, N.: Benthic foraminiferal Mg/Ca-paleothermometry: A revised core-top calibration, Geochim. Cosmochim. Acta, 66, 3375–3387, 2002.

Lear, C. H., Rosenthal, Y., Coxall, H. K., and Wilson, P. A.: Late Eocene to early Miocene ice sheet dynamics and the global carbon cycle, Paleoceanography, 19, PA4015, doi:10.1029/2004PA001039, 2004.

Leclercq, N., Gattuso, J. P., and Jaubert, J.: CO$_2$ partial pressure controls the calcification rate of a coral community, Glob. Change Biol., 6, 329–334, 2000.

Lewis, E. and Wallace, D. W. R.: Program developed for CO$_2$ system calculations ORNL/CDIAC-105, Carbon Dioxide Information Analysis Centre, Oak RIdge National Laboratory, US Department of Energy, 1998.

Lorens, R. B.: Sr, Cd, Mn and Co Distribution Coefficients in Calcite as a Function of Calcite Precipitation Rate, Geochim. Cosmochim. Acta, 45, 553–561, 1981.

Marchitto, T. M., Curry, W. B., and Oppo, D. W.: Millennial-scale changes in North Atlantic circulation since the last glaciation, Nature, 393, 557–561, 1998.

Marchitto, T. M., Curry, W. B., and Oppo, D. W.: Zinc concentrations in benthic foraminifera reflect seawater chemistry, Paleoceanography, 15, 299–306, 2000.

Martin, E. E., Shackleton, N. J., Zachos, J. C., and Flower, B. P. (1999), Orbitally-tuned Sr isotope chemostratigraphy for the late middle to late Miocene, Paleoceanography, 14, 74–83, 1999.

Martin, E. E., Lea, D. W., Rosenthal, Y., Schackleton, N. J., Sarnthein, M., and Papenfuss, T.: Quaternary deep sea temperature histories derived from benthic foraminiferal Mg/Ca, Earth Planet. Sci. Lett., 198, 193–209, 2002.

McCorkle, D. C., Martin, P. A., Lea, D. W., and Klinkhammer, G. P.: Evidence of a Dissolution Effect on Benthic Foraminiferal Shell Chemistry - Delta-C-13, Cd/Ca, Ba/Ca, and Sr/Ca Results from the Ontong Java Plateau, Paleoceanography, 10, 699–714, 1995.

Millero, F. J.: Thermodynamics of the Carbon-Dioxide System in the Oceans, Geochim. Cosmochim. Acta, 59, 661–677, 1995.

Mortyn, P. G., Elderfield, H., Anand, P., and Greaves, M.: An evaluation of controls on planktonic foraminiferal Sr/Ca: Comparison of water column and core-top data from a North At-

lantic transect, Geochem. Geophy. Geosy., 6(12), Q12007, doi:10.1029/2005GC001047, 2005.

Moy, A. D., Howard, W. R., Bray, S. G., and Trull, T. W.: Reduced calcification in modern Southern Ocean planktonic foraminifera, Nature Geosci., 2, 276–280, 2009.

Murray, J. W.: Ecology and paleoecology of benthic foraminifera, Longman, Harlow, 397 pp., 1991.

Nehrke G., Reichart G. J., Van Cappellen P., Meile C., and Bijma J.: Dependence of calcite growth rate and Sr partitioning on solution stoichiometry: Non-Kossel crystal growth, Geochim. Cosmochim. Acta, 71, 2240–2249, 2007.

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

Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., Feely, R. A., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., Key, R. M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R. G., Plattner, G. K., Rodgers, K. B., Sabine, C. L., Sarmiento, J. L., Schlitzer, R., Slater, R. D., Totterdell, I. J., Weirig, M. F., Yamanaka, Y., and Yool, A.: Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, Nature, 437, 681–686, 2005.

Pascal, P. Y., Dupuy, C., Richard, P., and Niquil, N.: Bacterivory in the common foraminifer Ammonia tepida: Isotope tracer experiment and the controlling factors, J. Exp.l Mar. Biol. Ecol., 359, 55–61, 2008.

Pascual, A., Rodriguez-Lazaro, J., Weber, O., and Jouanneau, J. M.: Late Holocene pollution in the Gernika estuary (southern Bay of Biscay) evidenced by the study of Foraminifera and Ostracoda, Hydrobiologia, 475, 477–491, 2002.

Pearce, N. J. G., Perkins, W. T., Westgate, J. A., Gorton, M. P., Jackson, S. E., Neal, C. R., and Chenery, S. P.: A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials, Geostandards Newsletter-the Journal of Geostandards and Geoanalysis, 21, 115–144, 1997.

R Development Core Team R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria, ISBN 3-900051-07-0, online available at: http://www.R-project.org., 2005

Raitzsch, M., Kuhnert, H., Groeneveld, J., and Bickert, T.: Benthic foraminifer Mg/Ca anomalies in South Atlantic core top sediments and their implications for paleothermometry, Geochem. Geophy. Geosy., 9, Q05010, doi:10.1029/2007GC001788, 2008.

Rathburn, A. E. and DeDeckker, P.: Magnesium and strontium compositions of Recent benthic foraminifera from the Coral Sea, Australia and Prydz Bay, Antarctica, Mar. Micropaleontol., 32, 231–248, 1997.

Rathmann, S. and Kuhnert, H.: Carbonate ion effect on Mg/Ca, Sr/Ca and stable isotopes on the benthic foraminifera Oridorsalis umbonatus off Namibia, Mar. Micropaleontol., 66, 120–133, 2008.

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.

Rickaby, R. E. M. and Elderfield, H.: Planktonic foraminiferal Cd/Ca: Paleonutrients or paleotemperature?, Paleoceanography, 14, 293–303, 1999.

Ridgwell, A., Zondervan, I., Hargreaves, J. C., Bijma, J., and

Lenton, T. M.: Assessing the potential long-term increase of oceanic fossil fuel CO$_2$ uptake due to CO$_2$-calcification feedback, Biogeosciences, 4, 481–492, 2007, http://www.biogeosciences.net/4/481/2007/.

Riebesell, U., Zondervan, I., Rost, B., Tortell, P. D., Zeebe, R. E., and Morel, F. M. M.: Reduced calcification of marine plankton in response to increased atmospheric CO$_2$, Nature, 407, 364–367, 2000.

Rosenthal, Y., Boyle, E. A., and Slowey, N.: Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography, Geochim. Cosmochim. Acta, 61, 3633–3643, 1997.

Rosenthal, Y., Lear, C. H., Oppo, D. W., and Linsley, B. K. (2006), Temperature and carbonate ion effects on Mg/Ca and Sr/Ca ratios in benthic foraminifera: Aragonitic species Hoeglundina elegans, Paleoceanography, 21(14), PA1007, doi:10.1029/2005PA001158, 2006.

Russell, A. D., Honisch, B., Spero, H. J., and Lea, D. W.: Effects of seawater carbonate ion concentration and temperature on shell U, Mg, and Sr in cultured planktonic foraminifera, Geochim. Cosmochim. Acta, 68, 4347–4361, 2004.

Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R., Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T. H., Kozyr, A., Ono, T., and Rios, A. F.: The oceanic sink for anthropogenic CO$_2$, Science, 305, 367–371, 2004.

Tesoriero, A. J. and Pankow, J. F.: Solid solution partitioning of Sr^{2+}, Ba^{2+}, and Cd^{2+} to calcite, Geochim. Cosmochim. Acta, 60, 1053–1063, 1996.

Toyofuku, T., Kitazato, H., Kawahata, H., Tsuchiya, M., and Nohara, M.: Evaluation of Mg/Ca thermometry in foraminifera: Comparison of experimental results and measurements in nature, Paleoceanography, 15, 456–464, 2000.

Walton, W. R. and Sloan, B. J.: The Genus Ammonia Brunnich, 1772 – Its Geographic Distribution and Morphologic Variability, J. Foramin. Res., 20, 128–156, 1990.

Zeebe, R. E. and Wolf-Gladrow, D. A.: CO$_2$ in Seawater: Equilibrium, Kinetics, Isotopes, Elsevier, Amsterdam, 346 pp., 2001.

Zondervan, I., Zeebe, R. E., Rost, B., and Riebesell, U.: Decreasing marine biogenic calcification: A negative feedback on rising atmospheric pCO(2), Global Biogeochem. Cy., 15, 507–516, 2001.