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Sulfur in foraminiferal calcite as a potential proxy for seawater carbonate ion concentration

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ABSTRACT

Sulfur (S) incorporation in foraminiferal shells is hypothesized to change with carbonate ion concentration [CO_3^{2-}], due to substitution of sulfate for carbonate ions in the calcite crystal lattice. Hence S/Ca values of foraminiferal carbonate shells are expected to reflect sea water carbonate chemistry. To generate a proxy calibration linking the incorporation of S into foraminiferal calcite to carbonate chemistry, we cultured juvenile clones of the larger benthic species *Amphistegina gibbosa* and *Sorites marginalis* over a 350–1200 ppm range of pCO_2 values, corresponding to a range in [CO_3^{2-}] of 93 to 211 µmol/kg. We also investigated the potential effect of salinity on S incorporation by culturing juvenile *Amphistegina lessonii* over a large salinity gradient (25–45). Results show $S/Ca_{CALCITE}$ is not impacted by salinity, but increases with increasing pCO_2 (and thus decreasing [CO_3^{2-}] and pH), indicating S incorporation may be used as a proxy for [CO_3^{2-}]. Higher S incorporation in high-Mg species *S. marginalis* suggests a superimposed biomineralization effect on the incorporation of S. Microprobe imaging reveals co-occurring banding of Mg and S in *Amphistegina lessonii*, which is in line with a strong biological control and might explain higher S incorporation in high Mg species. Provided a species-specific calibration is available, foraminiferal S/Ca values might add a valuable new tool for reconstructing past ocean carbonate chemistry.

1. Introduction

The interaction between the atmosphere and the ocean is a crucial component of the global climate system as the ocean and atmosphere exchange e.g. heat and gases. Due to the large size of the ocean it thereby acts as a reservoir and buffer for the atmosphere on geological timescales. Since the industrial revolution in the mid-18th century, ongoing anthropogenic burning of fossil fuels has resulted in a rapid increase of atmospheric CO_2 (Feely et al., 2009). Exchange of CO_2 between ocean and atmosphere has resulted in an uptake of approximately 25% of the anthropogenic carbon emissions by oceans over the last decades (Doney et al., 2009). When CO_2 enters the ocean, a suite of chemical reactions occur that lead to a decreased carbonate saturation state and the release of protons, a process called 'ocean acidification' (OA; Gattuso and Hansson, 2011). Carbonate precipitating organisms, including pteropods and coccolithophores, might be negatively impacted by these changes (Orr et al., 2005). Past ocean acidification events could provide valuable insight in the impact of ocean acidification on a global scale (Hönisch et al., 2012), but rely on our ability to accurately reconstruct carbon chemistry of the ocean. Different parameters of the ocean inorganic carbonate system are highly dependent on each other, allowing reconstruction of all parameters (e.g. pCO_2, total alkalinity, dissolved inorganic carbon [DIC] and pH) from the reconstruction of only two parameters (Zeebe and Wolf-Gladrow, 2001). Currently proxies permit reconstruction of some of these parameters (e.g. Foster, 2008; Hönisch and Hemming, 2005), whereas others are more difficult to assess. Therefore, development of new, and improvement of existing proxies is necessary to increase the accuracy and precision of such reconstructions.

Uptake of minor and trace metals in the shells of calcareous foraminifera provide a widely used toolbox to reconstruct past ocean conditions. For example, the relation between temperature and Mg incorporation in foraminiferal carbonate is reasonably well constrained (Nürnberg et al., 1996; Toyofuku et al., 2011 and references therein) and is frequently used as a paleothermometer (e.g. Elderfield and Ganssen, 2000). In comparison to temperature reconstructions, estimates of the inorganic carbon system in the past (seawater pH, alkalinity, saturation state, etc.) are less well constrained. The boron isotopic composition of

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foraminiferal shells is used as a proxy for pH (Henehan et al., 2016; Sanyal et al., 1996), while the concentrations of trace elements, including for instance U (Keul et al., 2013), Zn (Van Dijk et al., 2017) and B (Yu and Elderfield, 2007) in calcite correlate to carbonate ion concentration ($[CO_3^{2-}]$). However, partitioning of these elements is often not controlled by a single parameter (e.g., Allen and Hönisch, 2012), which is why (new) independent proxies are still needed to accurately reconstruct past ocean chemistry.

After chloride, sulfate (SO_4^{2-}) is the most abundant anion in the ocean and over geological time scales its concentration is largely controlled by the sulfur cycle (Walker, 1986). It is hypothesized that SO_4^{2-} in seawater is the only source of sulfur (S) in biogenic carbonate (Pingitore et al., 1995) and that S/Ca values change with carbonate ion concentration (Berry, 1998). Since the molar ratio of $Ca:CO_3$ in calcite is close to 1, SO_4/CO_3 can be approximated by S/Ca, which can be determined from foraminiferal shells. Over longer times scales, sulfate concentrations in the ocean have not been stable, ranging between ~10 and 30 mM during the Phanerozoic (Demicco et al., 2005), due to the balance between pyrite and shale formation/oxidation and the release of sulfur gasses (SO_2 and H_2S) by volcanic activity (Walker, 1986). Residence time of sulfate and Ca^{2+} in the ocean is currently estimated at, respectively 13–20 Ma (Bottrell and Newton, 2006) and ~1 Ma (Broecker and Peng, 1982), which implies that on timescales longer than 1 Ma foraminiferal S/Ca likely primarily reflects changes in seawater Ca^{2+} and $[SO_4^{2-}]$ (Paris et al., 2014). On shorter time scales, however, foraminiferal S/Ca values are most likely linked to seawater carbon speciation due to substitution of SO_4^{2-} for CO_3^{2-}.

Here we present and compare foraminiferal shell S/Ca data obtained from different species of benthic foraminifera cultured over either a range of pCO_2 (350–1200 ppm CO_2) or salinity (25–45), while keeping seawater S/Ca constant. Our culture set up allows us to independently quantify the impacts of these two environmental parameters on foraminiferal S/Ca, whereas in the field, these parameters are usually coupled. Furthermore, we investigate the micro-distribution of S within foraminiferal chamber walls to assess the potential biological imprint on S incorporation.

2. Methods

2.1. pCO_2-controlled experiment

2.1.1. Foraminifera collection

Macro-algae (*Dictyota* sp.) with attached larger benthic foraminifera were hand collected in November 2015 at a depth of 2–3 m in Gallows Bay, St. Eustatius (N 17°28′31.6″, W 62°59′9.4″), Caribbean Sea. Local salinity and temperature were ~34 and ~29 °C, respectively. Macro-algae samples were transported to the laboratory at the Caribbean Netherlands Science Institute (CNSI, St. Eustatius) and placed in a 5 L aquarium filled with unfiltered and aerated seawater. Algae debris was sieved over a 600 and 90 µm mesh to dislodge larger benthic foraminifera and the resulting 90–600 µm fraction was used as a stock to select specimens. Approximately 100–200 individuals of the rotaliid *Amphistegina gibbosa* and miliolid *Sorites marginalis*, characterized by yellow cytoplasm and pseudopodial activity, were isolated for the culturing experiments. Culture experiments are performed with juvenile specimens, to ensure that all calcite is grown under the set conditions of the experiment. To obtain juveniles, groups of 10–15 adults were transferred in 20 ml Petri dishes containing sand-filtered in-situ seawater and concentrated freeze-dried algae (*Dunaliella salina*) and stored at a constant temperature of 25 °C and a 12 h/12 h day/night cycle at a light intensity of approximately 300 par. After a reproduction event, juvenile clones were allowed to grow ~2 chambers before they were transferred to the culture vessel and incubated at experimental conditions.

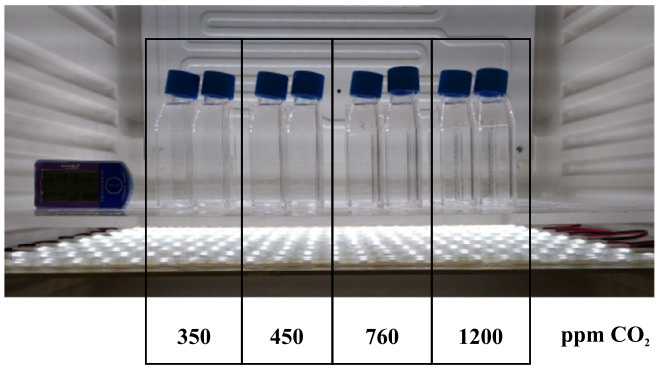

Fig. 1. Set-up of the culture experiment at 25 °C with LED shelves (300 par). Duplicate tissue bottles containing natural seawater pre-equilibrated to 350, 450, 760 or 1200 ppm CO_2 with juvenile foraminifera.

Table 1
Number of foraminifera in treatment A–D. Roman numbers indicate generation of juveniles.

Species	A	B	C	D
	350 ppm	440 ppm	760 ppm	1200 ppm
A. gibbosa	~20 (I)	~20 (I)	~20 (I)	~20 (I)
S. marginalis	~35 (I)	~35 (II)	~35 (III)	n.d.

2.1.2. Experimental set-up

Four 100 L barrels were filled with ~80 L of natural seawater (5 µm filtered). The pCO_2 in the headspace of these barrels was measured by a Li-Cor CO_2/H_2O analyzer (LI-7000), that was used to regulate addition of CO_2 and/ or CO_2-scrubbed air to keep the pCO_2 of each barrel at pre-set levels. Set-points for pCO_2 were 350 (A), 450 (B), 760 (C) and 1200 (D) ppm. This resulted in four batches of seawater with a range of pH, $[CO_3^{2-}]$ and saturation states, but with constant elemental composition, alkalinity and salinity. Salinity (34.0 ± 0.2) was measured with a salinometer (VWR CO310). Per condition, 2 L of culture water was stored bubble-free in eight 250 ml Nalgene bottles with Teflon lined Nalgene caps at 4 °C until further use. Nalgene was used because of its low gas permeability. At the start of the experiment, and for every water exchange, one of the 250 ml bottles for every of the four conditions was opened and used. This ensured that at the end of the experiment, media in the culture vessel were still in equilibrium with the pCO_2 set at the start of the experiment (see below for analytical checks).

Around eighty clones of juvenile of *A. gibbosa* and three generations (I–III) of clones of *S. marginalis* were divided in duplicates over the four pCO_2 treatments and placed in 70 ml tissue bottles with gas-tight caps (Falcon®) in a thermostat set at 25 °C (Fig. 1). This resulted in 8 tissue bottles with juvenile foraminifera (see Table 1 for specifications). Temperature within the thermostat was monitored by a temperature logger (Traceable Logger Trac, Maxi Thermal), measuring air temperature every minute. The average temperature over the whole experiment was 25 ± 0.2 °C. The shelves within the thermostat were equipped with customized LED shelfs to ensure that all foraminifera were cultured at similar light intensities. These shelves were designed to give similar amount of light (par) over a certain distance. The LED lights were controlled by a time controller and set to 30% for 12 h/12 h, which equals to 300 par (high-light condition). Light intensities were checked with an Odyssey logger (Dataflow Systems). Culture media was replaced every four days, to avoid build-up of organic waste and to obtain stable seawater element concentrations and carbon chemistry. Foraminifera were fed after every water change with 0.5 ml of freeze-dried cells of the algae *Dunaliella salina* cells, dissolved