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$^{88}Sr/^{86}Sr$ fractionation in inorganic aragonite and in corals

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Abstract

Conflicting results have been reported for the stable Sr isotope fractionation, specifically with respect to the influence of temperature. In an experimental study we have investigated the stable Sr isotope systematics for inorganically precipitated and biogenic (coral) aragonite (natural and laboratory-cultured). Inorganic aragonite precipitation experiments were performed from natural seawater using the CO_2 diffusion technique. The experiments were performed at different temperatures and different carbonate ion concentrations. $^{88}Sr/^{86}Sr$ of the inorganic aragonite precipitated in the experiments are 0.2‰ lighter than seawater, but showed no correlation to the water temperature or to CO_3^{2-} concentration. Similar observations are made in different coral species (*Cladocora caespitosa*, *Porites* sp. and *Acropora* sp.), with identical fractionation from the bulk solution and no correlation to temperature or CO_3^{2-} concentration. The lack of $^{88}Sr/^{86}Sr$ variability in corals at different environmental parameters and the similarity to the $^{88}Sr/^{86}Sr$ fractionation in inorganic aragonite may indicate a similar Sr incorporation mechanism in corals skeleton and inorganic aragonite, and therefore the previously proposed Rayleigh-based multi element model (Gaetani et al., 2011) cannot explain the process of Sr incorporation in the coral skeletal material. It is proposed that the relatively constant $^{88}Sr/^{86}Sr$ fractionation in aragonite can be used for paleo reconstruction of seawater $^{88}Sr/^{86}Sr$ composition. The seawater $^{88}Sr/^{86}Sr$ ratio reconstruction can be further used in calcite samples to reconstruct paleo precipitation rates.

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1. INTRODUCTION

Scleractinian coral skeletons are one of the main archives of paleoclimate information, such as sea surface temperature (SST), pH and ocean chemistry. A temperature dependency for the partitioning between seawater and corals was found for several elemental ratios such as Mg/Ca (e.g. Mitsuguchi et al., 1996), Sr/Ca (e.g. Beck et al., 1992) and B/Ca (e.g. Fallon et al., 1999; Montagna et al., 2007), and recently also Li/Mg (e.g. Case et al., 2010; Montagna et al., 2014). The isotope fractionation of oxygen, $\delta^{18}O$ (e.g. Weber and Woodhead, 1972), is also being used for SST reconstruction from coral skeletons. Among all geochemical proxies, Sr/Ca and $\delta^{18}O$ are the most widely used and established paleothermometers (Corrège, 2006). However, temperature may not be the only

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controlling factor for trace element partitioning and isotope fractionation (c.f. Gagnon et al., 2007). Sr/Ca ratios, for example, have been shown to differ significantly in neighboring colonies of the same species exposed to the same environmental conditions (Marshall and McCulloch, 2002). Similarly, the applicability of Mg/Ca as temperature proxy is undermined by recent studies showing a weak correlation between skeletal Mg/Ca and SST (Quinn and Sampson, 2002) and the fact that Mg is strongly correlated to organic materials in coral skeletons (Meibom et al., 2004; Finch and Allison, 2008). In addition to temperature $\delta^{18}O$ is known to be influenced by seawater salinity changes (e.g. Schmidt, 1999).

A new approach to extract temperature records from the geochemical signal in corals was recently proposed by Gaetani and Cohen (2006) and Gaetani et al. (2011) based on a Rayleigh-based multi element partitioning model. The Rayleigh-based model defines calcification in corals as a precipitation process from a renewable finite solution. Elements are depleted from the solution during precipitation according to their inorganic partitioning coefficient. Since the solution is finite, the coral's apparent fractionation factor is influenced by the Rayleigh effect. Temperature is strongly correlated to the Rayleigh-based mechanism (Gaetani et al., 2011), as the depletion or enrichment of elements is a function of increased precipitation rate as a consequence of increasing temperature. By combining information from two elemental ratios (Sr/Ca and Mg/Ca) Gaetani et al. (2011) were able to reconstruct the remaining fraction in the bulk solution and the temperature at which the *Acropora* sp. specimens were cultured.

The increasing interest in non-traditional stable isotopes (Johnson et al., 2004) and the search for a reliable paleo proxy record has led to several studies of $^{88}Sr/^{86}Sr$ fractionation as a possible paleo-temperature proxy. Fietzke and Eisenhauer (2006) first reported a measurable $^{88}Sr/^{86}Sr$ fractionation in the tropical coral *Pavona clavus* and in inorganic aragonites and showed a $\delta^{88/86}Sr$ dependency on temperature. In a follow up study Rüggeberg et al. (2008) found a similar trend between temperature and $\delta^{88/86}Sr$ in the cold water coral, *Lophelia pertusa*. Evidence of significantly different $\delta^{88/86}Sr$ between the precipitating mineral and the bulk solution were also found in terrestrial environments by Halicz et al. (2008).

While the earlier work of $\delta^{88/86}Sr$ used the sample-standard bracketing technique to reliably correct for instrumental mass fractionation using Multiple-Collector ICP-MS (MC-ICPMS) (Fietzke and Eisenhauer, 2006; Halicz et al., 2008; Rüggeberg et al., 2008), later studies applied the $^{87}Sr/^{84}Sr$ double spike method that was developed for Thermal Ionization Mass Spectrometry (TIMS) by Krabbenhöft et al. (2009). Measurements using the TIMS method did not confirm the significant positive $\delta^{88/86}Sr$-temperature trend in the tropical coral *Acropora* sp. (Krabbenhöft et al., 2010) and in the cold water coral *L. pertusa* (Raddatz et al., 2013). The discrepancies between the results of these studies may be due to methodological differences that produced erratic data in one set of measurements.

In the current study we measured $\delta^{88/86}Sr$ using the double spike method in modern natural *Porites* sp. from two different locations, cultured *Acropora* sp. and *Cladocora caespitosa* as well as inorganically-precipitated aragonite. A large range of temperatures and precipitation rates (obtained by different CO_3^{2-} concentrations) were applied to both the inorganic aragonite and the coral culturing experiments in order to detect environmental drivers of the Sr isotopes fractionation process. In addition, the comparison between inorganic aragonite and coralline aragonite through $^{88}Sr/^{86}Sr$ fractionation sheds some light on the enigmatic coral calcification process.

2. MATERIAL AND METHODS

2.1. Inorganic aragonite precipitation experiments

Inorganic aragonite precipitation experiments were conducted at the Graz University of Technology, Austria using the CO_2 diffusion technique as described in detail in Dietzel et al. (2004) and Tang et al. (2008). Briefly, CO_2 diffuses from an inner solution to an outer solution via a polyethylene (PE) membrane. For the experiments two different membranes thicknesses, 0.02 mm or 2 mm were used. The inner solution has a higher pCO_2 than the outer solution and consists of 35 g of $NaHCO_3$ dissolved in 0.5 L of double deionized water acidified to pH 7.5. In some experiments 10 ml 1 N HCl was added to the inner solution in order to increase the pCO_2 even more (Table 1). The outer solution (or bulk solution), from which the precipitation occurs, consists of 5 L of filtered natural seawater collected at 1000 m water depth from the Gulf of Aqaba using a CTD-Rosette system (19.09°N 39.49°E, salinity 40.7). Filtration was done using a Sartobram P. sterile MidiCap double filter (0.45 μm and 0.2 μm). The pH of the outer solution was kept constant at 8.30 ± 0.03 using 0.5 N NaOH titration, controlled using a Schott Blueline 28 pH meter combined with an automatic titration burette. The pCO_2 gradient between the inner and the outer solutions controls the CO_2 diffusion rate and the saturation state for $CaCO_3$ in the outer solution.

Nine different experiments (Table 1), which varied in temperature (15 °C, 25 °C and 30 °C) and CO_2 uptake rates (using different PE membranes of 0.02 mm or 2 mm thickness and different pCO_2 in the inner solution) were run. Water samples from the outer solution were collected at the beginning and at the end of the experiments for the analyses of Sr/Ca and $^{88}Sr/^{86}Sr$. The entire precipitated solid material was collected and dried at 80 °C for 24 h, and then analyzed with XRD and FTIR (PerkinElmer spectrum 100 FTIR) to determine its mineralogy and detect the presence of the poorly crystallized mineral brucite.

The precipitation rate (R in $\mu mol\ h^{-1}$) of aragonite was determined according the equation

$$R = ([Ca]_i - [Ca]_f) \cdot V/\Delta t \tag{2.1}$$

where $[Ca]_i$ and $[Ca]_f$ are the Ca concentration in the initial and the final solutions, respectively, V is the volume of the solution and Δt is the duration of the precipitation. Even though precipitation rates are influenced by the surface area and surface reactions (Wiechers et al., 1975), we could not include the surface area measurements in the calculation