



Environmental and biological controls on Mg and Li in deep-sea scleractinian corals

David H. Case^{a,*}, Laura F. Robinson^a, Maureen E. Auro^a, Alexander C. Gagnon^b

^a Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, 360 Woods Hole Road, Mail Stop 25, Woods Hole, MA 02543, USA

^b Earth Sciences Division and The Molecular Foundry, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Mail Stop 67R3208, Berkeley, CA 94720, USA

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ABSTRACT

Deep-sea scleractinian corals precipitate aragonite skeletons that provide valuable archives of past ocean conditions. During calcification biological mediation causes variability in trace metal incorporation and isotopic ratios of the aragonite such that signals caused by environmental controls can be overwhelmed. This complicates the interpretation of geochemical proxies used for paleo-reconstructions. In this study we examine the environmental controls on the Mg/Li ratio of 34 individuals from seven genera of deep-sea scleractinian corals: *Desmophyllum*, *Balanophyllia*, *Caryophyllia*, *Enallopsammia*, *Flabellum*, *Trochocyathus*, and *Lophelia*. In addition we examine the microscale distributions of Mg and Li in *Desmophyllum* and *Balanophyllia* using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Both Mg/Ca and Li/Ca ratios increased by more than a factor of two in the center of calcification regions compared to the outer, fibrous regions of the coral skeleton. As a result, replicate ~10 mg subsamples of coral show less variability in the Mg/Li ratio than Mg/Ca. Microscale Mg and Li results are consistent with Rayleigh-type incorporation of trace metals with additional processes dominating the composition within centers of calcification. Comparison of Mg/Li to seawater properties near the site of collection shows that the ratio is not controlled by either carbonate ion or salinity. It appears that temperature is the major control on the Mg/Li ratio. For all 34 samples the temperature correlation ($R^2 = 0.62$) is significantly better than for Mg/Ca ($R^2 = 0.06$). For corals of the family *Caryophyllidae* the R^2 value increases to 0.82 with the exclusion of one sample that was observed to have an altered, chalky texture. Despite this excellent correlation the scatter in the data suggests that the Mg/Li ratio of deep-sea corals cannot be used to reconstruct temperature to better than approximately ± 1.6 °C without better temperature control and additional calibration points on modern coral samples.

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1. Introduction

Ice core records show that there have been large and abrupt changes in atmospheric temperature in the past, as particularly well documented during the last deglaciation (Grootes et al., 1993). Since approximately half of the cross-equatorial heat transport occurs in the ocean (Ganachaud and Wunsch, 2000) there are likely to be important links between ocean circulation and climate (Rahmstorf, 2002). High-resolution, well-dated records of deep-water temperatures are difficult to obtain because of the challenges of bioturbation and constructing precise chronologies in sediment cores. Using the skeletons of deep-sea corals to reconstruct seawater temperature in the past would circumvent some of these challenges given a suitable geochemical proxy for temperature.

Deep-sea corals inhabit a wide variety of depths and geographic distributions, including high-latitude regions and all ocean basins (Cairns, 2007). Scleractinian corals are made of aragonite and are

datable using U/Th techniques, allowing accurate and precise ages to be calculated for each individual (Cheng et al., 2000). Solitary deep-sea scleractinians have been collected from diverse settings, and fossil specimens in existing collections span hundreds of thousands of years (e.g., Robinson et al., 2006). *Desmophyllum dianthus*, a species that has been used in a number of paleo-studies, live on the order of 100 years providing potential centennial-scale archives (Adkins et al., 1998).

Despite the promise of deep-sea corals for reconstructing past ocean circulation, paleoceanographic reconstruction of temperature has been complicated by vital effects. This broad term represents the influence of biomineralization on skeletal composition. The near constant environmental conditions of the deep sea over the roughly 100 year lifetime of modern corals, and the lack of photosymbionts mean that compositional variability in the coral skeleton can be attributed to the processes of coral biomineralization.

Stable isotopes and trace element ratios commonly used in paleoceanography, including $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Mg/Ca, Sr/Ca, and U/Ca all vary across deep-sea scleractinian skeletal features (Adkins et al., 2003; Cohen et al., 2006; Gagnon et al., 2007; Robinson et al., 2006; Sinclair et al., 2006; Smith et al., 2000, 2002). The magnitude of this variation is different from proxy to proxy, but for temperature reconstructions can

* Corresponding author. Tel.: +1 608 443 8880.

E-mail addresses: dcase@caltech.edu (D.H. Case), lrobinson@whoi.edu (L.F. Robinson), mauro@whoi.edu (M.E. Auro), acgagnon@lbl.gov (A.C. Gagnon).

overwhelm environmental controls. Much of the compositional variability in coral follows differences in skeletal architecture. On the macroscale, corals contain septal and thecal features, the former being comprised of septa radiating about the axis of the coral and the latter comprising the thick walls of the coral structure. Scleractinian coral skeletons have two distinctive micro-scale architectures: the Centers of Calcification (COCs) which contain small, granular, disorganized crystals, and the surrounding regions which are comprised of fibrous bundles of aragonite needles (Gladfelter, 1982, 2007; Stolarski, 2003). These features have also been documented in scleractinian deep-sea corals (Adkins et al., 2003; Gagnon et al., 2007; Robinson et al., 2006; Rollion-Bard et al., 2010). In the deep-sea coral *D. dianthus*, Mg/Ca nearly doubles in the COCs (Gagnon et al., 2007), while $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are depleted (Adkins et al., 2003). These results may be interpreted as evidence that separate mechanisms control composition in different regions of the coral skeleton. However, Sr/Ca seems unaffected by skeletal architecture (Gagnon et al., 2007) while [U] is lower in regions associated with, but extending beyond, the COCs (Robinson et al., 2006), suggesting some continuity of mechanism across the whole coral skeleton.

Geochemical models of biomineralization attempt to explain the mechanisms controlling the distribution of trace metals and isotopes in coral skeletons. Models can be distinguished by the most important step or process proposed to control skeletal composition. Some of these processes include ion transport, pH-driven solution chemistry (e.g.: Adkins et al., 2003; McConnaughey, 1989), precipitation from a closed system (e.g.: Cohen et al., 2006; Gaetani and Cohen, 2006; Gagnon et al., 2007), the role of an organic matrix during precipitation, and the presence of transient amorphous phases (Rollion-Bard et al., 2010). In this paper we examine Mg and Li in *D. dianthus* accompanied by a discussion of the mechanisms controlling the incorporation and variation of these elements.

Most existing models agree that coral skeletogenesis occurs in a biologically controlled space with a unique composition called the “extracytoplasmic calcifying fluid,” or ECF (Adkins et al., 2003; Johnson, 1982; McConnaughey, 1989). The source and transport of skeletal ions into the ECF has the potential to affect skeletal composition and cause vital effects. While the extent of seawater leakage and its influence on calcification is a matter of debate, transport of bulky fluorescent dyes to the skeleton implicates direct seawater transport (Erez and Braun, 2007).

Consideration of the ECF as a closed system has prompted the application of Rayleigh fractionation principles to trace metal incorporation (Cohen et al., 2006; Gaetani and Cohen, 2006; Gagnon et al., 2007; Rollion-Bard et al., 2009). This class of model describes a system in which trace metals are precipitated into the aragonite lattice from an ECF that initially matches the seawater composition, but is subsequently closed with regard to ion transport. As precipitation proceeds the ECF becomes depleted in calcium and depleted or enriched in trace metals depending on their distribution coefficient. Cohen et al. (2006) and Gagnon et al. (2007) have applied this theory to model Sr/Ca and Mg/Ca variability in deep-sea corals where Sr has a distribution coefficient >1 while that of Mg is $\ll 1$. Gagnon et al. (2007) concluded that Rayleigh fractionation is consistent with their correlated Me/Ca variability outside of obvious *D. dianthus* COCs. However, an equally important conclusion of that study is that large Mg/Ca variability associated with COCs is dominated by a mechanism other than a Rayleigh process.

The pathway for incorporation of Mg in aragonite is not well constrained (Fallon et al., 2003). While Mg^{2+} may be directly substituted for Ca^{2+} as has been documented in calcite (Politi et al., 2010), the relatively small ionic radius of Mg^{2+} severely distorts the 6-fold coordinated calcite lattice, and it is likely that the aragonite lattice of scleractinian corals would be even more severely distorted. Finch and Allison (2008) employed X-ray Absorption Fine Structure (XAFS) to determine the structural state of Mg in scleractinian coral samples and the authors interpret their results to indicate that Mg is not directly

hosted in aragonite. These data may mean Mg is located in a disordered site, consistent with either organic binding or the presence of amorphous calcium carbonate (ACC). Alternatively Mg^{2+} in corals may be loosely bound in the aragonite lattice or adsorbed to crystal surfaces (Amiel et al., 1973; Walls et al., 1977). Regarding Li incorporation, much less is known. Li^+ incorporation has been observed in inorganic aragonite experiments (Okumura and Kitano, 1986), but Li^+ substitution for Ca^{2+} is more complicated than Mg^{2+} because of the difference in charge. We compare some of these mechanisms to our data in the discussion.

Bryan and Marchitto (2008) discovered a strong Mg/Li-to-temperature correlation in the shells of calcitic and aragonitic foraminifera which was significantly better than that for Mg/Ca. This study evaluates major environmental controls on Mg/Li by comparing the measured ratio of seven genera of deep-sea corals with ambient seawater. We also build on our understanding of coral vital effects and geochemistry by analyzing the microscale distribution of Mg and Li in *D. dianthus* and *Balanophyllia*.

2. Materials and methods

2.1. Sample selection

Thirty-four separate coral individuals representing seven scleractinian genera were selected: *Desmophyllum* ($n=22$), *Balanophyllia* ($n=4$), *Caryophyllia* ($n=3$), *Flabellum* ($n=1$), *Trochocyanthus* ($n=1$), *Enallopsammia* ($n=2$), and *Lophelia* ($n=1$) (Table 1). The first five are solitary corals while the latter two are colonial. The samples were selected to represent diverse oceanographic settings in all major ocean basins (Fig. 1), and cover a depth range of 120 to 1818 m. Environmental parameters, including temperature, salinity, and carbonate ion concentration were derived from the GLODAP database (Key et al., 2004, Table 1). Typically, the match between coral and water column location was within 3.5° latitude and longitude and closer than 30 m in depth.

Corals in this study were either loaned from the Smithsonian Museum of Natural History by Stephen Cairns or collected on recent cruises to the North Atlantic or Southern Oceans. Corals from recent cruises were either collected live or were radiocarbon dated to be recently dead (Burke et al., 2010). For the case of the Southern Ocean samples temperature and salinity were also available from nearby CTD casts taken on the same cruise, *Nathaniel B. Palmer* 0805.

The temperature range for all samples is from 1.8 to 17.0°C . Salinity ranged from 34.04 to 36.54 and carbonate ion concentration from 1.2 to $192.7\ \mu\text{mol/kg}$ (Table 1). Samples from the Smithsonian museum were assumed to be modern, although two (48738 and 77019) exhibited a visibly chalky texture indicating that they may have experienced post-mortem alteration.

2.2. Sample preparation

Coral samples were prepared for two different types of analyses: bulk solution ICP-MS and laser ablation ICP-MS. For bulk solution ICP-MS, samples ranging from 10 to 136 mg were cut from the coral using a dremel tool. Subsamples came from both thecal and septal regions, and some coral individuals were subsampled more than once. At most four subsamples were taken from a single coral individual. All corals were chemically cleaned using the oxidative and reductive steps of Cheng et al. (2000). After cleaning, samples were dissolved in 5% Optima Grade nitric acid, diluted to 60 ppm Ca, and spiked to 0.5 ppb In.

To prepare for ICP-MS laser ablation, sections of coral were cut perpendicular to the coral growth axis with a dremel tool, bound to a microscope slide using epoxy (polymerized Araldite resin, Ernest F. Fullam, Inc.) and polished with $0.18\ \mu\text{m}$ silica. Images of each section were taken under reflected light.

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