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Calcium isotopes in scleractinian fossil corals since the Mesozoic: Implications for vital effects and biomineralization through time

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ABSTRACT

We present a Cenozoic record of $\delta^{44/40}$Ca from well preserved scleractinian fossil corals, as well as fossil coral $\delta^{44/40}$Ca data from two time periods during the Mesozoic (84 and 160 Ma). To complement the coral data, we also extend existing bulk pelagic carbonate records back to ~80 Ma. The same fossil corals used for this study were previously shown to be excellently preserved, and to be faithful archives of past seawater Mg/Ca and Sr/Ca since ~200 Ma (Gothmann et al., 2015). We find that the $\delta^{44/40}$Ca compositions of bulk pelagic carbonates from ODP Site 807 (Ontong Java Plateau) and DSDP Site 516 (Rio Grande Rise) have not varied by more than ~±0.20‰ over the last ~80 Myr. In contrast, the $\delta^{44/40}$Ca compositions of Mesozoic and Early Cenozoic fossil corals are ~1‰ lighter than those of modern corals. The observed change in coral $\delta^{44/40}$Ca does not likely reflect secular variations in seawater $\delta^{44/40}$Ca. Instead, we propose that it reflects a vital effect of calcification – specifically, a sensitivity of coral Ca isotope discrimination to changing seawater [Ca] and/or pH. Support for this hypothesis comes from the presence of an empirical correlation between our coral $\delta^{44/40}$Ca record and records of seawater [Ca] and pH since the Mesozoic (Lowenstein et al., 2003; Hönisch et al., 2012). We explore various mechanisms that could give rise to such a vital effect, including: (1) changes in calcification rate, (2) changes in proton pumping in exchange for Ca^{2+}, (3) variable Rayleigh distillation from an isolated calcifying fluid, and (4) changes in the calcium mass balance of the extracellular calcifying fluid (termed here the “leaky Ca model”). We test for the dependence of seawater $\delta^{44/40}$Ca on external seawater [Ca] by measuring the $\delta^{44/40}$Ca of cultured corals grown in seawater solutions with [Ca] ranging from 10 to 15 mmol/kg. Corals grown under elevated [Ca] conditions show a slight, ~0.15‰ depletion of $\delta^{44/40}$Ca at higher seawater [Ca] – a supportive but not definitive result.

1. Introduction

Diagenetically unaltered scleractinian fossil corals are useful archives of paleoenvironmental properties across a range of geologic timescales. For example, coral-based paleothermometers (Sr/Ca, δ^{18}O) have been applied to reconstruct high-resolution records of past climate (e.g., Corrège, 2006; Gaetani et al., 2011). Fossil corals have also been used to reconstruct the geochemical evolution of seawater (i.e., seawater Mg/Ca and Sr/Ca) on timescales of millions of years (Gothmann et al., 2015). The application of corals as paleoenvironmental indicators, however, can sometimes be confounded by the presence of ‘vital effects’ (Corrège, 2006; Gaetani et al., 2011).

‘Vital effects’ refer to departures in skeletal geochemistry away from the composition expected based on inorganic distribution coefficients, and they are thought to result from biological control by the coral organism over skeletal calcification (Weiner and Dove, 2003). Problematically, they may also vary between and within coral species, in which case constant correction factors cannot be employed (Weiner and Dove, 2003; Corrège, 2006; Gaetani et al., 2011).

The existence of vital effects in scleractinian coral has been very well documented, but a full mechanistic understanding of their origin has yet to be achieved (Weiner and Dove, 2003). Mechanisms that have been identified as potential sources of vital effects include, but are not limited to (1) Rayleigh fractionation from an

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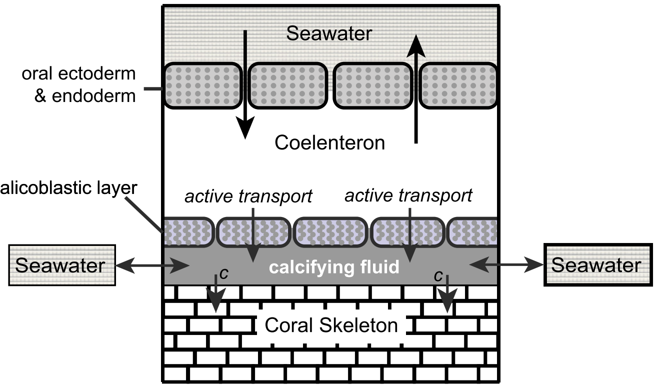

Fig. 1. Sketch of key skeletal compartments and reservoirs that play a role in coral calcification, modified from Böhm et al. (2006). Seawater transport to the site of calcification can occur via direct exchange, or can occur transcellularly by active transport with Ca-ATPase. The label 'c' denotes arrows marking calcification.

isolated calcifying fluid and/or other reservoir effects (e.g., Gaetani et al., 2011), (2) biologically-mediated ionic transport into the calcifying space (e.g., Böhm et al., 2006), (3) variable calcification rates (e.g., as discussed in Corrège, 2006) and (4) the influence of an organic matrix (e.g., Weiner and Dove, 2003).

Existing measurements of $\delta^{44/40}$Ca in modern corals suggest the presence of significant vital effects for Ca isotopes. Modern coral $\delta^{44/40}$Ca is on average ~0.4‰ heavier than inorganic aragonite (Chang et al., 2004; Böhm et al., 2006; Pretet et al., 2013; Inoue et al., 2015). For reference, inorganic aragonite is offset from seawater by about −1.7‰ (Blättler et al., 2012; Gussone et al., 2003). In addition, modern corals exhibit a ~0.4‰ range in $\delta^{44/40}$Ca compositions (Böhm et al., 2006; Blättler et al., 2012; Pretet et al., 2013; Inoue et al., 2015). This range cannot be attributed to variations in coral taxonomy, changes in salinity, or temperature.

Ca isotopes may offer unique insight into the mechanisms driving coral vital effects because calcium plays a critical role in calcification. There are two main pathways by which Ca may arrive at the site of coral calcification (Fig. 1). First, Ca^{2+} that has diffused into the coelenteron (the mouth of the coral animal) may be actively transported by Ca-ATPase to the site of calcification (e.g., Al-Horani et al., 2003). There are also suggestions that seawater may be transported paracellularly (i.e., via open channels or conduits) directly to the site of calcification (e.g., Tambutté et al. 2012). The calcification site may exist as a thin, seawater-like "calcifying fluid" beneath the calicoblastic layer (Al-Horani et al., 2003; Gaetani et al., 2011). Alternatively, calcification may occur directly from an organic matrix (e.g., Weiner and Dove, 2003).

It is possible that external seawater carbonate chemistry and seawater [Ca] influence each of the abovementioned pathways and the isotope effects associated with them. Ca isotope fractionation in inorganic calcite and aragonite precipitated from aqueous solutions has been found to depend on calcification rate (Lemarchand et al., 2004; Tang et al., 2008; Gussone et al., 2003), which in turn has been shown to depend on the $[CO_3^{2-}]/[Ca^{2+}]$ ratios of natural waters (Nielsen and DePaolo, 2013). Rayleigh distillation (e.g., Gaetani et al., 2011) may also lead to a dependence of Ca isotope discrimination on seawater [Ca]. Another possibility is that coral Ca isotope fractionation is dependent on seawater [Ca] in a way similar to the dependence of carbon isotope fractionation on $p\mathrm{CO}_2$ in plants. In plants cells, the ratio of carbon fixation by the enzyme RuBisCO, relative to the amount of CO_2 that diffuses back to the surrounding environment, is dependent on $p\mathrm{CO}_2$. Because the isotope effects associated with fixation and diffusion are distinct, the degree of carbon isotope fractionation expressed also depends on $p\mathrm{CO}_2$ (Pagani, 2014). Likewise, in coral, the ratio of Ca that is incorporated into coral aragonite from the calcifying fluid, relative to the amount of Ca returned to seawater, may be dependent on external seawater [Ca].

Böhm et al. (2006) hypothesize that Ca isotope fractionation in coral results, at least in part, from active biologically-mediated transport of Ca^{2+} to the site of calcification. As a result, changes in seawater [Ca] could presumably affect the proportion of Ca in the coral skeleton derived from active pumping by Ca-ATPase relative to Ca derived from a direct seawater pathway. As suggested by Gagnon et al. (2013), seawater pH, alkalinity and saturation state may also play a role in setting the proportion of skeletal Ca that comes directly from seawater, relative to the amount derived from Ca-ATPase. Studies of boron isotopes and pH-sensitive dyes in coral (McCulloch et al., 2012; Venn et al., 2013) present additional evidence in support of a relationship between proton pumping by Ca-ATPase and seawater carbonate chemistry.

We measured Ca isotopes in a suite of well preserved fossil aragonitic corals (Gothmann et al., 2015), bulk pelagic carbonates from ODP Site 807 and DSDP Site 516, and corals cultured under a range of seawater [Ca]. Collectively, the data allow us to examine how coral Ca isotope fractionation has responded to natural variations in seawater [Ca] and pH since the Mesozoic (Lowenstein et al., 2003; Hönisch et al., 2012). Our results provide new insights into the relationship between coral calcification and secular variations in seawater chemistry over million-year timescales.

2. Materials and methods

2.1. Fossil coral, bulk pelagic carbonate, and cultured coral samples

The fossil coral samples ($n = 38$) studied here were previously screened for diagenetic alteration and described by Gothmann et al. (2015). Fossil corals measured for Ca isotopes are as old as Jurassic in age and have been obtained from a variety of geologic localities to ensure that variations through time reflect global rather than local signatures. While our sample set includes a range of different species of coral, there are no trends in our sample set between coral taxonomy and geologic age. Details of sample taxonomy and provenance are presented in the supplementary materials (Table S1).

Bulk pelagic carbonate samples from ODP Site 807 (Ontong Java Plateau, ~2800 m water depth) and DSDP Site 516 (Rio Grande Rise, ~1300 m water depth) were also measured for $\delta^{44/40}$Ca. Samples range in age from Late Cretaceous to Recent. Cores from both sites are generally carbonate-rich, although some intervals of claystone and radiolarian siltstone are also present (Kroenke et al., 1991; Fantle and DePaolo, 2007; Barker et al., 1983). Sediments of Eocene age and younger are dominated by foraminifer oozes, nannofossil oozes, and chalk. Eocene and older sediments are dominated by lithified limestone (Kroenke et al., 1991; Barker et al., 1983). Bulk carbonate samples were washed and sieved prior to geochemical analysis as described in Higgins and Schrag (2015).

Cultured coral samples were grown for 9 weeks under controlled laboratory conditions at the University of Miami's Experimental Hatchery. Concentrations of calcium in the culture solutions were varied to assess the effect of past changes in seawater [Ca] on coral Ca isotope discrimination. Calcium concentrations of the growth solutions ranged from modern seawater concentrations (~10 mmol/kg) to concentrations similar to those expected for the late Oligocene or Early Miocene (~15 mmol/kg) (Lowenstein et al., 2003). (For reference, Early Cenozoic seawater [Ca] was ~25–30 mmol/kg, 250–300% of present: Lowenstein et al., 2003.) While some colonies were only subjected to elevated [Ca], others were also subjected to elevated [Mg] and [Sr].

Prior to starting experiments, 2 branches (>1.5 cm in length) of *Pocillopora damicornis* were fragmented from coral colonies us-