



Experimental determination of factors controlling U/Ca of aragonite precipitated from seawater: Implications for interpreting coral skeleton

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Abstract

The U/Ca ratio of aragonite coral skeleton exhibits coherent patterns of seasonal and interannual variability. In field-sampled corals and those grown in controlled culture experiments, strong correlations have been found between coral skeleton U/Ca and water temperature, pH, carbonate ion concentration, and salinity. However, the mechanism(s) underlying these different correlations remain unclear. We performed abiogenic precipitation experiments designed to evaluate the sensitivity of U partitioning between aragonite and seawater to temperature, pH, and the concentration of carbonate ion in seawater. Aragonite was precipitated from seawater by addition of carbonate alkalinity at rates set to maintain stable carbonate chemistry during precipitation. Experiments were conducted at 20–40 °C, with pH 7.8–9.0 and carbonate ion concentrations of 600–2600 $\mu\text{mol kg}^{-1}$. U/Ca ratios of the bulk precipitate and fluid were determined by inductively coupled plasma mass spectrometry. Our results show that the U/Ca ratio of aragonite precipitated from seawater decreases with increasing carbonate ion concentration, and is independent of pH and temperature. We use these results as a framework to interpret the skeletal composition of coral aragonite precipitated from a calcifying fluid that is semi-isolated from the external seawater environment. Accordingly, coral U/Ca ratios are consistent with calcifying fluid carbonate ion concentrations that are several times greater than those of ambient seawater. Correlations between coral U/Ca ratios and seawater temperature, carbonate chemistry, and other environmental variables arise indirectly, via the impacts of these variables on the carbonate ion concentration of the coral calcifying fluid.

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1. INTRODUCTION

Trace element-to-calcium ratios (E/Ca) in the skeletons of scleractinian corals, both deep and surface dwelling, are widely used as proxies for environmental conditions in the

oceans. The uranium-to-calcium ratio (U/Ca) of coral skeleton exhibits strong seasonality and covaries with other E/Ca ratios (Cardinal et al., 2001; Quinn and Sampson, 2002; Sinclair, 2005; Felis et al., 2009). In skeletons from field-sampled corals and those grown in controlled culture experiments, strong correlations have been found between U/Ca and seawater temperature (Min et al., 1995; Felis et al., 2009; Armid et al., 2011), pH (Inoue et al., 2011; Raddatz et al., 2014), carbonate ion concentration ($[\text{CO}_3^{2-}]$) (Shen and Dunbar, 1995; Armid et al., 2008;

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Anagnostou et al., 2011), and salinity (Ourbak et al., 2006). However, on the basis of existing data it is not possible to demonstrate conclusively which – if any – of these factors is directly responsible for U/Ca variability.

Observations of a link between aragonite U/Ca and seawater carbonate chemistry plausibly reflect the speciation of uranyl ion (UO_2^{2+}), which forms different complexes with CO_3^{2-} in seawater as a function of pH (Djogic et al., 1986) and/or $[\text{CO}_3^{2-}]$ (Kitano and Oomori, 1971; Saito and Miyauchi, 1982; Keul et al., 2013 and references therein). Uranyl speciation is potentially influenced by other factors in addition to carbonate chemistry. In freshwater at low ionic strength ($I=0.1$, whereas for seawater $I=\sim 0.7$), UO_2^{2+} forms complexes with both Ca^{2+} and CO_3^{2-} ($\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$) (Dong and Brooks, 2006; Endrizzi and Rao, 2014), and – at pH less than ~ 8 – with dissolved organic matter (DOM) (Gustafsson et al., 2009). Nevertheless, several studies have found that the dominant uranyl complex in seawater at pH ~ 8 is uranyl tricarbonate ($\text{UO}_2(\text{CO}_3)_3^{4-}$) (Saito and Miyauchi, 1982; Djogic et al., 1986; Kalin et al., 2005 and references therein), which was found to be incorporated directly into the aragonite lattice, substituting for CO_3^{2-} rather than Ca^{2+} (Reeder et al., 2000). Because the abundance of $\text{UO}_2(\text{CO}_3)_3^{4-}$ in seawater varies with pH and/or $[\text{CO}_3^{2-}]$, the U/Ca ratio of aragonite should be sensitive to one or both of these carbonate system variables.

Abiogenic precipitation experiments provide a means to investigate environmental controls on element partitioning between aragonite and seawater in the absence of physiological processes that can mask their influence. For example, Meece and Benninger (1993) used this approach to investigate the incorporation of a series of radionuclides into abiogenic aragonite precipitated from seawater at room temperature. Results from these experiments indicate that the aragonite–seawater exchange coefficient for U/Ca ($K_D^{\text{U/Ca}} = (C_U/C_{\text{Ca}})^{\text{Solid}} / (C_U/C_{\text{Ca}})^{\text{Fluid}}$) where C_i^j is

the concentration of j in phase i) decreases with increasing pH and/or precipitation rate. However, the relative importance of these two variables could not be resolved, and the influence of temperature was not evaluated. Gabitov et al. (2008) found that at relatively low pH (7.6–8), the $K_D^{\text{U/Ca}}$ of abiogenic aragonite increases with increasing precipitation rate and temperature. This precipitation rate dependence at low pH is opposite in sign to that found by Meece and Benninger (1993) at higher pH (8.0–8.8). As with the Meece and Benninger (1993) experiments, Gabitov et al. (2008) did not isolate temperature, pH, $[\text{CO}_3^{2-}]$, and precipitation rate, making it difficult to determine conclusively which factors control U partitioning between aragonite and seawater.

Here, we present results from abiogenic aragonite precipitation experiments designed to investigate the relative influence of temperature (T), pH, and $[\text{CO}_3^{2-}]$ on the U/Ca ratio of aragonite precipitated from seawater. We use these results to develop a biomineralization model that provides a framework for interpreting the U/Ca ratio of coral skeleton and its variability.

2. EXPERIMENTAL AND ANALYTICAL METHODS

2.1. Precipitation experiments

The seawater used in our experiments was collected from Vineyard Sound, Massachusetts, passed through a 0.2 μm filter, and stored in the dark. A concentrated seawater solution was prepared by evaporating an aliquot of filtered seawater to half of its initial mass and passing it through a 0.45 μm HAWP filter. The measured concentration of Ca^{2+} in the twice-concentrated seawater was approximately twice that measured in the filtered seawater (Table 1), indicating that CaCO_3 did not precipitate from the concentrated seawater. Solutions containing carbonate alkalinity (hereafter referred to as *Na solutions*) were prepared by dissolving Na_2CO_3 and/or NaHCO_3 powders in deionized water to achieve

Table 1
Summary of elemental concentrations and alkalinity of initial seawater and *Na solutions*.

Solution	[Ca] (mmol kg^{-1})	[Sr] ($\mu\text{mol kg}^{-1}$)	[U] (nmol kg^{-1})	TA ($\mu\text{eq kg}^{-1}$)
Filtered seawater	9.40	75.15	12.4	$2.132 (0.001) \times 10^3$
2X seawater	19.3	160.9	25.2	$4.25 (0.04) \times 10^3$
g13 acidified seawater	19.7	342	12.0	$42.4 (0.1) \times 10^3$
f08 acidified seawater	20.3	352	12.3	$28.3 (0.1) \times 10^3$
Na_2CO_3 batch 1	N.D.	0.30	N.D.	$76.8 (0.2) \times 10^3$
Na_2CO_3 batch 2	N.D.	0.28	N.D.	$79.6 (0.2) \times 10^3$
Na_2CO_3 batch 3	N.D.	0.27	N.D.	$79.8 (0.1) \times 10^3$
NaHCO_3 batch 1	8.8×10^{-3}	0.30	N.D.	$98.4 (0.1) \times 10^3$
NaHCO_3 batch 2	7.3×10^{-3}	0.28	N.D.	$96.8 (0.3) \times 10^3$
NaHCO_3 batch 3	8.1×10^{-3}	0.29	N.D.	$88.7 (0.1) \times 10^3$
NaHCO_3 batch 4	8.0×10^{-3}	0.29	N.D.	$115.4 (0.2) \times 10^3$
1:1 mix batch 1	4.4×10^{-3}	0.28	N.D.	$85.9 (0.5) \times 10^3$
1:1 mix batch 2	3.8×10^{-3}	0.29	N.D.	$88.0 (0.1) \times 10^3$

Notes: Experiments f08 and g13 were conducted by pumping acidified seawater enriched in Sr^{2+} and Ca^{2+} by dissolution of SrCO_3 and CaCO_3 . Not detectable (N.D.) measurements defined as less than 3 times the standard deviation of prediction of concentration from ICP-MS counts for Ca, Sr, and U, which were $2 \times 10^{-3} \text{ mmol kg}^{-1}$, $8 \times 10^{-2} \mu\text{mol kg}^{-1}$, and $2 \times 10^{-3} \text{ nmol kg}^{-1}$, respectively. Numbers in parentheses following TA values indicate $\pm 1\sigma$ of at least triplicate titrations.

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