1 Experimental determination of factors controlling U/Ca of aragonite precipitated from
2 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.

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; 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 tricarboxylate

($\text{UO}_2(\text{CO}_3)_3^{4-}$) (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 ($K_D^{U/Ca} = (C_{solid}^U / C_{solid}^{Ca}) / (C_{fluid}^U / C_{fluid}^{Ca})$ where C_j^i is the concentration of i in phase j) 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 $K_D^{U/Ca}$ 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 approximately 0.04 M Na_2CO_3 , 0.1 M NaHCO_3 , or a 1:1 combination of these two solutions (Table 1). A seawater solution containing elevated Ca and Sr concentrations was prepared by dissolving CaCO_3 and SrCO_3 powders in filtered seawater that had first been acidified by bubbling with CO_2 gas. This modified seawater solution was then passed through a 0.45 μm HAWP filter and divided into two aliquots, one of which (g13 acidified seawater) was spiked with NaHCO_3 (batch 4) to 4 % by volume to elevate the initial TA (Table 1).

Precipitation experiments were conducted at 20 - 40 °C as follows. First, between 400 and 800 g of seawater was added to a 1 L polypropylene container, placed into an isothermal bath, and stirred continuously at 120 or 130 rpm. For the majority of the experiments, the concentrated seawater solution and one of the *Na solutions* were added simultaneously to the filtered seawater at a constant rate using a Kd Scientific syringe pump. The initiation of aragonite precipitation was indicated by a decrease in the pH of the seawater solution (Fig. 1). Once precipitation began, only Na₂CO₃ solution and concentrated seawater were added, regardless of which *Na solution* was initially used. Different combinations of initial pumping rates (between ~0.06 and 10 mL hr⁻¹) and different *Na solutions* (Table 1) added to seawater controlled the pH and [CO₃²⁻] of the seawater solution when precipitation began. In order to maintain stable carbonate chemistry during aragonite precipitation, pumping rates were regularly adjusted so that CO₃²⁻ addition balanced removal by precipitation. Several of the experiments (g10, g11, and h09) were bubbled with a hydrated mixture of air containing 400-5000 ppm CO₂ at 25 mL min⁻¹ in order to stabilize pCO₂ and thus maintain pH in the beaker at levels below that of seawater. Two experiments (g13 and f08) were conducted by pumping Ca- and Sr-enriched seawater solution (Table 1) – rather than concentrated seawater and *Na solution* – and were bubbled with hydrated air at 25 mL min⁻¹ in order to strip CO₂ from the experimental solution. Over the course of each experiment, 8-10 samples of approximately 25 g each were typically collected for analysis of total alkalinity (TA). Each experiment was terminated after addition of approximately 100 g of Na₂CO₃ solution during aragonite precipitation. The final experimental solution was passed through a 0.45 µm HAWP filter and precipitate retained on the filter rinsed with

deionized water and ethanol. Precipitate on the beaker, stir rod, and bubbler was gently removed with a metal spatula. An aliquot of the final solution was analyzed for TA, pH, salinity, and the concentrations of Ca, Sr, and U.

The T of each experiment was continuously monitored (varying within $\pm \sim 0.1$ °C about the reported temperature during each experiment), and the pH of the experimental solution was regularly measured as follows. Approximately 7-8 g of experimental solution were removed and divided into two aliquots; one was used to rinse the electrode and the second to make a pH measurement of the solution while held at 25.5 °C and stirred with a magnetic stir bar. The electrode was calibrated against NBS (now NIST) buffers; this calibration was converted to the total pH scale (pH_T) through comparison of the intercept of the mV-pH regression (*i.e.* a constant offset was applied) to reference seawater provided by the laboratory of Andrew Dickson (batch 116; Scripps Institution of Oceanography).

Total alkalinity of initial seawater, experimental solutions, and *Na solutions* were determined by titrating 1 g of sample (measured to ± 0.0001 g) with 0.01 M HCl, following the technique of Holcomb et al. (2012). Concentration of the acid was calibrated by titrating reference seawater of known alkalinity provided by the laboratory of Andrew Dickson (batch 116; Scripps Institution of Oceanography). Samples were diluted with 0.7 M NaCl solution until TA was less than 6000 $\mu\text{eq kg}^{-1}$ before triplicate titrations, and TA was calculated by a non-linear least squares regression (Holcomb et al., 2012). At each sampling point, the expected solution TA was calculated from all equivalents of alkalinity added (initial seawater, concentrated seawater, and *Na solution*) and removed (sample collection) from the experiment. Alkalinity anomaly was quantified

as the difference between measured and calculated TA. The full carbonate chemistry of the experimental solution was calculated from pH_T (at the T of the experiment) and TA using the program CO2SYS (Lewis et al., 1998), with acidity constants of Mehrbach et al. (1973) refit by Dickson and Millero (1987).

Salinities of stock filtered seawater and final experimental solutions were measured using a Guildline autosal (accuracy ± 0.003 PSU) calibrated with IAPSO standard seawater (batch P-153). The salinity of the initial filtered seawater was 31.785 PSU. There was typically an increase in salinity of 0.5-1 PSU between the beginning and end of each experiment (Table 2), which was attributed to evaporation and/or addition of Na^+ from *Na solutions*. Salinity at solution sampling points was interpolated with respect to time between initial and final salinity measurements.

Prior to analysis, approximately 100 μg of precipitate was suspended in deionized water, centrifuged, and the supernatant removed. This cleaning step was performed in triplicate. A second set of subsamples was processed separately for U/Ca measurements. A duplicate washing of approximately 100 μg sample with 0.75 mL of 0.02 M NaOH solution (Fisher lot 975017) preceded duplicate deionized water washes in order to remove any adsorbed uranyl complexes.

Clean aragonite samples were dissolved in 5 % trace metal grade nitric acid before analysis by inductively coupled plasma mass spectrometry (ICP-MS). Long-term instrument precision (one standard deviation) determined on an in-house coral skeleton external consistency standard was $0.04 \text{ mmol mol}^{-1}$ (0.4 % relative) for Sr/Ca and $0.009 \mu\text{mol mol}^{-1}$ (0.8 % relative) for U/Ca. Counts of ^{48}Ca , ^{88}Sr , and ^{238}U were made in low-resolution on a Thermo-Finnegan Element2 ICP-MS at WHOI with 30 scans per sample

and a 3-minute wash with 5 % nitric acid between samples. Sample counts were corrected for background counts made on 5 % nitric acid blanks, and converted to Sr/Ca and U/Ca ratios by calibration with the *Porites* coral JCp-1 standard (Sr/Ca of 8.838 mmol mol⁻¹ and U/Ca of 1.192 μmol mol⁻¹) (Hathorne et al., 2013). We tested the homogeneity of precipitate subsamples by cleaning and analyzing five different aliquots in duplicate.

Concentrations of Ca, Sr, and U in filtered seawater, *Na solutions*, and the samples of solution collected at the end of each experiment were also determined by ICP-MS. High-Purity Standard simulated seawater (lot # 1221201) was used as the primary standard for seawater and experimental solution analyses, whereas High-Purity Standards single element solutions were used for analysis of *Na solutions*. Samples and standards were spiked with ¹¹⁵In at a concentration of 1.31 ppb as an internal standard. Background concentrations were subtracted based on analysis of a 5 % nitric acid blank. Instrument precision (1 σ) determined from repeated measurements of NASS-5 seawater was 0.06 mmol kg⁻¹ (0.7 % relative) for Ca, 0.3 μmol kg⁻¹ (0.4 % relative) for Sr, and 0.1 nmol kg⁻¹ (0.9 % relative) for U.

The mineralogy of the experimental precipitates was confirmed using Raman spectroscopy and X-ray diffraction (XRD). At least 3 grains per experiment were analyzed using a Raman microscope (Horiba Scientific LabRam HR800) with one 5-second acquisition. A subsample of each precipitate was also analyzed by XRD as follows: precipitates were loaded onto a Si holder on a rotating stage and diffraction patterns collected using a PANalytical Empyrean diffractometer (at the Centre for

Microscopy, Characterisation & Analysis, UWA) using Ni filtered Cu K α radiation (generator at 40 kV, current 40 mA).

Scanning electron microscope (SEM) images and experimental data, including solution pH and TA, aragonite element ratios, fluid element concentrations, sample masses, and solution pumping rates are provided in the supplementary material.

2.2 Determination of element partitioning in open-system experiments

The equilibrium distribution of two elements, such as Sr and Ca, between aragonite and fluid is described by an exchange reaction:

This reaction can be quantified through the use of a semi-empirical exchange coefficient:

$$K_D^{\text{Sr/Ca}} = (C_{\text{Sr}} / C_{\text{Ca}})^{\text{Aragonite}} / (C_{\text{Sr}} / C_{\text{Ca}})^{\text{Fluid}} \quad (2)$$

where C_i is the molar concentration of Sr or Ca in aragonite or fluid. During closed-system precipitation of aragonite at temperatures where diffusion is too slow for the interior of the crystal to maintain equilibrium with the external fluid, exchange coefficients are determined using the Doerner-Hoskin relationship:

$$\log \left(1 + \frac{\text{mol}_{\text{Sr}}^{\text{Aragonite}}}{\text{mol}_{\text{Sr}}^{\text{Fluid}}} \right) = K_D^{\text{Sr/Ca}} \log \left(1 + \frac{\text{mol}_{\text{Ca}}^{\text{Aragonite}}}{\text{mol}_{\text{Ca}}^{\text{Fluid}}} \right) \quad (3)$$

where $\text{mol}_i^{\text{Aragonite}}$ is the total number of moles of Sr or Ca in the bulk precipitate and $\text{mol}_i^{\text{Fluid}}$ is the total number of moles of Sr or Ca in the final fluid (Doerner and Hoskins, 1925). Our experiments represent open-system precipitation of aragonite (*i.e.* the bulk composition was modified by continuous addition of concentrated seawater and *Na* solutions and the removal of fluid samples), so that distribution coefficients could not be determined directly from the final (measured) fluid and solid compositions. Therefore,

aragonite-fluid exchange coefficients were determined through knowledge of element concentrations in the initial and final fluids, the aragonite precipitate, and all system inputs (concentrated seawater; *Na solutions*; Ca, Sr-enriched seawater) and outputs (fluid samples, aragonite precipitation).

Change in the total number of moles of element i in the solution during open-system precipitation is given by:

$$\frac{di_{total}}{dt} = \frac{dm_{ConcSW}}{dt} [i]_{ConcSW} + \frac{dm_{NaSol}}{dt} [i]_{NaSol} - \frac{dm_{Arag}}{dt} \left(K_D^{i/j} \right) \frac{[i]_{fluid}}{[j]_{fluid}} [j]_{Arag} \quad (4)$$

where i_{total} is the total moles of i in solution, t is time, m_k is mass, and $[i]_k$ and $[j]_k$ are the concentrations (mol kg^{-1}) of i (Sr or U) and j (Ca or CO_3^{2-}), respectively. The mass of aragonite precipitated per unit time (g hr^{-1}) is determined from the change in alkalinity anomaly per unit time (difference between measured TA and calculated sum of TA added, where 1 mole of aragonite precipitates per 2 equivalents of TA and where moles of aragonite are converted to mass using the molecular weight of CaCO_3). The inventory of Ca is calculated from the initial measured Ca concentration using alkalinity anomalies, and the concentration of CO_3^{2-} in aragonite is calculated from stoichiometry. Since the initial fluid composition was measured, the concentration of element i in the fluid can be solved numerically at any time t using the measured rates and the concentrations for inputs and precipitate. In practice, solution samples were periodically removed, so Eq. (4) was integrated separately between sampling points using the Runge-Kutta method (Dormand and Prince, 1980). The number of moles of Ca, Sr, and U removed by each sample was calculated as the product of concentration at the time of sampling and the measured mass of the sample. Because CO_3^{2-} is not conservative in seawater, any change

in $[\text{CO}_3^{2-}]$ between sampling points – as determined from pH_T and TA – was assumed to take place at a constant rate so that $[\text{CO}_3^{2-}]$ at any time t could be interpolated between sampling points.

The concentrations of Sr and U in the final fluid and bulk precipitate (aragonite) were used to constrain the $K_D^{\text{Sr/Ca}}$ and $K_D^{\text{U/CO}_3}$ values for each experiment. Forward modeling using initial guesses for $K_D^{\text{Sr/Ca}}$ and $K_D^{\text{U/CO}_3}$ – the only unknown variable in Eq. (4) – resulted in a predicted evolution for Sr and U in the fluid and the concentrations of Sr and U in the bulk aragonite. The calculated Sr and U concentrations in the final fluid and bulk aragonite were compared to the measured values, and a residual was calculated as follows:

$$residual = \left(\frac{i_{predicted} - i_{measured}}{\varepsilon_i} \right)_{solid}^2 + \left(\frac{i_{predicted} - i_{measured}}{\varepsilon_i} \right)_{fluid}^2 \quad (5)$$

where i is the total moles of Sr or U and ε_i is the measurement uncertainty of total Sr or U in the solid or fluid. Final values for $K_D^{\text{Sr/Ca}}$ and $K_D^{\text{U/CO}_3}$ were determined by minimizing Eq. (5) separately for Sr and U using Nelder-Mead unconstrained nonlinear optimization (Lagarias et al., 1998), implemented with MATLAB 2012a.

A Monte Carlo method was used to quantify the uncertainties associated with our estimates of $K_D^{\text{Sr/Ca}}$ and $K_D^{\text{U/CO}_3}$. The determination of $K_D^{\text{Sr/Ca}}$ and $K_D^{\text{U/CO}_3}$ for each experiment was repeated 1000 times, adding random measurement uncertainty (2σ assuming a Gaussian distribution) to the measurements of pH_T , TA, and Sr and U concentrations in the solid and fluid. Uncertainty in estimates of exchange coefficients was taken as the standard deviation of exchange coefficients from all Monte Carlo iterations.

The mean and standard deviation of carbonate system parameters for each experiment were weighted by change in alkalinity anomaly between sampling points:

$$w_k = \left(\frac{AA_k - AA_{k-1}}{AA_n} \right) \quad (6)$$

$$\bar{X} = \sum_{k=1}^n \left[\frac{X_{k-1} + X_k}{2} w_k \right] \quad (7)$$

$$\sigma_X = \sqrt{\frac{\sum_{k=1}^n [(X_k - \bar{X})^2 w_k]}{(n-2) \frac{\sum_{k=1}^n w_k}{n-1}}} \quad (8)$$

where w_k is the weighting coefficient assigned to the k th of n total samples, $k=0$ refers to the fluid prior to precipitation, AA is alkalinity anomaly, X_k is any carbonate system parameter at the k th sample, and σ_X is the sample standard deviation of parameter X . By this definition, weighting of measurements is determined by the change in alkalinity anomaly between sampling points so that the weighting coefficient represents the proportion of the bulk precipitate formed between consecutive measurements. For this reason, the estimated means are representative of only the time during aragonite precipitation, not the entire experiment. The mean of a given parameter is then estimated as the sum of the product of the weighting coefficient and the mean measured value from each consecutive pair of samples. Likewise, the sample standard deviation is estimated with the same weighting coefficients. Mean aragonite precipitation rate per surface area ($\mu\text{mol m}^{-2} \text{hr}^{-1}$) was estimated for each experiment using the mean aragonite saturation state (Ω_{Arag})¹ and T of the experiment and their relationships with aragonite precipitation rate reported by Burton and Walter (1987), where precipitation rate = $k(\Omega_{\text{Arag}} - 1)^n$ and where $k = -0.0177T^2 + 1.47T + 14.9$ and $n = 0.0628T + 0.0985$ (Table 2).

¹ $\Omega_{\text{Arag}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{\text{sp}}$, where K_{sp} is the apparent solubility product of aragonite

3. RESULTS

3.1 Precipitate mineralogy and homogeneity

All Raman spectra taken from experimental precipitates and an aragonite standard contain a double peak in Raman shift between 700 and 708 cm^{-1} characteristic of aragonite (Brahmi et al., 2010), and clearly distinct from the calcite peak at 712 cm^{-1} (Fig. 2). Further, XRD patterns collected on a subsample of each experimental precipitate are consistent with aragonite and show no contaminating phases, except for a small peak near 2θ of 30 for experiment h10 (Figure 2). Since this peak is very weak, only aragonite was found in the Raman spectra, crystal morphology is consistent with the other experiments (SEM images in supplementary), and elemental ratios are consistent with the other experiments (*i.e.* this experiment is not an outlier in $K_D^{\text{Sr/Ca}}$ or $K_D^{\text{U/CO}_3}$), this experiment is likely free of significant contamination.

Mean differences between duplicate subsamples of a given precipitate were 0.59 % and 1.15 % for measured Sr/Ca and U/Ca, respectively. The relative differences between duplicates were less than 2σ instrument precision for both Sr/Ca and U/Ca. Although composition may vary within individual crystals (*i.e.* the composition is zoned), for the purposes of this study where we calculate partitioning relative to the bulk aragonite and fluid compositions, sample heterogeneity was not considered a source of error in the Monte Carlo simulation.

3.2 Temperature dependence of element partitioning

Results from our experiments demonstrate that $K_D^{\text{Sr/Ca}}$ is significantly ($p < 0.05$) inversely correlated with T (Fig. 3), whereas $K_D^{\text{U/CO}_3}$ is independent of T ($p > 0.05$) at 20 to 40 $^{\circ}\text{C}$ after accounting for the effect of $[\text{CO}_3^{2-}]$ as described below in section 3.3 (*i.e.*

in multiple regression where the influences of T and $[\text{CO}_3^{2-}]$ on K_D^{U/CO_3} are evaluated together, there is no significant effect of T). Ordinary least-squares linear regression of mean $K_D^{\text{Sr/Ca}}$ at each T resulted in the following T dependence (numbers in parentheses indicate one standard error uncertainties):

$$K_D^{\text{Sr/Ca}} = -0.0047(0.0003)T + 1.24(0.01) \quad (r^2 = 0.99) \quad (9)$$

where T is in $^{\circ}\text{C}$.

The T dependence of $K_D^{\text{Sr/Ca}}$ determined between 20 and 40 $^{\circ}\text{C}$ is within uncertainty of that determined in three previous experimental studies employing different methodologies (Kinsman and Holland, 1969; Dietzel et al., 2004; Gaetani and Cohen, 2006). This clearly shows that the lack of T dependence for K_D^{U/CO_3} is not an artifact of our experimental design or sampling resolution masking the influence of T on element partitioning. Nevertheless, the $K_D^{\text{Sr/Ca}}$ variability at 25.5 $^{\circ}\text{C}$ (± 0.03 1 σ) is approximately twice as large as expected on the basis of the analytical uncertainties of individual experiments (Table 2), and this variability does not correlate with any of the measured parameters. Similar variability was reported by Dietzel et al. (2004) and Kinsman and Holland (1969) (± 0.02 and ± 0.05 1 σ respectively, determined from replicate experiments). Despite this, the T dependence of $K_D^{\text{Sr/Ca}}$ derived from averaging all experiments conducted at each T appears robust, indicating that $K_D^{\text{Sr/Ca}}$ likely follows a Gaussian distribution at a given T ($K_D^{\text{Sr/Ca}}$ from experiments conducted at 25.5 $^{\circ}\text{C}$ is not significantly different from a normal distribution, Kolmogorov-Smirnov test, $p > 0.05$). Our results also contrast the T dependence of Sr/Ca in abiogenic experiments (-0.039 to -0.044 mmol mol^{-1} Sr/Ca per $^{\circ}\text{C}$) with that of coral (typically -0.05 to -0.1 mmol mol^{-1}

Sr/Ca per °C), which reinforces previous conclusions that factors other than T , such as Rayleigh fractionation (Gaetani and Cohen, 2006), are driving a significant component of the Sr/Ca variability in coral skeletons.

3.3 Carbonate chemistry dependence of element partitioning

The influence of carbonate chemistry on $K_D^{Sr/Ca}$ was investigated using only the experiments conducted at 25.5 °C, whereas all experiments were used to evaluate the carbonate chemistry dependence of K_D^{U/CO_3} because of the lack of any discernible T effect. Mean solution pH and $[CO_3^{2-}]$ are only weakly correlated ($r^2 = 0.28$), whereas there are negligible correlations between $[CO_3^{2-}]$ and both $[HCO_3^-]$ and TA ($r^2 < 0.1$), allowing the influence of these variables on partitioning to be resolved from one another (Table 3). However, a strong correlation between $[CO_3^{2-}]$ and Ω_{Arag} ($r^2 = 0.95$) precludes resolving the influence of these two variables. In seawater, variation in Ω_{Arag} is dominated by variability in $[CO_3^{2-}]$ because of its dependence on biogeochemical processes, whereas $[Ca^{2+}]$ varies by only a few percent in accordance with changes in salinity. Corals change the $[Ca^{2+}]$ of their calcifying fluid by less than 10 % from the seawater concentration but elevate pH to greater than 9 (Al-Horani et al., 2003), implying that $[CO_3^{2-}]$ potentially increases to several times that of seawater. Thus, while future experiments could provide valuable insights regarding the relative importance of $[CO_3^{2-}]$ and Ω_{Arag} on element partitioning, in the context of aragonite precipitated from seawater, or the modified seawater of the coral calcifying fluid, these variables are not independent from one another.

350 There are no significant correlations between $K_D^{Sr/Ca}$ and carbonate system
 351 parameters (pH; $[CO_3^{2-}]$; Ω_{Arag} ; $[HCO_3^-]$; TA; dissolved inorganic carbon (DIC)) or
 352 precipitation rate, whereas K_D^{U/CO_3} is significantly positively correlated with $[CO_3^{2-}]$ ($p <$
 353 0.05), accounting for 83 % of the total variance (Fig. 4). There is also a significant
 354 correlation between K_D^{U/CO_3} and pH, but only 19 % of variance in K_D^{U/CO_3} can be
 355 accounted for in this way. Further, the residuals of K_D^{U/CO_3} regressed against $[CO_3^{2-}]$ are
 356 not significantly correlated with pH (*i.e.* multiple regression yields a significant $[CO_3^{2-}]$
 357 effect but no significant pH effect). Thus, $[CO_3^{2-}]$ is the variable influencing K_D^{U/CO_3} ,
 358 while the apparent pH effect is an artifact of the weak correlation between pH and
 359 $[CO_3^{2-}]$ in our experiments. The dependence of K_D^{U/CO_3} on $[CO_3^{2-}]$ was fit by logarithmic
 360 regression because the residual K_D^{U/CO_3} did not correlate with either $[CO_3^{2-}]$ or K_D^{U/CO_3} :
 361 $K_D^{U/CO_3} = 0.14(0.01)\ln([CO_3^{2-}]) - 0.70(0.09)$ ($r^2 = 0.83$) (10)
 362 where $[CO_3^{2-}]$ is in $\mu\text{mol kg}^{-1}$. The activity ratio $\{UO_2(CO_3)_3^{4-}\}/\{CO_3^{2-}\}$ is strongly
 363 correlated with the concentration ratio $[UO_2(CO_3)_3^{4-}]/[CO_3^{2-}]$ in our experiments ($r^2 =$
 364 0.978), meaning that the general relationship between K_D^{U/CO_3} and $[CO_3^{2-}]$ would not
 365 change if we defined K_D^{U/CO_3} with activity ratios instead of concentration ratios
 366 (supplementary Fig. S1).

367

368 4. DISCUSSION

369 4.1 Partitioning of U between abiogenic aragonite and seawater

370 Our experimental results indicate that $[\text{CO}_3^{2-}]$ has a significant influence on the
 371 partitioning of U between abiogenic aragonite and seawater. As $[\text{CO}_3^{2-}]$ increases from
 372 600 ± 100 to $2560 \pm 80 \text{ } \mu\text{mol kg}^{-1}$ in the experimental seawater, K_D^{U/CO_3} increases from
 373 0.154 ± 0.008 to 0.351 ± 0.009 . Conversely, our results do not indicate a direct link between
 374 K_D^{U/CO_3} and either T or pH. Here we discuss two potential mechanisms for explaining the
 375 dependence of K_D^{U/CO_3} on $[\text{CO}_3^{2-}]$: the kinetics of aragonite growth and the speciation of
 376 UO_2^{2+} in seawater. We then show how our experimental results bear on interpretation of
 377 U/Ca in aragonite.

378 The kinetics of aragonite growth provides one possible explanation for the
 379 influence of $[\text{CO}_3^{2-}]$ on the partitioning of U between aragonite and seawater. Gaetani
 380 and Cohen (2006) showed that the partitioning of Mg, Sr and Ba is consistent with the
 381 surface entrapment mechanism proposed by Watson (2004). At equilibrium, these
 382 elements are enriched in the near-surface region of an aragonite crystal relative to the
 383 lattice (Watson, 2004). As the near-surface region of the crystal is incorporated into the
 384 lattice, its composition must be modified in order to maintain equilibrium. In a slow-
 385 growing crystal, the elemental composition approaches equilibrium as enriched
 386 impurities are removed from the lattice via cation transport in the near surface region of
 387 the crystal. As crystal growth rate increases, the concentration of impurities “buried” as
 388 the near-surface region of the growing crystal advances increases, resulting in a larger
 389 apparent K_D . As noted above, Ω_{Arag} is positively correlated with $[\text{CO}_3^{2-}]$ in our
 390 experiments. Given the well established relationship between Ω_{Arag} and precipitation rate
 391 (Table 2) (Burton and Walter, 1987), the potential exists for a positive correlation

between $[\text{CO}_3^{2-}]$ and crystal growth rate and, thereby, increasing surface entrapment. This mechanism could explain the increase in K_D^{U/CO_3} with increasing $[\text{CO}_3^{2-}]$, and is consistent with the finding of Gabitov et al. (2008) that $K_D^{U/\text{Ca}}$ increases with increasing precipitation rate until reaching a plateau at high precipitate rate. However, given that cation transport is T dependent (Gaetani and Cohen, 2006), a surface entrapment mechanism implies that K_D^{U/CO_3} should be sensitive to both $[\text{CO}_3^{2-}]$ and T . Gabitov et al. (2008) found that $K_D^{U/\text{Ca}}$ increased from 22 °C to 53 °C, but this is potentially an artifact because those experiments did not isolate $[\text{CO}_3^{2-}]$ from T . Further, since aragonite was precipitated from aqueous chloride solutions with $[\text{U}]$ much higher than that of seawater in the experiments of Gabitov et al. (2008), U partitioning in that study may be influenced by different factors than our study, in which aragonite was precipitated from modified seawater. That our experimental results do not indicate any significant T dependence for K_D^{U/CO_3} at 20 to 40 °C makes a surface entrapment mechanism an unlikely explanation for our observations.

A second potential mechanism by which the partitioning of U between aragonite and seawater could be sensitive to $[\text{CO}_3^{2-}]$ derives from the tendency of UO_2^{2+} to form various complexes with CO_3^{2-} in seawater (UO_2CO_3 ; $\text{UO}_2(\text{CO}_3)_2^{2-}$; $\text{UO}_2(\text{CO}_3)_3^{4-}$) as a function of pH (Djogic et al., 1986) and/or $[\text{CO}_3^{2-}]$ (Kitano and Oomori, 1971; Saito and Miyauchi, 1982). The incorporation of UO_2^{2+} into aragonite involves exchange of $\text{UO}_2(\text{CO}_3)_3^{4-}$ — the dominant complex in seawater with pH ~8 (Djogic et al., 1986) — for CO_3^{2-} in the aragonite lattice (Reeder et al., 2000). This combination of factors

suggests that the incorporation of UO_2^{2+} into aragonite could be sensitive to pH and/or $[\text{CO}_3^{2-}]$ because the relative abundance of different uranyl-carbonate complexes varies with carbonate chemistry. A preliminary test of this hypothesis was performed by conducting speciation calculations using the PHREEQC database and software package (Parkhurst and Appelo, 1999) to predict the relative abundances of UO_2^{2+} complexes in our experimental fluids. The modeled abundance of $\text{UO}_2(\text{CO}_3)_3^{4-}$ ($\text{UO}_2^{2+} + 3\text{CO}_3^{2-} = \text{UO}_2(\text{CO}_3)_3^{4-}$; $\log_{10} K = 21.397$ at 25.5 °C) increases with increasing $[\text{CO}_3^{2-}]$ in a manner that is consistent with our experimental results ($r^2 = 0.89$ between $[\text{UO}_2(\text{CO}_3)_3^{4-}]$ and K_D^{U/CO_3}), although the magnitude of change predicted by the PHREEQC model is significantly less than that observed in our experiments (Fig. 5). However, without direct measurements of the speciation of UO_2^{2+} in the experimental solutions, this mechanism cannot be ruled out and remains the most plausible explanation for our data.

The relationship between K_D^{U/CO_3} and $[\text{CO}_3^{2-}]$ determined from our experimental results can be used to predict the sensitivity of aragonite U/Ca to seawater $[\text{CO}_3^{2-}]$. As discussed above, the exchange coefficient K_D^{U/CO_3} increases with increasing $[\text{CO}_3^{2-}]$, which serves to raise the $\text{U}/\text{CO}_3^{2-}$ ratio of aragonite with respect to that of seawater. While U is effectively conservative in seawater, changing only in proportion to salinity (e.g., Owens et al., 2011), $[\text{CO}_3^{2-}]$ is non-conservative and varies in response to changes in TA and/or DIC. Therefore, increasing $[\text{CO}_3^{2-}]$ at constant salinity decreases the $\text{U}/\text{CO}_3^{2-}$ ratio of seawater, resulting in a negative correlation between $\text{U}/\text{CO}_3^{2-}$ and K_D^{U/CO_3} .

(Fig. 6a). The U/Ca ratio of aragonite can be calculated from K_D^{U/CO_3} because it is approximately equal to the U/CO₃²⁻ ratio (*i.e.* Ca²⁺ and CO₃²⁻ are stoichiometrically linked by charge balance in the crystals). This allows the U/Ca ratio of aragonite to be calculated as a function of [CO₃²⁻]. Results from this calculation show that although K_D^{U/CO_3} increases with [CO₃²⁻] (Figure 4), the U/Ca ratio of abiogenic aragonite precipitated from an infinite reservoir of seawater decreases with increasing [CO₃²⁻] (Fig. 6b). In their abiogenic precipitation experiments, Meece and Benninger (1993) expressed U partitioning between aragonite and seawater as $K_D^{U/Ca}$, rather than K_D^{U/CO_3} , and found that the U/Ca ratio of aragonite decreases with increasing pH. Likewise, Kitano and Oomori (1971) precipitated aragonite from magnesium chloride and sodium chloride solutions and found that $K_D^{U/Ca}$ decreases as pH increases. The results of these previous experiments that related U partitioning to increasing pH (and by inference, increasing [CO₃²⁻]) are consistent with our result of an inverse relationship between the U/Ca ratio of aragonite and [CO₃²⁻]. However, our experiments are the first to isolate pH from [CO₃²⁻] to show that it is the latter that influences the U/Ca ratio of aragonite.

4.2 Implications for interpreting U/Ca in coral skeleton

By experimentally precipitating aragonite from seawater under controlled conditions, we show conclusively for the first time that the U/Ca ratio of abiogenic aragonite is strongly tied to [CO₃²⁻] and is independent of pH and *T* between 20 and 40 °C. While these results can be used to interpret U/Ca of coral skeletons, it is important to recognize that coral aragonite is not precipitated directly from an infinite reservoir of

seawater. Rather, there is strong evidence that skeleton is accreted in an isolated or semi-isolated space, and that the carbonate chemistry of the calcifying fluid is manipulated by the coral polyp during the biomineralization process (McConnaughey, 1989a,b; Gaetani and Cohen, 2006; Gagnon et al., 2007; Gaetani et al., 2011; Gagnon et al., 2012).

In corals, seawater is transported to an extracellular calcifying site between the base of the calicoblastic epithelium and the top of the existing skeleton or substrate. Evidence for the transport of seawater comes from tracer studies (Venn et al., 2011; Tambutté et al., 2012) and interpretation of skeletal geochemistry which is consistent with seawater being the initial fluid for aragonite nucleation and growth (Cohen and McConnaughey, 2003; Gaetani and Cohen, 2006; Cohen and Gaetani, 2010; Gagnon et al., 2012). Once in the calcification site, physiological processes modify the carbonate chemistry of seawater to significantly enhance the rate of aragonite precipitation (Cohen and McConnaughey, 2003; Cohen and Holcomb, 2009; Trotter et al., 2011; Venn et al., 2011; Holcomb et al., 2014). Specifically, evidence from crystal microstructure and geochemistry (Cohen et al., 2009; Holcomb et al., 2014), corals cultured with pH-sensitive dye (Venn et al., 2011) and microelectrodes inserted into the calcifying space (Al-Horani et al., 2003) indicates that calcifying fluid pH and Ω_{Arag} are elevated above that of seawater, likely achieved through proton removal from the calcifying fluid (McConnaughey, 1989a,b; Al-Horani et al., 2003; Cohen and McConnaughey, 2003).

Because the carbonate chemistry of the calcifying fluid differs from seawater, the U/Ca ratio of coral skeleton does not directly record seawater $[\text{CO}_3^{2-}]$. This is evident from comparing the dependence of U/Ca on $[\text{CO}_3^{2-}]$ in our abiogenic experiments to U/Ca ratios of shallow-water *Porites* corals, and the cold-water (~2-11 °C) coral

Desmophyllum dianthus (Anagnostou et al., 2011), along with the $[\text{CO}_3^{2-}]$ of the seawater in which these corals lived (Fig. 6b). This simple comparison suggests that both *Porites* and *D. dianthus* calcifying fluid $[\text{CO}_3^{2-}]$ is higher than that of seawater, and for *D. dianthus* its dependence on external seawater $[\text{CO}_3^{2-}]$ is stronger than observed in the abiogenic experiments.

To investigate further the relationship between coral U/Ca and the composition of the calcifying fluid, we developed a steady-state model of a simplified coral biomineralization process in which seawater is constantly replenishing the calcifying space, alkalinity and DIC are constantly added, and aragonite precipitates from the fluid (Fig. 7; Appendix). The model predicts the U/Ca ratio of coral aragonite based on the relative balance between alkalinity addition into the calcifying fluid and the ratio of alkalinity precipitated (removed) to alkalinity added, and using Eq. (10) to describe U partitioning between aragonite and seawater (Fig. 8). Model runs were carried out for different combinations of the amount of alkalinity added and the alkalinity precipitation to addition ratio in order to identify which combinations produced aragonite U/Ca ratios in agreement with the range measured in *Porites* sp. coral skeletons ($\sim 0.9\text{-}1.5 \mu\text{mol mol}^{-1}$) (Wei et al., 2000; Quinn and Sampson, 2002; Felis et al., 2009), while also predicting realistic coral Sr/Ca ratios ($9.68\text{ - }9.90 \text{ mmol mol}^{-1}$).

A subset of the alkalinity addition and the precipitation to alkalinity addition ratio combinations that are consistent with coral U/Ca and Sr/Ca are also consistent with measurements of the coral calcifying fluid pH between 8.5 and 9.3 (Al-Horani et al., 2003; Venn et al., 2011; Holcomb et al., 2014). Further, the steady-state model predicts that 14 - 30 % of C in coral skeleton is derived directly from seawater, consistent with

⁴⁵Ca and ¹⁴C labeling experiments that found between 25 % and 30 % of precipitated C is derived from ambient seawater in the coral *Stylophora pistillata* (Furla et al., 2000). Thus, the steady-state model reconciles the U/Ca ratios measured in coral skeleton with our experimentally determined partitioning for abiogenic aragonite, and agrees with measurements of coral calcifying fluid pH and the relative amount of seawater C incorporated in coral skeleton. According to our biomineralization model, calcifying fluid [U] decreases with respect to seawater as U is incorporated into aragonite during precipitation within the semi-enclosed calcifying space. However, calcifying fluid [CO₃²⁻] is elevated to several times that of seawater, above 700 μmol kg⁻¹ (Fig. 8), by a combination of alkalinity addition and DIC addition into the calcifying space. The model predicts that alkalinity and DIC are elevated, and pCO₂ decreased, relative to seawater, while Ω_{Arag} is elevated to at least 11 (Table 4), consistent with calcifying fluid Ω_{Arag} estimated from the crystal aspect ratio of aragonite coral skeletons (Cohen and Holcomb, 2009). These results show that corals exert control over their calcifying fluid [CO₃²⁻], and therefore strongly influence the U/Ca ratios of their skeleton.

U/Ca of corals has been investigated as a potential proxy for seawater [CO₃²⁻]. Our results imply that the utility of such a proxy will depend on whether corals maintain their calcifying fluid [CO₃²⁻] in proportion to that of seawater. Evidence to date suggests that the pH of the coral calcifying fluid, and likely its [CO₃²⁻], is proportional to that of the external seawater. Using boron isotopes as a pH proxy, McCulloch et al. (2012) showed that coral calcifying fluid pH is positively correlated with seawater pH. Further,

U/Ca ratios of the cold-water coral *D. dianthus* collected across the Atlantic and Pacific basins track differences in seawater $[\text{CO}_3^{2-}]$ (Anagnostou et al., 2011).

Our biomineralization model links coral U/Ca with $[\text{CO}_3^{2-}]$ of the calcifying fluid. Environmental and physiological factors that influence calcifying fluid $[\text{CO}_3^{2-}]$ will thus be reflected in the U/Ca ratio. Within this framework, U/Ca serves as a potentially valuable tool to investigate how changes in climate and/or seawater chemistry influence the coral biomineralization process.

5. CONCLUSIONS

Abiogenic precipitation of aragonite from seawater was carried out under controlled carbonate chemistry conditions in experiments conducted across a range of pH and $[\text{CO}_3^{2-}]$, and at different T . Our experiments confirm that in abiogenic aragonite, Sr/Ca is affected by T , while also demonstrating that it is independent of carbonate chemistry. The T dependence of Sr/Ca in our experiments agrees well with previous studies that were conducted with different methodologies. U/Ca in aragonite depends on $[\text{CO}_3^{2-}]$, and is independent of pH and T . Using the framework of a newly developed biomineralization model, the U/Ca ratio of coral skeleton provides a valuable tool to probe the sensitivity of coral biomineralization, specifically the $[\text{CO}_3^{2-}]$ of the calcifying fluid, to changes in the environment in which the coral lives, such as rising temperatures and increasing seawater CO_2 concentrations.

ACKNOWLEDGMENTS

We thank Rinat Gabitov and two anonymous reviewers for thorough and insightful comments that greatly improved the paper, and we thank Claire Rollion-Bard for editorial handling. We are grateful to Scot Birdwhistell (WHOI) for assistance with ICP-MS analyses, Frieder Klein (WHOI) for assistance with Raman analyses, Louie Kerr and the Central Microscope Facility at the Marine Biological Laboratory for assistance and equipment to collect SEM images, and Dan McCorkle (WHOI) for laboratory equipment to conduct alkalinity titrations. The authors acknowledge the facilities, and the scientific and technical assistance of the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy, Characterisation & Analysis, the University of Western Australia, a facility funded by the University, State and Commonwealth Governments. This work was supported by an NSF Graduate Research Fellowship to T.M.D., NSF grant OCE-1338320 to G.A.G. and A.L.C., and an ARC Super Science Fellowship awarded to M.H.

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729

FIGURES CAPTIONS

Fig. 1. Evolution of solution pH (squares) and $[\text{CO}_3^{2-}]$ (circles) during one experiment (“h01” – see Table 2). Shaded background indicates when aragonite precipitated during the experiment.

Fig. 2. Raman and XRD analysis of experimental precipitates. (a) Raman spectra focused on the peaks around 700 cm^{-1} of aragonite (solid black) and calcite (dashed black) grains, and five example spectra (gray) collected from different experimental precipitates. (b) XRD pattern for aragonite (black) from RRUFF database (ID R060195.1) and a pattern collected on a subset of the precipitate formed in experiment h10 (gray). Raman and XRD data collected on each experimental precipitate clearly indicate the presence of aragonite with no other contaminating phases.

Fig. 3. Temperature dependence of $K_D^{\text{Sr/Ca}}$. Solid line is regression performed with mean $K_D^{\text{Sr/Ca}}$ at each temperature, and shading is 95 % confidence interval. Error bars from this study are standard errors of mean $K_D^{\text{Sr/Ca}}$, and numbers in parentheses indicate the number of experiments, at each temperature. Note that $\pm$ standard error of two samples is equivalent to the range. Error bars on data from Gaetani and Cohen (2006) and Dietzel et al. (2004) are analytical error and standard deviation of replicate measurements, respectively.

Fig. 4. Dependence of K_D^{U/CO_3} on $[CO_3^{2-}]$ of the fluid. Solid line is logarithmic regression performed with all 27 experiments, and shading is 95 % confidence interval. Error bars show 1σ uncertainties. Note that $[CO_3^{2-}]$ is plotted on a logarithmic scale.

Fig. 5. The influence of UO_2^{2+} speciation in seawater on K_D^{U/CO_3} . (a) $[CO_3^{2-}]$ dependence of the concentration of $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$ in seawater with $13.9 \text{ nmol kg}^{-1} \text{ U}$, calculated with the program PHREEQC using the measured pH_T and TA conditions of each experiment. $[UO_2(CO_3)_3^{4-}]$ (squares) increases with increasing $[CO_3^{2-}]$, while the sum $[UO_2(CO_3)_3^{4-} + UO_2(CO_3)_2^{2-}]$ (triangles) remains approximately constant, indicating that the dominant change in speciation across our experiments is a conversion of $UO_2(CO_3)_2^{2-}$ to $UO_2(CO_3)_3^{4-}$ with increasing $[CO_3^{2-}]$. Concentration of all other UO_2^{2+} species calculated as less than $0.003 \text{ nmol kg}^{-1}$. (b) Correlation between measured K_D^{U/CO_3} and calculated concentration of $UO_2(CO_3)_3^{4-}$ for each experiment.

Fig. 6. Dependence of aragonite U/Ca on seawater $[CO_3^{2-}]$. (a) Correlation between the U/CO_3^{2-} ratio of seawater and the experimentally determined K_D^{U/CO_3} , where the U/CO_3^{2-} ratio is calculated from $[U]$ in seawater of salinity 35 ($[U] = 14.7 \text{ nmol kg}^{-1}$) and the $[CO_3^{2-}]$ of each experiment. (b) Predicted $[CO_3^{2-}]$ dependence of the U/Ca ratio of aragonite precipitating from an infinite reservoir of seawater (solid line), calculated as the product of K_D^{U/CO_3} from Eq. (10) and the seawater U/CO_3^{2-} ratio (shading is 95 %

confidence interval). The top abscissa shows how the U/CO_3^{2-} ratio changes with $[CO_3^{2-}]$ in seawater of salinity 35. Circles indicate the predicted aragonite U/Ca ratio from K_D^{U/CO_3} and $[CO_3^{2-}]$ of each experiment. The dashed line shows the observed relationship between seawater $[CO_3^{2-}]$ and U/Ca in the deep-sea coral *D. dianthus* (Anagnostou et al., 2011). The gray box indicates the approximate ranges of U/Ca ratios of shallow-water *Porites* skeletons ($\sim 0.9 - 1.5 \mu\text{mol mol}^{-1}$) and the $[CO_3^{2-}]$ of the seawater in which these corals live ($\sim 150 - 250 \mu\text{mol kg}^{-1}$). Error bars show 1σ uncertainties.

Fig. 7. Schematic diagram of the steady-state biomineralization model. The calcifying fluid is assumed to be in steady-state and is replenished by seawater exchange. Volume of the calcifying fluid is assumed constant, so fluid is removed at the same rate seawater is added. Alkalinity (A_C) and DIC fluxes (F), combined with aragonite precipitation, modify the carbonate chemistry of the calcifying fluid. Reservoirs are in bold and arrows indicate fluxes. U and Sr partitioning are functions of $[CO_3^{2-}]$ and temperature, respectively.

Fig. 8. Results from steady-state biomineralization model. Predicted coral U/Ca ($\mu\text{mol mol}^{-1}$ and indicated by solid black contours) and $[CO_3^{2-}]$ (colors) are functions of alkalinity addition and precipitation. Dashed lines indicate pH contours at 8.5 (right) and 9.3 (left) based on $\delta^{11}\text{B}$ of the skeleton (Holcomb et al. 2014), pH-sensitive dye studies (Venn et al., 2011), and microelectrode measurements of coral calcifying fluid pH (Al-Horani et al., 2003). $[CO_3^{2-}]$ is colored only for combinations of the amount of alkalinity

793 addition and the precipitation to alkalinity addition ratio that are consistent with measured
794 coral U/Ca ($0.9 - 1.5 \mu\text{mol mol}^{-1}$) and calcifying fluid pH (8.5 - 9.3). The primary vertical
795 axis is defined as the amount of alkalinity added during the residence time of a parcel of
796 calcifying fluid, and the horizontal axis is the ratio of precipitation to alkalinity addition
797 in the calcifying fluid. Secondary vertical axis shows percent DIC in coral skeleton
798 derived directly from seawater as a function of alkalinity added.

Table 1

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

Solution	[Ca] (mmol kg ⁻¹)	[Sr] (μmol kg ⁻¹)	[U] (nmol kg ⁻¹)	TA (μeq kg ⁻¹)
Filtered seawater	9.40	75.15	12.4	2.132 (0.001) x10 ³
2X seawater	19.3	160.9	25.2	4.25 (0.04) x10 ³
g13 acidified seawater	19.7	342	12.0	42.4 (0.1) x10 ³
f08 acidified seawater	20.3	352	12.3	28.3 (0.1) x10 ³
Na ₂ CO ₃ batch 1	N.D.	0.30	N.D.	76.8 (0.2) x10 ³
Na ₂ CO ₃ batch 2	N.D.	0.28	N.D.	79.6 (0.2) x10 ³
Na ₂ CO ₃ batch 3	N.D.	0.27	N.D.	79.8 (0.1) x10 ³
NaHCO ₃ batch 1	8.8 x10 ⁻³	0.30	N.D.	98.4 (0.1) x10 ³
NaHCO ₃ batch 2	7.3 x10 ⁻³	0.28	N.D.	96.8 (0.3) x10 ³
NaHCO ₃ batch 3	8.1 x10 ⁻³	0.29	N.D.	88.7 (0.1) x10 ³
NaHCO ₃ batch 4	8.0 x10 ⁻³	0.29	N.D.	115.4 (0.2) x10 ³
1:1 mix batch 1	4.4 x10 ⁻³	0.28	N.D.	85.9 (0.5) x10 ³
1:1 mix batch 2	3.8 x10 ⁻³	0.29	N.D.	88.0 (0.1) x10 ³

Notes: Experiments f08 and g13 were conducted by pumping acidified seawater enriched in Sr²⁺ and Ca²⁺ by dissolution of SrCO₃ and CaCO₃. 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 x10⁻³ mmol kg⁻¹, 8 x10⁻² μmol kg⁻¹, and 2 x10⁻³ nmol kg⁻¹, respectively. Numbers in parentheses following TA values indicate ± 1 σ of at least triplicate titrations.

Table 2

Summary of conditions and calculated $K_D^{Sr/Ca}$ and K_D^{U/CO_3} for each experiment.

Experiment	T (°C)	Final salinity	Precipitation rate ($\mu\text{mol m}^{-2} \text{hr}^{-1}$)	TA ($\mu\text{eq kg}^{-1}$)	pH_T	CO_3^{2-} ($\mu\text{mol kg}^{-1}$)	Ω_{Arag}	$K_D^{Sr/Ca}$	K_D^{U/CO_3}
h02	20.0	32.455	$3.4 (0.6) \times 10^3$	$7 (0.2) \times 10^3$	8.88 (0.01)	$2.06 (0.09) \times 10^3$	29 (4)	1.13 (0.01)	0.33 (0.01)
h08	20.0	32.750	$2.2 (0.6) \times 10^3$	$13.1 (0.9) \times 10^3$	8.20 (0.01)	$1.60 (0.09) \times 10^3$	21 (4)	1.17 (0.01)	0.36 (0.02)
f01	25.5	32.703	$4 (2) \times 10^3$	$5.8 (0.2) \times 10^3$	8.62 (0.02)	$1.31 (0.07) \times 10^3$	16 (4)	1.13 (0.02)	0.33 (0.01)
f02	25.5	32.523	$6 (2) \times 10^3$	$7.4 (0.3) \times 10^3$	8.48 (0.02)	$1.4 (0.1) \times 10^3$	19 (3)	1.14 (0.01)	0.32 (0.01)
f03	25.5	32.342	$13 (3) \times 10^3$	$6.8 (0.2) \times 10^3$	8.96 (0.02)	$2.1 (0.1) \times 10^3$	30 (4)	1.08 (0.01)	0.363 (0.009)
f04	25.5	32.686	$5 (2) \times 10^3$	$11.9 (0.7) \times 10^3$	8.16 (0.01)	$1.38 (0.07) \times 10^3$	19 (3)	1.10 (0.02)	0.32 (0.01)
f05	25.5	32.493	$16 (3) \times 10^3$	$7.8 (0.2) \times 10^3$	9.03 (0.01)	$2.56 (0.08) \times 10^3$	34 (3)	1.06 (0.01)	0.351 (0.009)
f06	25.5	32.764	$2.1 (0.5) \times 10^3$	$5.3 (0.3) \times 10^3$	8.38 (0.01)	$0.86 (0.06) \times 10^3$	11 (1)	1.13 (0.01)	0.25 (0.01)
f08	25.5	32.047	$2 (2) \times 10^3$	$8 (1) \times 10^3$	7.90 (0.07)	$0.6 (0.2) \times 10^3$	12 (4)	1.16 (0.01)	0.174 (0.009)
g01	25.5	32.269	$7 (2) \times 10^3$	$5.8 (0.3) \times 10^3$	8.80 (0.02)	$1.6 (0.1) \times 10^3$	21 (4)	1.13 (0.01)	0.34 (0.01)
g03	25.5	32.438	$5 (1) \times 10^3$	$7.0 (0.3) \times 10^3$	8.43 (0.01)	$1.23 (0.08) \times 10^3$	17 (3)	1.13 (0.01)	0.30 (0.01)
g04	25.5	32.514	$9 (2) \times 10^3$	$9.1 (0.3) \times 10^3$	8.48 (0.01)	$1.72 (0.06) \times 10^3$	25 (3)	1.11 (0.02)	0.36 (0.01)
g05	25.5	32.680	$5 (1) \times 10^3$	$14.7 (0.8) \times 10^3$	8.02 (0.02)	$1.32 (0.07) \times 10^3$	18 (2)	1.12 (0.03)	0.31 (0.01)
g06	25.5	32.541	$5 (2) \times 10^3$	$10.4 (0.6) \times 10^3$	8.24 (0.02)	$1.36 (0.06) \times 10^3$	18 (3)	1.15 (0.02)	0.29 (0.01)
g07	25.5	32.901	$8 (2) \times 10^3$	$20 (2) \times 10^3$	8.00 (0.01)	$1.7 (0.2) \times 10^3$	24 (3)	1.13 (0.01)	0.32 (0.01)
g08	25.5	32.470	$10 (3) \times 10^3$	$10.0 (0.6) \times 10^3$	8.49 (0.02)	$1.9 (0.1) \times 10^3$	26 (4)	1.09 (0.02)	0.35 (0.01)
g09	25.5	33.400	$8 (3) \times 10^3$	$30 (3) \times 10^3$	7.78 (0.02)	$1.7 (0.2) \times 10^3$	23 (5)	1.12 (0.02)	0.38 (0.02)
g10	25.5	32.772	$5 (2) \times 10^3$	$15 (2) \times 10^3$	8.06 (0.04)	$1.5 (0.1) \times 10^3$	18 (3)	1.03 (0.04)	0.29 (0.01)
g11	25.5	33.158	$4 (1) \times 10^3$	$22.9 (0.9) \times 10^3$	7.79 (0.02)	$1.29 (0.07) \times 10^3$	17 (2)	1.13 (0.01)	0.31 (0.01)
g13	25.5	32.250	$1.7 (0.9) \times 10^3$	$8 (1) \times 10^3$	7.89 (0.02)	$0.6 (0.1) \times 10^3$	10 (3)	1.07 (0.02)	0.154 (0.008)
h01	25.5	32.486	$7 (2) \times 10^3$	$5.9 (0.2) \times 10^3$	8.86 (0.01)	$1.69 (0.08) \times 10^3$	21 (4)	1.14 (0.01)	0.34 (0.01)
h09	25.5	33.041	$3 (1) \times 10^3$	$16 (1) \times 10^3$	7.89 (0.03)	$1.1 (0.1) \times 10^3$	14 (3)	1.09 (0.02)	0.26 (0.01)
h10	25.5	33.297	$7 (3) \times 10^3$	$30 (2) \times 10^3$	7.78 (0.03)	$1.6 (0.1) \times 10^3$	21 (4)	1.10 (0.03)	0.35 (0.02)
h03	33.0	32.471	$18 (8) \times 10^3$	$5.2 (0.2) \times 10^3$	8.69 (0.03)	$1.3 (0.1) \times 10^3$	17 (3)	1.07 (0.01)	0.34 (0.01)
h07	33.0	32.501	$13 (3) \times 10^3$	$9.9 (0.5) \times 10^3$	8.13 (0.03)	$1.07 (0.07) \times 10^3$	15 (1)	1.10 (0.01)	0.29 (0.01)
h05	40.0	32.532	$40 (20) \times 10^3$	$4.7 (0.1) \times 10^3$	8.67 (0.01)	$1.10 (0.04) \times 10^3$	15 (2)	1.05 (0.01)	0.31 (0.01)
h06	40.0	32.572	$22 (9) \times 10^3$	$8.0 (0.4) \times 10^3$	8.12 (0.04)	$0.85 (0.06) \times 10^3$	12 (2)	1.04 (0.02)	0.24 (0.01)

Notes: Numbers in parentheses indicate $\pm 1 \sigma$. T , salinity, TA, and pH_T are measured, while CO_3^{2-} , and Ω_{Arag} are calculated with CO2SYS. pH reported on the total scale, calculated as $\text{pH}_{\text{NBS}} - 0.099$. Precipitation rate is calculated based upon results of Burton and Walter (1987) where uncertainty is reported as $\pm 1 \sigma$ by propagating uncertainty from the estimate of mean Ω_{Arag} .

Table 3

Coefficient of determination (r^2) matrix for carbonate system parameters across all experiments (n=27).

	TA	pH _T	HCO ₃ ⁻	CO ₃ ²⁻	Ω_{Arag}
DIC	0.995	0.581	0.996	0.004	0.000
TA		0.513	0.981	0.019	0.007
pH _T			0.638	0.278	0.283
HCO ₃ ⁻				0.000	0.002
CO ₃ ²⁻					0.954

Table 4
Range of coral calcifying fluid carbonate system parameters predicted by
biomineralization model.

	Min	Max
CO_3^{2-} ($\mu\text{mol kg}^{-1}$)	0.7×10^3	4.2×10^3
TA ($\mu\text{eq kg}^{-1}$)	3.2×10^3	10.2×10^3
DIC ($\mu\text{mol kg}^{-1}$)	2.6×10^3	6.1×10^3
$p\text{CO}_2$ (μatm)	24	150
Ω_{Arag}	11	68

Notes: Calculations performed at salinity of 35 and temperature of 25 °C. Minimum and maximum values correspond to the region consistent with calcifying fluid U/Ca and pH (Fig. 8). Ω_{Arag} calculated assuming the Ca^{2+} concentration of the calcifying fluid is elevated above seawater by ~10% to 11 mmol kg^{-1} . (Al-Horani et al., 2003).

Figure 1

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Figure 7

Figure 8