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SIMS OF SYNTHETIC AND BIOLOGICAL CARBONATES

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Nicola Allison is a marine biogeochemist with a multidisciplinary background (BSc Biology, Imperial College; PhD Geology and Geophysics, University of Edinburgh). She studies how organisms mediate the precipitation of calcium carbonate and control its chemistry. She cultures calcifying organisms under conditions analogous to those of past oceans e.g., varying temperatures and seawater pCO_2, and precipitate calcium carbonate minerals under simulated biological conditions e.g., in the presence of biomolecules. She works to deconvolve the impacts of environment and biology on carbonate geochemistry. Secondary ion mass spectrometry has been a fundamental technique in her research. Her research group also studies the impact of rising seawater temperatures and atmospheric CO_2 (ocean acidification) on biomineralisation. This is a key to predicting the future of coral reefs and other economically important calcareous species.

ABSTRACT

The trace element and isotope geochemistry of biocarbonates is a rich source of biological and environmental information. For example, the Sr/Ca of aragonitic coral skeletons and Mg/Ca of calcitic foraminifera tests are influenced by seawater temperatures while the $\delta^{18}O$ of both these carbonate materials reflects seawater temperature and seawater $\delta^{18}O$ composition (an indicator of global ice volume). SIMS has a high spatial resolution (typically ≤ 30 μm beam diameter) and precision e.g. ≤ 0.3 % aragonite Sr/Ca, equivalent to ~0.3 °C on the coral Sr/Ca palaoethermometer and ≤ 0.5 % calcite Mg/Ca, typically equivalent to <0.2 °C on the foraminifera Mg/Ca palaoethermometer. The SIMS spatial resolution permits the analysis of carbonate structures at a high temporal resolution (up to daily increments in coral) and indicates that seawater temperature is not the predominate control on coral skeletal Sr/Ca. The spatial resolution can be further utilised to analyse the small volumes of carbonate deposited during short term coral culturing experiments which employ biochemical inhibitors to identify how biomineralisation processes affect skeletal chemistry. Finally, the SIMS spatial resolution allows the selective analysis of the primary (original biocarbonate minerals) independently of any secondary cements, facilitating the reconstruction of accurate past seawaters temperatures from even diagenetically altered specimens.

1. INTRODUCTION

Calcium carbonate structures are produced by a range of organisms including corals, molluscs, foraminifera, coralline algae and coccolithophores. The chemistry of these structures frequently encodes information on the local environmental conditions e.g., temperature, salinity and nutrient concentration, at the time of their deposition and fossil carbonates can be analysed to estimate past climate/environment. Bio-carbonate chemistry can also yield information on how organisms mediate the precipitation of calcium carbonate and gives insight into the response of calcifying organisms to present and future climate change e.g. rising temperatures and ocean acidification. Secondary ion mass spectrometry (SIMS) analysis has been instrumental in the development of coral, mollusc and foraminifera palaeoproxies. SIMS has a high spatial resolution (Fig. 1) permitting the analysis of samples at a high temporal resolution, the selective analysis of pristine primary carbonate in diagenetically altered samples and the analysis of small volumes of material deposited during culturing experiments. Here I consider some of the challenges inherent in SIMS analysis of carbonate materials and I present 2 case studies of applications.

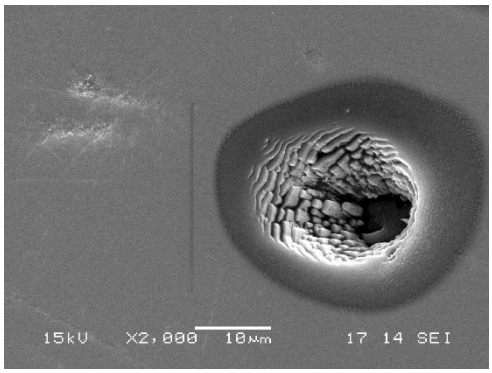

Figure 1. SIMS pit in a polished thin section of coral skeleton. The main SIMS pit has a maximum depth of 20 µm and a diameter of ~20 µm although some sputtering occurs across a larger area, generating a dark halo around the main pit.

2. CARBONATE STANDARDS AND THE PRECISION OF SIMS ANALYSES

Ideal standards should be matrix-matched i.e., carbonates, and chemically similar to the samples. However it is not possible to produce fused carbonate standards and natural carbonate materials are usually geochemically heterogeneous, either within or between crystals (Table 1). Heterogeneity between crystals compromises the accuracy of SIMS as the chemistry of grains determined by wet chemistry methods is likely different from that of the grains retained for SIMS. Heterogeneity within crystals can limit the identification of instrumental drift, both within and between SIMS sessions (Table 1). Haxby grain 1 is relatively homogenous with respect to Sr/Ca and is currently used for SIMS calibration.

Table 1. Sr/Ca of carbonate standards analysed by SIMS. Replicate SIMS analysis of each standard indicates that analytical precision (1σ) varies from 0.3 - 10 %.

Carbonate Standard	Approximate Sr/Ca (mmol mol^{-1})	Standard deviation of repeat Sr/Ca SIMS analyses (mmol mol^{-1})	Coefficient of variation (%)
NCC	1.18	0.118	10
Haxby grain 1	2.86	0.00858	0.3
Haxby grain 2	2.97	0.0299	1.0
M93	9.50	0.285	3.0
OKA carbonatite	13.6	0.135	1.0

3. BIOLOGICAL CONTROLS ON CORAL Sr/Ca CHEMISTRY

The Sr/Ca of aragonite inorganically precipitated from seawater exhibits a temperature dependence (~0.04 mmol mol^{-1} $°C^{-1}$ [1]) and coral skeleton Sr/Ca has become a commonly used palaeothermometer, used to infer seasonal sea surface temperatures (SST), glacial-interglacial temperature changes [2] and the amplitude and frequency of interdecadal climate events [3]. Such high resolution palaeoproxy data are critical for understanding global palaeoclimate and in testing and validating global climate models for predicting 21st century climate change. However coral Sr/Ca-SST sensitivity is greater than that observed in inorganically precipitated aragonites (ranging from 0.05 to 0.08 mmol mol^{-1} $°C^{-1}$ [4]) and varies significantly between localities. Significant variations in skeletal Sr/Ca can also occur between different coral colonies from the same reef site, equating to errors in reconstructed SST of up to ~3 ºC [5].

The high spatial resolution of SIMS permits the analysis of skeletons at a high temporal resolution (up to ~daily, Fig. 2) and the precision of analyses (≤ 0.3 %) enables identification of Sr/Ca changes equivalent to ~0.3 °C on the coral Sr/Ca-SST palaeothermometer. The Sr/Ca chemistry of massive *Porites* spp. coral skeletons, typically used for palaeoenvironmental reconstruction, is dominated by large variations (≥ 1 mmol mol^{-1}; Fig. 3) deposited over short periods (days-weeks). Such variations are nominally equivalent to SST changes of ≥ 12 °C but do not reflect seawater temperatures. This indicates that the predominant control on coral skeletal Sr/Ca is not temperature.

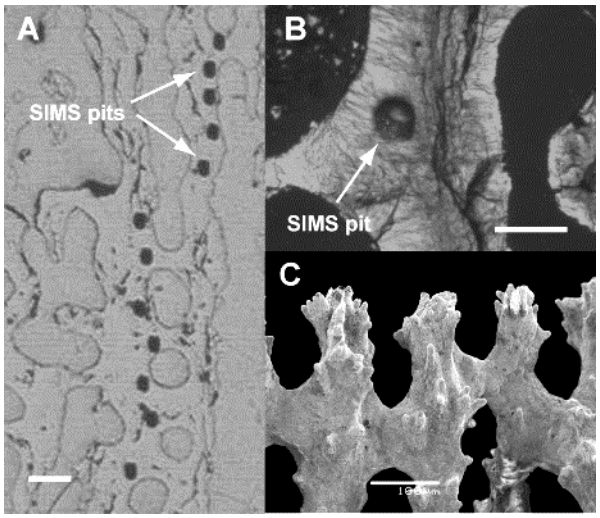

Figure 2. a) and b) reflected and transmitted light micrographs of a coral thin section after SIMS analysis, and c) scanning electron micrograph of the growing skeletal surface. In all images the skeleton growth direction is up the page and the SIMS pits in a) form a time series. Scale bars are 100, 50 and 100 µm, respectively. From Allison *et al.* [6].

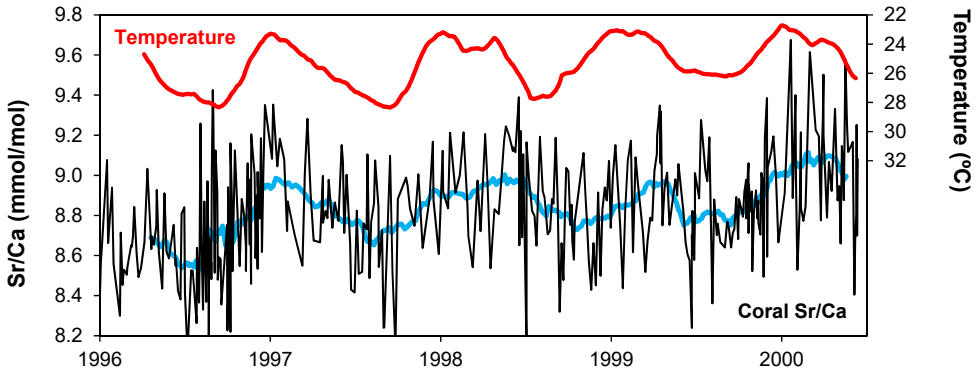

Figure 3. SIMS record of skeletal Sr/Ca (black line) across a *Porites lobata* coral from Oahu, Hawaii (after Allison and Finch [7]). The record is 48 mm long and analyses are spaced ~120 µm apart, equating to 3 - 4 days of skeletal accretion. The record is dominated by large Sr/Ca variations deposited over periods of days-weeks which do not correlate with sea surface temperatures (red line). Averaging the SIMS record at ~2 monthly resolution yields a trend (in blue) in broad agreement with the temperature record.

The coral skeleton is formed from a fluid enclosed in a semi-isolated space (the calcification site) between the base of the coral tissue and the underlying skeleton. The fluid appears to be seawater based but its exact composition is affected by the pathways and rates of solute transport to the calcification site. Ca^{2+} is transported across the coral tissues to the calcification site by the enzyme Ca-ATPase and by Ca channels (pore- forming membrane proteins which allow the passage of selective ions). To investigate the impact of transcellular Ca transport processes on skeletal Sr/Ca, a suite of *Pocillopora damicornis* corals were cultured in the presence of inhibitors of Ca-ATPase (ruthenium red) and Ca channels (verapamil hydrochloride). During the treatments the corals extended their skeletons by ~100 µm or less. The skeleton deposited in the presence of the inhibitors was identified (by ^{42}Ca spike) and analysed for Sr/Ca by SIMS (Fig. 4). The Sr/Ca of the aragonite deposited in the presence of either of the inhibitors was not significantly different from that of the solvent (dimethyl sulfoxide, DMSO) control. Sr^{2+} has a similar ionic radius to Ca^{2+} and either Ca-ATPase and Ca channels transport Sr^{2+} and Ca^{2+} in virtually the same ratio in which they are present in seawater or transcellular processes contribute little Ca^{2+} to the skeleton and most Ca is derived from seawater transported directly to the calcification site. Variations in the activities of these Ca transport processes are not responsible for the short-term (days-weeks) Sr/Ca oscillations observed in skeletal chronologies. The origin of these is currently unresolved.

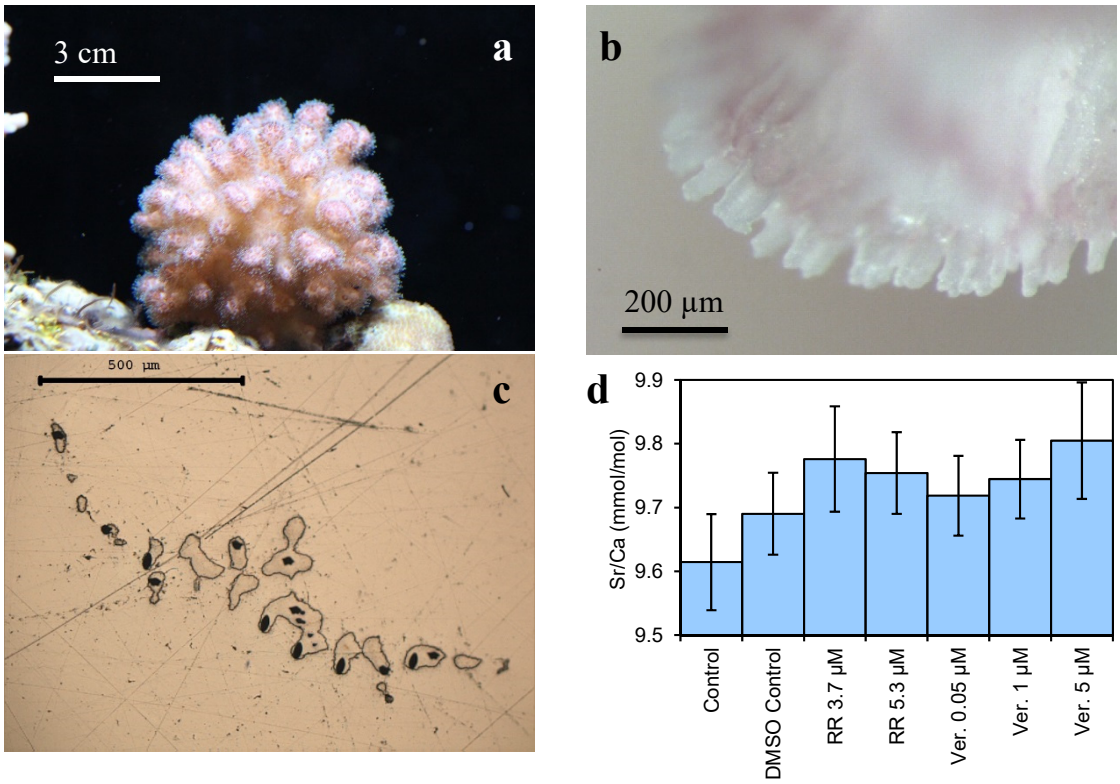

Figure 4. a) Small *Pocillopora damicornis* coral colony. b) Tip of one skeletal branch after tissue removal. The branch was incubated in Alizarin red S dye for several hours 4 days before sacrifice and the skeleton deposited after the stain line represents carbonate accreted during the experiment. c) Polished block of branch tip after SIMS analysis. Skeletal tips appear as islands surrounded by epoxy resin. SIMS pits appear as dark ovals ~30x20 µm. d) Sr/Ca of coral skeletons cultured for 4 days in the seawater control, the DMSO (solvent) control and in multiple concentrations of ruthenium red (RR, the Ca-ATPase inhibitor) and verapamil hydrochloride (Ver., the Ca channel blocker) from Allison *et al.* [8]. Bars indicate means and error bars indicate 95% confidence limits.

4. DIAGENETIC INFLUENCES ON CORAL SKELETAL Sr/Ca

Fossil corals can be preserved in both uplifted and drowned reef terraces and may undergo post depositional diagenesis during which parts of the original coral skeleton (the primary aragonite) dissolve and secondary minerals (e.g., aragonite and low- and high-Mg calcite, depending on the diagenetic environment) are deposited. Secondary minerals, even aragonites, have significantly different geochemistry compared to the primary coral aragonite (e.g., [9, 10]) and their inclusion in drilled (bulk) coral samples may lead to erroneous estimates of past climate. SIMS can be used for the selective analysis of primary aragonites in altered coral samples.

For example, petrographic examination of a 130 ky fossil coral (Fig. 5), which is 100 % aragonite (by XRD) and appears pristine in hand specimen, indicates subtle alteration compared to a modern analogue. Coral skeletons are comprised of two key features: centres of calcification (COCs),

composed of granular submicron crystals, and fasciculi, composed of bundles of larger acicular crystals which radiate out from the COCs and make up the bulk of the coral skeleton. In unaltered corals, COCs appear as fine dark lines with diameters of 5 - 10 mm (Fig. 5a). In the fossil coral some COCs have dissolved, leaving voids in the section (Fig. 5b) but most appear opaque with diameters of up to 20 mm (Figs. 5b and 5d), indicating some alteration. The opacity may reflect minute intercrystalline pores which provide significant scattering of light. Growth lines, which may record successive positions of the basal coral tissue that secretes the skeleton, are visible in both corals, suggesting the fasciculi are unaltered (e.g., Fig. 5d).

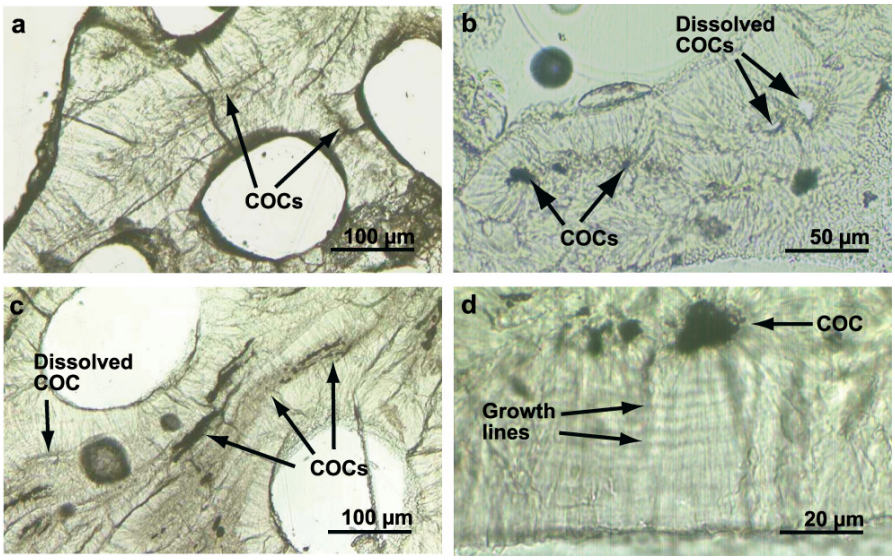

Figure 5. Transmitted light micrographs of a) a modern and b-d) a 130 ky fossil coral specimen from Papua New Guinea. Coral skeletons are composed of two key features: centres of calcification (COCs), composed of granular submicron crystals, and fasciculi, composed of bundles of larger acicular crystals and make up the bulk of the coral skeleton. In the fossil specimen some centres of calcification (COCS) have dissolved, leaving voids in the section (b) but most appear opaque with enlarged diameters (b - d), indicating some alteration. Growth lines, which may record successive positions of the secretory coral tissue, are visible in both corals, suggesting the fasciculi are unaltered. From Allison *et al.* [11].

The 2 skeletal structures (fasciculi and COCs) were analysed by SIMS in both corals (Fig. 6). In the modern coral the Sr/Ca of the COCS is slightly higher (4 %) than that of the fasciculi, in line with observations of other modern corals [7]. In contrast, Sr/Ca is 14 % higher in the COCs of the fossil coral compared to the fasciculi. The original COCs in the fossil coral may have been replaced by secondary aragonite cements which are typically higher in Sr/Ca than coral aragonite [7]. Bulk Sr/Ca analyses of drilled samples, combining both fasciculi and COCs, suggest that the fossil coral grew in seawater temperatures 6 °C cooler than the present day (Fig. 6). Comparison of the Sr/Ca of the unaltered fasciculi of both corals suggests that the temperature difference is only 1 °C. The

fossil coral lived in the mid to late stages of SST warming during the penultimate deglaciation and this 1 °C temperature difference is reasonably consistent with the total glacial-interglacial temperature change of 3 °C inferred from other palaeoproxies in this region (Lea et al., 2000).

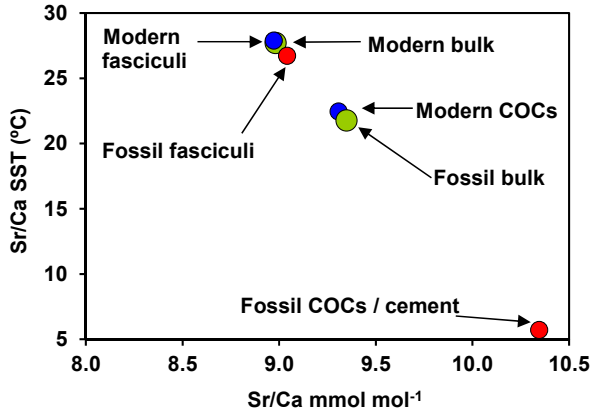

Figure 6. Mean Sr/Ca records and reconstructed SSTs from both the modern and fossil corals depicted in Fig. 5. Bulk Sr/Ca, combining fasciculi and COCs, was determined on drilled samples by TIMS (green) while SIMS was used to analyse the fasciculi and COCs of the modern (blue) and the fossil (red) corals separately.

5. *CONCLUSIONS*

SIMS has been a core technique in the development of carbonate palaeoproxies. The high spatial resolution of the techniques allows detailed investigation of the likely controls on trace elements and isotopes. The high spatial resolution of SIMS also permits the analysis of pristine areas which encode the original climate signal in diagenetically altered carbonate specimens.

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