

CaCO₃ diagenesis and palaeoproxy relationships in marine biominerals

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Overview: Marine fossil carbonates are invaluable archives of past climate information, recording information on seawater composition, temperature and pH in their geochemistry. As examples, the Sr/Ca of aragonite coral skeletons and Mg/Ca of calcite foraminifera tests are influenced by seawater temperatures while the $\delta^{18}\text{O}$ of both carbonate materials reflects seawater temperature and $\delta^{18}\text{O}$ composition (an indicator of global ice volume).

During post-depositional diagenesis parts of the original primary carbonate dissolve (Figure 1) and secondary minerals can be deposited. Diagenesis affects carbonate geochemistry when elements/isotopes are heterogeneously distributed within the primary carbonate and preferential dissolution of specific structures therefore alters the palaeoproxy signature. Secondary cements can contaminate the primary mineral (Allison et al., 2007) or geochemical re-equilibration can occur (Bernhard et al., 2017). Dissolution of calcium carbonate is a function of the seawater CaCO₃ saturation state (itself a function of the concentrations of calcium and carbonate in seawater and the solubility product of the calcium carbonate phase at the relevant temperature, salinity and pressure). However calcium carbonate biominerals are composites in which the mineral phases are intimately associated with soluble and insoluble organic materials including proteins, polysaccharides and lipids (Falini et al., 2015). The biomolecule composition of coral skeletons varies significantly between specimens cultured at different seawater pCO₂ (Figure 2). These biomolecules are implicated in the mediation of precipitation and can inhibit calcium carbonate dissolution (Naviaux et al., 2019).

This project will explore how biomolecules influence carbonate diagenesis and thereby alter palaeoproxy estimates of past seawater temperatures. Accurate estimates of past temperatures are essential in shaping our understanding of past climate and are critical in validating global climate models for predicting 21st century climate change.

Figure 1. SEM micrographs of modern (left) and fossil (right) *Porites* spp. coral skeletons. The skeletons are perforate and composed of interconnecting skeletal units with diameters of 100-200 μm . In the fossil specimen the centres of the skeletal units (termed the centres of calcification) have dissolved leaving voids in the skeleton. Centres of calcification are enriched in Sr/Ca compared to the remaining aragonite and their selective dissolution decreases the bulk Sr/Ca of the skeleton and offsets Sr/Ca seawater temperature estimates to higher values.

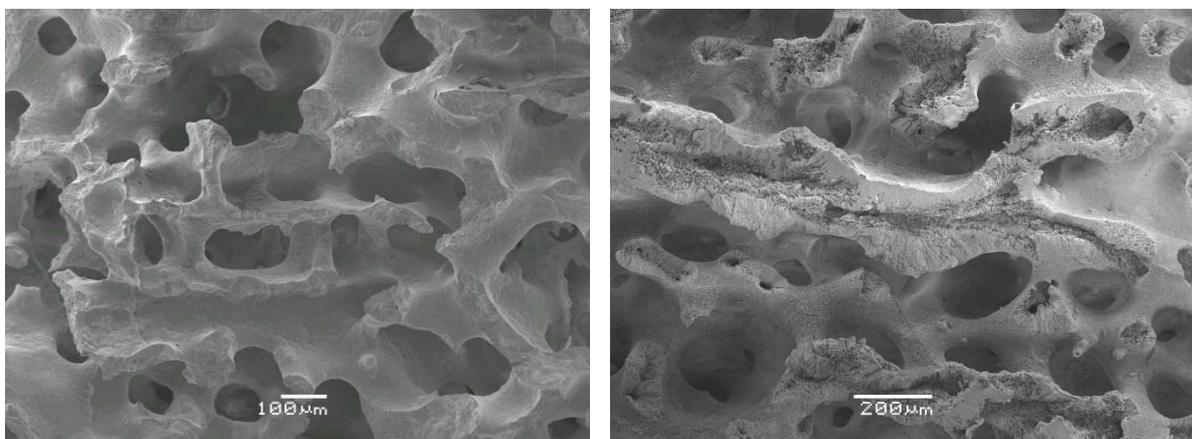
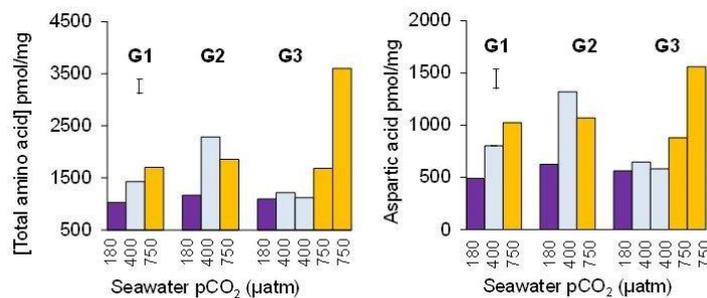


Figure 2. Skeletal total amino acid concentrations (left) and aspartic acid (right) of three coral genotypes (G1, G2 and G3) cultured at 25°C and over a range of seawater pCO₂. Two replicate colonies of G3 were cultured at 400 and 750 μatm. Error bars indicate the mean standard deviation of analyses of duplicate drilled samples. Both total amino acid and aspartic acid concentrations vary significantly between corals and treatments.



Methodology: The methodology is divided into 3 parts.

1. The student will produce and characterise a suite of natural and synthetic biominerals with varying biomolecule compositions for further study. The student will select natural coral aragonites and foraminifera calcites from our existing collection. The modern corals span a wide range of depositional temperatures (18-30°C), skeletal growth rates and are sampled from a wide geography of the tropics and sub-tropics. The concentration and composition of skeletal organic materials varies significantly between specimens (Figure 2). The student will also produce synthetic aragonites and calcites at the University of St. Andrews using a pH stat titrator adapted to precipitate calcium carbonates with tightly controlled chemistries. They will precipitate calcium carbonates in the presence/absence of a range of organic materials in order to later identify the roles of individual biomolecules in diagenesis and re-precipitation.
2. The student will artificially diagenetically alter both field and synthetic calcium carbonates to identify how the biomolecules influence calcium carbonate dissolution and re-precipitation. Selected materials will be exposed to increased temperature and pressure to induce artificial dissolution in an autoclave engineers hydrothermal reactor and will be used as a substrate for re-precipitation from natural seawater. The student will calculate the rates of dissolution/re-precipitation and compare the morphologies of altered carbonates to determine if biomolecules inhibit or accelerate dissolution/re-precipitation and to identify potential action pathways for this response. The student will characterise the calcium carbonates before and after diagenesis using SEM and thin section observations (to observe crystal structure), BET (to determine surface area) and Raman spectroscopy (to investigate chemical structure).
3. The student will determine how diagenesis affects palaeoproxy signatures. They will analyse the geochemistry of the natural and synthetic biominerals before and after artificial diagenesis. The student will analyse Sr, Mg and δ¹⁸O as the key aragonite and calcite palaeothermometer proxies however analysis of other proxies of interest is also possible.

Training and skills: The student will develop a series of skills in the preparation, characterisation and analysis of biogenic and synthetic carbonates. Analytical methods include Brunauer-Emmett-Teller (BET) technique, XRD, SEM, Raman spectroscopy, confocal microscopy, ICP-MS and IR-MS. The student will also develop an understanding of the seawater carbonate system and controls on carbonate dissolution and precipitation. The student will receive full training in all required techniques. We will consider applicants from a range of environmental, marine and geological backgrounds. The student will present results at national & international workshops and conferences and will be assisted in preparing scientific manuscripts to be published in international peer-reviewed journals. The student will join a NERC-funded team studying biomineralisation in the School of Earth and Environmental

Sciences at the University of St Andrews and will be a member of the Marine Alliance for Science and Technology for Scotland (www.masts.ac.uk) with access to wider training and networking opportunities. All project supervisors are highly research-active and the student will have opportunities to learn other techniques and research areas which may be applicable to their interests.

Applications: General information about eligibility, studying at the University of St Andrews, and the online application form can be found at <http://www.st-andrews.ac.uk/study/pg/apply/>. This project is eligible for funding from [NERC IAPETUS 2](#). Contact Nicola Allison for further enquires (na9@st-andrews.ac.uk).

References:

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