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The skeletal geochemistry of the sclerosponge *Astrosclera willeyana*: Implications for biomineralisation processes and palaeoenvironmental reconstruction

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ABSTRACT

To investigate the controls on the geochemistry of aragonitic sclerosponge skeletons, we used secondary ion mass spectrometry (SIMS) to analyse an *Astrosclera willeyana* specimen. The high spatial resolution of SIMS allows the independent analysis of the two key crystal structures in the skeleton i.e. the fused spherulites (formed intracellularly and fused together at the surface of the skeleton) and the epitaxial backfill (deposited extracellularly at the base of the sponge tissue). We analysed Sr/Ca, Mg/Ca and Ba/Ca across a short (~5 mm) transect of fused spherulites which represented several years growth. We observe cyclical variations (with a length of 0.1 to 0.6 mm in both Sr/Ca and Mg/Ca in some (but not all) sections of the transect. The observed ranges of Sr/Ca and Mg/Ca over the presumed seasonal cycles are ~9.5 to 11.5 mmol mol^{-1} and 0.6 to 1.0 mmol mol^{-1} respectively. The annual seawater temperature range at the study site is ~4.3 °C, so the inferred temperature sensitivity of skeletal Sr/Ca and Mg/Ca is ~0.5 mmol mol^{-1} °C (or 5%°C^{-1}) and ~0.1 mmol mol^{-1}°C (or 13%°C^{-1}) respectively. This is higher than observed in most previous sclerosponge studies or anticipated from studies of synthetic aragonite. This indicates that the chemistry of the *A. willeyana* skeleton is affected by one or more additional influences, besides temperature, which are currently unresolved. The pH of the precipitating fluid, estimated from skeletal $\delta^{11}B$, is ~8.1–8.2 for both fused spherulites and epitaxial backfill. Epitaxial backfill contains significantly higher Sr/Ca, Mg/Ca and B/Ca and significantly lower Ba/Ca than the fused spherulites but Sr/Ca and Mg/Ca are positively correlated by the same relationship in both skeletal features. This suggests that the geochemistry of each feature is predominantly controlled by a common process. This is unlikely to be Rayleigh fractionation, which is indicated by negative correlations between Sr and Mg in aragonite.

1. Introduction

The isotope and trace element chemistry of marine calcite and aragonite skeletons is used frequently to infer past environmental conditions. Sclerosponges are long-lived and their skeletons may provide archives of environmental conditions over periods of 100–1000 years. The Sr/Ca of synthetically precipitated aragonite is temperature dependent (e.g. Kinsman and Holland, 1969) and sclerosponge skeletal Sr/Ca may indicate seawater temperatures (e.g. Haase-Schramm et al., 2003). Seasonal variations in skeletal Sr/Ca and seawater temperature correlate well ($r^2 = 0.67$) in a specimen of the Caribbean sclerosponge, *Ceratoporella nicholsoni*, (Rosenheim et al., 2004) but less well ($r = \sim 0.5$) in specimens of the Indo-Pacific species, *Astrosclera willeyana* (Fallon et al., 2005).

Accurate calibration of the relationship between skeletal Sr/Ca and seawater temperature is complicated by the growth habit of sclerosponges. The sponge tissue occupies calicles in the outermost 0.5–1 mm of the skeleton in *C. nicholsoni* (Swart et al., 2002; Rosenheim et al., 2009) and ~5 mm in *A. willeyana* (Fallon et al., 2005). Skeletal deposition occurs both at the skeleton surface and towards the base of the calicle. Annual linear extension rates are 0.1–0.4 mm yr^{-1} for *C. nicholsoni* (Böhm et al., 1996, 2002; Swart et al., 2002) and 0.2–1.8 mm yr^{-1} for *A. willeyana* (Worheide 1998; Moore et al., 2000; Fallon and Guilderson 2005; Fallon et al., 2005; Grottoli et al., 2010). Consequently aragonite deposited at the base of the tissue layer serves to thicken and infill structures which may have been deposited up to several years previously and drilled or milled sampling horizons, cut parallel to the sponge surface, combine mixtures of materials of significantly different ages. In *C. nicholsoni* backfill is precipitated in the bottom quarter of the tissue layer and backfilled skeleton may consist of ~20% older calicle wall material, originally deposited at the skeleton surface, and ~80% younger backfill (Böhm et al., 1996). In contrast, in *A. willeyana*, skeletal density increases gradually over most of the depth of the tissue layer suggesting that backfilled skeleton represents material which has been deposited and thickened almost continuously (Fallon et al., 2005). Variations in the timing and relative placement of skeletal accretion may explain the different success of each species in recording seasonal seawater temperatures.

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The aragonite deposited at the skeleton surface consists of intracellularly formed spherulites which are fused by epitaxial growth while the aragonite deposited at the base of the tissue layer consists of epitaxial backfill which precipitates extracellularly. In *A. willeyana* the spherulites form within vacuoles inside mobile large vesicle cells in the ectosome, the upper tissue layer of the sponge (Worheide 1998). As the membrane of the large vesicle cell lyses (breaks down), the spherulite is released and subsequently enveloped by one or more basopinacocyte cells which have invaded the sponge tissue. The basopinacocytes transport the spherulites to the skeleton where they are attached to the vertically growing skeletal pillars. These spherulites are then fused by epitaxial processes. Epitaxial backfill is deposited at the base of the tissue layer as the sponge tissue is slowly drawn upwards, vacating the skeletal pore spaces. Any variation in Sr/Ca partitioning between the fused spherulites and the epitaxial backfill will complicate the Sr/Ca–seawater temperature relationship preserved in the skeleton.

To further investigate controls on the geochemistry of *A. willeyana* skeletons, we used secondary ion mass spectrometry (SIMS) to analyse a single skeleton at a high spatial resolution. We used a primary beam diameter of 15–35 μm allowing us to characterise the geochemistry of the different skeletal features i.e. the fused spherulites and epitaxial backfill. We analysed a transect, along the fused spherulites, perpendicular to the skeleton surface, to investigate if these features record any seasonal environmental signal. We determined Sr/Ca, Mg/Ca, Ba/Ca and B/Ca. All of these elements may have some potential as palaeoenvironmental indicators in biogenic aragonites (Shen and Sanford, 1990, Beck et al., 1992, Mitsuguchi et al., 1996, Fallon et al. 1999). In addition, correlations between trace and minor elements have been used to infer controls in biogenic carbonate chemistry e.g. inverse correlations between Sr and Mg in deep sea corals may indicate Rayleigh fractionation (Gagnon et al., 2007) while trace element incorporation may be correlated with crystal growth rate in synthetic aragonites (e.g. Gabitov et al., 2008). We also made a preliminary suite of $\delta^{11}B$ analyses on this skeleton. The $\delta^{11}B$ of experimentally precipitated calcite and cultured foraminifera reflects the pH of local seawater (Sanyal et al., 1996, 2000) and the analysis of $\delta^{11}B$ in fossil foraminifera has been used to estimate past seawater pH (Sanyal et al., 1995). We estimate the likely pH of the fluids present during deposition of fused spherulites and epitaxial backfill.

2. Methods and materials

2.1. Sample preparation

We analysed an *A. willeyana* sponge (our reference NOM-1) collected from Nomuka Ika (174º49' W; 20º16′S), Tonga in November 2004. The specimen was found at a water depth of 9.5 m on the roof of a cave, under an overhang, on a modern coral reef framework. The sponge was collected from ~3.5 m into the cave. This cave had one large entrance (under the overhang) and several smaller conduits (from the back and sides of the cave) ensuring that is was well flushed with local sea water. The SST at the study site has an annual mean of 25.8 °C with a range of 4.3 °C, from ~24 °C (in August) to ~28 °C (in February/March) and we assume that this is reflective of water temperatures in the cave.

The sclerosponge was approximately hemi-spherical (with dimensions 34×20 mm) and was living when collected. After collection, the specimen was air-dried and returned to the UK for analysis. The sponge was sectioned along the axis of maximum vertical growth. One half of the sponge skeleton was divided into two and one of the resulting quarters was embedded in epoxy resin, mounted onto a 2.5 cm diameter glass slide and ground to a thickness of ~50 μm (Fig. 1) using silicon carbide papers and 0.3 μm polishing alumina lubricated with water.

2.2. SIMS

All analyses were made using a Cameca ims-4f ion microprobe in the School of GeoSciences at the University of Edinburgh. The section was gold coated and analysed with a $^{16}O^-$ beam, accelerated at 15 kV. Trace and minor element ratios were determined using 2 sets of instrument conditions. Instrument conditions, isotopes studied and typical count rates are summarised in Table 1. Annual cycles in trace/minor element composition were not obvious in preliminary analyses made using trace element conditions 1. Consequently the instrument conditions were adjusted, resulting in a smaller primary beam diameter and a higher analytical spatial resolution (trace element conditions 2). We estimate no significant isobaric interference for any of the isotopes studied (Allison 1996; Allison et al., 2007). Background counts were determined at mass 4.7 and were insignificant (<0.1 cps).

Trace element data were collected over two days and relative ion yields (RIY) for Mg/Ca, Sr/Ca and Ba/Ca were calculated from multiple analyses on the carbonate standard, OKA carbonatite (Mg/Ca = ~2.75 mmol mol^{-1}; Sr/Ca = ~13.66 mmol mol^{-1}; Ba/Ca = ~0.95 μmol mol^{-1}, see Allison et al., 2007). Instrument drift was insignificant over the 2 days. The accuracy of our SIMS estimates is affected by uncertainty in the composition of the standard (e.g. reflecting variations in the different OKA crystals used for SIMS and characterised by bulk analytical methods) and by potential matrix effects resulting from chemical and physical differences between the standard and samples, i.e. calcite and aragonite. To reduce this uncertainty, we have compared estimates of Mg/Ca, Sr/Ca and Ba/Ca along adjacent coral transects by SIMS and by bulk methods of analysis and calculated standardisation factors to apply to SIMS data (Allison et al., 2007). We have normalised all the SIMS data presented here using these factors. A relative ion yield for B/Ca was calculated from multiple analyses on the fasciculi of a *Porites* coral standard (M93-TB-FC-1, B/Ca = 0.36 mmol mol^{-1}, Kasemann et al., 2009).

Internal reproducibility (the precision at a single point) was calculated from the standard deviation (σ) of all cycles (n = number of cycles) in each sclerosponge analysis as ($\sigma/(\sqrt{n})$) and was typically 3%, 1.5%, <0.4% and 3% for B/Ca, Mg/Ca, Sr/Ca and Ba/Ca respectively, for

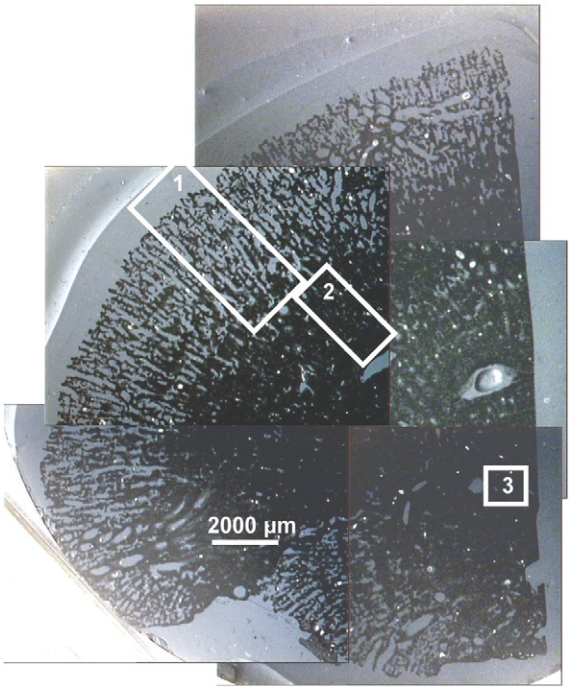

Fig. 1. Transmitted light micrograph of the sclerosponge section. The areas denoted by 1, 2 and 3 indicate the regions analysed for the spherulite transect, the epitaxial backfill and the spherulites at the centre of the skeleton, respectively.