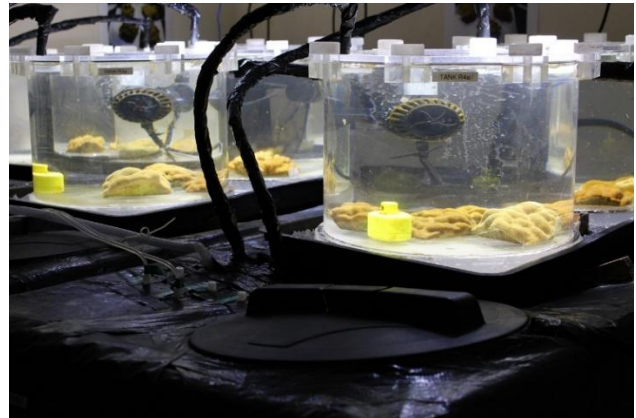


## XMaS CASE STUDIES:

### Ba speciation in Biominerals

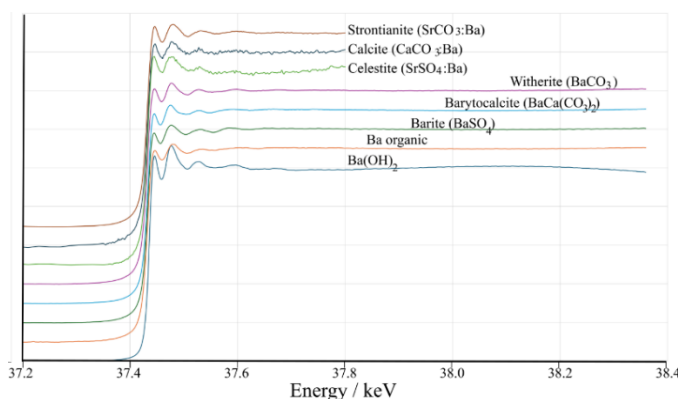
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Trace element geochemistry of the skeletons of marine organisms such as foraminifera, corals (Figure CS1) and bivalves capture key aspects of the seawater environment in which these organisms grew. By analysing fossil skeletons, we can reconstruct a powerful archive of past marine conditions, provided we understand how the trace metals are incorporated into the mineral phase. However, biominerals are complex nanocomposites of organic matrices and crystalline material, both of which have significant binding capacity resulting in trace elements following distinct partitioning pathways. For example, strontium, substitutes directly into the crystalline lattice and using inorganic partitioning models can be used as a proxy for sea surface temperature. Magnesium, by contrast, is predominantly bound to organic components, rendering Mg based paleoclimate reconstructions inherently flawed.



**Figure CS1:** Corals encode the environments in which they live in the geochemistry of their skeletons – conversely, those of fossils can be used to reconstruct marine conditions into the prehistorical past.

Barium is another environmentally sensitive trace element in biominerals, widely used to infer variations in terrestrial run off to the oceans. Yet because Ba is present only at ppm concentrations, its structural environment within biogenic carbonates has remained difficult to resolve. Our initial attempt to characterise Ba using XAFS (Finch et al., 2010) was ultimately inconclusive, as only the Ba L<sub>3</sub> edge was experimentally accessible. With the recent extension of the energy range on XMaS, however, Ba K edge XAFS has now become feasible. Coupled with the capability of the new Ge detector to operate efficiently at such high energies, this development opens a new metrological pathway for probing Ba incorporation in biominerals for the first time.



**Figure CS2:** Ba K-edge XAS of a variety of Ba-containing solids, including some in those in which Ba is a minor element.

Using XMaS, we collected Ba K-edge EXAFS spectra for a set of mineral and organic standards—an experimental capability our team has anticipated for more than 15 years (Figure CS2). The resulting datasets, from both standards and inorganic unknowns, are of excellent quality, with usable k-ranges extending to 11 Å<sup>-1</sup>. Refinements resolve up to three coordination shells around the central Ba atom, providing tightly constrained local structural information. These measurements now allow us to quantify the lattice relaxation and dilation associated with Ba substitution in carbonate minerals, offering unprecedented insight into the mechanisms of Ba incorporation. Coral samples proved more challenging, unfortunately. At natural concentrations of ~5 ppm, the Ba signal fell just below the detection limit, preventing reliable EXAFS extraction. Even so, the study marks a major step forward in understanding Ba behaviour in carbonate lattices and we now have a far more sophisticated understanding of Ba substitution in carbonate minerals and can predict the effect of Ba substitution. Working with the facility, we are currently assessing whether new diffraction-based detectors can isolate Ba K-edge signals in ultra dilute systems. If successful, this approach would enable the first structural characterisation of Ba in biominerals at natural abundances and open a new window onto paleoenvironmental reconstructions.