Strontium in Coccoliths

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Coccolithophores – an introduction

- Coccolithophores are single-celled marine algae that produce intricate structures – coccoliths – which are made from a mineral called calcite.
- Coccoliths are grown inside the cell and assembled into a coccosphere which surrounds the cell.
- Coccolithophores are responsible for ~10% of global annual carbon fixation.[1]
- Trace element concentrations – particularly strontium – in fossil coccoliths are used to model prehistoric ocean temperatures and dynamics.[2]
- When forming coccoliths, coccolithophores show amazing control of crystal growth which could influence new synthetic methods inspired by biology.
- Studying trace metal distribution and environment could shed light on the formation process.

False colour scanning electron micrographs of different coccolithophore species (Figure 1) and their coccoliths (Figure 2); *Scyphosphaera apsteinii* with cup-shaped lopadoliths and disk shaped muroliths, *Coccolithus braarudii*, *Helicosphaera carteri* and *Calcidiscus leptoporus*

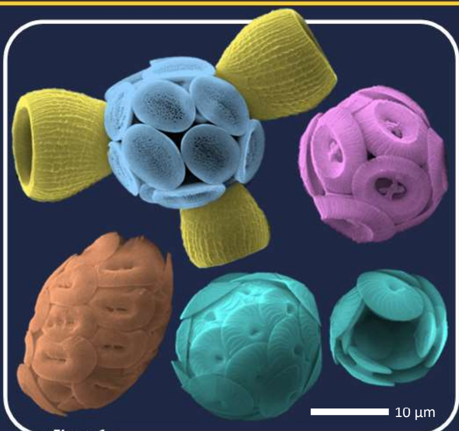


Figure 1

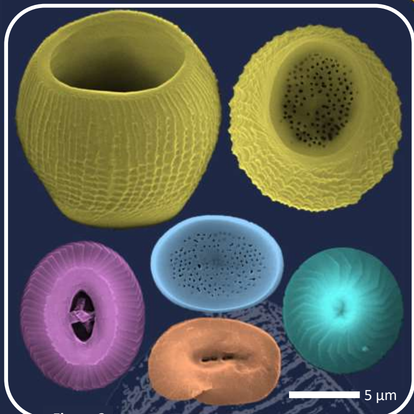


Figure 2

Sr distribution in *Scyphosphaera apsteinii* revealed by XRF tomography

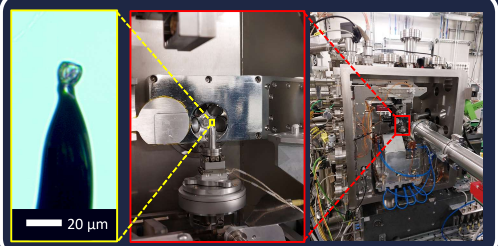


Figure 3

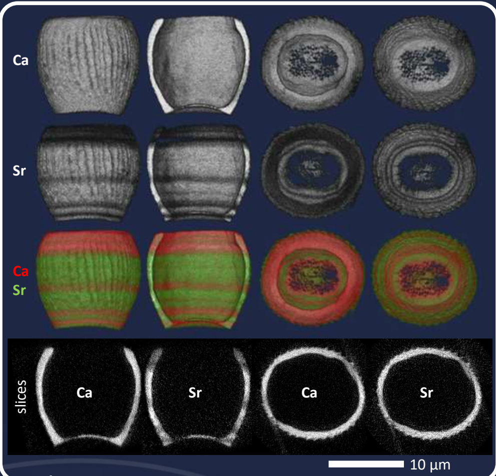


Figure 4

- The distribution of Sr within the cup-shaped lopadoliths of *S. apsteinii* had previously been shown to be non-uniform.[3]
- To study distribution in 3 dimensions, we used X-ray fluorescence (XRF) tomography.
- A single lopadolith was glued on the tip of a pin and mounted on the I14 beamline – the hard X-ray nanoprobe (Figure 3).
- The sample was rotated through 180° at 2° intervals and scanned at 60 nm resolution at each rotation – a 50-hour scan!
- Reconstruction of the data into a digital 3D model showed the 3D structure of the lopadolith, including features such as vertical ridges, and showed that Sr was arranged in rings or stripes of different concentrations (Figure 4).
- By measuring how the Ca and Sr XRF signal changed along the length of the lopadolith we were able to estimate that the Sr/Ca ratio varied by over 2.5× within the structure (Figure 5).
- Stripes of different Sr concentrations still appeared when the cells were grown in Sr-enriched seawater (Figure 6).
- The observation of stripes of different concentration cannot be explained by current models of coccolith formation and minor element fractionation which predict an even distribution.[4]

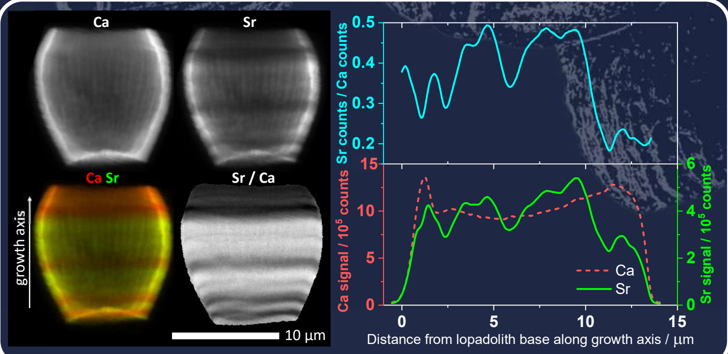


Figure 5

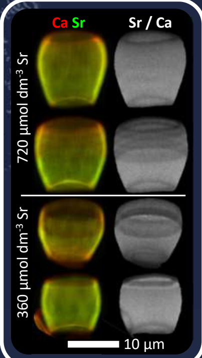


Figure 6

Sr distribution in other species

- Other species were scanned by 2D XRF at 2 orientations.
- The Sr distribution was found to be mostly uniform.
- There is a slight distribution in *C. leptoporus* where Sr/Ca in the proximal shield appears to be 1.2× that of the distal shield.

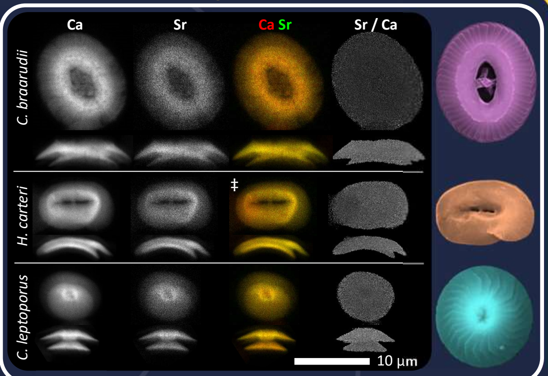


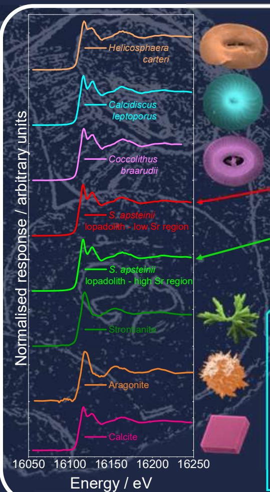
Figure 7

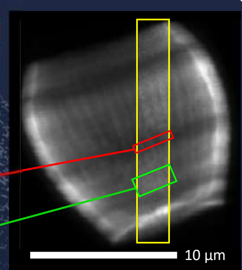
Apparent low Sr/Ca ratio of area of *H. carteri* coccolith visible in map marked ‡ likely artefact from overlap with mounting needle

Electron micrographs not to scale and not of measured samples – provided for illustrative purposes only

Sr environment in coccoliths – XANES

- To study the chemical environment of the Sr we used X-ray absorbance near edge structure (XANES) at the Sr K-edge.
- The XANES from different coccoliths and from different regions of the stripy lopadolith all best match the spectrum from calcite.
- Sr appears to be in a Ca site within the calcite structure.





Sr XRF map showing a transect of the stripy lopadolith scanned at energies around the Sr K-edge, from which XANES spectra were constructed from areas of high and low Sr abundance

Figure 8

Acknowledgements

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References

1. G. Langer, A. R. Taylor, C. E. Walker, E. M. Meyer, O. Ben Joseph, A. Gal, G. M. Harper, I. Probert, C. Brownlee and G. L. Wheeler, *New Phytol.*, 2021, **231**, 1845-1857.
2. 1. H. M. Stoll and P. Ziveri, in *Coccolithophores: From Molecular Processes to Global Impact*, eds. H. R. Thierstein and J. R. Young, Springer, Berlin, Heidelberg, 2004, DOI: 10.1007/978-3-662-06278-4_20, pp. 529-562.
3. E. M. Meyer, G. Langer, C. Brownlee, G. L. Wheeler and A. R. Taylor, *Geochim. Cosmochim. Acta*, 2020, **285**, 41-54.
4. G. Langer, N. Gussone, G. Nehrke, U. Riebesell, A. Eisenhauer, H. Kuhnert, B. Rost, S. Trimborn and S. Thoms, *Limnol. Oceanogr.*, 2006, **51**, 310-320.

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