

2.7.P11

Submicron-scale coccolith chemistry revealed by NanoSIMS

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To probe record and forcing mechanisms of past climate change, we rely on indirect chemical proxies encapsulated within biominerals. In order to apply proxies reliably, we need to know how biomineralisation processes, including the transport of ions from seawater across a membrane(s) and the precipitation of calcite on an organic matrix, exert control on trace metal chemistry. ICPMS analyses of cultured cells suggest that coccolith calcite is most influenced by biological discrimination compared to the chemistry of e.g. foraminifera. We exploit the high spatial resolution ability of NanoSIMS to investigate trace metal selectivity of coccolith calcite. First, we obtain sub-micron scale maps of trace metal distribution (e.g. Sr) in coccoliths to investigate whether organic mineral templates control the selection and assembly of Ca and similarly sized trace ions into the calcite (Fig. 1c,d). Second, we map the intracellular distribution of metals in cells grown in spiked media to resolve discriminatory steps associated with ion transport during mineralisation (Fig. 1a,b).

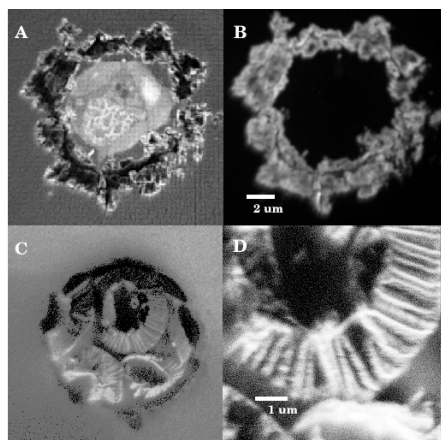


Fig 1. (a) $^{12}\text{C}^{14}\text{N}^-$ and (b) $^{16}\text{O}^-$ image of semithin ($1\mu\text{m}$) section of resin-embedded *Coccolithus pelagicus* obtained with Cs^+ beam of Oxford NanoSIMS. $^{12}\text{C}^{14}\text{N}^-$ beam resolves intracellular organelles and intricate relationship between organic template and calcite. $^{16}\text{O}^-$ is produced from external calcite platelets encircling cell. (c) $^{16}\text{O}^-$ image of an entire *C. pelagicus* (d) $^{12}\text{C}^{14}\text{N}^-$ at higher magnification demonstrates sub-micron scale mapping potential of NanoSIMS.

2.7.P12

A ghost haunts mass spectrometry: Real isotope fractionation or analytical paradox?

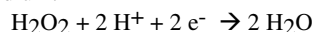
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Ca isotope paleothermometry based on planktonic foraminifera *N. pachyderma* (sin.) and *G. sacculifer* has been recently established, the latter by comparison with other reliable sea-surface temperature proxies and by the systematic analysis of cultured individuals [1]. This result has been challenged by [2], who dispute the regular fractionation trend of *G. sacculifer*. For analysis of Ca isotopes we use high-precision thermal ionization mass spectrometry. Ionization (and therefore fractionation) depend critically on the purity of the Ca fraction. Moreover, aliphatic fragments with 3 and 4 C atoms produce quasi-isobaric interferences in the Ca mass range. To avoid bias by organic molecules, we completely removed them (see below) and obtained reproducible results.

A similar problem is encountered in U-Th dating of speleothems, where microbial colonization can give rise to organic contamination. In the case of U-Th, there is no isobaric interference, but organic molecules adversely affect the desolvating nebulizer, and the ionization of U and particularly of Th in the plasma source is likely impaired as well. U and Th isotope ratios of organic-contaminated samples are inaccurate and irreproducible. We speculate that unresolved organic interferences may affect the fractionation of any element in plasma source mass spectrometry.

To eliminate organic molecules, oxidation is the method of choice. Dissolution of samples in nitric acid can oxidize some organic molecules, but by far not all, as the oxidation potential of the nitrate anion is at most 0.957 V, while biomass contains numerous molecular species which require > 1 V for oxidation. Hydrogen peroxide has an oxidation potential of 1.776 V for the following reaction in an acid medium:



Use of a hydrogen peroxide + nitric acid mixture for sample dissolution (and, if needed, also on the column eluate) has resulted in elimination of all organic interference in most samples. The mass ratio of the oxidizing mixture is not decisive, as long as (1) hydrogen peroxide is in excess of organic molecules, and (2) a low pH is maintained throughout.

References

- [1] Nägler et al. (2000) *G³*, paper 2000GC000091.
[2] Sime et al. (2003) *AGU* Fall abstract PP11A-0203.