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Probing the trace metal proxies of coccolithophores

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In order to probe the record and forcing mechanisms of past climate change, we rely on indirect chemical proxies often encapsulated within exquisitely crafted biominerals. Accurate interpretation of such proxy records requires a mechanistic understanding of the interaction of environmental parameters with the biological control of the precipitation process. Coccolithophores provide an outstanding model for investigating the biochemical discrimination between the similarly sized trace metals and calcium during mineralization, due to their intracellular calcification and extreme biological influence over the chemistry of the calcite. An understanding of these biological controls enhances the potential application of trace metal proxies in coccolith calcite for reconstruction of coccolithophore productivity and environment in the past ocean. In the present ocean, coccolithophores are one of the most important pelagic calcifying organisms to contribute to both the organic carbon and carbonate pump of $p\mathrm{CO}_2$into the deep ocean.

Here, we apply the high spatial resolution analytical capability of NanoSIMS, coupled with flow-through analyses, to map the heterogeneity of trace metals within coccolithophore calcite. Whilst the incorporation of Sr appears to show no spatial variability, our data imply that the Mg concentration is heterogeneous across the liths. Due to the similar charge densities of Sr and Ca, we suggest that the transport and incorporation of Sr into coccoliths is via the same pathway as that of Ca but with a differing affinity, such that the Sr is incorporated as a mistaken Ca. This mechanism further supports a rate dependent uptake of Sr. By contrast, the heterogeneity of Mg incorporation indicates that the coccolithophores exert a strong biological control over Mg uptake

and transport, perhaps even utilising the precipitation-inhibiting properties of Mg as a control over the biomineralisation process.

Down-core records of coccolith Sr/Ca from the global ocean add further confidence to its use for reconstruction of coccolithophore growth rates. These records show a near 400 kyr secular trend as the overwhelming signature over the last 1 Myrs. High coccolithophore Sr/Ca is correlated closely with the global zenith of the bloom forming species *Gephyrocapsa caribbeanica*, and the more recent rise to dominance of *Emiliania huxleyi*. We hypothesise that these long term trends in coccolithophore production could be related to orbital controls on the number of daylight hours.