

Trace element and Ca isotope ratios in calcareous dinoflagellate cysts of *Thoracosphaera heimii*

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Dinoflagellates are important marine primary producers, which significantly contribute to the global carbon-cycle. They can form cysts, composed of organic-material, silicate or calcium carbonate, which are used as stratigraphic and paleoenvironmental indicators.

The export flux of calcareous dinoflagellate cysts is of particular importance in temperate to tropical waters and is dominated by the species *Thoracosphaera heimii*. Providing a significant calcium sink, their Ca isotope fractionation is an important factor for the Ca isotope ratios of the locally deposited carbonate oozes, but might also be important for defining the isotopic Ca budget of the ocean. In addition, *T. heimii* cysts provide the potential to record long-term changes in the ocean chemistry, because their first occurrence dates at the K/T boundary [1].

The CaCO₃ cysts of *T. heimii* might be particularly useful as proxy archive recording ocean surface conditions (e.g. temperature, pH) due to their formation at the deep chlorophyll maximum depth in the water column and the ease in which a monospecific assemblage can be isolated from sediments [2]. Furthermore, they are comparatively insensitive to dissolution.

The dominant calcareous dinoflagellate *T. heimii* was grown in lab cultures at varying temperatures ranging from 12 to 30 °C as described earlier [3]. Trace element to Ca and Ca isotope ratios were analysed on the CaCO₃ cysts, previously cleaned from organic components.

The Ca isotope fractionation for *T. heimii* cysts resembles previous calibrations of other marine calcifiers, including coccolithophores [4], foraminifers and corals [5], in respect to absolute fractionation and temperature sensitivity. In contrast, trace element to Ca ratios and their temperature dependence differ from trends observed for coccolithophores and planktonic foraminifera. These results will be discussed in terms of biomineralisation of *T. heimii* and potential use for paleoceanographic applications.

References

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Mechanisms of iron(III) binding to organic matter and its competitive effect on trace metals

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Organic complexation of iron(III) is important for the binding of trace metals in natural environments because of competition effects. We have investigated the binding mode of iron(III) in the presence of O horizon soil material and isolated fulvic acid by means of EXAFS spectroscopy. The spectra for the O horizon samples showed Fe-O/N interactions at 2.02(2) Å, second-shell Fe-C interactions at 3.00(4) Å, and a mean Fe-Fe distance at 3.37(3) Å (Gustafsson *et al.*, 2007). This showed that the major part of the organically complexed iron(III) was hydrolyzed, and comparisons with literature data revealed that iron(III) had formed a mixture of di- and trimeric complexes with soil organic matter. The results were used to constrain a model for organic complexation, the Stockholm Humic Model. Observed competition effects on Cd²⁺, Cu²⁺, Ni²⁺ and VO²⁺ were well described with a single dimeric iron(III) complex in the model. In another set of experiments iron(III) was equilibrated with isolated fulvic acid at different initial pH:s, and the mixtures were analyzed with EXAFS spectroscopy after different time periods. These spectra lacked the Fe-Fe distance at 3.37 Å, instead Fe formed a monomeric iron(III) complex with FA or was reduced to Fe(II) after prolonged equilibration times. Our results indicate that the iron(III) binding modes to organic matter need not be identical in soils and aquatic environments. In soil suspensions any added iron(III) is quickly polymerized, whereas in solutions significant amounts of iron(III) complexes may remain as monomeric organic complexes. This shows that much remains to be done before the aquatic geochemistry of iron(III) is fully understood.

Reference

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