

Tracking single coccolith dissolution with picogram resolution: Implications for CO₂ sequestration and ocean acidification

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Coccoliths are micrometer scale shields made from 20 to 60 individual calcite (CaCO₃) crystals that are produced by some species of algae. Chalk deposits, the fossil remains of ancient algae, have remained remarkably unchanged by diagenesis. Even after 60 million years, the fossil coccolith crystals are still tiny (<1 μm), compared with inorganically produced calcite, where one day old crystals can be 10 times larger. This raises the question if the biogenic nature of coccolith calcite gives it different properties than inorganic calcite? And if so, can this protect coccoliths in CO₂ challenged oceans? By recording the changes in resonant frequency of a cantilever coccolith setup the dissolution of individual specimens, can be tracked with picogram (10⁻¹² g) resolution.

The results show that the behaviour of modern and fossil coccoliths is similar and both are more stable than inorganic calcite. However, ancient and modern coccoliths, that resist dissolution in Ca-free artificial seawater at pH > 8, all dissolve when pH is 7.8 or lower. Ocean pH is predicted to fall below 7.8, by 2100, in response to rising CO₂ levels. Our results imply that at these conditions, the advantages offered by the biogenic nature of calcite will disappear, putting coccoliths on algae and in the calcareous bottom sediments at risk [1].

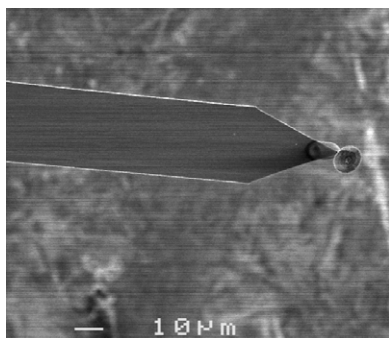


Figure 1: AFM cantilever with a single coccolith attached to the end. Mass 500 pg

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Online preconcentration ICP-MS analysis of rare earth elements in seawater

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The rare earth elements (REEs) with their systematically varying properties are useful tracers of continental inputs, particle scavenging activity and the oxidation state of seawater. However, their generally low (~pmol/kg) concentration and fractionation potential during chemical treatment makes them difficult to measure. Here we report initial results for GEOTRACES samples obtained using an automated preconcentration system, which separates the matrix and elutes the preconcentrated sample directly into the spray chamber of an ICP-MS instrument.

The commercially available SeaFAST system (Elemental Scientific Inc.) uses a resin with ethylenediaminetriacetic acid and iminodiacetic acid functional groups to preconcentrate REEs and other metals while alkali and alkaline earth elements are washed out. Importantly, time resolved analysis of the elution peaks demonstrates that this resin does not fractionate the REEs. The technique we developed for the analysis of REEs in seawater samples loads 4 mL of undiluted, filtered and acidified (pH ~2), seawater sample onto the column. The column is flushed with water and a pH 6 buffer solution for ~10 mins to wash the matrix away before the REEs are eluted with nitric acid into the ICP-MS for measurement. Using this technique each analysis takes about 15 mins and we obtain sub ppt limits of detection (3 times the standard deviation of blank measurements). Repeated measurements of a sample from 2000 m water depth in the Southern Ocean allows the external precision of the technique to be estimated at < 10% for all REEs and < 5% for many others. Comparison of Nd concentrations with isotope dilution measurements for 30 samples shows the techniques agree within 10%. To assess the accuracy of the technique for all REEs mine water standards have been diluted with NaCl matrix and analysed as unknowns. The results for most elements agree well with values in the literature. This makes the online preconcentration ICP-MS technique advantageous for the minimal sample preparation required and the relatively small sample volume consumed. Further development of the technique is underway to ensure accurate results even for the least abundant REEs in seawater samples.