

UPTAKE OF Cd²⁺ DISSOLVED IN SEAWATER BY PARTICULATE CALCITE

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Several experiments concerning the interaction of cadmium with calcite have been carried out by various investigators (e.g. Chiarello et al., 1997; Prieto et al., 2003). These researches have demonstrated the effectiveness of this mineral in removing cadmium from freshwater solutions, by sorption onto the crystal surfaces and/or surface precipitation of (Cd,Ca)CO₃ solid solutions with a calcite-type structure. However, analogous experimental work has not yet been performed to evaluate the potential inorganic removal of Cd²⁺ by calcite from seawater, by a similar sorptive process. The issue is relevant, as the bio-limiting profile of cadmium in the oceans needs an explanation.

Previously, in order to thermodynamically assess this last hypothesis, we have calculated the saturation state of equatorial Pacific surface waters with respect to the (Cd,Ca)CO₃ solid solution. Using the geochemical computer code PHREEQC (Parkhurst and Appelo, 2003), we have observed that these waters are supersaturated with respect to pure calcite, and subsaturated with respect to pure otavite. Yet, with the stoichiometric supersaturation function (Prieto et al., 2003), we have seen that the solid solution composition for which this aqueous solution is most supersaturated does not exactly correspond to the pure calcite end-member. As can be noticed in the inset graph in figure 1, the supersaturation peak slightly departs from X_{CdCO₃}=0, implying that some cadmium in the aqueous solution would have been incorporated into the precipitating solid phase. Also, the obtained high distribution coefficients of cadmium between the solid and the aqueous solution (in the range of 3900-4700) corroborate the fact that cadmium would always partition to the solid phase.

Although this hypothesis of inorganic uptake of cadmium seems to be thermodynamically plausible, it needs to be further substantiated by experimental work in order to conclude if there is a decrease in the concentration of cadmium in a seawater solution, in the presence of particulate calcite. Here we present a preliminary study of the uptake of cadmium by particulate calcite. The experiments have been carried out at 25±0.1°C and at ambient partial pressure of CO₂, by reacting 0.02 g of calcite particles

(with diameters in the range 1-25 µm) with 450 cm³ of artificial seawater (Instant Ocean® Sea Salts dissolved in MilliQ® deionized water), with a CdCl₂ concentration of 0.001 mM. This interaction was conducted in a continuously stirred reaction flask (100 rpm) and samples were taken before adding the calcite seeds and after 8h, 24h, 72h, 1 week and 2 weeks from the beginning of the experiments. The concentrations of dissolved cadmium have been measured by inductively coupled plasma mass spectrometry (ICP-MS).

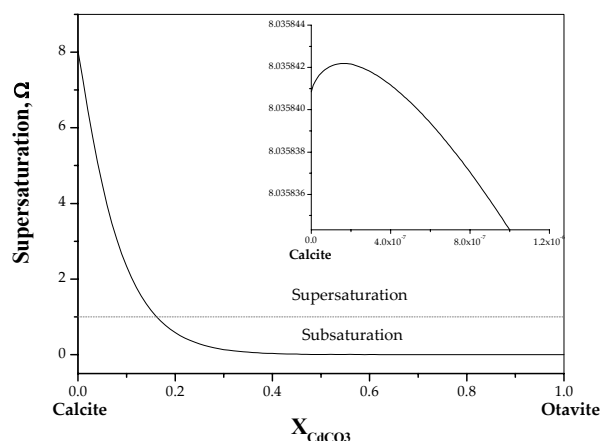


Figure 1: Supersaturation of seawater, at 20 m, in relation to the entire compositional range of the (Cd,Ca)CO₃ solid solution. Inset graph shows the supersaturation maximum, close to the calcite endmember.

REFERENCES

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