The mechanism for inhibition of calcite recrystallisation by organic molecules

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The inhibitory effect of biopolymers, particularly by polysaccharides, could explain the extremely slow recrystallization rates of biominerals such as the calcite coverings on some species of algae that make chalk. Recrystallization can be considered as a series of simultaneous and consequent elementary events of dissolution and precipitation that leads to the diagenetic phenomenon known as grain coarsening. A driving force of recrystallization in geological environments is usually either the difference between lithostatic and hydrostatic pressures or the dependence of the chemical potential of the interface on the grain size. This coarsening process, where larger particles grow at the expense of smaller ones, is called Ostwald ripening.

It is well known [1] that the presence of aqueous organic anions (such as alginate) negligibly affects calcite dissolution rate. On the other hand, there is evidences that alginate significantly inhibits calcite precipitation [2]. Thus, it can be supposed that precipitation is the rate-limiting stage of the overall process of recrystallization, which, in turn should be affected by the presence of alginate. This conclusion is supported by our experimental study of ^{14}C isotope uptake during calcite recrystallization in a pure system and in the presence of alginate. Isotope concentration was monitored during the experiment, yielding the total amount of isotope uptake into the solid phase. An assumption about the mechanism of isotope uptake (i.e. burial into calcite layers newly formed during recrystallization) allows us to quantify the amount of newly formed material. Extent of inhibition of the calcite recrystallization rate because of alginate adsorption is comparable with that of calcite precipitation. This inhibition would take place as long as alginate is present in the solution. If there is no effective alginate supply, inhibition would sooner or later be decreased by exhausting the solution and burying the alginate molecules under the newly formed calcite layers, the more so, because adsorbed alginate could function as a substrate for calcite growth, initiated by the interaction of Ca with the negative end of the –C=O bond of the alginate functional group.

[1] Oelkers et al. (2011) *Geochim. Cosmochim. Acta*, **75**, 1799-1813. [2] Lakshtanov et al. (2011) *Geochim. Cosmochim. Acta*, **75**, 3945-3955.

Photochemical alteration of $\delta^{13}C$ of dissolved organic matter in big rivers

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Organic matter (OM) depleted in $\delta^{13}C$, is considered an excellent tracer for terrestrial OM in aquatic systems. As a bulk measurement, it was also thought that $\delta^{13}C$ is less susceptible than molecular biomarker proxies toward bacterial reworking and degradation. It has been shown however, that $\delta^{13}C$ in total dissolved organic matter (DOM) can change as a result of photochemical reactions, with coloured, aromatic-rich terrestrial OM most susceptible to these reactions [1,2]. Here we further assess the viability of $\delta^{13}C$-DOM as a tracer for terrestrial OM in coastal systems by assessing the susceptibility of this proxy to UV radiation, which causes the photochemical destruction of chromophoric DOM. Our data set comprises 10 large rivers, which cumulatively account for approximately 1/3 of the world's freshwater discharge to the global ocean. We show that irradiation causes a 1.5‰ enrichment in $\delta^{13}C$ in almost all riverine DOM samples, demonstrating that riverine DOM, almost entirely terrestrial in nature, can artificially be branded as a mixture of terrestrial and marine DOM due to photochemical reactions. Photochemical alterations in $\delta^{13}C$ therefore bias mass balance calculations of terrestrial OM discharge and degradation in coastal oceans towards the marine end-member.

[1] Vahatalo et al. (1998) *Limnology and Oceanography* **53**, 1387-1392.
2] Osburn et al. (2022) *Marine Chemistry* **126**, 182-294.