Alginate control on calcite precipitation rate

L.Z. LAKSHTANOV[1,2]*, N. BOVET[1] AND S.L.S. STIPP[1]

[1]Nano-Science Center, Deptartment of Chemistry, University of Copenhagen, Denmark (bovet@nano.ku.dk, stipp@nano.ku.dk)
[2]Inst of Experimental Mineralogy, 142432 Chernogolovka, Russia (*correspondence: leonid@iem.ac.ru)

The kinetics of calcite precipitation in the presence of alginate was investigated using the constant composition technique. In the concentration range investigated (0.0002 to 0.005 g L^{-1}), alginate inhibits calcite precipitation. The extent of inhibition increased with increased alginate concentration and decreased solution supersaturation.

Alginate adsorption, derived from normalized calcite precipitation rates, is described satisfactorily by the Langmuir adsorption model.

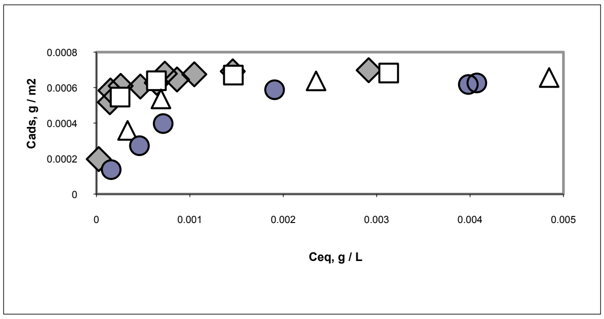

Figure 1: Alginate adsorption isotherms for four supersaturation values: Rhombs, σ = 1.40; squares, σ= 2.02; triangles, σ = 2.65; circles, σ = 3.55.

At lowest supersaturation, alginate adsorption onto calcite probably reaches its maximal uptake of 7.5E-4 g m^{-2}, corresponding to surface coverage of one molecule for each 200 to 300 nm^2, depending on the molecular mass of alginate. This means that one alginate molecule can be bound over 100 to 150 Ca surface sites. Initially, on the surface of the inhibited calcite.

XPS identified alginate but after further time in solution, when the system had recovered, XPS demonstrated that it disappeared from the surface, presumably buried under the newly formed calcite.

The alginate affinity constant decreases with increasing supersaturation, evidence for incomplete adsorption. A simple model based on competition between growth and desorption effectively describes the observed change in the adsorption constant.

Molybdenum and vanadium abundances in banded iron formation and the onset of oxidative continental weathering

STEFAN V. LALONDE[1]*, NOAH J. PLANAVSKY[2], OLIVIER J. ROUXEL[1,3], ERNESTO PECOITS[4] AND KURT O. KONHAUSER[4]

[1]Institut Universitaire Européen de la Mer (IUEM), Université Européene de Bretagne (UEB), Plouzané 29280, France (*correspondence: stefan.lalonde@univ-brest.fr)
[2]Department of Earth Sciences, University of California-Riverside, Riverside, CA 92521, USA
[3]IFREMER, Géoscience Marines, Plouzané 29280, France
[4]Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB T6G 2E3, Canada

The enrichment and isotopic composition of molybdenum in black shales provide insight into the history of atmospheric oxygenation via the coupling of molybdenum supply with the oxidative weathering of terrestrial sulfides [e.g. 1, 2]. However, the fidelity of preservation of Mo oxidative proxies in black shales may also be related to the degree to which euxinic conditions enable their capture [3, 4]. Similar to molybdenum, vanadium is also enriched in sediments deposited under euxinic conditions [4], but its marine supply should be independent of the oxidative weathering of terrestrial sulfides. Here we consider their combined history in order to better understand the black shale Mo record [2] in terms of changing oxidative sources and euxinic sinks in the geological past. We present a complimentary dataset for Mo and V abundances in banded iron formations (BIF), where the ferruginous conditions necessary for BIF deposition preclude euxinia, and sequestration of Mo and V likely occur by adsorption of their anions onto highly reactive ferric hydroxides. While V abundances remain relatively stable throughout the Precambrian, notable Mo enrichments are observed ca. 2.5-2.3 Ga; combined, these data point to the importance of changing sources, and reaffirm assertions that the Great Oxidation Event was marked by increased marine Mo supply driven by oxidative continental weathering. The BIF dataset is further evaluated in light of experimentally-determined Mo- and V- iron oxide partition coefficients that enable back-calculation to dissolved Mo and V concentrations in paleoseawater.

[1] Anbar *et al.* (2007) *Science* **317**, 1903–1906. [2] Scott *et al.* (2008) *Nature* **452**, 456–459. [3] Neubert *et al.* (2008) *Geology* **36**, 775–778. [4] Tribovillard *et al.* (2006) *Chem. Geol.* **232**, 12–32.