

Reactivity of detrital silicates and carbon storage in the ocean margins

S.R. GISLASON^{1*}, E.H. OELKERS^{1,2}, M.T. JONES¹,
D. WOLFF-BOENISCH¹, H.A. ALFREDSSON¹
AND K.G. MESFIN¹

¹Institute of Earth Sciences, University of Iceland, Reykjavik, Iceland (*sigrg@raunvis.hi.is, morgan@hi.is, boenisch@raunvis.hi.is, haa4@hi.is, kgm1@hi.is)

²Géosciences Environnement Toulouse, GET/CNRS, Université de Toulouse, Toulouse, France (oelkers@get.obs-mip.fr)

A recent survey of chemical denudation of continental silicates at the global scale suggests that riverine particulate material-seawater interaction may be essential to the feedback between weathering and atmospheric CO₂ content/climate over geological timescales [1]. Moreover substantial evidence indicates that this particulate material is reactive once it arrives in the coastal oceans, in part due to its high surface area [2,3]. This study explores the possibility of using the detrital silicate material, located at the continental and volcanic island margins for carbon storage via *in-situ* mineral carbonation.

Continental margin silicate sediments offer a number of advantages to potential carbon storage efforts. In addition to the large surface area of reactive solids, they have substantial porosity available for carbonate mineral precipitation. The carbonation of silicate sediments can be enhanced by injecting CO₂ fully dissolved in water, which in turn limits the risk associated with buoyancy. The CO₂ dissolution requires large water volumes that may not be available on land. Moreover, public acceptance of ocean sediments storage may be easier than for land storage.

Of particular interest is the carbonation of basaltic and ultramafic sediments [4,5], which comprise a significant proportion of the particulate material transported to the oceans. Natural analogues, laboratory experiments, and reactive transport models suggests that such material is readily transformed into carbonates at low temperature and high CO₂ partial pressure [e.g. 6]. Laboratory experiments suggest that seawater/basaltic sediment interaction is particularly well suited for long-term CO₂ storage [7].

[1] Gislason *et al.* (2006) *Geology* **34**, 49–52. [2] Wallmann *et al.* (2008) *Geochim. Cosmochim. Acta* **72**, 2895–2918. [3] Jones *et al.* (2012) *Geochim. Cosmochim. Acta* **77**, 108–120. [4] Oelkers *et al.* (2008) *Elements* **4**, 333–337. [5] Gislason *et al.* (2010) *Intern. Jour. Greenhouse Gas Control* **4**, 537–545. [6] Roger *et al.* (2006) *Lithos* **92**, 55–82. [7] Wolff-Boenisch *et al.* (2011) *Geochim. Cosmochim. Acta* **75**, 5510–5525.

Controls of polysaccharide chemistry on kinetics and thermodynamics of calcium carbonate nucleation

ANTHONY J. GIUFFRÉ^{1*}, LAURA M. HAMM¹,
AND PATRICIA M. DOVE¹

¹Department of Geosciences, Virginia Tech, Blacksburg, USA, giuffre@vt.edu (* presenting author)

Living organisms produce skeletal structures within a complex matrix of organic macromolecules. These compounds are proposed to actively guide the nucleation and growth of crystalline structures into the organic-inorganic composites we know as biominerals. Good examples are seen in calcareous algae and stromatolite-forming cyanobacteria. An extensive effort has investigated the influence of proteins on calcium carbonate (CaCO₃) mineralization. The polysaccharides, however, have received little attention despite their near-ubiquitous occurrence in mineralized tissues and intimate associations with proteinaceous compounds of the organic matrix.

The polysaccharides found at sites of microbial mineralization have complex monosaccharide sequences with various carbohydrate stereochemistries and functionalities (carboxylated, acetylated, sulfonated, methylated). This study tests the hypothesis that polysaccharides influence the rate of calcite nucleation by systematic and predictable differences in their chemistry. Using high purity polysaccharides with regular monomer sequences as simple model compounds for more complex macromolecules, we quantify the effect of functional group chemistry (chitosan, hyaluronic acid, heparin, alginic acid) and monomer sequencing (two stereoisomers of alginic acid) on the kinetic and thermodynamic barriers to CaCO₃ formation. Substrates were prepared by electrodeposition of these polysaccharides as thin gel-like films onto gold-coated silicon wafers. Using a flow-through cell, heterogeneous nucleation rates of calcite were measured for a suite of supersaturation conditions.

The kinetic measurements show rates of calcite nucleation are dependent on polysaccharide functional group chemistry and monomer sequence. Analysis of the data indicate the kinetic and thermodynamic barriers to nucleation are correlated with surface charge as the number of carboxyl groups per monomer of polysaccharide. Nucleation rates are also correlated with independent measurements of surface free energy of the polysaccharide substrates. These findings indicate polysaccharides may have active roles in promoting the formation of calcite and suggest their presumed function as inert framework molecules should be revisited.