Calcium carbonates distribution in experimentally carbonated Portland cement cores

F. BRUNET[1], J. CORVISIER[1], A. FABBRI[1,2], S. BERNARD[1], N. FINDLING[1], G. RIMMELE[3], V. BARLET-GOUEDARD[3], O. BEYSSAC[1] AND B. GOFFE[4]

[1]Laboratoire de Géologie de l'ENS, CNRS-UMR8538, Paris – France (brunet@geologie.ens.fr)
[2]BRGM, Orléans – France
[3]SRPC, Schlumberger, Clamart – France
[4]CEREGE, CNRS-UMR6635, Aix-en-Provence – France

Portland cement strongly reacts with wet supercritical CO_2 or CO_2-satured water, especially in the context of deep geological storage. The corresponding alteration process is characterized by a complex series of dissolution/carbonation fronts related to the diffusion of aqueous species, which have an impact on the hydromechanical cement properties.

Using Raman micro-spectrometry and X-ray micro-diffraction on polished sample sections, we investigated the spatial distribution of $CaCO_3$ polymorphs formed during the experimental carbonation of water saturated Portland cement cores (30-mm in diameter) with supercritical CO_2 at 90°C and 28 MPa. Calcite, aragonite and vaterite, the three calcium carbonate polymorphs were clearly identified with these two techniques. Moreover, using a dynamic line-scanning Raman mapping tool, their distribution along the main CO_2 diffusion direction could be mapped at millimetre-scale area. The calcium carbonate 2-D distribution then shows that vaterite is mostly located in a 500-µm wide ring ahead of the carbonation front. This feature indicates that vaterite, which is the least stable $CaCO_3$ polymorph, first crystallizes within the cement sample in the course of the carbonation process consistently with the Ostwald rule. The presence of a *vaterite front* indicates that local mineral-solution equilibration can be slower than species transport, even above ambient conditions, and that kinetics cannot be ignored in the cement carbonation process.

A computer program based on purely diffusive 1-D transport with simple boundary conditions (e.g. infinite source of pure CO_2-H_2O fluid) has been build; it is able to model the coupled effects of chemical reactions and fluid transport and also to handle the competition between their respective kinetics. For example using calcite and vaterite precipitation kinetic data from the literature and assuming a water-mineral kinetics based on the Transition State Theory, the width of the vaterite front inferred from Raman mapping could be reproduced and, vaterite dissolution kinetic constant could, in turn, be adjusted.

Dissimilatory sulfate reduction: Why is the oxygen isotope equilibrium value where it is?

B. BRUNNER[1]*, T. GOLDHAMMER[2], S.P. TEMPLER[3] AND S.M. BERNASCONI[3]

[1]Biogeochemistry Research Group, Max Planck Institute for Marine Microbiology Bremen, Germany (*correspondence: bbrunner@mpi-bremen.de)
[2]Marum, University of Bremen, Germany (goldhammer@uni-bremen.de)
[3]ETH Zurich, Switzerland (stefanie.templer@erdw.ethz.ch, stefano.bernasconi@erdw.ethz.ch)

Dissimilatory sulfate reduction (DSR) causes oxygen isotope exchange between sulfate and water. The oxygen isotope composition approaches an apparent equilibrium value, where sulfate is enriched in ^{18}O by approximately 28 to 32‰ compared to water. This value is close to the predicted oxygen equilibrium isotope fractionation between sulfate and water (33.4‰ at 4°C [1]). However, DSR does not catalyze direct oxygen isotope exchange between water and sulfate. Instead, oxygen isotope exchange appears to take place between metabolic intermediates (i.e. sulfite) and water, and during reversible enzymatic sulfate reduction steps. Thus, there is no direct link between predicted oxygen isotope fractionation and equilibrium values during DSR. We discuss three potential causes for the observed isotope fractionation: oxygen isotope exchange between sulfite and water [2], oxidation of sulfite with adenosinemonophosphate (AMP) to adenosinephosphosulfate (APS) [3] and a combination of these processes with kinetic oxygen isotope fractionation during the reduction of APS [4]. We conclude that none of the above scenarios can be excluded as cause for the apparent oxygen isotope equilibrium between sulfate and water. However, our calculation of the isotope fractionation between AMP and water based on the framework of oxygen isotope equilibrium calculations between phosphate and water [5, 6] demonstrates that AMP has a temperature dependent oxygen isotope composition close to the equilibrium values for sulfates, which makes it the prime candidate as controller in the oxygen isotope fractionation between sulfate and water during DSR.

[1] Mitzutani (1972) *Japan. Geochem. J.* **6**, 67-73. [2] Brunner *et al.* (2006) *Eos Trans. AGU* **87**, V11C-0601. [3] Peck & Stulberg (1962) *J. of Biological Chem.* **237**, 1648-1652. [4] Turchyn *et al.* (2009) *GCA subm.* [5] Colman *et al.* (2005) *PNAS* **102**, 13023–13028 [6] Lecuyer *et al.* (1999) *GCA* **63**, 855–862.