Micro- and nanoscale studies of Mn incorporation in bivalve shells

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Numerous studies have shown that the chemical composition of bivalve shells is strongly controlled by physiology. Because some elements fulfil physiological functions, metals may be incorporated both, in the inorganic and the organic part of the material. Knowledge of element speciation is therefore crucial for the application of thermodynamically controlled element exchange relationships in calcite or aragonite to composite biominerals.

The speciation of Mg, for example, was shown to vary between bivalve species and sizeable portions (>130 ppm) were found to reside in the organic shell parts of *Arctica islandica* [1]. Additionally, different $CaCO_3$ polymorphs (vaterite, amorphous $CaCO_3$) contain differing concentrations of elements which are thought to be necessary for stabilization of the specific mineral structure [2].

Freshwater bivalves incorporate Mn seasonally into their shells which can potentially be used to track primary productivity and upwelling in the water mass [3, 4]. Aragonitic *Diplodon chilensis patagonicus* shells have seasonal Mn patterns with increasing concentrations towards the organic-rich growth lines, raising the question of the speciation of this element in the shells.

Here we present combined results of LA-ICP-MS, Nano-SIMS, XANES and FIB/TEM measurements to address the mechanisms of Mn incorporation into bivalve shells. First XANES results [5] imply that manganese is incorporated as Mn^{2+} in the carbonate phase and not in the organic part.

[1] Schöne *et al*. (2010) *Geochem. J*. in press. [2] Jacob *et al*. (2008) *Geochim. Cosmochim. Acta* **72**, 5401–5415. [3] Soldati *et al*. (2009) *J. Mollusc. Stud*. **75**, 75–85. [4] Langlet *et al*. **2006**, *Biogeosci. Disc*. **3**, 1453–1471. [5] Soldati *et al*. (2010*) J. Synchrotron Rad*. **17**, 193–201.

Gases in managed aquifer recharge

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Dissolved gases can play an important role in Managed Aquifer Recharge (MAR), as illustrated by field studies in southwestern U.S.A. The Sand Hollow Reservoir in southern Utah was constructed in 2002 to provide surface-water storage and recharge to the underlying Navajo Sandstone Aquifer. Prior to filling the reservoir, a gas partitioning tracer test was conducted in a 60 m-diameter infiltration test-pond [1]. Very strong attenuation of a dissolved helium tracer was observed as it partitioned into a gas phase that had been trapped below the pond during filling. The trapped gas resulted in much lower infiltration rates than expected based on measurements of the saturated hydraulic conductivity. Similarly, infiltration rates 10 to 100 times less than expected beneath the 600 hectare Sand Hollow Reservoir, along with large increases in total dissolved gas pressure (TDGP) and significant fractionation of dissolved noble gases, suggest large amounts of trapped interstitial air. Sampling for environmental tracers (^3H, CFCs, TDGP, DO, SpC, Cl/Br) began in 2001 at observation wells located between 20 and 1, 500 m downgradient of the reservoir to monitor the movement of recharged water. Elevated TDGP and other tracers have migrated less than 1 km downstream in 8 years. Since 2002, infiltration rates have progressively declined possibly due to *in situ* generation of CO_2 and CH_4, along with other clogging mechanisms such as siltation and biofilm development.

[1] Heilweil V., Solomon K., Perkins K. & Ellett K. (2004) 'Gas-partitioning tracer test to quantify trapped gas during recharge.' *Groundwater* **42**(4), 589–600.