

X-ray pair distribution function and NMR studies of biogenic amorphous calcium carbonate

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Introduction and Approach

Amorphous calcium carbonate (ACC) is known to serve multiple functions during biomineralization processes: as a transient precursor to crystalline CaCO₃, as structural components of functional hard parts, and as temporary storage of calcium. Minor additives play important roles in stabilization of ACC as well as in transformation to crystalline forms. Yet, the specific interactions of the additives with the ACC remain largely unknown. One of the main limitations in understanding ACC stabilization and transformation mechanisms is a lack of knowledge of short- and medium-range structure in the amorphous phase. Recent application of synchrotron total X-ray scattering and pair distribution function analysis has allowed characterization of short- and medium-range structure extending up to length scales of 15 Å in synthetic hydrated ACC [1]. NMR studies provide insight to the role of hydrogen bonding in the local structure. We have applied these same experimental approaches to examine structure in hydrated biogenic ACC to provide a comparison with synthetic ACC. American lobsters produce gastroliths that are composed almost entirely of hydrated ACC.

Results and Conclusions

X-ray PDFs for gastrolith ACC exhibit a weak, sharp peak at 1.3 Å and a strong, sharp peak at 2.4 Å, resulting from first-shell C-O and Ca-O bonds. A weak peak is also evident at ~2.9 Å, appearing as a small shoulder to the 2.4 Å peak. In addition, there are two broad peaks of lower amplitude centered at ~4 and ~6 Å, with even weaker oscillations extending up to ~12 Å. Comparison with the PDF for synthetic hydrated ACC shows essentially identical features, in both position and amplitude. Reverse Monte Carlo refinement has shown that the broad features at 4 and 6 Å represent dominantly Ca-Ca and Ca-O pair correlations [2]. NMR data likewise closely resemble those for synthetic ACC, showing a broad ¹³C peak near +169 ppm, 3.6 ppm FWHM. Phosphorus present at minor concentrations in the gastrolith yields a ³¹P NMR peak at 2.8 ppm, similar in position to phosphate in crystalline CaCO₃ but much broader (5.5 ppm FWHM), indicating a wide range of local environments. ³¹P-detected ¹H NMR spectra contain a broad sideband envelope characteristic of rigid structural water, similar to ¹H spectra of synthetic ACC, suggesting intimate association of phosphate in the gastrolith ACC.

[1] Michel (2008) *Chem. Mater.* **20**, 4720-4728. [2] Goodwin (2010) *Chem. Mater.* **22**, 3197-3205.

The role of lead (Pb) in highly saline fluids of a deep geothermal system: complexation and precipitation

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At the geothermal in situ laboratory in Groß Schönebeck (North German Basin) fluid of a Permian sandstone reservoir is produced from about 4.4 km depths, where the temperature is about 150°C at 45 MPa pressure. The brine is characterized by a very high salt content of 265 g/L total dissolved solids, which is mainly composed of NaCl and CaCl₂ [1]. During the initial testing phase of the geothermal fluid loop between April and October 2011, fluid was produced from one well at temperatures below 100 °C. After passing a gas separator and two filter units (< 20 µm), the fluid was re-injected into a second well. During that phase, fluid samples were collected with a special sampling device, allowing to take fluid at in-situ pressure and temperature from the above ground installations after the production well. Fluid samples were collected at various temperatures between 20 and 100 °C. Additionally, filter residues as well as mineral scalings, which precipitated within the well bore have been collected and analyzed. One of the compounds of interest both in fluid and in solid phase is lead (Pb), which was found to be highly enriched (up to 1 mM) in the fluid solution as well as in most of the solid samples.

Solid samples were analyzed by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and, after acid extraction by ICP-MS or OES for total elemental composition. Although a large quantity of the material was weakly crystalline or amorphous, some crystalline phases were identified in the samples. Lead occurred in different minerals such as laurionite (PbOHCl), galena (PbS), native Pb and PbO, indicating that redox processes play an important role in the borehole.

Fourier Transform Infrared Spectroscopy (FTIR) spectra were collected both on samples of the geothermal brine and on synthetic Pb containing solutions of various composition to identify Pb complexation in the solution.

The aim of these investigations was to understand Pb mobility and the factors affecting Pb solution and precipitation at geothermal conditions.

[1] Regenspur et al. (2010) *Chemie der Erde* **70(S3)**, 3-12.