Structural characteristics of synthetic amorphous calcium carbonate

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Amorphous calcium carbonate (ACC) is an important precursor phase involved in biomineralization by a wide variety of invertebrate organisms and is of technological interest in the development of functional materials. An understanding of the transformation of ACC to crystalline forms and the selection of final product polymorph has been hindered by the difficulty is assessing structure of the amorphous phase. This is mainly due to its metastability and limitations of conventional structure determination methods. We present new findings from the application of two techniques, synchrotron X-ray based pair distribution function (PDF) analysis and nuclear magnetic resonance spectroscopy, to synthetic, hydrated analogs of ACC and provide new insight to short and intermediate range structure. PDF results for ACC formed *in vitro* using two common preparation methods show that structural coherence extends over less than ca. 15 Å, confirming that the synthetic ACC is truly amorphous. Results also demonstrate that the short- and intermediate-range structure shows no distinct match to any crystalline structure in the calcium carbonate system. NMR results show that most of the hydrogen in ACC is present as structural H_2O, about one-half of which undergoes restricted motion on the millisecond timescale near room temperature. NMR results also demonstrate that most of the carbonate in ACC is monodentate, making it distinctly different from monohydrocalcite. These results complement X-ray absorption spectroscopy studies and provide a baseline for future experiments evaluating biogenic ACC and samples containing additives that may play a role in stabilization of ACC, crystallization kinetics, and final polymorph selection.

Speciation of REE(III) in chloride-, fluoride-, and sulphate-bearing solutions: Solubility and spectroscopic studies

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Experimental studies of REE speciation at elevated temperatures have been largely restricted to a few REE in chloride-bearing solutions, and consequently our understanding of the behaviour of other REE in hydrothermal fluids comes primarily from theoretical predictions [1, 2]. In order to evaluate the stability of REE complexes with atomic number and to verify theoretical estimates, we have therefore conducted a systematic experimental investigation of REE speciation in chloride-, fluoride-, and sulphate-bearing solutions.

Experiments were performed at temperatures up to 250 °C and pressures up to 100 bar, and initially consisted of spectroscopic studies of REE speciation in homogenous chloride- and sulfate-bearing solutions containing one of the REE (e.g. Nd(III), Sm(III), and Er(III)) and one of the ligands. Later experiments involved determination of the solubility and speciation of Nd(III) fluoride in F-bearing aqueous solutions. Finally, we evaluated the solubility of REE fluorides in multi-component systems involving all REE (except Pm) and one to two ligands (F^-, or F^-+Cl^-, or F^-+HSO_4^-). The resulting data were used to derive formation constants of the corresponding aqueous complexes.

The experimental data obtained in this study show that the theoretical predictions of Wood [1] and Haas *et al*. [2] overestimate the stability of fluoride complexes of REE at elevated temperatures, and that this overestimation increases with increasing temperature. Formation constants obtained for chloride species are in fair agreement with the predictions of Haas *et al*. [2] for HREE, but show higher stabilities for LREE at elevated temperatures. The first formation constants for sulphate complexes are in reasonably good agreement with those predicted by both Haas *et al*. [2] and Wood [1], but the data indicate that $REE(SO_4)_2^-$ is progressively more stable than predicted as temperatures above 150 °C.

[1] Wood (1990) *Chem. Geol*. **88,** 99-125. [2] Haas *et al*. (1995) *Geochim. Cosmochim. Acta* **59,** 4329-4350.