Experimental report

26/09/2016

Proposal: 6-06-464 **Council:** 4/2015

Title: Unraveling the structural ordering of water in amorphous calcium carbonate using neutron pdf-analysis

Research area: Materials

This proposal is a new proposal

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Samples: CaCO3*H2O
CaCO3*D2O

Instrument	Requested days	Allocated days	From	To
D4	7	7	29/10/2015	05/11/2015

Abstract:

Amorphous calcium carbonates (ACC) are interesting materials, serving as metastable intermediates for crystalline calcium carbonate formation, but also form stable storage units in biological samples. Studying the structure of this material therefore provides us information on how nature produces intricate hierarchical structures and provides us control over the chemical and structural properties of the final crystalline product. In this study we intend to investigate the structure of water inside the ACC (~CaCO3*H2O) using neutron pdf-analysis, where previous investigations using X-ray diffraction and NMR were unable to give a trustworthy image of the water structure. We plan to compare deuterated and non-deuterated samples with different extent of hydration as well as ACC samples with two different particle sizes and with or without the presence of magnesium.

PRINCIPLE INVESTIGATOR

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EXPERIMENT DETAILS

Reference Number: 6-06-464
Title: Unraveling the structural ordering of water in amorphous calcium carbonate using neutron pdf-analysis
Equipment/Facility Used: D4

Dates Scheduled: 29 Okt 2015 to 05 Nov 2015 Days: 7

Date of Experimental Report: 26.09.2016

OBJECTIVES AND EXPERIMENT REPORT

Background & Objectives: Calcium carbonates make up some of the most abundant minerals in the world. They are of great importance in geology and in the field of biomaterials as well as having several industrial applications. Despite the high interest, detailed structural information on several calcium carbonates still does not exist. This is especially true for amorphous calcium carbonate (ACC), a kinetically stabilized intermediate, also in biological mineralization. Therefore, solving the structure of ACC would increase our understanding of the formation of complex hierarchical biomaterials. Traditionally this has been attempted with MAS-NMR, EXAFS, RAMAN and many other techniques. However, this only gives information on the closest coordination sphere. By performing Neutron PDF on standardized ACC, we intent to characterize the structure of ACC with emphasis on the structure of water inside the ACC.

Experimental report: To investigate the structure of the water inside ACC, different samples were measured. As a standard ACC we used ACC described in our previous paper (see Zou et al.), which crystallizes in mostly vaterite and a bit of calcite upon solution crystallization. This sample was measured in native state as well as dehydrated and deutorated to visualize the water.

From here on small adaptations were performed including samples obtained after a reverse addition reaction, resulting in only calcite upon crystallization, samples obtained from a reaction at higher concentration (250mM) with only slightly smaller particle sizes but much more Na^{+} incorporated, which result in only vaterite upon crystallization, a reaction at higher pH (pH 13) resulting in the incorporation of a small amount of OH- groups that directs the crystallization towards calcite, and a 10% Mg ACC sample where the addition of 10% Mg^{2+} again directs the crystallization towards calcite.

Unfortunately, the high incoherent scattering of H made the data difficult to reduce and unsuitable for further analysis. Isotope substitution was attempted but samples quickly exchanged D with H when exposed to air. A fully deutorated ACC was produced using a

glovebox, but could not be stabilized in time to give a fully amorphous sample. Hence, the experiment was unsuccessful.

Literature:

Zou et al. Chem. Mater., 2015, 27 (12), pp 4237–4246