Experimental Report

Proposal: **7-04-123** **Council:** 10/2012

Title: Vibrational study of the role of Mg2+ in the increased thermodynamic stability of Mg2+-doped amorphous calcium carbonate

This proposal is resubmission of: 7-04-118

Researh Area: Other...

Main proposer: **FERNANDEZ-MARTINEZ Alejandro**

Experimental Team: FERNANDEZ-MARTINEZ Alejandro
BATAILLE Benjamin

Local Contact: JIMENEZ-RUIZ Monica

Samples: MgxCa1-xCO3 nH2O

Instrument	Req. Days	All. Days	From	To
IN1 LAG	9	8	26/06/2013	30/06/2013

Abstract:

Calcium carbonate (CaCO3) is a widely studied inorganic compound very abundant in nature as a mineral and a bio-mineral. In recent years, it has been observed that the formation of stable crystalline polymorphs of CaCO3 is preceded by the precipitation of an amorphous phase -Amorphous Calcium Carbonate (ACC)-, which contains structural water. ACC is found in the first steps of formation of many organisms. ACC usually contains a small weight fraction of some organic and inorganic additives, whose role is not yet fully understood. One of them, Mg2+, is also known to play a role as stabilizer of the amorphous structure, preventing its crystallization. Here we will test whether this stabilization mechanisms is mediated by enhanced strength of hydrogen bonding of water molecules. The residence time of water in Mg2+ is longer, and thus it is expected that this makes Mg2+-doped ACC more persistent. The IINS technique is perfectly suited to study water librational modes, whose frequencies should be affected in the case of stiffer hydrogen bonding network as the one hypothesized for Mg2+-doped ACC.

ILL EXPERIMENTAL REPORT

Ex N°: 7-04-123

TITLE: Vibrational study of the role of Mg2+ in the increased thermodynamic stability of Mg2+-doped amorphous calcium carbonate

INSTRUMENT: IN1-LAGRANGE

DATES: From: 26/06/2013 To: 30/06/2013

EXPERIMENTAL TEAM:

Alejandro Fernandez-Martinez

Benjamin Bataille

LOCAL CONTACT: Monica Jimenez-Ruiz

Results:

Amorphous calcium carbonate (ACC), the precursor to a wide variety of biominerals, has a highly hydrated and disordered structure. Modeling studies have pointed to an important role of water in the stability of this amorphous phase. However, there is a lack of experimental studies addressing the structure and dynamics of water in ACC. In this experiment, we probed the vibrational density of states of water in a variety of hydrated amorphous calcium and magnesium carbonates using Incoherent Inelastic Neutron Scattering (IINS). These experiments designed with the aim of obtaining dynamical information that can be used to ascertain the stability and the environment of water in the amorphous structures of ACC and Mg-bearing ACC.

TGA and FTIR results revealed that different types of water are present in the structure. The use of IINS is specially interesting, since this technique gives information about the strength of the hydrogen bond network around the hydrated cations. The results indicate that a strong H-bond network is present whose stability is independent on the amount of Mg^{2+} in the ACC. This indicates that water is preferentially coordinated with the Mg^{2+}, revealing a mechanism for the increased kinetic persistence of the Mg^{2+}-bearing amorphous structure.

More experiments will be performed with the aim of completing the dataset and to unveil the dynamics of water in the pure ACC form. This sample (pure ACC) could not be measured

during the first visit to ILL due to difficulties in the transportation (it crystallized during sample handling).

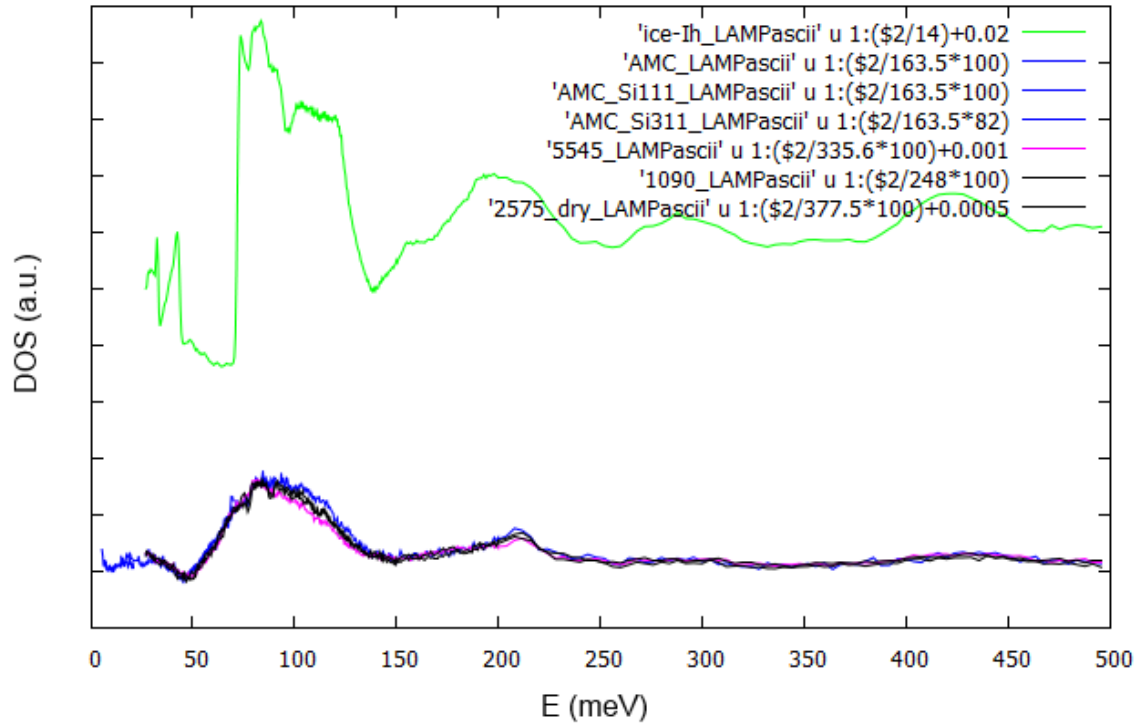

Figure 1. Top (green curve): vDOS of ice Ih. Bottom: vDOS of Mg-bearing ACCs with different Mg contents ranging from pure Mg amorphous carbonate to 10% Mg. Measurements shown here were done with the Cu(220) monochromator. The position of the librational edge (~65 meV, i.e., the start of the librational band of water that ranges from 50 to ~150 meV) does not change with the Mg^{2+} content. This suggests that water is preferentially partitioned with Mg^{2+} and that Ca^{2+} is coordinated with CO_3^{2-}.

A second visit to LAGRANGE will be scheduled for the next cycle due to technical problems during the last cycle that did not allow us to use our full time allocation. Samples with organics such as pAsp will be measured in order to see the effect of the organic on the vibrational properties of water (pAsp is known to prevent crystallization of ACC in short time scales).