	Experiment title: Microscopic dynamics in amorphous calcium carbonate	**Experiment number**: HC-1964
Beamline: ID10	**Date of experiment**: from: 8 July 2015 to: 13 July 2015	**Date of report**: 9 Septembre 2015
Shifts: 18	**Local contact(s)**: Beatrice Ruta, Federico Zontone	*Received at ESRF:*

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Report:

In this experiment, a series of samples of mixed Ca^{2+} - Mg^{2+} amorphous carbonates were studied using the XPCS technique, with the aim of quantifying changes in the atomic dynamics of the solids as a function of their Mg^{2+} content. The working hypothesis used was that the presence of Mg^{2+} slows down the dynamics of the solids, preventing atomic scale reorganization of the amorphous structure and crystallization. The effect of Mg^{2+} as retardant of crystallization has been observed in the laboratory: addition of Mg^{2+} makes the amorphous structure more persistent; our past studies have shown that the amorphous structure becomes also thermodynamically more stable, see (Radha et al., 2012)).

In December 2014 we had the opportunity to make a test experiment with one sample ($MgCO_3 \cdot H_2O$). XPCS measurements were performed at a Q ~ 2.45 $Å^{-1}$ (maximum of the static structure factor). The observed dynamics were too fast to be quantified with the available detector (CCD camera with a reading out time of 1s). It was decided to look at small angle for the actual experiment in July 2015.

The experiment was performed with an incident energy of 8 keV, and a Q range of 0.001 to 0.03 $Å^{-1}$. The first three days of beamtime were devoted to the study of beam damage. Parameters such as beam attenuation, acquisition time and sleeping time after each measurement were varied systematically to prevent beam damage to the sample. An example of 2-times correlation fuctions for an amorphous sample with 50% Mg^{2+} in the solution synthesis (real Mg^{2+} concentration remains to be determined at our lab, but it is expected at ~25%, i.e., sample stoichiometry is close to $Ca_{0.75}Mg_{0.25}CO_3 \cdot H_2O$, sample '5050') is shown in Figure 1.

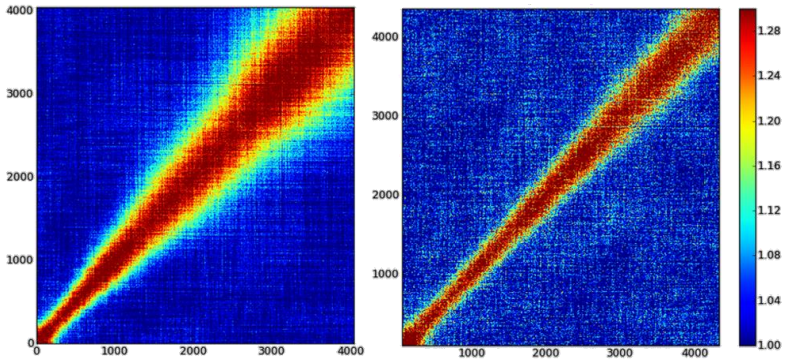

Figure 1*. 2-times correlation function for sample 5050 using acquisition times of 0.16 s (left) and 0.08 s (right), measured at q = 0.022 Å). Significant 'aging' is observed in the left graph, with relaxation times increasing one order of magnitude. The effect is reduced when reducing the dose (sleeping time was increased to keep same time lapse between two consecutive images).*

Besides this aging effect, that could be due to beam damage, another aging effect was observed when measuring the same sample at different spots, and even when measuring the same sample after three days in the dessicator. This is exemplified in Figure 2, in which two intensity autocorrelation functions are shown for the sample of Amorphous Magnesium Carbonate (AMC: $MgCO_3 \cdot H_2O$). The difference between these two measurements is just that one was performed 4 days before the other. In the meantime, the sample was stored in a dessicator. It is well known that the water content of these solids is variable, and it depends on the external relative humidity.

These results suggest the hypothesis that the presence of water in the structure has a strong influence on the microscopic dynamics of these amorphous materials. These effects will be studied systematically in a forthcoming experiment (proposal submitted on September 2015) using samples with different degrees of hydration. μ-FTIR will be used at our lab to quantify the amount of water for each sample before and after the experiments.

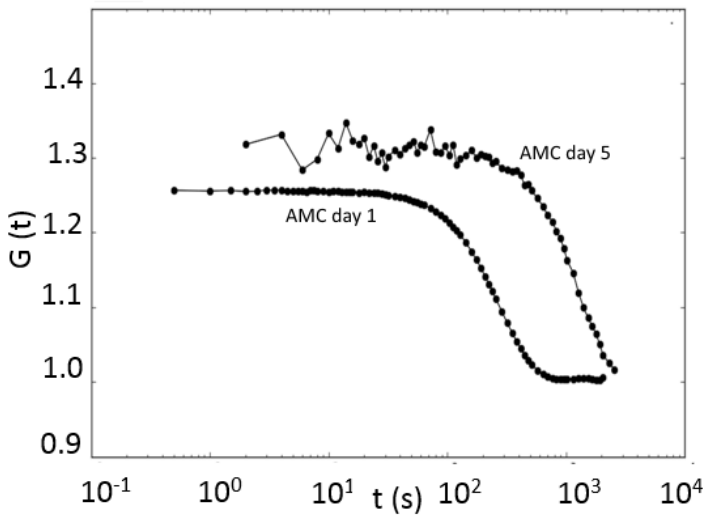

Figure 2*. Intensity autocorrelation functions of AMC measured on day 1 after synthesis and at day 5. The sample was stored in a dessicator.*

References

Radha A. V, Fernandez-Martinez A., Hu Y., Jun Y. S., Waychunas G. A. and Navrotsky A. (2012) Energetic and Structural Studies of Amorphous Ca1-xMgxCO3 nH2O ($0 \leq x \leq 1$). *Geochim. Cosmochim. Acta* **90**, 83–95.