The role of Mg in the formation of monohydrocalcite

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Monohydrocalcite (MHC, $CaCO_3 \cdot H_2O$) is a calcium carbonate mineral which forms by biological and abiotic processes in a number of environments including caves or lake-bed sediments. MHC often forms in Mg-rich aqueous environments, but is metastable with respect to aragonite and calcite [1]. However, the mechanisms of its formation and the role or effect of Mg on its nucleation and growth are not understood. Hence, using a combination of *in situ* and real-time synchrotron-based scattering and off-line micro-spectroscopic characterization, we followed and quantitatively assessed the formation mechanism of MHC.

Experiments were carried out by mixing equimolar Ca, Mg and CO_3 solutions (0.7:0.3:1) and reacting them at 21°C for 12 hours. The MHC crystallisation reaction was followed *in situ* (1 min/frame) using Small and Wide Angle Scattering (SAXS/WAXS, Diamond Light Source, UK), and equivalent off-line experiments were quenched at various times for solids and solution analysis.

The WAXS profile (Fig. 1 main plot) revealed after ~ 50 minutes MHC crystals grew via a two-step reaction. Step 1 is the transformation of a poorly-ordered amorphous calcium carbonate precursor (inset 1) into MHC nanocrystals (inset 2). This stage is followed by a second growth step after ~8.5 hr of reaction (inset 3) which occurs concomitantly with the formation of minor hydromagnesite (HMg). The combined on- and off-line data have allowed us to elucidate the key role of Mg^{2+} in both the precursor stabilization as well as in the structure, crystallinity and growth mechanisms of MHC.

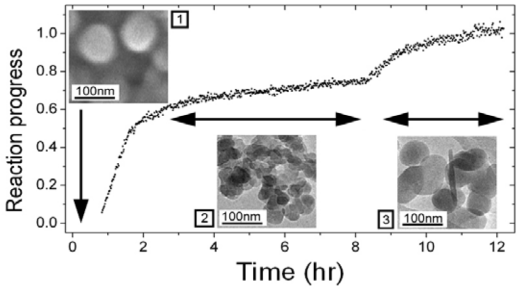

Figure 1: Reaction progress profile (***1***) precursor (***2***) MHC spheres at 3 h (***3***) MHC and HMg (plates) at 11 hr.

[1] Munemoto and Fukushi (2008) *Journal of Mineralogical and Petrological Sciences* **103**, 345-349.

High-pressure phases and dynamical properties of $ZnAl_2O_4$ and $ZnGa_2O_4$

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The structural dependence of oxide spinel AB_2O_4 compounds (A: divalent cation and B: trivalent cation) under pressure has received a lot of attention, mainly due to their occurrence in many geological settings of the Earth's crust and mantle, as well as in lunar rocks and meteorites. Many AB_2O_4 compounds crystallize in the cubic spinel structure (*Fd*3*m*), exemplified by $MgAl_2O_4$. In this work, we report first-principles calculations of the structural, electronic, and vibrational properties of the cubic spinels $ZnAl_2O_4$ and $ZnGa_2O_4$ compounds under hydrostatic pressure. Besides, we report the variation in the structural parameters under pressure and compare directly with recent experimental results. Finally, we study the possible pressure induced structural phase transitions for both compounds that have been confirmed from X-Ray diffraction experiments [1] and from *ab initio* studies [2]. Total energy calculations were done within the framework of the density functional theory (DFT) and the projector-augmented wave (PAW) method. The exchange and correlation energy was described within the local density approximation (LDA). We use a plane-wave energy cutoff of 500 eV to ensure a high precision in the calculations. Monkhorst-Pack scheme was employed for the Brillouin-zone (BZ) integrations with dense meshes to ensure convergence. We will report the Raman and IR phonon modes as well as the pressure coefficients and Grüneisen parameters of the spinel structure and the pressure dependence of the Raman and IR active modes in other high-pressure structures.

[1] Errandonea, D. Kumar, R.S. Manjon, F.J. Ursaki, V.V. & Rusu, E.V. (2009) *Phys. Rev. B* **79**, 024103. [2] López, S. Romero, A.H. Rodríguez-Hernández. P. & Muñoz, A. (2009) *Phys. Rev. B* **79**, 214103.