

The Mechanism of Monohydrocalcite formation

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Monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$) is a rare and unique CaCO_3 phase, which often forms as an intermediate to calcite and aragonite in a variety of environments including lacustrine deposits, mine galleries, limestone-dolomite caves and marine polar areas [1]. In these settings, monohydrocalcite is frequently associated with other Ca-Mg carbonates including Mg-calcite, Ca-rich dolomite, hydromagnesite or nesquehonite [1]. Monohydrocalcite has also been found as a biomineral in living organisms where biogenic amorphous calcium carbonate (ACC), a precursor of crystalline CaCO_3 , has also been found [2,3]. However, so far the main factors controlling the formation and stability of monohydrocalcite are as yet unknown.

In this work we present a study in which we elucidated (i) the mechanisms of monohydrocalcite formation from solution; and (ii) the role of Mg during its crystallization. We have followed the nucleation and crystallization reactions in real-time using *in situ* synchrotron-based small and wide angle X-ray scattering (SAXS/WAXS). We complemented the scattering data with off-line spectroscopic, microscopic and wet chemical analyses of reaction products during the monohydrocalcite formation stages. These include conventional X-ray diffraction, high-resolution transmission electron microscopy, thermogravimetric analysis and aqueous solution analysis. This way we characterized both the resulting solids and equivalent solution at every step in the reaction.

Our results show that the formation of monohydrocalcite takes place via a 4-stage process that starts with the formation of an Mg-rich ACC precursor. This amorphous precursor crystallized to monohydrocalcite through a dissolution-reprecipitation reaction, with monohydrocalcite forming via a constant nucleation process. The so formed monohydrocalcite further ages through Ostwald-ripening. The kinetics of these reaction stages are essentially driven by the Mg/Ca ratio and the initial supersaturation of the aqueous solution. These parameters also control the chemical composition of monohydrocalcite (i.e., the Mg/Ca ratio, hydration), its crystallite size, unit-cell dimensions, particle size and shape. Furthermore, the transformation pathways into more stable Ca(Mg) carbonates (calcite or aragonite) is also dependent on the Mg/Ca ratio in the solids and the $\text{Mg}_{(aq)}$ in the supernatant solution. Interestingly, our data reveal that monohydrocalcite forms at conditions (Mg/Ca ratio in solution, supersaturations) that are equivalent to many other biogenic carbonates [4]. Therefore we hypothesize that some (Mg)-calcite and aragonite deposits in the geologic past that have formed through biomineralization could indeed be secondary in origin and may have been originally formed via a metastable monohydrocalcite intermediate.

[1] Taylor (1975) *American Mineralogist*, **60**, 690-697.

[2] Señorale-Pose et al (2008) *Experimental Parasitology*, **118**, 54-58.

[3] Rodriguez-Blanco et al (2008) *Mineralogical Magazine*, **72**, 283-286.

[4] Kimura and Koga (2011) *Crystal Growth & Design*, **11**, 3877-3884.