

Effect of magnesium on monohydrocalcite formation and unit-cell parameters

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ABSTRACT

Monohydrocalcite (MHC) is hydrated calcium carbonate, which plays an active role in many geological processes, carbonate biomineralization, and can be used for fundamental science (as a paleoenvironmental indicator) and industry (for removal of hazardous anions). Despite a great number of works, the conditions preferable for MHC formation/stabilization and MHC crystal chemical patterns in relation to Mg and H₂O are not clarified yet. In the course of current work, we conducted 38 syntheses to obtain information on MHC formation at different Mg/Ca ratios (0–12), pH (~9–12), and temperature (23 and 3 °C). Newly formed carbonate precipitates were studied by means of X-ray powder diffraction, optical, and scanning electron microscopy, energy-dispersive X-ray spectroscopy, Raman, and Fourier-transform infrared (FTIR) spectroscopies. The phase diagram for MHC, calcite, aragonite, and dypingite as a function of pH and Mg concentration in solution at $T = 23$ °C and $\text{Ca}/\text{CO}_3 = 0.5$ was obtained. We demonstrated that MHC could be stable in dry conditions for up to two years and that the time of crystallization is important for the transformation of amorphous calcium carbonate to MHC. Our results on synthetic MHC stability show that the widespread idea that MHC is a short-lived intermediate phase is wrong. For the first time, on the basis of a regular changes in the unit-cell parameters the possibility of significant incorporation of magnesium in MHC has been demonstrated. According to FTIR data, it is shown to be accompanied by an increase in the water content, which leads to multidirectional change in a and c MHC parameters.

Keywords: Monohydrocalcite, aragonite, dypingite, amorphous Ca carbonate, phase diagram, Mg/Ca