



Chemical characterization of amorphous calcium magnesium carbonates

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The formation of crystalline calcium carbonate minerals (e.g. calcite and aragonite) via an amorphous calcium carbonate (ACC) precursor represents an alternative pathway for calcium carbonate formation in biotic and abiotic environments. Magnesium ions are well-known to play a significant role in the temporal stabilization of ACC and the presence of Mg-rich ACC has been documented for a variety of biominerals [1]. More recently, it has been suggested that amorphous calcium magnesium carbonates ($\text{Ca}_{(1-x)}\text{Mg}_x\text{CO}_3$) with near 50 mol% Mg may serve as proto-dolomite precursors in modern hypersaline settings [2]. Considering that the formation of amorphous $\text{Ca}_{(1-x)}\text{Mg}_x\text{CO}_3$ is of huge relevance in many natural surroundings, rigorous experimental work is needed to systematically describe their chemical composition, occurrence and metastability. In the present study amorphous $\text{Ca}_{(1-x)}\text{Mg}_x\text{CO}_3 \cdot n\text{H}_2\text{O}$ was synthesized in the range $0 \leq x \leq 1$ in order to examine the elemental distribution between the solid phase and the precipitating solution as well as to investigate the relation between chemical composition and water content of the solids. Our results show a preferential uptake of Ca versus Mg in the amorphous phase. This behavior stems from the strong free energy of hydration of the Mg^{2+} ion compared to Ca^{2+} . The thermogravimetric analyses of the amorphous $\text{Ca}_{(1-x)}\text{Mg}_x\text{CO}_3 \cdot n\text{H}_2\text{O}$ reaction products revealed a linear correlation between the Mg content of the amorphous solid and the $n\text{H}_2\text{O}$ content with the values of the latter to continuously increase from the ACC end-member to amorphous MgCO_3 . Our results can numerically describe the chemical composition of amorphous $\text{Ca}_{(1-x)}\text{Mg}_x\text{CO}_3 \cdot n\text{H}_2\text{O}$ with respect to the composition of the forming solution and thus have significant implications for the characterization of amorphous precursors in biotic and abiotic precipitation environments.

[1] Politi Y., Batchelor D. R., Zaslansky P., Chmelka B. F., Weaver J. C., Sagi I., Weiner S., and Addadi L. (2010). *Chem. Mater.* **22**, 161-166

[2] Rodriguez-Blanco J. D., Shaw S. and Benning L. G (2015). *American Mineralogist* **100**, 1172-1181