

## Solubility Consideration on the Amorphous Calcium Magnesium Carbonate System

B. PURGSTALLER<sup>1</sup>, K. GOETSCHL<sup>1</sup>, V. MAVROMATIS<sup>1</sup>,  
C. PFARRMAIER<sup>1</sup> AND M. DIETZEL<sup>1</sup>

<sup>1</sup>Institute of Applied Geosciences, Graz University of  
Technology, Rechbauerstraße 12, 8010 Graz, Austria  
(\*correspondence: [bettina.purgstaller@tugraz.at](mailto:bettina.purgstaller@tugraz.at))

Earlier experimental studies have shown that calcium carbonate formation from a highly supersaturated solution proceeds via the formation of an intermediate amorphous phase. With respect to natural environments, the presence of amorphous calcium carbonate (ACC) has been observed in various calcifying organisms and in aqueous settings where high local supersaturation degrees with respect to carbonate minerals are induced in particular by microbial metabolism. In this context, it has been suggested that Mg ions play a significant role in temporarily stabilizing ACC. Although ACC can incorporate various amounts of Mg, the solubility of Mg-rich ACC was not yet determined.

In order to shed light on the solubility of the amorphous calcium magnesium carbonate system, amorphous  $\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 \cdot n\text{H}_2\text{O}$  (ACMC) with  $0 \leq x \leq 1$  and  $0.5 \leq n \leq 1.0$  was synthesized by mixing equimolar solutions of  $\text{Na}_2\text{CO}_3$  and  $(\text{Ca,Mg})\text{Cl}_2$ . Subsequently, the freeze-dried ACMC was dispersed into a stirring glass reactor containing a  $\text{MgCl}_2$ - $\text{NaHCO}_3$  buffer solution ( $\text{pH} = 8.3$ ;  $T = 23.5 \pm 0.5^\circ\text{C}$ ). The mineral composition of the suspension was monitored by *in situ* Raman spectroscopy. In order to follow the chemical composition of the solution and precipitate, homogeneous sub-samples of the experimental solution were collected at certain reaction times.

The results reveal a significant change in the molar Mg/Ca ratio of the solution and solid, only 10 sec after ACMC was dispersed into the experimental solution, indicating a dynamic exchange between the amorphous solid and the aqueous solution. The calculated ion activity products for ACMC clearly document that the solubility of ACMC increases as a function of the Mg content. *In situ* Raman results show that the lifetime of ACMC in aqueous solution does not increase at elevated Mg content of the ACMC. In contrast, the lifetime of ACMC is mainly controlled by the chemical composition of the experimental solution, e.g. its aqueous Mg concentration. Obtained results are discussed in the light of published literature data on ACC solubility and formation conditions of ACMC in biogeochemical settings.