

Probing the amorphous-to-crystalline transition in the calcium-magnesium carbonate system as a function of time and temperature

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Summary

Calcium-magnesium carbonate minerals are known to form via a non-classical pathway from amorphous precursor phases. Previous work has focused on characterizing these amorphous phases [1][2], but little is known about how the composition of amorphous calcium magnesium carbonate (ACMC) influences (1) rate of crystallization and (2) which crystalline solids are ultimately produced. We synthesized ACMC with different molar ratios of Ca and Mg to study the impact of stoichiometry on the crystallization rate, final elemental compositions, and crystal structures of carbonate minerals.

We determined the chemical formula for each ACMC sample (n=6, with compositions from 0–100 mol% Mg), including hydration state, using inductively coupled plasma mass spectrometry (ICP-MS), thermogravimetry (TGA) and differential scanning calorimetry (DSC). We examined the crystallization of ACMC as a function of time at two temperatures (i.e., 20–23°C and 75°C). During the first few weeks, X-ray diffraction (XRD) was used to analyze high temperature samples daily and low temperature samples weekly. Samples that had been incubated for at least 3 months were analyzed with scanning electron microscopy (SEM). Our XRD and SEM results show that the crystallization of calcium carbonate polymorphs (calcite, aragonite and vaterite, CaCO₃) from ACMC was much faster than formation of magnesium carbonates. ACMC samples with higher mol% Ca crystallized calcium carbonates quicker, from one day (100 mol% Ca) to 10 weeks (61 mol% Ca) at room temperature. Mg-carbonate minerals like hydromagnesite formed more quickly from Mg-rich than Mg-poor ACMC, but the shortest crystallization period still took 8–10 weeks at room temperature. The Mg/Ca ratio was an important parameter controlling mineralogy, especially for determining which of the calcium carbonate polymorphs formed; stoichiometric calcite and vaterite were only found together in 100 mol% Ca samples and aragonite formed only in 15–53 mol% Mg samples. The crystallization products of amorphous carbonates depend on the initial Mg/Ca ratio such that final mineral assemblages can be used to determine the identity of precursor phase. At 75°C, the tendency for Mg to substitute for Ca in the calcite group structure increased, producing an assemblage of aragonite, hydromagnesite and VHMC more commonly than at room temperature. In addition, higher temperature incubations allowed for the formation of magnesite, and sped up all crystallization rates. Although this research was based on ideal laboratory experiments, it provides new insights into the complex carbonate mineralogy of natural systems such as carbonate playa lakes and formation of carbonate sediments at the seafloor.

REFERENCE

- [1] Purgstaller et al. (2019) CrystEngComm 21, 155–164.
- [2] Rhada et al. (2012) GCA 90, 83–95.

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