

Crystallization of amorphous Ca-, Ca-Mg, and Mg- Carbonates in water-limited systems

AVNIS PATEL¹, MAIJA RAUDSEPP², SIOBHAN A. WILSON² AND ANNA HARRISON³

¹University of Alberta - EAS

²University of Alberta

³Géosciences Environnement Toulouse

Presenting Author: avni1@ualberta.ca

Ca- and Mg-carbonate minerals are pervasive in the geological record and represent important paleoarchives and vast reservoirs for long-term CO₂ storage. Amorphous Ca-, Ca-Mg- and Mg-carbonate (ACC, APMC and AMC, respectively) are important precursors to crystalline carbonate minerals in low-temperature environments that may be kinetically inhibited. These amorphous phases undergo stepwise re-crystallization, typically via several metastable intermediates, until the most stable crystalline configuration is reached. The crystallization pathways of amorphous carbonates are diverse and often result in multi-phase carbonate assemblages. It is known that the lifetime of the amorphous precursors and the phases forming along these transformation pathways are controlled by [Mg], pH, temperature and alkalinity. However, few studies have considered the effect of water activity on crystallization rates and pathways. In this study, we synthesized amorphous Ca_{1-x}Mg_xCO₃·nH₂O (APMC) with variable compositions (0 ≤ x ≤ 1) at 21.0 ± 0.8 °C. The dry amorphous solids were placed under relative humidity (RH) conditions of 2, 29, 53, 75 and 100 ± 2% for up to 210 days. Results from X-ray Diffraction analysis show preservation of the amorphous phase for compositions 20% < MgCO₃ ≤ 100% at RH ≤ 53% for the duration of the experiment. At 75% RH, the amorphous–crystalline transformation occurs within 210 days for both Mg-rich and Mg-poor APMC; however, APMCs with compositions of 30% < MgCO₃ < 80% do not transform over the experimental duration. At 100% RH, crystallization is observed within 14 days of reaction, which indicates that crystallization is significantly accelerated at RH >75%. The first phases to crystallize at 100% RH are highly hydrated Ca- and Mg-carbonates and very high Mg-carbonate (VHMC); these hydrated carbonate phases gradually transform into aragonite, dypingite and hydromagnesite. Notably, we also observe distinct spatial segregation on the micrometre scale of Ca-rich and Mg-rich phases at 100% RH. These findings offer new insights on cation transport and mineral phase transitions mediated by adsorbed water films. Reactions in thin films of water are key to understanding mineralogy and element cycling in important water-undersaturated systems including carbonate deposits on Earth and Mars, CO₂ sequestration projects, and cement and concrete infrastructure.