Towards a mechanistic understanding of the transformation of amorphous calcium magnesium carbonate to high magnesium calcite

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Calcite containing >4 mol% $MgCO_3$ is typically referred to as high magnesium calcite (HMC). Although HMC with > 10 mol% $MgCO_3$ is thermodynamically unstable under ambient conditions, skeletal HMC with up to 40 mol% $MgCO_3$ and inorganic HMC cements near to dolomite-stoichiometry can be found in modern marine environments. Several studies documented that the classical model of crystal growth cannot explain the formation of such HMC. Recent literature, however, suggests that the formation of HMC via the transformation of an amorphous calcium magnesium carbonate (ACMC) phase overcomes the limitations imposed by the classical terrace-ledge-kink crystal growth model. In the latter case, a large gap of knowledge exists with respect to the mechanisms involved during this transformation process.

In the present study, the transformation of ACMC to HMC was experimentally studied by dispersion of synthesized ACMC standard material with 48 ±1 mol% $MgCO_3$ into a $NaHCO_3$-$MgCl_2$ solution. Experiments were performed under controlled pH conditions (pH 7.6 ±0.2) in the temperature range from 10 to 80°C. X-ray diffraction patterns showed that the reaction products in experiments performed at 10 to 60°C consist of HMC, while at 80°C additionally hydromagnesite and aragonite were found. The Mg content of the final HMC increases from 15 to 40 mol% $MgCO_3$ with increasing temperature, thus it is significantly lower than the Mg content of the ACMC precursor. Our results suggest that the transformation of ACMC into HMC takes place via a dissolution-reprecipitation process and is strongly controlled by the Mg/Ca ratio of the reactive solution rather than by the precursor material. In our experiments, the incorporation of Mg in calcite is favored at higher temperatures most likely due to the faster dehydration kinetics of the aqueous Mg^{2+} ion at high versus low temperature. These observations suggest that the ACMC precursor is not a prerequisite for the formation of HMC, but can provide aqueous surroundings suitable for its formation.