NANO-SCALE INVESTIGATION OF AMORPHOUS Ca-Mg CARBONATE BY STEM

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Amorphous calcium carbonate (ACC) is a highly soluble mineral phase that commonly occurs as a precursor of calcite and aragonite in modern biotic and abiotic precipitation environments (ADDADI et al., 2003). Considering that the formation of ACC is of high relevance in many natural surroundings and of eminent concern for medical and industrial applications (MATSUNUMA et al., 2014), the effect of environmental factors, such as temperature, pH and organic and inorganic additives, on the stability and transformation pathway of ACC was investigated in numerous studies. Special focus therein was given on investigating the incorporation of Mg^{2+} ions in ACC, because Mg^{2+} plays an important role in the temporal stabilization of both natural and synthetic ACC. Although the molecular structure of amorphous calcium magnesium carbonate (ACMC) was recently studied, significant gaps in knowledge exist with respect to the distribution of Mg^{2+} and Ca^{2+} ions in the ACMC structure on the nano-scale. Thermogravimetric results of a previous study on synthetic ACMC by RADHA et al. (2012) point towards the presence of discrete $MgCO_3$ phases in the ACMC crystals. Such heterogeneity could be induced during the heating process (thermally driven $MgCO_3$ segregation), but may also be valid for the amorphous nano-particles.

In order to assess the chemical heterogeneity of ACMC on the nano-scale, amorphous $Ca_{0.89}Mg_{0.11}CO_3{\cdot}0.46H_2O$ (ACMC_11) and $Ca_{0.46}Mg_{0.54}CO_3{\cdot}0.60H_2O$ (ACMC_54) materials were synthesized by a batch method using $(Ca,Mg)Cl_2$ and Na_2CO_3 solutions and analysed by STEM coupled with EDX. TEM images of ACMC_11 and ACMC_54 reveal spheroidal particles with a size range from 30 to 90 nm. Based on TEM observation, ~14 individual spheroidal particles of ACMC_11 and ACMC_54, respectively, were examined by EDX. The EDX results reveal that the average Mg content of the spheroidal particles is 12.7 ±3.6 mol% for ACMC_11 and 63.4 ±7.7 mol% for ACMC_54, which is in good agreement with the Mg content determined by ICP-OES analyses of the digested solids of ACMC_11 (11.4 ± 0.6 mol%) and ACMC_54 (53.9 ±2.7 mol%). Overall, the results did not confirm the presence of discrete $MgCO_3$ and $CaCO_3$ particles in the ACMC solids. In contrast, our findings suggest that the distribution of Ca^{2+} and Mg^{2+} ions in the ACMC solids is compatible with the concept of an “amorphous solid-solution”, which has significant implications for developing transformation mechanisms as well as strategies for industrial applications.

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