

Experimental and theoretical determination of the density of amorphous Ca/Sr carbonate solid solutions

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Minor or trace element incorporation in minerals is of interest to both industrial and environmental applications. Charge density and size of the impurity generally determine the stability of the mixed phase. This solid solubility of minority components is well-studied for many crystalline systems, enabling predictive models of element fractionation into the solid. In the case of carbonate minerals, however, formation of metastable intermediates prior to crystallization significantly affects the impurity concentration in the final crystalline products. For example, Sr and Mg solubilities in calcite (CaCO_3) are greatly enhanced when the mineral forms via amorphous calcium carbonate (ACC) relative to direct formation. Thus, a physical understanding of ACC properties as a function of composition is crucial to developing a quantitative predictive model of these amorphous solid solutions and how they may control the solid compositions upon transformation to more stable phases.

In this study, we measure the composition, structure, and density of an amorphous Sr/Ca carbonate solid solution using thermogravimetry, inductively coupled plasma mass spectroscopy, small-angle X-ray scattering, and X-ray pair distribution function analysis. Results indicate non-linear water content of the amorphous solid as a function of cation composition. Density measurements demonstrate this non-linearity collapses onto a single trend, however, when the molecular volume is plotted against both cation and water composition. This suggests amorphous carbonate density can be predicted from the composition in the Ca-Sr-H₂O-CO₃ system, akin to crystalline carbonates. Additional work is underway to determine the atom-level mechanism that enables additive molecular volumes in an amorphous solid solution using ab initio molecular dynamics models. Initial results from simulations reproduce experimental trends. Using advanced computational models together with high-resolution synchrotron X-ray scattering experiments, our work provides important insights into how solid solutions in amorphous materials enable greater compositional compatibility while retaining the fundamental volumetric constraints observed in crystalline materials.