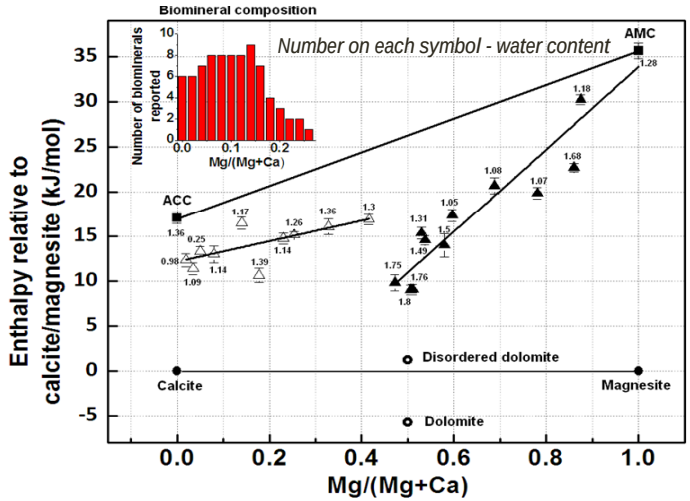
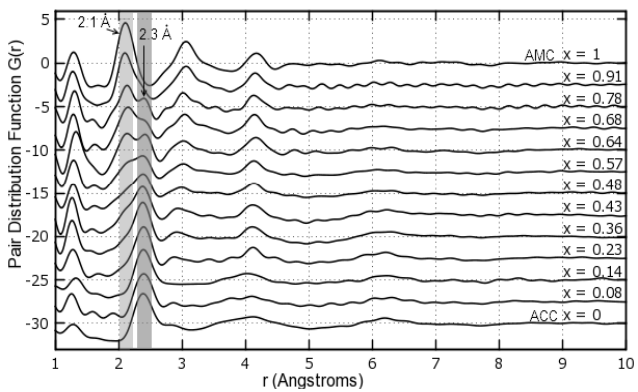
Energetic and structural studies of amorphous $Ca_{1-x}Mg_xCO_3 \cdot nH_2O$ ($0 \le x \le 1$)

By isothermal acid solution calorimetry and synchrotron X-ray scattering with pair distribution function (PDF) analysis



Relative stabilities of amorphous $Ca_{1-x}Mg_xCO_3 \cdot nH_2O$. Inset is a histogram of number of binominals as function of their Mg contents. Open triangles - homogeneous single phase and filled triangles - heterogeneous two phase region



The PDFs of amorphous $Ca_{1-x}Mg_xCO_3 \cdot nH_2O$, Arrows indicate the first O neighbor correlations for Ca and Mg

Scientific Achievement

This work documents the thermodynamic underpinnings for significant amounts of Mg inclusion in many sedimentary and biogenic calcium carbonate minerals. The Mg containing amorphous carbonate precursors are shown to provide a low energy pathway in the early stages of mineralization that has implications for biominealization and dolomite formation.

Significance and Impact

The energetic study indicates that organisms take advantage of a single phase low energy amorphous precursor pathway to crystallize biogenic carbonates. There are some thermodynamic clues for the existence of an amorphous precursor for dolomite that support previous observations. The thermodynamic data from this study help in geochemical modeling studies for reactions relevant to CO_2 sequestration.

Research Details

Calorimetric studies: *Amorphous $MgCO_3$ (AMC) is more metastable than ACC but more persistent. All intermediate compositions are more stable than a mixture of ACC and AMC*

- *There are two distinct regions of amorphous $Ca_{1-x}Mg_xCO_3 \cdot nH_2O$ ($0 < x < 1$) phases: homogeneous single phase ($x < 0.47$) and heterogeneous two phases ($x > 0.47$)*
- *There are two distinct amorphous precursors: a) $x = 0 - 0.2$ is a less metastable single phase frequently found in biogenic carbonates and b) $x \sim 0.5$ is least metastable and most hydrated, could be a dolomite precursor*

Synchrotron X-ray scattering and PDF analysis: *$Ca_{1-x}Mg_xCO_3 \cdot nH_2O$ ($0 \le x \le 1$) forms a continuous X-ray amorphous series. The short range order in these phases is limited to about 1 nm. but the structural heterogeneity leading to the two observed energetic regions may occur at longer length scales*

A.V. Radha, A. Fernandez-Martinez, Y. Hu, Y. Jun, G.A. Waychunas, A. Navrotsky, Geochimica et Cosmochimica Acta 90 (2012) 83–95