

## **Geochemistry of calcite grown from seawater on a substrate at sub-micron spatial resolution.**

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Precipitation of calcium carbonate minerals and their geochemistry was extensively studied for the last few decades because of importance of naturally occurring carbonates as paleorecorders. The most of those studies employed bulk experimental approach where batches of small crystals were examined for their morphological, crystallochemical, and geochemical properties. However, in case of precipitation of multiphase  $\text{CaCO}_3$  missing one or more of non-abundant ( $<1\%$ ) a  $\text{CaCO}_3$  phase is possible, for example if bulk X-ray diffraction is used. Therefore, geochemical analyses of  $\text{CaCO}_3$  mineral mixture can yield significant offset from geochemistry of an individual phase. For example presence of 1% of aragonite in 99% calcite causes elevation of Sr content to about factor of two compare to Sr in 100% calcite bulk. In the present work experiments on crystals growth were conducted on calcite substrate in order to eliminate nucleation effect on crystal structure and geochemistry of the precipitated carbonate mineral. Unlike other *in situ* studies we anticipate to present not only element:calcium ratios but also partition coefficients between calcite and seawater.

Experiments proceeded for 1 and 8 months where high magnesium (high-Mg) calcite was grown on low magnesium calcite substrate and *in situ* techniques were applied to evaluate elemental partitioning between calcite and artificial seawater. Seawater saturation states with respect to calcite were elevated by addition of  $\text{Na}_2\text{CO}_3$  aliquots and varied from 5.6 to 19.2 in initial fluids (before crystallization started). After a month of experimental duration one cleavage fragment was collected from each of the five runs, mounted into epoxy to expose sections parallel to calcite growth direction, and examined with micro-Raman spectroscopy and scanning electron microscopy (SEM). Experiments were continued for the next 7 months and rare earth elemental spikes were introduced to mark growth zones and determine calcite growth (extension) rate. Overgrowth layers on calcite surface perpendicular to growth direction were examined with LA-ICP-MS using depth profiling technique.

In four experiments micro-Raman spectroscopy yielded that the rims of calcite substrates contains both calcite and aragonite minerals. SEM examination with energy dispersive spectroscopy (EDS) and electron backscattered diffraction (EBSD) yielded thin ( $< 5$  microns) layer of high-Mg calcite ( $\text{Mg}=1.35\pm 0.13$  wt%,  $\text{Sr}=0.07\pm 0.03$  wt%) coating the substrate and chunks of aragonite (up to 20 micron in length) ( $\text{Mg}=0.09\pm 0.02$  wt%,  $\text{Sr}=0.98\pm 0.05$  wt%) adjacent to calcite substrate or high-Mg calcite overgrowth. Morphology of aragonite changed with decreasing of seawater saturation state from fibrous to monocrystalline. Presentation of successfully collected LA-ICP-MS data (Li, B, Mg, Al, Ca, Mn, Cu, Zn, Sr, Y, La, Ce, Nd, Sm, and U), partition coefficients between calcite overgrowth and seawater, and calcite growth rates are anticipated.