

Uptake of ammonium and nitrate by calcium carbonate polymorphs

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The abundance of nitrogen ionic species in natural waters is linked to drivers of environmental change at the global and local scale throughout the anthropogenic era. The potential for calcium carbonate minerals, as a resistant host material, to record the reactive nitrogen composition of natural waters is driving a requirement to understand incorporation mechanisms, and for developing absolute analytical techniques which operate at the micron scale. To assess the capacity of calcium carbonate in the uptake of dissolved nitrogen compounds, we conducted an experimental study on ammonium and nitrate incorporation into inorganic carbonate crystals. Calcium carbonate polymorphs were synthesized in nitrogen containing growth media and used to quantify nitrate and ammonium uptake by calcium carbonates. Calcite crystals were typically presented as rhomboids; aragonite and vaterite formed hemispherical bundles of needle like crystals radiating outward from the center (spherulites). Calcite, aragonite, and vaterite were identified with powder X-ray diffraction and Raman spectroscopy on individual crystals/spherulites. Nitrate and ammonium concentrations in post experimental products (solids and liquids), were analyzed with automated colourimetry (SEAL AQ2 analyzer). Secondary ion mass spectrometry (SIMS) was used to assess the degree of heterogeneity in nitrogen partitioning within individual carbonate crystals and thus the suitability of the technique for establishing carbonate polymorph standards for calibration of SIMS and the enabling of absolute nitrogen concentrations in the carbonate palaeorecord at the micron scale. Nernst partition coefficients (D) were calculated as a ratio of ammonium or nitrate in CaCO_3 to ammonium or nitrate in growth media.

Our experimental study revealed:

- 1) Although calcite crystals are highly heterogeneous, a calibration curve was developed using AQ-2 and SIMS data of multiple synthetic calcite samples with $R^2 > 0.99$;
- 2) Individual large aragonite spherulites are much more homogeneous than calcite crystals and can be used as a carbonate reference material with precision $< 10\%$;
- 3) Ammonium is more compatible with vaterite ($D=0.009$) and especially with aragonite ($D=0.01-0.028$) compared to calcite ($D=0.002-0.006$);
- 4) Nitrate is much more compatible with calcite ($D=0.02-0.7$) compared to ammonium.

