

Effect of solution saturation state on diopside dissolution

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Among all the physico-chemical variables that control mineral dissolution, the effect of solution saturation state has received the least attention. At present, two rate laws have received wide applicability. One rate law invokes etch pit nucleation at dislocations at a critical degree of undersaturation and the other is based on a cation exchange mechanism. In this study, the dissolution rate of diopside is measured as a function of temperature, pH, and solution saturation state using a flow-through reactor. Insights into the dissolution mechanism are gathered by imaging freshly cleaved diopside surfaces undergoing dissolution with hydrothermal Atomic Force Microscopy and Vertical Scanning Interferometry. At 150°C and pH 7.5, the dissolution rate is found to be congruent with respect to Ca, Mg, and Si. Dissolution rate continuously decreases, without reaching any apparent dissolution plateau, as solution conditions approach equilibrium. A generalized rate law for diopside dissolution will be presented.

Preliminary experimental results for ¹⁸O and ¹³C uptake in calcite and at 32°C and various precipitation rates

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Experimental studies have revealed that the growth rate of calcite affects the uptake of trace and minor elements into the crystal lattice [1-3]. The factor(s) responsible for this disequilibrium effect might also apply to stable isotope incorporation during calcite growth; however, this particular suggestion [4] has yet to be confirmed by experiment. Oxygen-18 and ¹³C contents of carbonates (expressed as ¹⁸O/¹⁶O and ¹³C/¹²C) are widely used in paleothermometry, yet it is clear from comparison of experimental results and marine samples that chemical (isotopic) equilibrium is not always maintained in nature. This observation underscores the importance of exploring possible effects of growth rate on isotopic fractionation, which is the focus of this study.

We controlled the rate of calcite precipitation by injecting solutions of CaCl₂ and Na₂CO₃ into a NaCl solution at different speeds using a syringe pump. Mass spectrometric analysis of the resulting samples revealed that δ¹⁸O dropped from -12 to -15‰ with increasing injection rate from 7.23·10⁻¹⁰ to 7.20·10⁻⁷ mol/min and remained constant over further increases in rate. Carbon-13 also decreased from -1.6 to -2.8‰ over a pumping rate increase from 7.23·10⁻¹⁰ to 7.20·10⁻⁷ mol/min, but returned to -1.6‰ at a pumping rate of 2.3·10⁻⁵ mol/min. These trends (decreasing δ¹⁸O and δ¹³C with increasing calcite growth rate) are not inconsistent with growth entrapment of an isotopically distinct near-surface region of the calcite crystals: if the rate of calcite growth exceeds a minimum value required to maintain equilibrium, then the crystal surface may be “captured” by the newly-formed lattice (4). Our results provide the first suggestive evidence that under equilibrium conditions ¹⁸O and ¹³C may be depleted in the near-surface region of calcite relative to the bulk crystal lattice. More work is required to confirm and evaluate this effect.

References

- [1] Lorens 1981.
- [2] Tesroeiro and Pankow 1996.
- [3] Gabitov and Watson 2004.
- [4] Watson 2004.