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# Cobalt Reactive Transport and Solid Solution At the Calcite-Water Interface At 40 Degrees C

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## 2.1.44

### Development of surface reactivity during crystal dissolution: Direct observations vs. model predictions

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Mineral reactivity reflects the distribution of reactive sites over the surface and the relationship of those sites to the underlying bulk structure. Recognition of the statistical nature of this distribution thus makes stochastic approaches inherently useful in investigations of crystal dissolution mechanism, and the insights that accrue may be difficult to achieve through more deterministic models parameterized by simple free energy relations.

We study dissolution and growth kinetics of crystalline materials through coupling of experimental and modeling techniques (Fig. 1). The complementary use of both AFM and vertical scanning interferometry (VSI) allow direct observations of the crystal surface over a wide range of length and time scales. Although these methods do not typically permit the direct observation of kink site distribution (e.g., [1]), this information can be provided by Monte Carlo simulations and associated modeling techniques [2].

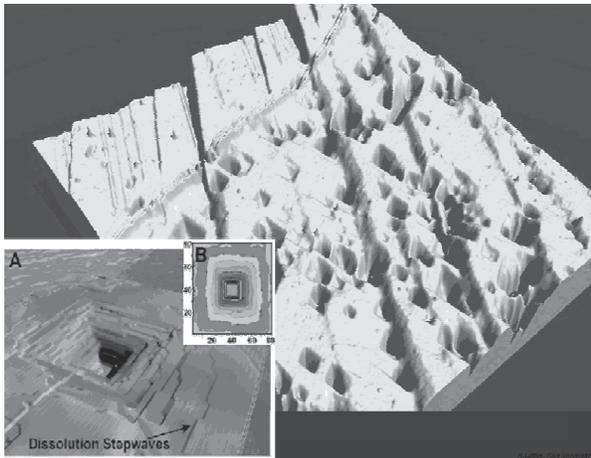


Figure 1. Comparison of Monte Carlo model results with an experimentally dissolved calcite 104 cleavage surface (25C, pH8, 4 hours).

Both model results and direct observations of crystal dissolution rates show that the overall rate varies as a function of time, and thus imply that the site population and distribution continually change as dissolution proceeds.

#### References

- [1] Arvidson R.S., Ertan I.E., Amonette J.E. and Luttge A. (2003) *GCA* **67**,1623-1634.
- [2] Lasaga A.C. and Luttge A. (2003) *EJM* **15**, 603-615.

## 2.1.45

### Cobalt reactive transport and solid solution at the calcite-water interface at 40° C

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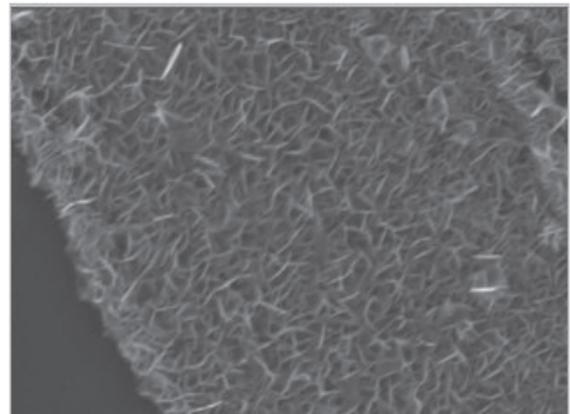
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The reactive transport of cobalt at the calcite surface in starting solutions undersaturated with respect to  $\text{CoCO}_3$  was explored at 40° C in a flowing system. Hydrothermal Atomic Force Microscopy experiments in which calcite dissolution flux is measured as a function of solution flow rate reveal mass transport dependence, indicating that diffusive mass transport cannot be ignored in these experiments. Well defined laminar flow conditions in the HAFM allow modeling of the coupled heterogeneous kinetics/mass transport that affect calcite dissolution flux and, therefore, local saturation state with respect to  $\text{Co}_x\text{Ca}_{1-x}\text{CO}_3$  solid solutions and precipitate distribution in time and space.

Precipitation of  $\text{Co}_x\text{Ca}_{1-x}\text{CO}_3$  solids on the calcite surface occurred despite the initial undersaturation with respect to  $\text{CoCO}_3$ . The presence and distribution of  $\text{Co}_x\text{Ca}_{1-x}\text{CO}_3$  solids on the calcite surface was confirmed using SEM/Microprobe after the HAFM experiment. Co- rich solids on the calcite surface consisted of euhedral and twinned  $\text{Co}_x\text{Ca}_{1-x}\text{CO}_3$  plates, dominated by {001} and {100} on the calcite surface.

Lippmann diagrams are used to further discuss the range of solid solutions that could exist. Consideration of the most thermodynamically stable phase reveals a narrow range ( $x > 0.98$ ) of rhombohedral  $\text{Co}_x\text{Ca}_{1-x}\text{CO}_3$  solids that would form in the system at 40° C.



SEM secondary electron image of a cobalt carbonate precipitation front on calcite after exposure to 0.1 mM Co solution at 40C.  
Width = 26.4  $\mu\text{m}$