

Calcite nucleation and growth on basaltic glass and silicate minerals

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Mineral substrates and their effect on calcite nucleation and growth

Calcite was precipitated in flow-through experiments at 25 °C from supersaturated aqueous solutions in the presence of seeds of calcite and six different silicates: augite, basaltic glass, enstatite, labradorite, olivine, and peridotite. The aim of the experiments was to determine how calcite nucleation and growth depends on the identity and structure of the growth substrate. Calcite saturation was achieved mixing a CaCl₂-rich solution with a NaHCO₃-Na₂CO₃ buffer in a mixed-flow reactor containing 0.5-2 grams of mineral grains. This led to a calcite saturation index of 0.6 and pH 9.1 for the reactive solution inside the reactor.

Although chemical conditions, flow rate and temperature were identical for all experiments, the onset of calcite nucleation and the amount of calcite being precipitated depended on the identity of the mineral substrate. With calcite as the growth substrate, new calcite crystals formed instantaneously. Calcite nucleated relatively rapidly on olivine, enstatite, and peridotite (mainly composed of Mg-olivine). Scanning Electron Microscope images showed silicate crystals to be almost completely covered with calcite coatings at the end of the experiments. Less calcite growth was found on labradorite and augite, and least on basaltic glass. In all cases, calcite precipitation occurs on the mineral substrate and not adjacent to them.

Results and Conclusion

These findings indicate that calcite nucleation and its subsequent growth depends on the crystal structure of the silicate substrate. Orthorhombic silicate minerals (olivine and enstatite) are the easiest for trigonal calcite to nucleate on. Monoclinic augite and triclinic labradorite show intermediate behavior, whereas basaltic glass with its non-ordered crystal structure is the least favorable platform for calcite growth. The results have implications for CO₂ mineralization in ultramafic and basaltic rocks [1,2] indicating that trigonal carbonates easier precipitate on crystalline rather than glassy rocks, but even glass surfaces can serve as a substrate for calcite nucleation.

[1] Oelkers *et al.* (2008) *Elements* **4**, 333-337. [2] Gislason *et al.* (2010) *Int. J. Greenhouse Gas Control* **4**, 537-545.

Smart K_d-concept based on Surface Complexation Modeling

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Methodology

Sorption on mineral surfaces of sediments is one important retardation process for radionuclides to be considered in long-term safety assessments for radioactive waste repositories. Previously, the K_d-concept with temporally constant values was applied to describe the radionuclide retardation in the far field of a repository.

In this study, pre-calculated distribution coefficients (K_ds) based on surface complexation models (SCM) are implemented in the existing 3D transport program r³t [1]. The so-called smart K_d-values are calculated as a function of important environmental parameters to reflect changing geochemical conditions. Respective multi-dimensional K_d-matrices are generated and stored a-priori to any r³t run. The calculations follow a bottom-up approach, i.e. the sorption of an element on each single mineral phase contributes to the distribution coefficient for a sediment.

Results

As an exemplary proof-of-concept, the Gorleben site (a potential repository site in Germany) was selected. Figure 1 shows the 3D plot for the logK_d-matrix of UO₂²⁺ in the upper aquifer (UAF) at the Gorleben site as a function of pH, [Ca], and [DIC] (logarithmic scale).

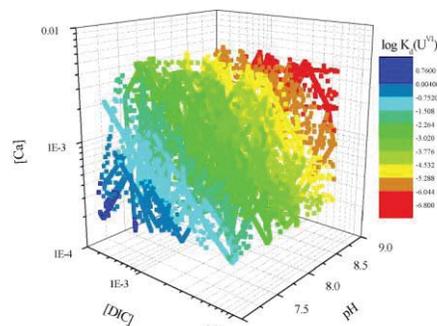


Figure 1: Multidimensional K_d-matrix for UO₂²⁺ in UAF as a function of pH, [Ca], and [DIC] (K_d in m³/kg, logarithmic scale).

These pre-calculated logK_d-values vary between -6.8 and 0.75. Comparing to the temporally constant conservative logK_d of -2.7 from [2], which was previously used in r³t for the retention of UO₂²⁺ in fresh water in the upper aquifer at the Gorleben site, the resulting mean logK_d of -2.74 shows a good general agreement, but account now for geochemical variations.

[1] Fein (2004) *Report GRS-192, BMWi-FKZ 02E9148/2*. [2] Suter *et al.* (1998). *Proceedings DisTec 98*.