Mineral growth and dissolution from rare event methods

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Computational theory and hardware have advanced sufficiently to allow in-depth examination of free energy landscapes for complex, geologically important reactions. Here, we used two rare event theories, metadynamics and reactive flux, to probe the attachment and detachment of barium ions to the [120]-oriented monomolecular step on barite and compare these reaction rates and mechanisms to those measured experimentally. This reaction was chosen because attachment and detachment of barium ions to these step-edges is thought to be rate limiting and barite scale has been found to inhibit production of oil and geothermal energy in some cases.

Using metadynamics, we found that detachment and attachment of ions does not occur directly to and from solution, but several intermediate states are observed. Starting from a barium kink site making five bonds to three surface sulfates, detachment first proceeds to a bidentate state containing two bonds to two surface sulfates, followed by an inner-sphere adsorbed species (making one bond), then an outer-sphere adsorbed species before completely dissolving.

Reactive flux calculations of the transitions between each of these states revealed that moving from the inner-sphere adsorbed species to outer-sphere adsorbed is limiting the rate of detachment. For attachment, the transition from inner-sphere adsorbed to the bidentate species is rate limiting. Arrehenius activation energies of each of these rate limiting steps were calculated by performing the reactive flux calculations at multiple temperatures. The activation energies and rate constants, compare favorably to those measured experimentally by atomic force microscopy in the case of dissolution.

The implications this study are two-fold. Firstly, the observation of multiple intermediates states implies that mineral growth and dissolution reactions can lead to pools of labile or recalcitrant material in variou states of adsorption onto mineral surfaces. This addresses the longstanding issue of non-steady state dissolution rates. Secondly, the ability to quantitatively probe complex reaction mechanisms on surfaces accurately will be a powerful technique in addressing mineral reactivity and mechanisms.

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A multi-isotope study for identifying groundwater movement near disturbed salt domes: Case study Stassfurt, Germany

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An area of the German part of the Southern Permian basin affected by anthropogenically induced subrosion was investigated for its potential for ongoing salt dissolution induced by groundwater movement. A set of environmental tracers supported by hydrochemical analyses was applied to establish aquifer fingerprints of the covering layers (Quaternary and Triassic) and of flooded parts of the mining area (Zechstein), and revealed prevailing mixing components: A modern groundwater component was identified by the presence of ^{3}H and $^{3}He_{tri}$ which indicates young apparent groundwater ages (0 - 50 a) in the covering layers. Using this, percentages of modern water could be derived for each sample. The presence or absence of ^{14}C in the samples represents an age classification between the modern groundwater component (<50 a) given above, and an old groundwater component (apparent groundwater ages <50 000 a). The trends derived from radiocarbon could generally be validated by low $^{4}He_{rad}$ contents in samples from the modern groundwater component and elevated $^{4}He_{rad}$ contents in the old groundwater. Contact between meteoric water and Zechstein salts could be identified by the presence or absence of Permian crystallization water from the dissolution of e.g. Carnallite and/or Kieserite in the samples. We developed a conceptual model of groundwater flow and interactions between groundwater of the different aquifers in the studied area and discuss potential implications for ground subsidence.