Classical nucleation theory predicts dissolution kinetics of silica

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Issue

Silicate mineral weathering has a primary control on biogeochemical cycles of elements through earth systems. This has motivated studies of dissolution for more than 50 years. Current rate 'laws' are largely empirical, sometimes with apparent, serious inconsistencies. We show that dissolution of silica and silicate minerals can be understood across broad conditions through the same nucleation rate theory that was originally developed for crystal growth. This theory should, in principle, also apply to dissolution but, before now, has never been tested.

Methods

Kinetic measurements were conducted at 200°C using quartz sand (Destin, FL) using established flow-through reactor methods for measuring H_4SiO_4 production rate at steady state. Undersaturated solutions were prepared with and without reagent grade NaCl or $CaCl_2 \cdot 2H_2O$ and additions of silicic acid. All solutions had circumneutral pH and calculated $pH_{T,200} = 5.7$.

Parallel experiments exposed natural (100) surfaces of a euhedral quartz crystal to four experimental conditions that, according to theory, should give distinct dissolution mechanisms. Samples were restrained using Ti screen. Durations of each treatment were determined from measured rates to calculate reaction time necessary to give equal silica production at 200°C. Thus, etching times ranged from 28 days to four hours. Resulting nanoscale structures were examined under a drop of water using atomic force microscopy.

Findings

By generalizing nucleation theory across the potential energy continuum of growth to dissolution, we present a quantitative and mechanistic model that predicts how quartz dissolution processes change with increasing undersaturation from simple step edge retreat, to dislocation and defect-driven pit nucleation. We further show that the origin of the so-called salt effect that was recognized almost 100 years ago arises from increases in surface energy to activate dissolution by two-dimensional nucleation of vacancy islands, to greatly increase site density. This process has not been heretofore recognized as possible for oxide or silicate minerals. Nucleation rate theory also predicts the dissolution kinetics of dominant aluminosilicates, kaolinite and K-feldspar to resolve controversial discrepancies in 80 & 150°C data reported for kaolinite. The differences naturally arise from temperature-activated changes in the dominant dissolution mechanism. Nucleation rate theory may be the missing link to understanding the dissolution-growth continuum.

Hydration and dissolution of nano-particulate silicate surfaces

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A range of complementary computer modelling techniques has been employed to study a series of silicate/water interfaces. Firstly, density functional theory (DFT) calculations as well as interatomic potential-based simulations have been employed to study the adsorption of water at two α-quartz (0001) surfaces, where the different methods are found to be in good agreement, both as to modes and energies of adsorption. When under-coordinated silicon and oxygen atoms are present at the surface, water molecules adsorb dissociatively at the surface, thereby annihilating dangling bonds by the formation of surface hydroxy groups. However, when the surface species are linked by Si-O-Si bridges and fully coordinated, water adsorbs associatively, releasing approximately 40 kJ mol^{-1}. The comparison study shows that the potential model for hydrated silica performs sufficiently well to be suitable for use in our further simulations of the hydration of a silicate nano-tube. Results of these calculations show that the side of the nano-tube is relatively resistant against dissociative chemisorption and silicon dissolution, but that the end of the nano-tube is highly reactive towards water and amenable to dissolution. Secondly, classical molecular dynamics simulations have been carried out to investigate the dissolution of the same quartz (0001) surfaces in a more realistic, liquid water environment. Preliminary results suggest that on thermodynamic grounds the complete dissolution of silicon atoms from the quartz surfaces in liquid water is unlikely to occur.