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Mechanisms controlling albite dissolution/precipitation kinetics as a function of chemical affinity: New insights from experiments in ^{29}Si spiked solutions at 150 and 180 °C

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Abstract

Knowledge of the rates of dissolution of rock-forming minerals close to equilibrium and their dependence on ΔG_r, the Gibbs free energy of reaction, is essential for describing the temporal and spatial evolution of many environmental and engineering processes involving solid/fluid interactions. In the present study we used the isotope-doping method to quantify albite forward and net dissolution rates. Batch experiments were performed at 150, 180 °C and pH = 9 at near equilibrium and equilibrium conditions ($-25 \leq \Delta G_r \leq +8.2$ kJ/mol) in ^{29}Si spiked solutions which were undersaturated with the secondary Al-Si solid phases likely to precipitate.

The forward dissolution rates normalized to the initial BET surface area were found to decrease continuously and monotonically with increasing time and ΔG_r, achieving values 1.3 to 2.4 orders of magnitude lower at chemical equilibrium than initial far from equilibrium values, with the highest rate decrease for the highest solid to fluid ratio. These rate drops were accompanied by an increase in BET specific surface areas associated with the formation of widespread dissolution features. A decrease of albite forward dissolution rate together with an increase of its BET surface area was also observed as a function of reaction time at far from equilibrium conditions ($\Delta G_r \leq -65$ kJ/mol). These observations are consistent with a continuous decrease with time and increasing ΔG_r of albite effective surface area linked to the formation of unreactive negative crystal facets, in addition to etch pits stopping nucleating above a critical value of ΔG_r. Thus, the observed decrease in albite dissolution rate as equilibrium is approached is not linked primarily to the increase in the contribution of the backward reaction but rather to the decrease of the forward reaction rate in conjunction with the decrease in the density of reactive sites at the mineral surface.

The results of this study show that the characterization of the effective surface area and its evolution with reaction time and chemical affinity is crucial to deriving robust dissolution rates of well-crystallized minerals like feldspars. Dissolution experiments in ^{29}Si spiked solutions of samples with different history and well-characterized effective surface area and surface morphology should help to better quantify the rate laws controlling silicate minerals weathering.