

Experimental studies on the thermodynamics and kinetics of fluid-mineral interactions: Applications to hydrothermal systems and geological CO₂ sequestration

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Accurate experimentally derived thermodynamic and kinetic data on mineral dissolution/precipitation are critical in modeling a wide variety of fluid-rock interactions, mass-transport and deposition in a number of natural and industrial systems. Since the last 15 years, the solubility of metal hydroxides and oxides (e.g. [1-4]) and the dissolution/precipitation rates of aluminum solid phases [5] very near equilibrium have been measured by taking advantage of *in situ* pH monitoring.

More recently, increasing fundamental researches have also focused on the short and long-term effects of injections of anthropogenic CO₂ in various geological environments to assess the feasibility of its sequestration in the form of stable solid carbonate phases. However, accuracy of geochemical modeling depends strongly on reliable thermodynamic and kinetic data for carbonate-bearing minerals. The primary goal of our research is to provide the fundamental basis for predicting the degree to which stable carbonate will precipitate in the subsurface. This includes the solubility of dawsonite, siderite [6, 7] and magnesite; the dissolution rates of various carbonates [8, 9] as well as their precipitation rates at abiotic and biotic conditions over a wide range of temperature and pCO₂ [10, 11].

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***Ab initio* calculations of He diffusion in apatite**

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The diffusion of He in zircon and apatite is important for the interpretation of He-loss measurements used in thermochronology. Recent simulations and experimental determinations of the diffusion of He in zircon found that it is strongly anisotropic [1-3]. However, the He diffusion mechanisms and rates for apatite are not well known. *Ab initio* quantum mechanical methods are used to calculate the diffusion of He in ideally crystalline fluoroapatite Ca₅(PO₄)₃F. A 168-atom unit cell with 1 He atom is used to simulate the dilute limit of He in apatite. The most energetically favored position for He is along the column of F atoms, [001]. The Nudged Elastic Band (NEB) method was used to calculate the energy barriers to He diffusion along [001] and [110]. The activation energy along [001] is 0.8 eV (77 kJ/mol), and the barrier along [110] is 1.2 eV (116 kJ/mol). These calculations suggest that there is much less anisotropy for apatite than has been observed and calculated for zircon. From the activation energies in apatite the tracer diffusion coefficients (*D*^{*}) were calculated. *D*^{*} describes the diffusion pathway of a single He atom in pure crystalline bulk apatite. Along [001] *D*^{*}=3.38x10⁻⁸exp (-77 kJ*mol⁻¹/RT) m²/s and along [110] *D*^{*}=5.72x10⁻⁸exp (-116 kJ*mol⁻¹/RT) m²/s. The calculated *D*^{*} exhibit slight anisotropy. The calculated values for *D*^{*} are in good agreement with the experimental measurements for He diffusivity [3].

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