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Experimental Determination of Hydrogen Diffusion Rates in Hydrous Minerals Using the Ion Microprobe

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Accurate determination of hydrogen diffusion rates are necessary to understand the mechanism of hydrogen isotope exchange between hydrous minerals and water, and to interpret H isotopes from natural systems. However, hydrogen diffusion coefficients, knowledge of transport mechanisms of hydrogen, and reaction kinetics between fluids and hydrous phases such as epidote, amphibole, and the micas are poorly determined at present. Hydrogen diffusion rates have been almost entirely determined empirically from bulk powder-fluid exchange experiments, using different grain geometry models to estimate the rates of fast and slow diffusion (Graham, 1981). A better approach is to react deuterated water with hydrous crystals and measure the D/H using secondary ion mass spectrometry. Single crystals of museum-quality epidote and pargasite were mineralogically characterized (e.g., SEM; electron microprobe), cut and polished perpendicular to mineralogical axes prior to hydrothermal experimentation. The single crystals were placed in gold capsules with 50 - 100 mg of 99% deuterated water. Experiments were conducted in cold seal vessels, typically at 2 kbar (±25 bars) for durations of 6hrs to 18 days depending on the temperature. The surface of each reacted crystal was carefully examined both optically and by SEM, for the presence of epitaxial crystal growth or surface roughness resulting from dissolution. Only those crystals that exhibited minimal roughness (<0.1μm) and an absence of surface mineral growth were selected for SIMS analysis. The samples were sputtered using a ^{16}O- primary ion beam with an impact energy of 17 keV. Primary beam currents were 25-100 nA with a diameter of 30-60μm and the beam was rastered over 100x100 to 150x150 μm2 areas. A field aperture was used to restrict analysis to ions sputtered from the central ~33μm diameter of the crater. Crater depths, measured using a profilometer, ranged from 0.2 to several μm. Two methods have been used for calculating the diffusion coefficients from the ion probe data. In the first approach, self-diffusion of deuterium is modeled as transport into a semi-infinite medium whose surface is maintained at a constant isotopic composition different from that initially in the crystal (Crank, 1975; Gilleti et.al., 1978). A second related method uses the Levenberg-Marquardt algorithm, a non-linear least-squares technique (Labotka et al., 2000). Both approaches give essentially the same diffusivities. Using SIMS we are also determining hydrogen diffusivity in phlogopite, muscovite, chlorite and brucite. We have measured D/H profiles parallel to the *b* crystallographic orientation (faster direction) in epidote reacted with deuterated water between 200 and 600 C at 2 kbar. For example, the range of diffusion coefficients between 200 - 600 C and 2 kb for epidote is between the values of log D = -13.6 to -17 cm ^{2}/sec. Similarly, we measured the D/H profiles in pargasite (calcic amphibole) reacted with deuterated water at 300 - 400 C and 2 kbar, but parallel to the faster *c* crystallographic direction. The diffusion coefficient at 400 C and 2 kb for pargasite is log D = -15.2 cm ^{2}/sec. Preliminary activation energies for both of these experimental systems are ~67 kJ/mol. The diffusion coefficients for epidote (200 - 600 C) and pargasite (300 - 400 C) are significantly slower than those estimated from either a plate or cylinder model using the bulk exchange data (Graham, 1981; Graham et. al, 1980,1984). A mixed recrystallization-diffusional process in bulk exchange experiments compared to a purely self-diffusion process in single crystals may in part account for the faster rates in the bulk experiments. Additionally, selection of the grain size, grain geometry and diffusion model can have profound influence on the estimates of diffusivity from the powdered experiments. Results obtained with the present single-crystal technique have broad ramifications for the applications of hydrogen isotopes not only in geothermometry, but also in coupling natural isotopic distribution with rate data to quantify the duration of a particular fluid-rock interaction.

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