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An experimental study of the diffusion of C and O in calcite in mixed CO_2-H_2O fluid

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Abstract

The diffusivity of C and O in calcite in mixed CO_2-H_2O fluid was determined over the range in x_{CO_2} from 1.0 to about 0.2 at 700 °C, 100 MPa, with selected experiments conducted at pressures to 250 MPa and temperatures of 600 and 800 °C. The diffusivity of C, D_C, varies little with x_{CO_2}, although there is some evidence for a slight increase in D_C from ~5×10^{-18} to ~5×10^{-17} cm^2/s with decreasing x_{CO_2}. Our data and those of others are consistent with a model for $D_C \propto 1/f_{CO_2}$. Despite the large uncertainty, we observed that the diffusivity of O, D_O, increases from ~2×10^{-16} to ~5×10^{-14} cm^2/s with x_{CO_2} decreasing from 1.0 to 0. There is a good correlation at 700 °C between log D_O and log f_{H_2O} regardless of the total pressure, matching the observations of previous workers. The data are consistent with a simple two-component model for the diffusion of O in calcite, one component for diffusion in the presence of CO_2 and one in the presence of H_2O: $D_O = D_O^{CO_2} + D_O^{H_2O} a_{H_2O}$. The activity of H_2O is relative to the fugacity at 100 MPa, 700 °C. $D_O^{CO_2}$ is 3.45×10^{-16}, and $D_O^{H_2O}$ is 3.8×10^{-14} cm^2/s. The data indicate that the rate of diffusion of C and O in calcite is controlled by reactions at the surface of calcite. Adsorption of H_2O and the creation of vacancies at the surface account for the dependence of the diffusivity on the fugacity of the fluid components. There is little evidence that H itself diffuses into calcite. With this model and the values of D_O in pure CO_2 (Labotka et al. 2000) and in pure H_2O (Farver 1994), the value of D_O is predicted over the temperature range 600–800 °C and p_{H_2O} up to 300 MPa, the range of the data. Calculated closure temperatures for diffusive exchange of O between calcite and fluid are reduced by about 150 °C in the presence of an aqueous fluid.

Keywords: O isotope, C isotope, calcite, diffusion, experiment