

## **Diffusion of C and O in calcite from 0.1 to 200 MPa**

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### **ABSTRACT**

We measured the diffusivity of C and O in calcite over the pressure range 0.1–200 MPa at 600–800 °C in a pure CO<sub>2</sub> atmosphere. The experiments were conducted on single, preannealed crystals of Chihuahuan calcite in an isotopically labeled atmosphere, and the diffusion profiles were measured by secondary ionization mass spectrometry (SIMS). At 800 °C,  $D_C$  and  $D_O$  are identical at 0.1 MPa at a value of  $\sim 10^{-13.5}$  cm<sup>2</sup>/s. The value of  $D_C$  decreases to  $\sim 10^{-16}$  cm<sup>2</sup>/s with an increase in pressure to  $\sim 50$  MPa and remains at that value to 200 MPa, but  $D_O$  remains nearly constant at a value of  $\sim 10^{-14}$  cm<sup>2</sup>/s to 200 MPa. The identical values at low pressure indicate that C and O are migrating together as a carbonate anion. A simple model relates the diffusivity of carbonate anions to the formation of vacancies at the crystal surface, which predicts that  $D_C \propto 1/f_{CO_2}$ . The prediction matches the observed decrease in  $D_C$  with increasing pressure to 50 MPa. The shapes of the diffusion profiles for the low-pressure experiments indicate compositional dependence of  $D$ , which also suggests the influence of CO<sub>2</sub> sorption on the diffusivity. The value of  $D_C$  at 0.1 MPa can be fitted to the relation  $D_C = 0.62 \exp[(-291 \text{ kJ/mol})/RT]$ . The activation energy is nearly twice the value determined for  $D_C$  at 100 MPa,  $\sim 166$  kJ/mol. The change in slope for  $\log D_C$  vs.  $P$  and the change in  $E_a$  between 0.1 and 100 MPa suggest that the migrating C species changes from carbonate anions at low pressure to carbon atoms at  $P \geq 50$  MPa. The values of  $D_O$  at 0.1 MPa can be fitted to  $D_O = 0.017 \exp[(-261 \text{ kJ/mol})/RT]$ , approximately the same as for C at 0.1 MPa and similar to the relation for  $D_O$  at 100 MPa:  $D_O = 0.008 \exp[(-242 \text{ kJ/mol})/RT]$ .