Diffusion of C and O in calcite

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Diffusion of C and O in calcite depends strongly on the presence of defects in the calcite and of H_2O in an accompanying fluid phase. Previous experimental studies of the diffusion of O at 700°C, for example, show that the diffusion coefficient D ranges over nearly three orders of magnitude from 10^{-13} to 10^{-16} as p_{H_2O} ranges from 400 to 0.1 MPa. Values of D for C also depend on p_{H_2O}, although the dependence isn't as well determined as it is for O. We have attempted to isolate the extrinsic effects on C and O self diffusion in calcite by determining the diffusion coefficients from single crystals of annealed calcite that were heated in an atmosphere of isotopically labeled CO_2.

Experimental methods

Single crystals of calcite from Chihuahua, Mexico, were annealed in an atmosphere of NBS-20 CO_2 at 700°C for 24 h. For each experiment, two or three crystals were placed in either a platinum or a gold capsule. The capsule was evacuated, and 6–12 mg of $^{13}C^{18}O_2$ were introduced into the capsule. Experiments were conducted at 100 MPa, 600–800°C, and 7–72 d. The crystals were extracted from the capsules and analysed with a Cameca 4f ion microprobe, during which isotopic ratios were monitored with depth in the crystal. Depth profiles were measured with a profilometer and were

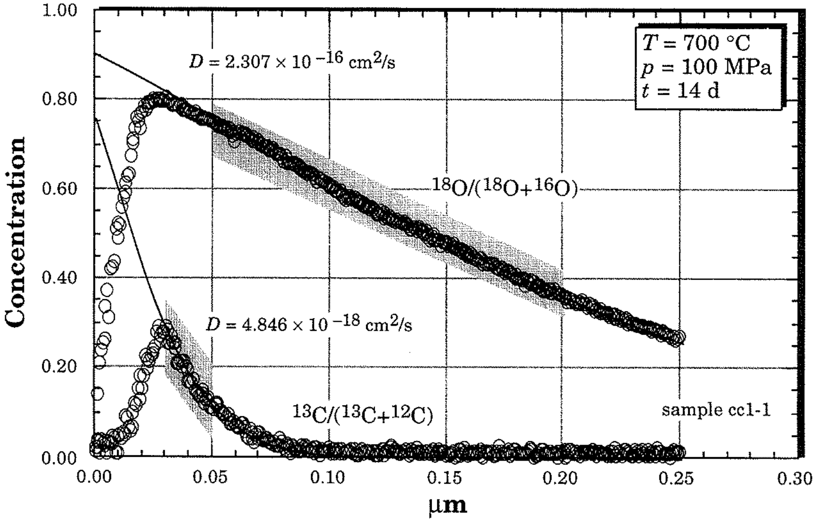

FIG. 1. Ion microprobe depth profile for a calcite crystal heated to 700°C at 100 MPa for 14 d. The two data profiles represent simultaneous measurements of ^{13}C, ^{12}C, ^{18}O, and ^{16}O. The curves represent fits to $C = C_0 \mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$. The shaded regions on each profile show the range in values fitted to the function. Least-squares values of D are indicated next to the profiles. The least-squares values of the apparent surface concentrations are indicated by the curves at $x = 0$.

generally <0.5 μm.

Results

Figure 1 shows the results from one experiment conducted at 700°C, 14 d. The use of labelled CO_2 allows simultaneous measurement of the diffusion coefficients for C and O, although the great difference in the values of D for C and O results in concentration profiles that can be too deep for O or too shallow for C. The concentration profiles are characterized by an initial increase in the concentration of the heavy isotope through the gold coat on the sample, followed by a decrease with depth, mimicking an error-function profile. The shaded portions of the curves were fit to the function $C = C_0 \mathrm{erfc}(bx)$, in which C_0 is the apparent surface concentration and $b = \frac{1}{2\sqrt{Dt}}$. These parameters were fitted with the use of the Levenberg-Marquardt algorithm, which predicts values of C_0 and b with $\chi^2 \approx 3 \times 10^{-3}$, corresponding to a Pearson's r ~ 0.99. The error in D from the fitting procedure is < 5%, much less than that from the error in measuring the depth, $< \pm 30\%$.

Preliminary results from experiments conducted at 600, 700, 750, and 800°C indicate an activation energy of ~205.4 and 148.7 kJ/mol and preexponential factors of $\sim 5.1 \times 10^{-5}$ and 8.3×10^{-10} cm^2/s for O and C, respectively. These values are smaller than previously determined activation energies by Anderson (1969) and Kronenberg *et al.* (1984), although the O values are similar to those determined by Farver (1994). The values of D are smaller than previously measured values. Some of the differences may result from the preannealing, the pressure, and the simultaneous direct measurement of C and O. It is clear, though, that the absence of H_2O severely restricts the diffusivities of C and O in calcite.

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