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 H₂O 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 pH₂O ranges from 400 to 0.1 MPa. Values of D for C also depend on pH₂O, 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 CO₂.

Experimental methods

Single crystals of calcite from Chihuahua, Mexico, were annealed in an atmosphere of NBS-20 CO₂ 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 ¹³C/¹⁸O 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

![Graph](image)

**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 ¹³C, ¹²C, ¹⁸O, and ¹⁶O. The curves represent fits to \( C = C₀ \text{erfc} \left( \frac{x}{2\sqrt{D}t} \right) \). 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 \( x = 0 \).
Results

Figure 1 shows the results from one experiment conducted at 700°C, 14 d. The use of labelled CO₂ 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 \( C = C_0 \text{erfc}(bx) \), in which \( C_0 \) is the apparent surface concentration and \( b = \frac{1}{2D} \). 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 \( r \approx 0.99 \). The error in \( D \) from the fitting procedure is < 5%, much less than that from the error in measuring the depth, < ±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 ~5.1 × 10⁻⁵ and 8.3 × 10⁻¹⁰ cm²/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 H₂O severely restricts the diffusivities of C and O in calcite.


References