Carbon and Oxygen Diffusion in Calcite: Effects of Mn Content and \( P_{H_2O} \)

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Abstract. The diffusion rates of carbon and oxygen in two calcite crystals of different Mn contents have been studied between 500° and 800°C in a \( CO_2 - H_2O \) atmosphere (\( P_{CO_2} = 1-5 \) bars, \( P_{H_2O} = 0.02-24 \) bars) labeled with \( ^{13}C \) and \( ^{18}O \). Isotope concentration gradients within annealed specimens were measured using a secondary ion microprobe by depth profiling parallel and perpendicular to the \( c \) axis. Despite the anisotropic structure of calcite, the diffusion of carbon and oxygen are both very nearly isotropic. Least-squares fitting of the carbon data to an Arrhenius relation gives an activation energy of 87±2 kcal/mole, with \( D_o \) terms dependent only slightly upon direction:

\[
D_o(\parallel c) = \left( \frac{9 + 12}{-5} \right) \times 10^2 \text{ cm}^2/\text{s},
\]

\[
D_o(\perp c) = \left( \frac{5 + 6}{-3} \right) \times 10^2 \text{ cm}^2/\text{s}.
\]

These results are in close agreement with previous determinations. Results for oxygen diffusion, however, give \( D \) values much larger than those previously reported for dry conditions; at 650° to 800° C the \( D \) values are two orders of magnitude larger. The diffusion of oxygen, unlike carbon, is strongly dependent on water pressure, as well as Mn content, and does not fit an Arrhenius relation over the entire temperature range. On the basis of these observations and considerations of the defect chemistry of calcite, it is proposed that carbon migrates as a Frenkel pair. The diffusion of oxygen, however, appears to be more complicated and may depend upon several simultaneous mechanisms.

Introduction

The kinetics of solid state processes in limestones and marbles, such as the rates of ductile deformation and the chemical and isotope equilibration with intergranular fluids, can only be understood fully if the self-diffusion rates of the various ions in calcite are known. Hauff and Stein (1955) first measured the diffusion of carbon in calcite. Haul and Stein (1955) measured the \( ^{13}C \) and \( ^{18}O \) concentration gradients within samples parallel to and perpendicular to the \( c \) axis using an ion microprobe. Mechanisms for \( C \) and \( O \) diffusion are considered based upon the observed effects of crystalllographic direction, temperature, \( P_{H_2O} \), Mn content, and the expected defect chemistry of calcite.

Experimental Procedures

Starting Materials

Two large rhombs of optically clear calcite from Yakutsk, U.S.S.R. (Wards Scientific Co.) were chemically analyzed by atomic absorption spectrophotometry. Crystal \( \# Ygb-2 \) is a high purity calcite, containing only 100 ppm Mn (100 Mn/10⁶ Ca), 90 ppm Fe, and 30 ppm Mg, whereas crystal \( \# Ygb-1 \) is manganese rich with 1,180 ppm Mn, 90 ppm Fe, and 40 ppm Mg. Ion microprobe analyses of five separate chips taken from each crystal indicate that their compositions are relatively uniform; Fe and Mg concentrations in both crystals, as well as the Mn content of \( \# Ygb-2 \), vary by no more than 20 ppm, and the Mn content of \( \# Ygb-1 \) varies by no more than 70 ppm (or 6% of its average Mn content).

Each crystal was oriented by making thin sections of successive cuts and determining the optic axis orientation using a universal stage. Oriented cores (3 mm diam.) were drilled and surfaces \( \parallel \) and \( \perp \) to the \( c \) axis were ground and polished using \( Al_2O_3 \) with particle sizes down to \(~ 0.05 \mu m \). Surfaces were routinely examined using an optical interferometer and a few were observed using a scanning electron microscope. Examination of one sample with a
transmission electron microscope revealed no signs of damage or high dislocation density near the polished surface. In addition, two samples were simply cleaved, in order to compare diffusion rates \( \perp \) to the cleavage surface with the results for polished surfaces. Despite the excellent \{10\{1\} cleavage of calcite, these surfaces were found to have many ledges when observed by interferometry.

**Annealing Experiments**

Calcite samples were annealed in a CO\(_2\)-H\(_2\)O atmosphere labeled with either \(^{13}\)C or \(^{18}\)O (or both) using the experimental set-up shown in Figure 1. Two to four samples were placed in an open Au tube, and into a thick (2 mm wall) fused SiO\(_2\) glass tube. Carefully weighed quantities of H\(_2\)O, sealed in an Au tube, and MnCO\(_3\) powder (typically 0.05 g each) were added, separated from the samples by a 5 cm long SiO\(_2\) glass rod. H\(_2\)O labeled with 98.3 atom percent \(^{18}\)O and MnCO\(_3\) labeled with 90 atom percent \(^{13}\)C were used for the oxygen and carbon diffusion experiments, respectively.

For each experiment, the SiO\(_2\) tube was evacuated to 45 \(\mu\)Hg, sealed, and placed into a furnace with a well-determined temperature gradient. Upon heating, the H\(_2\)O was released from its Au tube (usually before 200\(^\circ\)C) and CO\(_2\) was generated by MnCO\(_3\) dissociation at low temperatures (complete dissociation by 400\(^\circ\)C) relative to those of calcite decomposition (Goldsmith, 1959). Temperatures were monitored continuously, both at the hot end \(T_h\) and cold end \(T_c\) of the SiO\(_2\) tube using chromel-alumel thermocouples. \(T_h\) varied by no more than \(\pm 2^\circ\)C, whereas \(T_c\) varied by as much as \(\pm 6^\circ\)C. CO\(_2\) pressures were estimated from the amount of MnCO\(_3\) used and by integrating for the molar density variation in the temperature gradient, assuming ideal gas behavior. H\(_2\)O pressures were controlled by liquid-vapor equilibrium at the cold end of the tube \(T_c\) where water droplets formed. \(^{18}\)O concentrations of the CO\(_2\)-H\(_2\)O gas mixtures were calculated assuming complete isotopic exchange (Epstein and Mayeda, 1953). No corrections have been made for either carbon or oxygen isotope fractionation between the solid and gas phases (Usdowski, 1982), because such effects cannot be detected using current ion probe techniques. Because of the large \(^{13}\)C and \(^{18}\)O concentrations of the gases used, fractionation should lead to negligible errors in the determination of diffusion coefficients.

**Fig. 1.** Experimental design for C and O diffusion experiments. Calcite crystals and Mn\(^{13}\)CO\(_3\) in separate unsealed Au and SiO\(_2\) tubes, respectively; H\(_2\)SO in sealed Au tube that ruptures during heating. The temperatures at both ends of the scaled SiO\(_2\) glass tube were monitored continuously. The CO\(_2\) pressure was determined from the known quantity of MnCO\(_3\) and the volume of the tube. The H\(_2\)O pressure was controlled by the liquid-vapor equilibrium at the cold tube end \(T_c\).

**Fig. 2A, B.** A multibeam interferometer was used to measure the depths of holes produced by the ion probe. (A) Ion probe hole in sample \# cp-17 (annealed at 800\(^\circ\)C for 348 h). The primary O\(^{-}\) beam, 20 \(\mu\)m in diameter, was rastered over an area \~100 \(\mu\)m square and secondary ions were collected from the central, imaged area. Each fringe represents \(1/2 \lambda\) of the monochromatic light source \(\lambda=5.440 \text{ Å}\). (B) Plot of final hole depth vs. sputtering time. The sputtering rate appears to be constant for the machine conditions used, so that sputtering times can be converted directly to depths.