Diffusion of C and O in calcite at 100 MPa

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ABSTRACT

The diffusivities of C and O in calcite were determined in a pure CO₂ atmosphere at 100 MPa and temperatures ranging from 600 to 800 °C. The calcite crystals were preannealed and H₂O was excluded from the system to determine the self-diffusion coefficients. The CO₂ consisted of 99% ¹³C and 90% ¹⁸O. After heating for 7–147 d, diffusion profiles were measured with the use of secondary ion mass spectrometry. The results indicate that the diffusivity of C is \( D_C = 7.77 \times 10^{-9} \exp(-166 \pm 16 \text{kJ/mol/}R \text{)} \) cm²/s and of O is \( D_O = 7.5 \times 10^{-13} \exp(-242 \pm 39 \text{kJ/mol/}R \text{)} \) cm²/s. In comparison with other determinations of diffusivities in calcite, diffusion of O under the experimental conditions is consistent with vacancy migration in the intrinsic region, and diffusion of C seems to occur by diffusion of carbonate anions. Increased pressure appears to reduce the activation energy and the value of \( D_\text{an} \), and the presence of H₂O greatly increases the diffusivity of O without appreciably changing the activation energy. Closure temperatures calculated for isotopic exchange by diffusion predict that C isotope compositions of calcite are preserved during cooling in most geologic environments, but that O isotope compositions in H₂O-rich environments are preserved only in rapidly cooling environments, such as contact metamorphic aureoles.

INTRODUCTION

The stable isotope composition of calcite is the most significant monitor of the interaction between carbonate rocks and aqueous fluids, whether the environment is a sedimentary basin, carbonate-hosted ore deposit, or contact-metamorphic aureole. The isotopic composition of calcite, however acquired during the fluid-rock interaction, is subject to continued exchange with its environment during uplift and cooling by diffusion and recrystallization. We have determined C and O self-diffusion coefficients in calcite by exchange with isotopically labeled CO₂ in a completely dry environment at elevated temperatures and geologically relevant pressure to place an upper limit on the possible conditions under which C and O exchange by diffusion can occur.

Previous studies of C and O diffusion in calcite have shown the dependence of the diffusion coefficients on the H₂O content of fluid and the Mn content in the crystal. Farver (1994) demonstrated the strong effect that \( f_{H_2O} \) has on the O diffusion coefficient, and Kronenberg et al. (1984) documented the effects of both \( f_{H_2O} \) and \( X_{Mn} \) on C and O diffusion. In our study, we have kept the system free from H₂O by using pure CO₂ instead of silver oxalate as the source of labeled isotopes, and we used a single sample material to isolate the influence of fluid and crystal composition on the diffusion coefficients. We used preannealed crystals to reduce the effects of any nonequilibrium defects on the diffusion rates.

The experiments of Haul and Stein (1955) and Anderson (1969) were also dry, but they had to estimate the diffusion distances indirectly. Our experimental design is different from theirs, because we measured the C and O diffusion profiles directly and simultaneously with the ion microprobe. Our experiments were designed to come as close as possible to measuring the C and O self-diffusion coefficients in calcite in a completely H₂O-free environment. The results of the experiments give well-defined activation energies and indicate diffusion coefficients similar to, but lower than those determined in H₂O-bearing systems.

EXPERIMENTAL METHODS

The starting material was Chihuahuan Iceland spar with polished cleavage faces and with normal isotopic composition. The crystals were annealed in an atmosphere of pure CO₂ having natural values of ⁸¹³C and ⁸¹⁸O in a platinum capsule at 700 °C for 24 h. Two or three crystals, approximately 2 mm across, were placed in a platinum capsule; the crystals were separated from each other by platinum mesh. Several milligrams of ¹³C¹⁸O₂ were loaded cryogenically into the evacuated platinum capsules; the isotopic concentrations in the gas were 99% ¹³C and 90% ¹⁸O. The CO₂ was passed through two dry-ice + propanol traps to remove any H₂O that may have been present. Two capsules were placed on a vacuum line after experimentation to extract the CO₂ and to determine whether any H₂O was present. In both cases, CO₂ recovery was better than 99%, and there was no detectable H₂O. The capsules were heated in cold-seal hydrothermal vessels at 100 MPa and temperatures of 600, 650, 700, 750, and 800 °C for periods ranging from 7 to 147 d.