

Stable isotope exchange kinetics in the system calcite $\pm$ CO₂ $\pm$ H₂O to 700°C, 1000 bar: The effect of fluid composition

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Introduction

Experimental determination of the rates and mechanisms of stable isotope exchange between minerals and fluids is of great importance for the development of accurate quantitative models of water-rock interaction in the Earth's crust. Crustal fluids are composed of varying amounts of electrolytes (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, HCO₃⁻), dissolved gases (CO₂, CH₄, H₂S), and organics. A number of mineral phases have been studied isotopically, but with the exception of a few electrolytes, systematic rate studies have been conducted primarily in either pure H₂O or

pure CO₂ fluid. Mixed-volatile CO₂-H₂O fluids are important in studies of regional and contact metamorphism, the alteration of carbonates by hydrothermal fluids in geothermal areas, and the evolution of C-O-H gases during diagenesis of carbonates in hydrocarbon-bearing sedimentary basins. We report the results of ¹³C and ¹⁸O exchange experiments between calcite and supercritical and two-phase CO₂-H₂O fluids.

Methods

The calcite was reagent-grade calcium carbonate that had been annealed in H₂O at 300°C, 500 bar

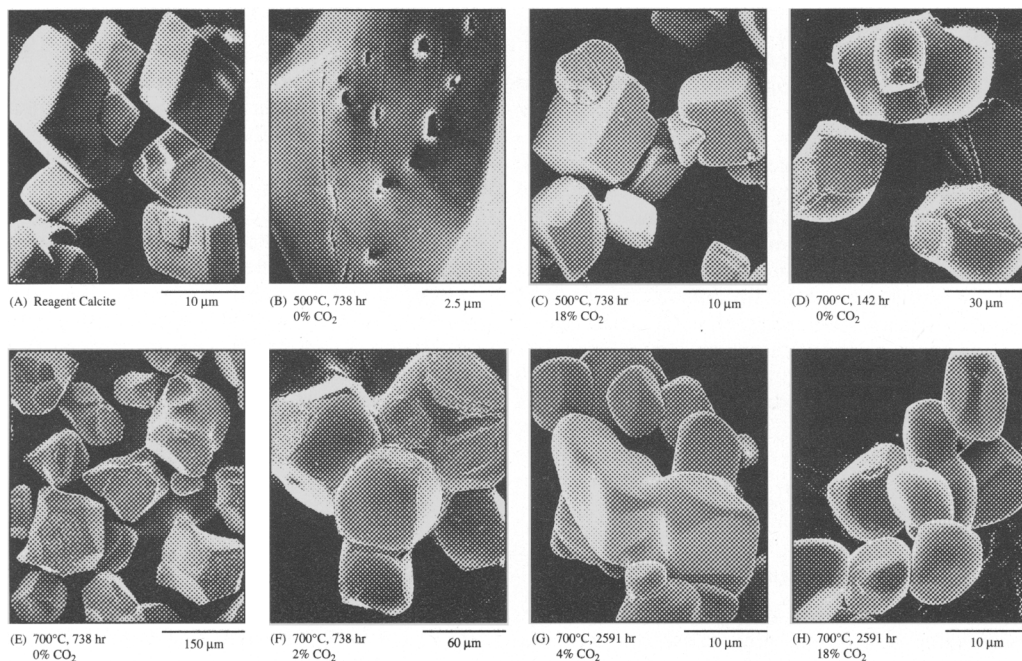


FIG. 1. SEM photomicrographs of calcite before and after reaction with CO₂-H₂O fluid. At 500°C, pitting is evident in pure H₂O (B), but little change is found with increasing X_{CO_2} (C). At 700°C, extensive mass transfer is seen. In pure H₂O, the mean diameter increases from 14 μ m to approximately 30 μ m after 142 hr (D) and 100 μ m after 738 hr (E). With increasing X_{CO_2} , the degree of grain coarsening is dramatically reduced, although rounding and coalescing of grains is evident (F)-(H).

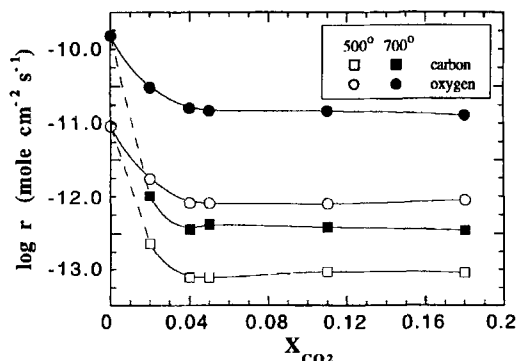


FIG. 2. Initial rates of carbon and oxygen exchange. For each X_{CO_2} , the ratio $r_{oxy}/r_{carb} \gg 1$ and increases with increasing temperature.

for 3 weeks and subsequently rinsed, sieved, and settled in H_2O several times. The calcite was examined by XRD and SEM to verify the absence of aragonite and ultrafine grains. The specific surface area and grain size distribution were determined by N_2 -BET and laser particle size analysis, respectively. Approximately 30 mg calcite was sealed in Pt capsules along with NBS-SLAP[†] and $Ag_2C_2O_4$ in appropriate amounts to yield the fluid compositions $X_{CO_2} = 0.0, 0.02, 0.04, 0.05, 0.11, 0.18$, and 1.0 . Experiments were conducted for 72 to 2600 hr at temperatures (T) and pressures (P) of 300°C, 250 bar and 500°C and 700°C at 1000 bar, using Ti (250 bar) or cold-seal (1000 bar) pressure vessels.

Results

SEM images of calcite after exchange are shown in Fig. 1. For pure CO_2 and the experiments at 300°C, 250 bar, little change in morphology was observed. At 500°C, dissolution and growth features were seen in pure H_2O (Fig. 1B). At 700°C, 1000 bar, grain growth and mass transfer between adjacent grains was extensive in pure H_2O (Fig. 1 D,E, and decreased with increasing X_{CO_2} of the fluid (Fig. 1 F-H).

The fractional exchange of carbon and oxygen, F , was calculated for each experiment from the measured $\delta^{13}C$ and $\delta^{18}O$ values of calcite and CO_2 . Plots of F vs. time, for each X_{CO_2} at T and P , revealed systematic trends. Initially steep F vs. time slopes were followed by a gradual approach (shallow, subparallel F vs. time slopes) toward equilibrium ($F = 1$) over several hundred hours. This change in slope of the F vs. time curve is common in exchange experiments, but does not require a change in reaction mechanism. Rather, the rate of the overall exchange reaction decreases

with time between the short and long duration experiments as chemical equilibrium between calcite and fluid is approached closely. The near-equilibrium rate is governed by Ostwald ripening of calcite and the number of grains decreases as the mean grain size increases (Fig. 1. D-F). Quantitative modeling of the exchange reaction requires knowledge of the functional dependence of calcite dissolution and growth rates on the saturation state of the CO_2 - H_2O fluid. Because this dependence is unknown at high T and P , initial rates of exchange were calculated using the rate expression of Cole *et al.* (1983). This equation was modified to incorporate the change in surface area with time evident in Fig. 1. Surface areas were calculated from the SEM images using a geometric model and averaged over a large number (> 25) of grains. Carbon and oxygen exchange rates are shown in Fig. 2 as a function of X_{CO_2} .

At each temperature, exchange rates decrease with increasing CO_2 in the fluid. The rate decrease is greatest between $X_{CO_2} = 0$ and 0.04 , in accordance with the reduction in grain growth with increasing X_{CO_2} in Fig. 1. For each CO_2 - H_2O composition investigated, the rate of carbon exchange is much slower than the rate of oxygen exchange. The activation energy for oxygen exchange between 300°C and 700°C, $E_a \approx 13.5$ kcal mole⁻¹, is of the magnitude expected for surface reactions.

The difference in rate calculated for carbon and oxygen exchange at a given temperature suggests that: (1) the exchange mechanisms may be decoupled, and (2) it is unlikely that a single surface species, with the approximate stoichiometry of CO_3^{2-} or HCO_3^- , controls the rate of both carbon and oxygen exchange (at 700°C, $r_{oxy}/r_{carb} > 10$). Speciation calculations indicate that $[HCO_3^-]_{aq} \ll [CO_2]_{aq}^*$ at T and P . $[CO_2]_{aq}^*$ is the dominant source of carbon in the fluid, hence the overall carbon exchange reaction must involve this species. Since H_2O is the dominant oxygen reservoir in the CO_2 - H_2O fluid, it is proposed that the overall rate of oxygen exchange is faster than that of carbon, because the exchange mechanism – involving H_2O and the calcite surface – operates at an intrinsically faster rate than does the carbon exchange mechanism involving $[CO_2]_{aq}^*$.

[†]U.S. National Bureau of Standards, Standard Light Antarctic Precipitation water

* $[CO_2]_{aq}^*$ refers to dissolved molecular CO_2 and to hydrated neutral species