

**DATA ON THE CRYSTAL GROWTH OF CALCITE FROM CALCIUM
BICARBONATE SOLUTIONS AT 34°C AND CO₂ PARTIAL
PRESSURES OF 0.101, 0.0156 AND 0.00102 ATMOSPHERES**

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CONVERSION FACTORS

Temperature can be converted to degrees Celsius (°C) or degrees Fahrenheit (°F) by the following equations:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32)/1.8$$

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$$

DATA ON THE CRYSTAL GROWTH OF CALCITE FROM CALCIUM BICARBONATE SOLUTIONS AT 34°C AND CO₂ PARTIAL PRESSURES OF 0.101, 0.0156 AND 0.00102 ATMOSPHERES

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ABSTRACT

Calcite crystal growth was studied in the laboratory by determining the weight gain of single crystals of Iceland spar in Ca-HCO₃ solutions at 34 °C and CO₂ partial pressures of 0.101, 0.0156 and 0.00102 atm, and calcite saturation indices of 0.2 to 1.9. At constant CO₂ partial pressure, P_{CO2}, and temperature, the rate of crystal growth varied linearly with the activity product of Ca²⁺ and HCO₃⁻ in solution. At constant saturation state, growth rate was nearly independent of P_{CO2} between 0.00102 and 0.0156 atm, but increased at the highest P_{CO2}. The maximum calcite growth rate was 25,000 mm/ka at SI_c=1.6 and P_{CO2} of 0.101 atm. Growth rate decreased with decreasing saturation state, but rates less than 100 mm/ka could not be reliably measured by the laboratory weight-gain method. Near-equilibrium laboratory rates of calcite dissolution and crystal growth in "clean" Ca-HCO₃ solutions decrease abruptly, and remain very small over the range of SI_c = 0 ± 0.2.

INTRODUCTION

The kinetics of calcite dissolution and crystal growth have been extensively studied in the laboratory (see for example, Nancollas and Reddy, 1971; Sjöberg, 1978; Morse, 1978; Plummer and others, 1978, 1979; Reddy and others, 1981; Morse, 1983; Sjöberg and Rickard, 1984; Inskeep and Bloom, 1985; Busenberg and Plummer, 1986; Chou and others, 1989; Compton and Unwin, 1990; Compton and Pritchard, 1990; Wollast, 1990; Morse and Mackenzie, 1990; Svensson and Dreybrodt, 1992; Van Cappellen and others, 1993; Arakaki and Mucci, 1995; and references therein). The study described here builds on the earlier work of Busenberg and Plummer (1986) in which rates of dissolution and crystal growth of calcite were measured by change in weight of single crystals of Iceland spar calcite after contact with aqueous calcium bicarbonate solutions.

DESCRIPTION OF CRYSTAL GROWTH EXPERIMENTS

Supersaturated solutions of calcium bicarbonate were prepared by dissolving calcite in CO₂-saturated water at approximately 4 °C. The solution was filtered and stored in refrigerated, sealed glass containers until used (see Reddy and others, 1981 for further details). The solution was analyzed by EDTA titration (Plummer and Busenberg, 1982), diluted to the desired range, placed in a stirred, constant temperature reaction vessel at 34 °C, and equilibrated with a CO₂-N₂ gas mixture by continuous bubbling. Three gas mixtures were used-- 10.1, 1.56, and 0.102 percent CO₂. The partial pressure of CO₂ in the reaction solution was calculated by assuming that the total pressure of the CO₂-N₂ gas mixture plus saturated water vapor was equal to the room barometric pressure (Plummer

and Busenberg, 1982; Busenberg and Plummer, 1986).

Single crystals of calcite were prepared from rhombohedral cleavage fragments of Iceland spar with total surface areas of 3 to 6 cm². Each crystal was tied with fine Pt-Ir wire with a small loop used to suspend the crystal in aqueous solutions. Surface area was calculated from the measured dimensions of the rhomboid faces. The crystals were reacted initially with 1N HCl, washed with de-ionized water, dried, tied with the Pt-Ir wire, reacted with 0.1N HCl for approximately 30 seconds, washed with de-ionized water, and dried overnight in an oven at 80 °C. The crystals, tied with Pt-Ir wire, were weighed on a Mettler electronic balance (Model ME22-BA25-BE22) to the nearest µg, recording room barometric pressure, temperature, and relative humidity. Each weight was corrected to *in vacuo*. All weights were reproducible within 2 µg or less.

The single crystals of calcite were suspended in the supersaturated calcium bicarbonate solutions. Many of the measurements were made in duplicate, that is, two crystals were suspended in the same reaction vessel. Measurements made in duplicate are identified in Table 1 as pairs of experiments with identical run times and solution composition. The experimental design constitutes a nearly constant-composition system, as the amounts of calcite formed were usually less than 1 mg from solution volumes of approximately 500 ml. Rates were determined by weight gain of the single crystals reacted over periods of approximately 20 to nearly 400 minutes. Further details of the experimental procedures are given in Busenberg and Plummer (1986). The experimental conditions and rates of the 91 measurements at calcite saturation indices of 0.15 to 1.87 are summarized in Table 1.

RESULTS OF EXPERIMENTS

Laboratory measurements of calcite growth were used to determine the dependence of growth rate in calcium bicarbonate solutions to variations in CO₂ partial pressure and calcite saturation state at 34 °C as equilibrium is approached. Three CO₂ partial pressures were used in the experiments (10.1, 1.56 and 0.102 % CO₂ in N₂). Table 1 summarizes the solution compositions, saturation states with respect to calcite, masses of calcite grown, and growth rates. Crystal surface area ranged from 3.4 to 6.6 cm² and averaged 4.3 cm². Reaction times were typically 20 to 60 minutes. The calcite saturation index ranged from 0.15 to 1.87, and weight gain ranged from about 0 to nearly 2000 µg. Three crystals actually lost weight (runs 28, 33, and 103; of 2, 9, and 3 µg, respectively). Although this weight loss may be from physical loss of solid from the samples prior to weighing, both runs involving weight loss occurred nearest equilibrium for reactions in 0.102 and 10.1 % CO₂. However, these observations were not reproducible (see run 34, Table 1, which was a duplicate of run 33) and are likely due to sample damage.

Maximum rates of approximately 25,000 mm/ka were obtained from calcite growth at saturation indices of about 1.6 in calcium bicarbonate solutions saturated with 10.1 % CO₂. Figure 1 shows that at constant saturation state, calcite growth rate decreases with decreasing CO₂ partial pressure in calcium bicarbonate solutions, but the rate dependence on P_{CO2} is relatively small at CO₂ partial pressures in the range of 1.56% CO₂ and lower.

Table 1: Laboratory results of calcite crystal growth, 34 °C

[Ca, Calcium; mmol/kg, millimoles per kilogram of water; Calc., Calculated; pH, -log activity of hydrogen ion; IAP, Ion Activity Product of CaCO_3 ; p, -log activity; H, hydrogen ion; CO_3 , carbonate ion; HCO_3 , bicarbonate ion; cm^2 , square centimeters; Min., minutes; mg, milligrams; $\text{mg/cm}^2/\text{sec}$, milligrams per centimeter squared per second; mm/ka, millimeters per 1000 years, SI, Saturation Index of calcite = $\log \text{IAP/K}$, where K is the calcite equilibrium constant]

| Exp. No. | % CO_2 | Ca mmol/kg | Calc. pH | -Log IAP | pCa | p CO_3 | p HCO_3 | Area cm^2 | Time Min. | Wt. Gain mg | Rate 10^5 $\text{mg/cm}^2/\text{sec}$ | Rate mm/ka | SI |
|----------|-----------------|---------------|-------------|-------------|------|-----------------|------------------|-----------------------|--------------|-------------------|--|---------------|------|
| 69 | 0.102 | 2.66 | 8.52 | 6.92 | 2.79 | 4.13 | 2.39 | 5.56 | 22 | 0.735 | 10.01 | 11601 | 1.62 |
| 70 | 0.102 | 2.66 | 8.52 | 6.92 | 2.79 | 4.13 | 2.39 | 4.42 | 22 | 0.463 | 7.94 | 9193 | 1.62 |
| 13 | 0.102 | 2.42 | 8.48 | 7.02 | 2.82 | 4.20 | 2.42 | 4.00 | 35 | 0.783 | 9.32 | 10798 | 1.52 |
| 14 | 0.102 | 2.42 | 8.48 | 7.02 | 2.82 | 4.20 | 2.42 | 4.01 | 35 | 0.755 | 8.97 | 10386 | 1.52 |
| 75 | 0.102 | 2.12 | 8.44 | 7.15 | 2.86 | 4.29 | 2.46 | 4.22 | 20 | 0.313 | 6.18 | 7160 | 1.39 |
| 76 | 0.102 | 2.12 | 8.44 | 7.15 | 2.86 | 4.29 | 2.46 | 4.05 | 20 | 0.245 | 5.04 | 5840 | 1.39 |
| 40 | 0.102 | 1.89 | 8.39 | 7.27 | 2.90 | 4.37 | 2.51 | 4.92 | 51 | 0.858 | 5.70 | 6602 | 1.26 |
| 39 | 0.102 | 1.89 | 8.39 | 7.27 | 2.90 | 4.37 | 2.51 | 5.56 | 51 | 1.182 | 6.95 | 8048 | 1.26 |
| 60 | 0.102 | 1.84 | 8.39 | 7.30 | 2.91 | 4.39 | 2.52 | 4.22 | 20 | 0.184 | 3.63 | 4209 | 1.24 |
| 59 | 0.102 | 1.84 | 8.39 | 7.30 | 2.91 | 4.39 | 2.52 | 3.77 | 20 | 0.212 | 4.69 | 5428 | 1.24 |
| 61 | 0.102 | 1.74 | 8.37 | 7.36 | 2.93 | 4.43 | 2.54 | 4.19 | 20 | 0.188 | 3.74 | 4331 | 1.18 |
| 62 | 0.102 | 1.74 | 8.37 | 7.36 | 2.93 | 4.43 | 2.54 | 4.05 | 20 | 0.223 | 4.59 | 5315 | 1.18 |
| 53 | 0.102 | 1.65 | 8.34 | 7.42 | 2.95 | 4.47 | 2.56 | 4.32 | 50 | 0.418 | 3.23 | 3736 | 1.12 |
| 54 | 0.102 | 1.65 | 8.34 | 7.42 | 2.95 | 4.47 | 2.56 | 5.20 | 50 | 0.501 | 3.21 | 3720 | 1.12 |
| 45 | 0.102 | 1.43 | 8.29 | 7.57 | 2.99 | 4.58 | 2.61 | 4.22 | 64 | 0.355 | 2.19 | 2538 | 0.97 |
| 46 | 0.102 | 1.43 | 8.29 | 7.57 | 2.99 | 4.58 | 2.61 | 4.05 | 64 | 0.273 | 1.76 | 2033 | 0.97 |
| 21 | 0.102 | 1.34 | 8.26 | 7.65 | 3.02 | 4.63 | 2.63 | 4.00 | 53 | 0.253 | 1.99 | 2304 | 0.89 |
| 22 | 0.102 | 1.34 | 8.26 | 7.65 | 3.02 | 4.63 | 2.63 | 4.01 | 53 | 0.256 | 2.01 | 2326 | 0.89 |
| 36 | 0.102 | 1.19 | 8.22 | 7.77 | 3.06 | 4.72 | 2.68 | 3.77 | 237 | 0.51 | 0.95 | 1102 | 0.76 |
| 28 | 0.102 | 0.98 | 8.14 | 8.00 | 3.13 | 4.87 | 2.76 | 3.36 | 58 | -0.002 | -0.02 | -20 | 0.54 |
| 7 | 1.56 | 8.81 | 7.81 | 6.66 | 2.38 | 4.28 | 1.87 | 3.81 | 12 | 0.107 | 3.90 | 4518 | 1.87 |
| 1 | 1.56 | 8.81 | 7.84 | 6.66 | 2.38 | 4.28 | 1.87 | 5.20 | 22 | 1.023 | 14.90 | 17265 | 1.87 |
| 6 | 1.56 | 8.81 | 7.84 | 6.66 | 2.38 | 4.28 | 1.87 | 4.00 | 22 | 0.783 | 14.83 | 17179 | 1.87 |
| 44 | 1.56 | 5.93 | 7.70 | 7.07 | 2.50 | 4.58 | 2.02 | 3.36 | 41 | 0.979 | 11.84 | 13720 | 1.46 |
| 43 | 1.56 | 5.93 | 7.70 | 7.07 | 2.50 | 4.58 | 2.02 | 4.22 | 41 | 1.15 | 11.08 | 12832 | 1.46 |
| 68 | 1.56 | 5.77 | 7.69 | 7.10 | 2.50 | 4.60 | 2.03 | 5.20 | 20 | 0.834 | 13.37 | 15482 | 1.44 |
| 67 | 1.56 | 5.77 | 7.69 | 7.10 | 2.50 | 4.60 | 2.03 | 4.32 | 20 | 0.848 | 16.36 | 18949 | 1.44 |
| 88 | 1.56 | 5.58 | 7.68 | 7.14 | 2.51 | 4.62 | 2.04 | 4.92 | 21 | 0.332 | 5.36 | 6204 | 1.40 |
| 87 | 1.56 | 5.58 | 7.68 | 7.14 | 2.51 | 4.62 | 2.04 | 6.56 | 21 | 0.481 | 5.82 | 6741 | 1.40 |
| 80 | 1.56 | 5.45 | 7.67 | 7.16 | 2.52 | 4.64 | 2.05 | 5.20 | 20 | 0.435 | 6.97 | 8075 | 1.37 |
| 79 | 1.56 | 5.45 | 7.67 | 7.16 | 2.52 | 4.64 | 2.05 | 4.32 | 20 | 0.383 | 7.39 | 8558 | 1.37 |
| 90 | 1.56 | 5.25 | 7.65 | 7.20 | 2.53 | 4.67 | 2.06 | 4.01 | 20 | 0.263 | 5.47 | 6331 | 1.33 |
| 89 | 1.56 | 5.25 | 7.65 | 7.20 | 2.53 | 4.67 | 2.06 | 4.00 | 20 | 0.257 | 5.35 | 6202 | 1.33 |
| 74 | 1.56 | 5.12 | 7.65 | 7.23 | 2.54 | 4.69 | 2.07 | 3.77 | 20 | 0.423 | 9.35 | 10831 | 1.31 |
| 73 | 1.56 | 5.12 | 7.65 | 7.23 | 2.54 | 4.69 | 2.07 | 4.19 | 20 | 0.43 | 8.55 | 9907 | 1.31 |
| 12 | 1.56 | 5.04 | 7.64 | 7.25 | 2.55 | 4.70 | 2.08 | 4.92 | 35 | 0.570 | 5.52 | 6391 | 1.29 |
| 11 | 1.56 | 5.04 | 7.64 | 7.25 | 2.55 | 4.70 | 2.08 | 5.56 | 35 | 0.887 | 7.60 | 8800 | 1.29 |
| 51 | 1.56 | 4.99 | 7.63 | 7.26 | 2.55 | 4.71 | 2.08 | 5.56 | 51 | 1.69 | 9.93 | 11507 | 1.28 |
| 52 | 1.56 | 4.99 | 7.63 | 7.26 | 2.55 | 4.71 | 2.08 | 4.92 | 51 | 1.308 | 8.69 | 10064 | 1.28 |
| 81 | 1.56 | 4.95 | 7.63 | 7.27 | 2.55 | 4.72 | 2.08 | 4.19 | 23 | 0.251 | 4.34 | 5029 | 1.27 |
| 82 | 1.56 | 4.95 | 7.63 | 7.27 | 2.55 | 4.72 | 2.08 | 3.77 | 23 | 0.205 | 3.94 | 4564 | 1.27 |

Table 1 (continued)

| Exp. No. | % CO ₂ | Ca mmol/kg | Calc. pH | -Log IAP | pCa | pCO ₃ | pHCO ₃ | Area cm ² | Time Min. | Wt. Gain mg | Rate·10 ⁵ mg/cm ² / sec | Rate mm/ka | SI |
|----------|-------------------|---------------|-------------|-------------|------|------------------|-------------------|-------------------------|--------------|-------------------|---|---------------|------|
| 80 | 1.56 | 4.94 | 7.63 | 7.27 | 2.55 | 4.71 | 2.09 | 4.09 | 20 | 0.427 | 8.70 | 10078 | 1.27 |
| 79 | 1.56 | 4.94 | 7.63 | 7.27 | 2.55 | 4.71 | 2.09 | 3.81 | 20 | 0.481 | 10.52 | 12187 | 1.27 |
| 91 | 1.56 | 4.84 | 7.62 | 7.29 | 2.56 | 4.73 | 2.09 | 4.22 | 20 | 0.295 | 5.83 | 6748 | 1.25 |
| 92 | 1.56 | 4.84 | 7.62 | 7.29 | 2.56 | 4.73 | 2.09 | 3.36 | 20 | 0.216 | 5.36 | 6206 | 1.25 |
| 83 | 1.56 | 4.40 | 7.58 | 7.40 | 2.59 | 4.81 | 2.13 | 4.22 | 20 | 0.174 | 3.44 | 3980 | 1.14 |
| 84 | 1.56 | 4.40 | 7.58 | 7.40 | 2.59 | 4.81 | 2.13 | 3.36 | 20 | 0.126 | 3.13 | 3620 | 1.14 |
| 50 | 1.56 | 4.20 | 7.56 | 7.45 | 2.61 | 4.84 | 2.15 | 4.09 | 61 | 0.781 | 5.22 | 6044 | 1.09 |
| 49 | 1.56 | 4.20 | 7.56 | 7.45 | 2.61 | 4.84 | 2.15 | 3.81 | 61 | 0.879 | 6.30 | 7302 | 1.09 |
| 57 | 1.56 | 4.09 | 7.56 | 7.47 | 2.61 | 4.86 | 2.16 | 4.32 | 20 | 0.176 | 3.40 | 3933 | 1.06 |
| 58 | 1.56 | 4.09 | 7.56 | 7.47 | 2.61 | 4.86 | 2.16 | 5.20 | 20 | 0.223 | 3.57 | 4140 | 1.06 |
| 85 | 1.56 | 4.04 | 7.55 | 7.49 | 2.62 | 4.87 | 2.16 | 3.81 | 22 | 0.177 | 3.52 | 4077 | 1.05 |
| 86 | 1.56 | 4.04 | 7.55 | 7.49 | 2.62 | 4.87 | 2.16 | 4.09 | 22 | 0.173 | 3.20 | 3712 | 1.05 |
| 64 | 1.56 | 3.95 | 7.54 | 7.51 | 2.62 | 4.89 | 2.17 | 3.36 | 20 | 0.124 | 3.08 | 3563 | 1.02 |
| 63 | 1.56 | 3.95 | 7.54 | 7.51 | 2.62 | 4.89 | 2.17 | 4.22 | 20 | 0.149 | 2.94 | 3408 | 1.02 |
| 66 | 1.56 | 3.83 | 7.53 | 7.55 | 2.64 | 4.91 | 2.19 | 4.09 | 21 | 0.183 | 3.55 | 4114 | 0.99 |
| 65 | 1.56 | 3.83 | 7.53 | 7.55 | 2.64 | 4.91 | 2.19 | 3.81 | 21 | 0.184 | 3.83 | 4440 | 0.99 |
| 17 | 1.56 | 3.73 | 7.52 | 7.58 | 2.64 | 4.94 | 2.20 | 4.22 | 49 | 0.236 | 1.90 | 2203 | 0.96 |
| 18 | 1.56 | 3.73 | 7.52 | 7.58 | 2.64 | 4.94 | 2.20 | 4.05 | 49 | 0.183 | 1.54 | 1780 | 0.96 |
| 19 | 1.56 | 3.03 | 7.44 | 7.81 | 2.71 | 5.10 | 2.28 | 5.56 | 52 | 0.240 | 1.38 | 1603 | 0.72 |
| 20 | 1.56 | 3.03 | 7.44 | 7.81 | 2.71 | 5.10 | 2.28 | 4.92 | 55 | 0.168 | 1.03 | 1199 | 0.72 |
| 26 | 1.56 | 2.44 | 7.35 | 8.06 | 2.79 | 5.27 | 2.36 | 4.05 | 62 | 0.041 | 0.27 | 315 | 0.47 |
| 25 | 1.56 | 2.44 | 7.35 | 8.06 | 2.79 | 5.27 | 2.36 | 4.22 | 62 | 0.05 | 0.32 | 369 | 0.47 |
| 31 | 1.56 | 2.14 | 7.30 | 8.21 | 2.83 | 5.38 | 2.42 | 5.20 | 387 | 0.218 | 0.18 | 209 | 0.32 |
| 32 | 1.56 | 2.14 | 7.30 | 8.21 | 2.83 | 5.38 | 2.42 | 5.56 | 387 | 0.242 | 0.19 | 217 | 0.32 |
| 94 | 1.56 | 1.99 | 7.27 | 8.29 | 2.86 | 5.43 | 2.45 | 5.20 | 125 | 0.022 | 0.06 | 65 | 0.24 |
| 93 | 1.56 | 1.99 | 7.27 | 8.29 | 2.86 | 5.43 | 2.45 | 4.32 | 125 | 0.017 | 0.05 | 61 | 0.24 |
| 97 | 1.56 | 1.83 | 7.24 | 8.39 | 2.89 | 5.50 | 2.48 | 4.09 | 99 | 0.012 | 0.05 | 57 | 0.15 |
| 98 | 1.56 | 1.83 | 7.24 | 8.39 | 2.89 | 5.50 | 2.48 | 4.92 | 99 | 0.023 | 0.08 | 91 | 0.15 |
| 3 | 10.1 | 12.94 | 7.20 | 7.01 | 2.25 | 4.76 | 1.70 | 5.56 | 20 | 1.484 | 22.24 | 25765 | 1.53 |
| 55 | 10.1 | 10.46 | 7.12 | 7.24 | 2.31 | 4.92 | 1.78 | 4.00 | 49 | 1.931 | 16.42 | 19021 | 1.30 |
| 56 | 10.1 | 10.46 | 7.12 | 7.24 | 2.31 | 4.92 | 1.78 | 4.01 | 49 | 1.984 | 16.83 | 19494 | 1.30 |
| 78 | 10.1 | 9.50 | 7.09 | 7.33 | 2.34 | 4.99 | 1.82 | 3.36 | 20 | 0.565 | 14.01 | 16233 | 1.20 |
| 77 | 10.1 | 9.50 | 7.09 | 7.33 | 2.34 | 4.99 | 1.82 | 4.22 | 20 | 0.641 | 12.66 | 14663 | 1.20 |
| 10 | 10.1 | 7.97 | 7.02 | 7.52 | 2.40 | 5.13 | 1.89 | 5.20 | 40 | 1.023 | 8.20 | 9496 | 1.01 |
| 9 | 10.1 | 7.97 | 7.02 | 7.52 | 2.40 | 5.13 | 1.89 | 4.32 | 40 | 0.761 | 7.34 | 8503 | 1.01 |
| 41 | 10.1 | 7.48 | 6.99 | 7.60 | 2.42 | 5.18 | 1.91 | 4.00 | 51 | 0.717 | 5.86 | 6786 | 0.94 |
| 42 | 10.1 | 7.48 | 6.99 | 7.60 | 2.42 | 5.18 | 1.91 | 4.01 | 51 | 0.718 | 5.85 | 6778 | 0.94 |
| 48 | 10.1 | 6.78 | 6.95 | 7.70 | 2.45 | 5.26 | 1.95 | 3.77 | 65 | 0.617 | 4.20 | 4861 | 0.83 |
| 47 | 10.1 | 6.78 | 6.95 | 7.70 | 2.45 | 5.26 | 1.95 | 4.19 | 65 | 0.595 | 3.64 | 4218 | 0.83 |
| 15 | 10.1 | 5.77 | 6.89 | 7.88 | 2.50 | 5.38 | 2.01 | 4.19 | 49 | 0.256 | 2.08 | 2407 | 0.66 |
| 16 | 10.1 | 5.77 | 6.89 | 7.88 | 2.50 | 5.38 | 2.01 | 3.77 | 49 | 0.132 | 1.19 | 1380 | 0.66 |
| 24 | 10.1 | 5.00 | 6.83 | 8.04 | 2.54 | 5.50 | 2.07 | 5.20 | 55 | 0.296 | 1.72 | 1998 | 0.50 |
| 23 | 10.1 | 5.00 | 6.83 | 8.04 | 2.54 | 5.50 | 2.07 | 4.32 | 55 | 0.229 | 1.61 | 1861 | 0.50 |
| 30 | 10.1 | 4.37 | 6.78 | 8.19 | 2.59 | 5.60 | 2.12 | 3.77 | 66 | 0.029 | 0.19 | 225 | 0.35 |
| 29 | 10.1 | 4.37 | 6.78 | 8.19 | 2.59 | 5.60 | 2.12 | 4.19 | 66 | 0.056 | 0.34 | 391 | 0.35 |
| 34 | 10.1 | 4.10 | 6.75 | 8.26 | 2.61 | 5.66 | 2.15 | 4.01 | 386 | 0.017 | 0.02 | 21 | 0.27 |
| 33 | 10.1 | 4.10 | 6.75 | 8.26 | 2.61 | 5.66 | 2.15 | 4.92 | 386 | -0.009 | -0.01 | -9 | 0.27 |
| 71 | 10.1 | 1.09 | 7.11 | 7.27 | 2.33 | 4.94 | 1.80 | 4.00 | 17 | 0.482 | 11.81 | 13685 | 1.27 |

Table 1 (continued)

| Exp. No. | % CO ₂ | Ca mmol /kg | Calc. pH | -Log IAP | pCa | pCO ₃ | pHCO ₃ | Area cm ² | Time Min. | Wt. Gain mg | Rate 10 ⁵ mg/cm ² /sec | Rate mm/ka | SI |
|----------|-------------------|-------------|----------|----------|------|------------------|-------------------|----------------------|-----------|-------------|--|------------|------|
| 72 | 10.1 | 1.09 | 7.11 | 7.27 | 2.33 | 4.94 | 1.80 | 4.01 | 17 | 0.437 | 10.68 | 12376 | 1.27 |
| 103 | 10.1 | 5.13 | 6.77 | 8.14 | 2.53 | 5.61 | 2.61 | 4.00 | 20 | -0.003 | -0.06 | -72 | 0.40 |

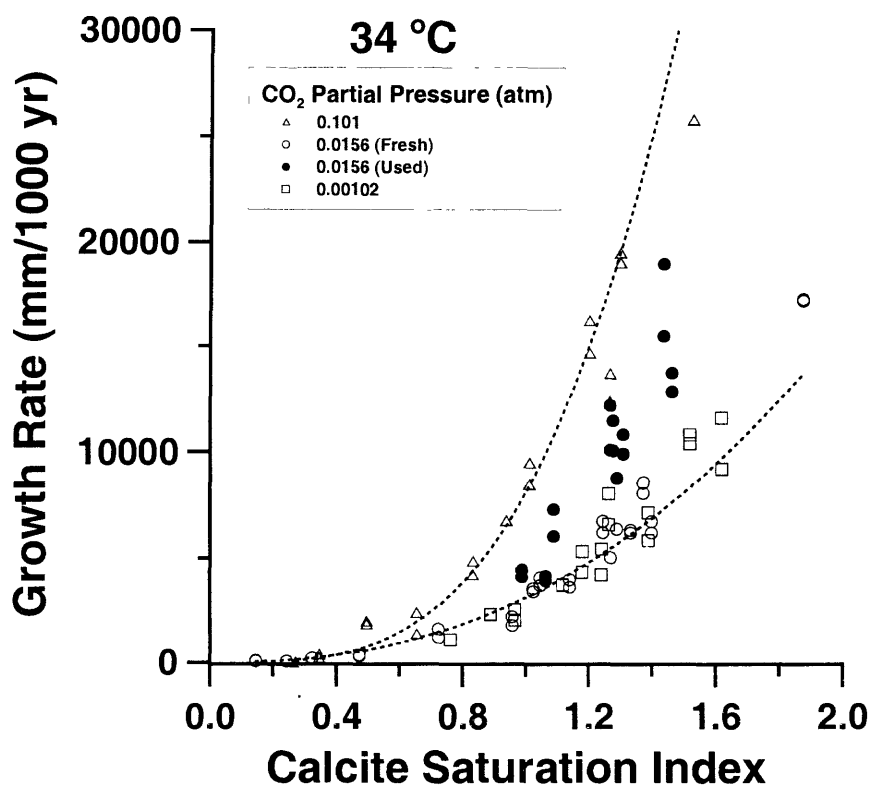


Figure 1: Laboratory rates of calcite growth at 34 °C and CO₂ partial pressures of 0.101, 0.0156, and 0.00102 atmospheres, for calcite saturation indices of 0.2 to 2.0. Solid circles denote rates obtained from Iceland spar crystals that were re-used in successive growth experiments without acid washing (1.56 % CO₂ only). The dashed lines are fits to the experimental data at 0.101 and 0.00102 atm.CO₂.

In other experiments, crystals that had grown previously in laboratory solutions saturated with 1.56 % CO₂ were re-used in successive growth experiments without acid treatment. The previously reacted crystals (denoted “used” on Figure 1) usually grew faster than clean, fresh crystals by as much as a factor of 2 (Figures 1 and 2).

Using Scanning Force Microscopy, Dove and Hochella (1993) found that precipitation of calcite began with the formation of surface nuclei that spread and coalesced as growth continued, and spiral growth began only after several hours of reaction in near-equilibrium CO₂-saturated solutions. The increase in rate we observe for previously reacted crystals relative to fresh, unreacted crystals may be due to increase in surface area as the surface evolves during growth.

Uncertainties in the laboratory rates become very large below rates of 100 mm/ka. On the log rate scale of Figure 2, the rate curve must decrease steeply to $-\infty$ as SI calcite approaches 0.

RATE MODELS AND NEAR-EQUILIBRIUM RATES

Considerable progress has been made in developing mechanistic rate laws that describe both dissolution and growth of calcite crystals, obey the principle of microscopic reversibility, and predict rates under a wide range of pH, P_{CO2}, and calcite-saturation state conditions (Plummer and others, 1978, 1979; Chou and others, 1989; Van Cappellen and others, 1993; Zuddas and Mucci, 1994; Arakaki and Mucci, 1995).

Plummer and others (1978) studied the dissolution of calcite in the CaCO₃-H₂O-CO₂-HCl system both far from equilibrium using pH-stat methods, and as equilibrium was approached in “free-drift” dissolution experiments. From measurements of the forward rate dependence on H⁺, CO_{2(aq)} and H₂O, the overall net rate of reaction (positive for dissolution, negative for precipitation) was defined as

$$R = k_1 a_{H^+} + k_2 a_{H_2CO_3} + k_3 a_{H_2O} - k_4 a_{Ca^{2+}} a_{HCO_3^-},$$

where k_1 , k_2 and k_3 are first-order rate constants for the forward reaction dependent on temperature, and k_4 is a second-order back-reaction rate constant dependent on P_{CO2} and temperature. A theoretical expression was derived for k_4 by assuming that the composition of the fluid in the boundary layer adjacent to the crystal surface was in equilibrium with calcite at the bulk-fluid CO₂ partial pressure. This assumption may be valid for relatively high CO₂ partial pressures (P_{CO2} > 0.03 atm), but could fail at lower CO₂ partial pressures if the boundary layer P_{CO2} deviates from the bulk fluid and is a function of the reactant flux between the mineral surface and bulk fluid (Plummer and others, 1979). Theoretical values of k_4 compared favorably with experimental values from dissolution experiments in CO₂-H₂O solutions (Plummer and others, 1978). The

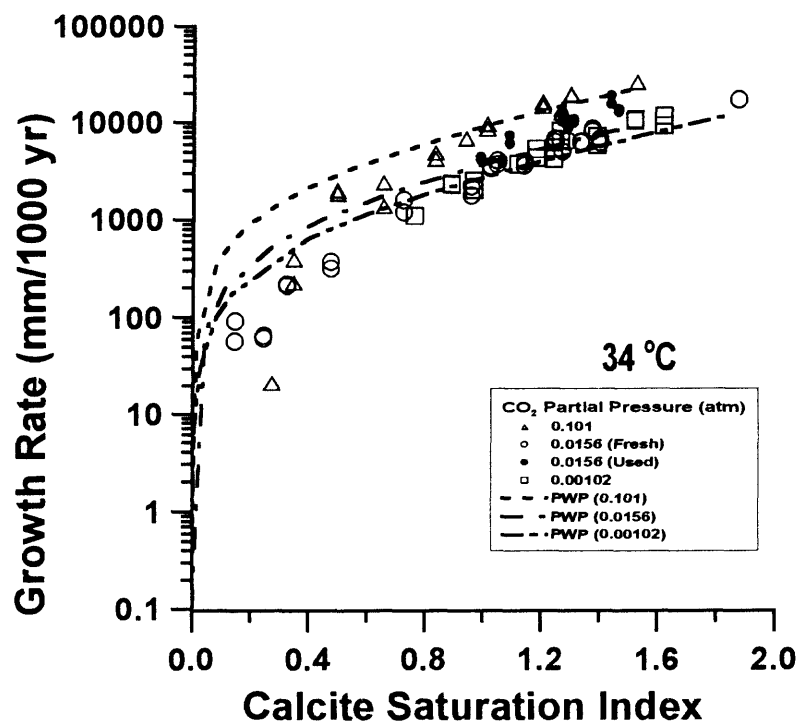


Figure 2: Log rate of calcite crystal growth as a function of calcite saturation index. The experimental data indicate that crystal growth rates fall rapidly as equilibrium is approached. The dashed lines show rate calculated from the mechanistic model of Plummer and others (1978), PWP, which adequately describes the growth rate at $SI_c > 0.4$, but over-estimates rates near equilibrium.

rate expression, derived solely from dissolution data, was shown to describe calcite crystal growth in controlled laboratory experiments (Reddy and others, 1981; Busenberg and Plummer, 1986). The dashed lines on Figure 2 show rates calculated from the model of Plummer and others, (1978) at the 3 CO₂ partial pressures used here and 34 °C. In the calculations, the rate constants and thermodynamic data were from Plummer and others (1978, 1982), except for k_3 (the rate constant for the water reaction, see Plummer and others, 1978)) which was taken from Chou and others (1989). The laboratory rates, and the dependence of growth rate on P_{CO2} and saturation state, are adequately described by the Plummer and others (1978) model at calcite saturation indices above about 0.4, but fall below the calculated rates as equilibrium is approached at saturation indices below 0.4 (Figure 2).

Studies by Inskeep and Bloom (1985), and Chou and others (1989) identified problems with the Plummer and others (1978) rate law above pH of about 8. (The experimental data of the present study range in pH from 7.0 to 8.5). Chou and others (1989) proposed dependence of the back reaction on the activity product of Ca²⁺ and CO₃²⁻. As evidence for backward reaction dependence on the Ca²⁺ and CO₃²⁻ activity product, Chou and others (1989) presented a non-linear relation between backward rate (obtained at variable P_{CO2}) as a function of the Ca²⁺ HCO₃⁻ activity product, and linear dependence on the activity product of Ca²⁺ and CO₃²⁻ (see Figure 4b of Chou and others, 1989). The comparison of Figure 4b of Chou and others (1989) is considered to be misleading, however, because it does not account for the P_{CO2} dependence of k_4 .

Only one reaction is needed to describe the forward rate at low P_{CO2} and high pH. Plummer and others (1978) chose to represent the reaction with water as reactant,



to maintain consistency with the predominant Ca²⁺ and HCO₃⁻ speciation in their laboratory fluids. The reaction could equally have been written as



Because the dissociation of HCO₃⁻ to CO₃²⁻ can be assumed to occur instantaneously during the dissolution and crystal growth of calcite, either reaction can be applied in the mechanistic model of Plummer and others (1978) for dilute solutions where the $a_{\text{H}_2\text{O}}$ is virtually unity. The reason for this is that the forward rate is known from experiments far from equilibrium in compositional regions where rate is independent of P_{CO2} and pH. The principle of microscopic reversibility and data on the thermodynamic stability of calcite then equally define the backward reaction rate for either rate expression. As shown by Plummer and others (1978), the backward rate constant for the reaction of calcite with H₂O as reactant is large at low P_{CO2}, and thus, in principle, either reaction can describe the rate of backward reaction. Nevertheless, the performance of the mechanistic model of Plummer and others (1978) could be improved at high pH if modified to define more accurately the CO₂ partial pressure in the boundary layer adjacent to the mineral surface during reaction.

Van Cappellen and others (1993) derived a surface complexation model for the chemical speciation at the carbonate mineral-water interface. They proposed that two species ($>\text{CaOH}^\circ$ and $>\text{CO}_3\text{H}^\circ$) form at hydration sites on the calcite surface when fresh calcite comes in contact with water. The model then predicts the development of surface charge and surface speciation as these sites interact with aqueous solutions. These authors showed that the surface-complexation model provided a framework that was capable of describing the pH and CO_2 dependence of calcite dissolution. Arakaki and Mucci (1995) expanded the surface-complexation model of Van Cappellen and others (1993) to include both dissolution and crystal growth of calcite, incorporating aspects of the mechanistic models of Plummer and others (1978) and Chou and others (1989).

The mechanistic models (Plummer and others, 1978; Chou and others, 1989), and surface complexation models (Van Cappellen and others, 1993; Arakaki and Mucci, 1995) provide theoretical frameworks for describing experimental kinetic results and predicting rates beyond experimental conditions. Both approaches can be enhanced to account for inhibiting effects of foreign ions, by including additional terms to describe the effects of adsorption of foreign ions on rate (Busenberg and Plummer, 1986; Svensson and Dreybrodt, 1992), or by including reactions for the formation of additional surface complexes (Van Cappellen and others, 1993). Both approaches have also, with some success, adequately described the rates of dissolution and crystal growth of calcite in aqueous solutions where the driving force for reaction was relatively large. Specifically, these models are most reliable when applied to aqueous solutions where calcite saturation is approximately $-0.2 > \text{SI}_c > 0.2$. But in the region near equilibrium ($\text{SI}_c = 0 \pm 0.2$), rates of crystal growth and dissolution are very small and not described by either the mechanistic model or surface-complexation approach.

Both the mechanistic and surface-complexation models overestimate the rate of dissolution in the sub-saturated region nearest equilibrium ($-0.2 > \text{SI}_c > 0$), and overestimate growth rates in the over-saturated region nearest equilibrium ($0.2 > \text{SI}_c > 0$). Figure 3 shows calcite dissolution and growth rate data from Busenberg and Plummer (1986) as a function of the CaHCO_3 activity product in calcium bicarbonate solutions saturated with CO_2 at 25 °C and covering a range in SI_c of nearly $-\infty$ to 1.0. The experimental data show that the measured rate in “pure” laboratory fluids plateaus in the near-equilibrium region. It is possible that trace impurities are still present and inhibit the laboratory rate near equilibrium. If this is so, then all near-equilibrium calcite rates in natural environments will be inhibited. It is also possible that the free energy of reaction must exceed the adsorption energy of water and aqueous species at the calcite surface for net reaction to proceed. The mechanistic model (Plummer and others, 1978) was derived from rate measurements at substantial undersaturation where surface energies could be ignored. Near equilibrium, the surface energies of adsorption of water and all aqueous species, including adsorbed inhibitors, compete with the net reaction energy and slow the rate as equilibrium is approached. At present, there are no models that adequately describe both near and far from equilibrium the rates of calcite dissolution and crystal growth. Rates calculated from the models of Plummer and others (1978) and Arakaki and Mucci (1995) vary smoothly between the dissolution and precipitation fields, passing directly through

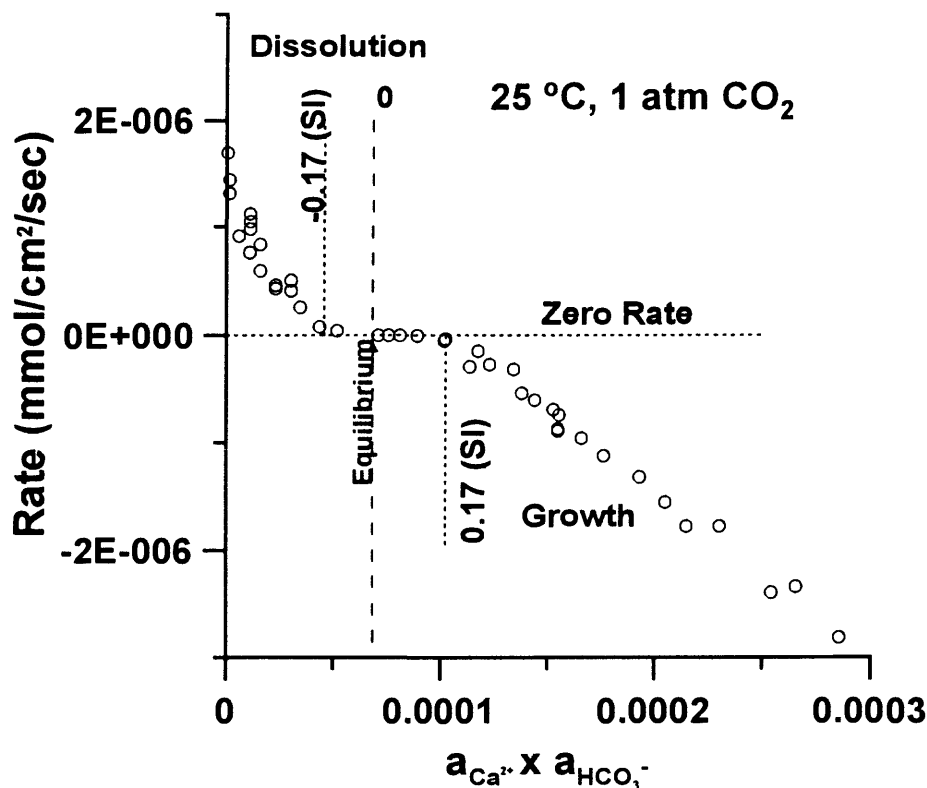


Figure 3: Rates of dissolution and crystal growth of calcite at 25 °C in CO_2 -saturated water as a function of the CaHCO_3 activity product in solution (Busenberg and Plummer, 1986). The plot shows a plateau in rate in the near-equilibrium region ($\text{SI}_c = 0 \pm 0.17$). The forward rate far from equilibrium occurs at 0 for the CaHCO_3 activity product ($\text{SI}_c = -\infty$). Equilibrium occurs at zero rate where the CaHCO_3 activity product is 0.68×10^{-4} . The maximum CaHCO_3 activity product shown corresponds to a saturation index of approximately 1.0.

the point of zero rate at $SI_c=0$, as required by microscopic reversibility. Consequently, these models over-estimate both rates of dissolution and crystal growth, which decrease abruptly and plateau near equilibrium. Calcium bicarbonate solutions saturated with CO_2 were chosen to make this point in Figure 3 because the rate departures are more evident at high concentrations than at low concentrations. The plateau in rate near equilibrium occurs at all CO_2 partial pressures, but is usually overlooked at low P_{CO_2} values.

Figure 4 shows the calcite growth rates reported here at 34 °C and CO_2 partial pressures of 0.101, 0.0156, and 0.00102 atm as a function of the calcium bicarbonate activity product. In all three cases, the growth rate varies linearly with the calcium bicarbonate activity product (at constant P_{CO_2}), but extrapolates to zero at solution compositions that are slightly supersaturated with respect to calcite. Although the compositional width of the near-equilibrium region, where the rate plateaus, decreases with decreasing CO_2 partial pressure, the range corresponds thermodynamically to the near-equilibrium region of $0 < SI_c < 0.2$ in calcite saturation index (Busenberg and Plummer, 1986). Calcite saturation is commonly observed in the range $SI_c = 0 \pm 0.2$ in waters from limestone aquifers. Further work is needed to develop theoretical models of calcite dissolution and growth in near-equilibrium solutions.

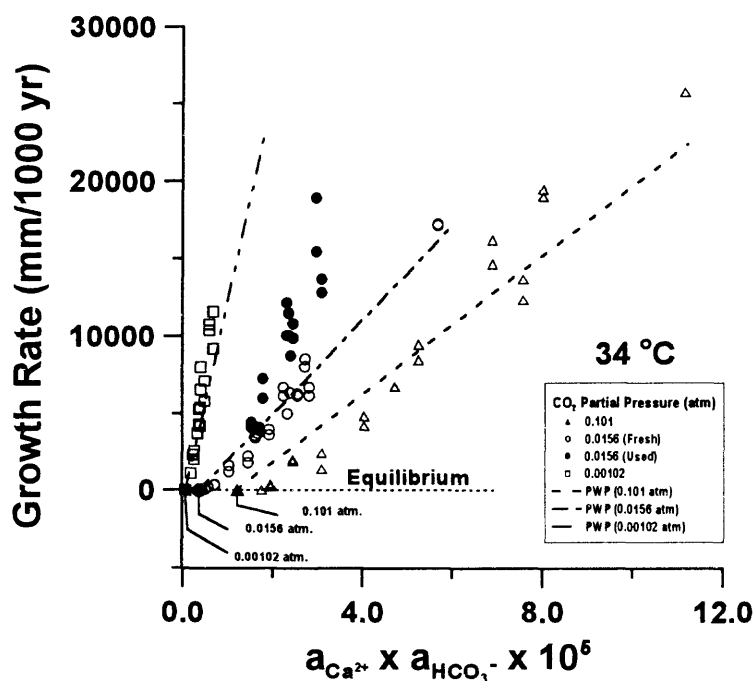


Figure 4: Rate of calcite growth at CO_2 partial pressures of 0.101, 0.0156, and 0.00102 atm and 34°C as a function of the $CaHCO_3$ activity product in solution. The plateau in rate near equilibrium (also seen in Figure 3) is evident at the lower CO_2 partial pressures. The dashed lines show rate calculated from the mechanistic model of Plummer and others (1978). The solid symbols at zero rate correspond to equilibrium for each CO_2 partial pressure. Other symbols are as described in Figures 1 and 2.

CONCLUSION

Calcite crystal growth was studied in the laboratory by determination of weight gain of single crystals of Iceland spar in Ca-HCO_3 solutions at 34 °C and CO_2 partial pressures of 0.101, 0.0156 and 0.00102 atm and calcite saturation indices of 0.15 to 1.87. The rate of crystal growth varied linearly with the activity product of Ca^{2+} and HCO_3^- in solution. At constant saturation state, growth rate was nearly independent of P_{CO_2} between 0.00102 and 0.0156 atm, but increased at the highest P_{CO_2} . The maximum calcite growth rate was 25,000 mm/ka at $\text{SI}_c=1.6$ and P_{CO_2} of 0.101 atm. Growth rates less than 100 mm/ka could not be reliably measured by the laboratory weight-gain method. If not treated with acid between use, growth rate of individual Iceland spar crystals increased by as much as a factor of 2 with re-use, possibly due to increase in surface area.

At calcite saturation indices greater than 0.4, the laboratory rates of crystal growth were adequately described by the mechanistic model of Plummer and others (1978). The laboratory rates for fresh Iceland spar crystals show that growth rate is extremely sensitive to saturation state near equilibrium. In the near-equilibrium region of $\text{SI}_c = 0 \pm 0.2$, rates of calcite dissolution and crystal growth are very small and are not described by either the mechanistic model or the surface-complexation model of calcite dissolution and crystal growth.

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