

# An experimental study of calcite dissolution rates at acidic conditions and 25 °C in the presence of NaPO<sub>3</sub> and MgCl<sub>2</sub>

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## Abstract

Dissolution rates of single calcite crystals were determined from sample weight loss using free-drift rotating disk techniques. Experiments were performed at 25 °C in aqueous HCl solutions over the bulk solution pH range – 1 to 3 and in the presence of trace concentrations of aqueous NaPO<sub>3</sub> and MgCl<sub>2</sub>. These salts were chosen for this study because aqueous magnesium and phosphate are known to strongly inhibit calcite dissolution at neutral to basic pH. Reactive solutions were undersaturated with respect to possible secondary phases. Neither an inhibition or enhancement of calcite dissolution rates was observed in the presence of aqueous MgCl<sub>2</sub> at pH 1 and 3. The presence of trace quantities of NaPO<sub>3</sub>, which dissociates in solution to Na<sup>+</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, decreased the overall calcite dissolution rate at pH ≤ 2. This contrasting behavior could be attributed to the different adsorption behavior of these dissolved species. As calcite surfaces are positively charged in acidic solutions, aqueous Mg<sup>2+</sup> may not adsorb, whereas aqueous phosphate, present as either the anion H<sub>2</sub>PO<sub>4</sub><sup>-</sup> or the neutral species H<sub>3</sub>PO<sub>4</sub><sup>0</sup>, readily adsorbs on calcite surfaces leading to significant dissolution inhibition.

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*Keywords:* Calcite dissolution rates; NaPO<sub>3</sub>; MgCl<sub>2</sub>

## 1. Introduction

The motivation of this work is the improved understanding of the rates and mechanism of calcite dissolution in acidic solutions. Toward this goal, the dissolution rates of calcite crystals have been measured as a function of aqueous NaPO<sub>3</sub> and MgCl<sub>2</sub> at a temperature of 25 °C and – 1 < pH < 3. Comparison

of these rates with those reported in the literature illustrates the effect of these salts as a function of their concentration and pH. The purpose of this manuscript is to report the results of this experimental and comparative study.

Due to its widespread presence in crustal rocks and its role in CO<sub>2</sub> cycle, the dissolution/precipitation kinetics of calcite have been studied more than perhaps any other mineral (c.f. King and Liu, 1933; Tominaga et al., 1939; Weyl, 1958, 1967; Berner, 1967, 1975, 1978; Nestaas and Terjesen, 1969; Griffin and Jurinak, 1973; Berner and Morse, 1974; Plummer and Mackenzie, 1974; Lund et al., 1975; Plummer and Wigley, 1976; Sjöberg, 1976,

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1978, 1983; Plummer et al., 1978, 1979; Dreybrodt, 1981; Plummer and Busenberg, 1982; Rickard and Sjöberg, 1983; Morse, 1974a,b, 1983; Mucci and Morse, 1983; Sjöberg and Rickard, 1983, 1984a,b, 1985; Walter, 1983; Amrhein et al., 1985; Buhman and Dreybrodt, 1985a,b; Busenberg and Plummer, 1986; Mucci, 1986; Burton and Walter, 1987; Guy, 1989; Murphy et al., 1989; Schott et al., 1989; Chou et al., 1989; Compton and Pritchard, 1990; Compton and Unwin, 1990; Wollast, 1990; MacInnis and Brantley, 1992; Dreybrodt et al., 1996; Liu and Dreybrodt, 1996; Alkattan et al., 1998). Several studies were aimed at determining the degree to which various dissolved aqueous species inhibit calcite dissolution or precipitation at near to seawater conditions (Nestaas and Terjesen, 1969; Morse and Berner, 1972; Berner and Morse, 1974; Sjöberg, 1978; Kier, 1980). The presence of two dissolved components, aqueous magnesium (Weyl, 1967; Berner, 1967; Sjöberg, 1978) and aqueous phosphate (Morse and Berner, 1972; Berner and Morse, 1974; Sjöberg, 1978) were noted to have marked inhibitory effects on calcite dissolution rates at neutral to basic pH. One of the aims of the present study is to evaluate to what extent these two components affect calcite dissolution rates at acidic conditions.

Calcite dissolution at acidic conditions plays a major role in a variety of natural and industrial processes. In the petroleum industry, calcite dissolution rates are of interest to better predict and optimize acid fracturing of carbonate petroleum reservoirs (Van Poolen and Argon, 1968; Cheung and Van Arsdale, 1989; Daccord et al., 1989; Gdanski and Lee, 1989; Hung et al., 1989; Tinker, 1989; Hoefner and Folger, 1989; Van Domelen, 1992; Wang et al., 1993; Yan et al., 1993; Hill et al., 1994). Other systems in which calcite dissolution by acidic solutions play a major role include the neutralization of acid mine waste water and spent pickling liquors by carbonates (Hoak et al., 1945; Hill, 1969; Hill and Wilmoth, 1971; Volpicelli et al., 1982; Maree et al., 1992), and the destruction of building facades by acid rain.

## 2. Materials and methods

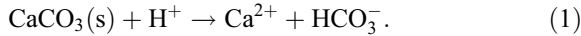
All dissolution rates obtained in the present study were from the weight loss of Pourtalet calcite dis-

solved in HCl-rich solutions using rotating disk techniques. The rotating disk reactor and disk preparation techniques are described in detail by Alkattan et al. (1998); the interested reader is referred to this previously published description. Pourtalet calcite is comprised of 55.8 wt.% CaO, 43.9% CO<sub>2</sub>, 0.32% Al<sub>2</sub>O<sub>3</sub>, 0.72% SiO<sub>2</sub>, 0.29% Fe<sub>2</sub>O<sub>3</sub> and 0.7% MgO. Calcite disks exposing faces either parallel to the cleavage plane or perpendicular to the *c*-crystallographic axis were dissolved. Reactive solutions were composed of pure analytical grade HCl,  $\pm$  NaPO<sub>3</sub> or MgCl<sub>2</sub> dissolved in deionized H<sub>2</sub>O. All reactive solutions were undersaturated with respect to secondary phases. For experiments conducted at pH  $\sim$  3, 0.09 mol/kg KCl was added to these solutions to insure an ionic strength of 10<sup>-2</sup> molal. Neither the pH nor the ionic strength of the reactive solutions was controlled during the experiments. At pH  $\geq$  2, the bulk reactive solution pH was measured in the reactor during the dissolution experiments with a Schott H63 combined electrode calibrated using DIN 19266/NIST standards (pH=4.008 and 6.865 at 25 °C) at the temperature of interest. pH values at more acidic conditions were computed using equations reported by Pitzer (1991, see Alkattan et al., 1998) because of the low accuracy of standard glass electrodes at these conditions (Bates, 1973). The difference between the pH of the reactive solution before and following the experiments was 0.01 pH unit for experiments conducted at pH  $\approx$  -1, increasing to as much as 0.32 pH unit for experiments conducted at pH  $\approx$  3. The ionic strength of the reactive solutions increased by a maximum of 15% for the experiments performed at pH  $\approx$  2, but by less than 5% at all other pH. All experiments were controlled so that sample dissolution did not change the hydrodynamic conditions near the disk surface (Alkattan, 1996) and the reactive solutions were highly undersaturated with respect to all solid phases including calcite. The rotation speed was kept at 340  $\pm$  4 revolutions per minute (rpm) for all experiments.

## 3. Theoretical background

The overall reaction rate of a rapidly dissolving mineral, such as calcite in acidic solutions stems from

two distinct effects: detachment from the mineral surface, and diffusional transport of dissolved aqueous species from this surface through an interfacial layer into the bulk solution (Dibble and Tiller, 1981; Guy and Schott, 1989; Murphy et al., 1989). Detachment of solutes from the calcite surface at acidic conditions can be described using



The chemical reaction rate ( $r_c$ ) of this reaction is given by (Busenberg and Plummer, 1986; Chou et al., 1989; Wollast, 1990; Alkattan et al., 1998)

$$r_c = k_2 a_{\text{H}^+,s} = k_2 \gamma_{\text{H}^+,s} c_{\text{H}^+,s} \quad (2)$$

where  $k_2$  stands for a chemical rate constant, and  $a_{\text{H}^+,s}$ ,  $\gamma_{\text{H}^+,s}$  and  $c_{\text{H}^+,s}$  represent the activity, activity coefficient, and concentration of aqueous  $\text{H}^+$  adjacent to the calcite surface. The symbol  $k_2$  was chosen to be

consistent with formalism presented by Wollast (1990) and adopted by Alkattan et al. (1998). Protons consumed by reaction (1) leads to diffusion concentration gradients near the calcite surface that can be described using

$$r_t = k_t (c_{\text{H}^+,b} - c_{\text{H}^+,s}), \quad (3)$$

where  $r_t$  signifies the transport rate,  $c_{\text{H}^+,b}$  refers to the hydrogen ion concentration in the bulk solution, and  $k_t$  denotes a transport rate constant. The transport rate constant for the rotating disk reactor at disk rotation speeds  $\gg 0$ , can be computed from Gregory and Rid-diford (1956), Pleskov and Filinovski (1976), and Alkattan et al. (1997a,b)

$$k_t = D/\delta = 0.62D^{2/3}v^{-1/6}\omega^{1/2}, \quad (4)$$

where  $\delta$  signifies the thickness of the diffusion layer,  $v$  corresponds to the kinematic solution viscosity,  $\omega$

Table 1

Measured calcite dissolution rates as a function of  $\text{MgCl}_2$  concentration at a disk rotation speed of  $340 \text{ min}^{-1}$

Sample number	Mass dissolved (g)	Experiment duration (min)	Dissolution rate ( $\text{mol/m}^2/\text{s} \times 10^3$ )	pH	$\text{MgCl}_2$ concentration (mol/kg)
<i>pH ~ 1</i>					
1023	0.25545	20	5.13	1.028	0
1027	0.28825	20	5.78	1.021	0
923	0.27605	20	5.54	0.989	0.001
927	0.27885	20	5.60	1.001	0.001
920	0.2648	20	5.31	1.010	0.01
919	0.26785	20	5.38	1.012	0.01
1025	0.28540	20	5.73	0.989	0.05
1029	0.27680	20	5.56	1.002	0.05
917	0.29475	20	5.92	1.013	0.1
<i>pH ~ 3</i>					
1035	0.01885	110	0.0688	3.095	0
938	0.01705	120	0.0570	3.095	0.001
939	0.01915	120	0.0641	3.095	0.001
921	0.02220	120	0.0743	3.073	0.001
922	0.02460	120	0.0823	3.088	0.001
925	0.02320	120	0.0776	3.111	0.01
918	0.02175	120	0.0727	3.087	0.01
931	0.02740	120	0.0916	3.143	0.01
934	0.02425	120	0.0811	3.107	0.01
1034	0.02225	120	0.0744	3.137	0.05
1032	0.02210	120	0.0739	3.223	0.05
1019	0.01945	120	0.0651	3.090	0.1

All disks were oriented such that the calcite face perpendicular to the  $c$ -crystallographic axis was exposed to solution.

represents the disk rotation speed, and for the case of calcite dissolution at acidic conditions,  $D$  stands for the  $H^+$  diffusion coefficient.

At stationary state, the rate of product diffusional transport away from the surface equals the rate at which these products are released from the calcite surface such that

$$r = r_c = r_t. \quad (5)$$

Eqs. (2), (3), and (5) can be combined to yield

$$c_{H^+,s} = \frac{k_t c_{H^+,b}}{k_2 \gamma_{H^+,s} + k_t}, \quad (6)$$

and

$$r = \frac{k_t k_2 \gamma_{H^+,s}}{k_t + k_2 \gamma_{H^+,s}} c_{H^+,b}. \quad (7)$$

Combining Eq. (7) with Eq. (4) results in

$$\frac{1}{r} = \frac{1}{k_2 c_{H^+,b} \gamma_{H^+,s}} + \frac{1}{0.62 D^{2/3} \nu^{-1/6} c_{H^+,b}} \omega^{-1/2}. \quad (8)$$

Eq. (8) suggests that at constant bulk solution pH, the reciprocal overall dissolution rate ( $1/r$ ) is a linear function of the reciprocal square root of the rotating disk speed ( $\omega^{-1/2}$ ). The intercept of this straight line yields  $k_2$ , the chemical rate constant, and the slope allows determination of  $D$ , the diffusion coefficient. Calcite dissolution has been demonstrated to be consistent with Eq. (8). Sjöberg and Rickard (1985) showed that 25 °C reciprocal calcite dissolution rates plot as a linear function of  $\omega^{-1/2}$  at both pH=3.92 and 8.4; Alkattan et al. (1998) showed that 25 °C reciprocal calcite dissolution rates plot as a linear function of  $\omega^{-1/2}$  at  $-1 < \text{pH} < 3$ . The consistency of measured rates with Eq. (8) supports the application of the formalism described above to interpreting calcite dissolution rates obtained using rotating disk techniques in the present study. Note, however, that at  $\text{pH} < 3$ , the intercepts of reciprocal rate versus  $\omega^{-1/2}$  plots were sufficiently close to zero, so that it was impossible to unambiguously determine values of the chemical rate constant ( $k_2$ ) for calcite dissolution in pure HCl solutions. Nevertheless, if (1) the presence of an inhibiting aqueous species decreases calcite dissolution rates during a rotating disk experiment

and (2) the aqueous  $H^+$  diffusional transport rate from this surface is unchanged by the presence of this inhibitor, a value of the chemical rate constant ( $k_2$ ) can be generated from the data by rearranging Eq. (7) to obtain

$$k_2 = \frac{1}{\gamma_{H^+}} \left( \frac{r k_t}{k_t c_{H^+,b} - r} \right). \quad (9)$$

Eq. (9) will be used below to quantify the degree of calcite dissolution rate inhibition in response to the presence of aqueous species.

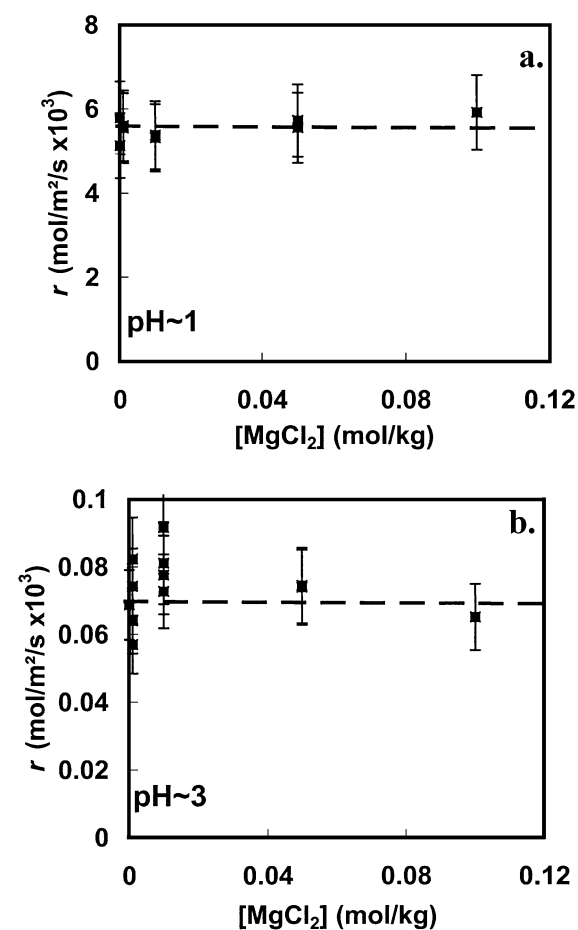


Fig. 1. Measured calcite dissolution rates at 25 °C and  $\text{pH} \approx 1$  and 3 as a function of the aqueous  $\text{MgCl}_2$  concentration of the reactive fluid. The symbols represent measured rates, the error bars correspond to a  $\pm 15\%$  uncertainty in these rates and the dashed lines denote calcite dissolution rates in the  $\text{MgCl}_2$ -free solutions.

#### 4. Experimental results and discussion

Disk weight loss, elapsed times, average bulk solution pH, and computed dissolution rates for all experiments are presented in Tables 1 and 2. Dissolution rates listed in these tables were computed from

$$r = \frac{\Delta m}{stW}, \quad (10)$$

where  $\Delta m$  represents the weight loss of the solid,  $s$  designates the geometric surface area of the disk

( $4.154 \text{ cm}^2$ ),  $t$  represents elapsed time, and  $W$  signifies the molecular weight of calcite (100.1 g/mol). Several experimental results previously reported by Alkattan et al. (1998) have also been included in these tables for comparison. As the pH and ionic strength were allowed to drift in all of these experiments, computed  $r$  values in Tables 1 and 2 represent an integrated average of the dissolution rates during each experiment. The uncertainties of each individual dissolution rate stem from corresponding uncertainties in sample weighting, experiment duration, disk rotation speeds, and temperature. Slight irregularities in sample sur-

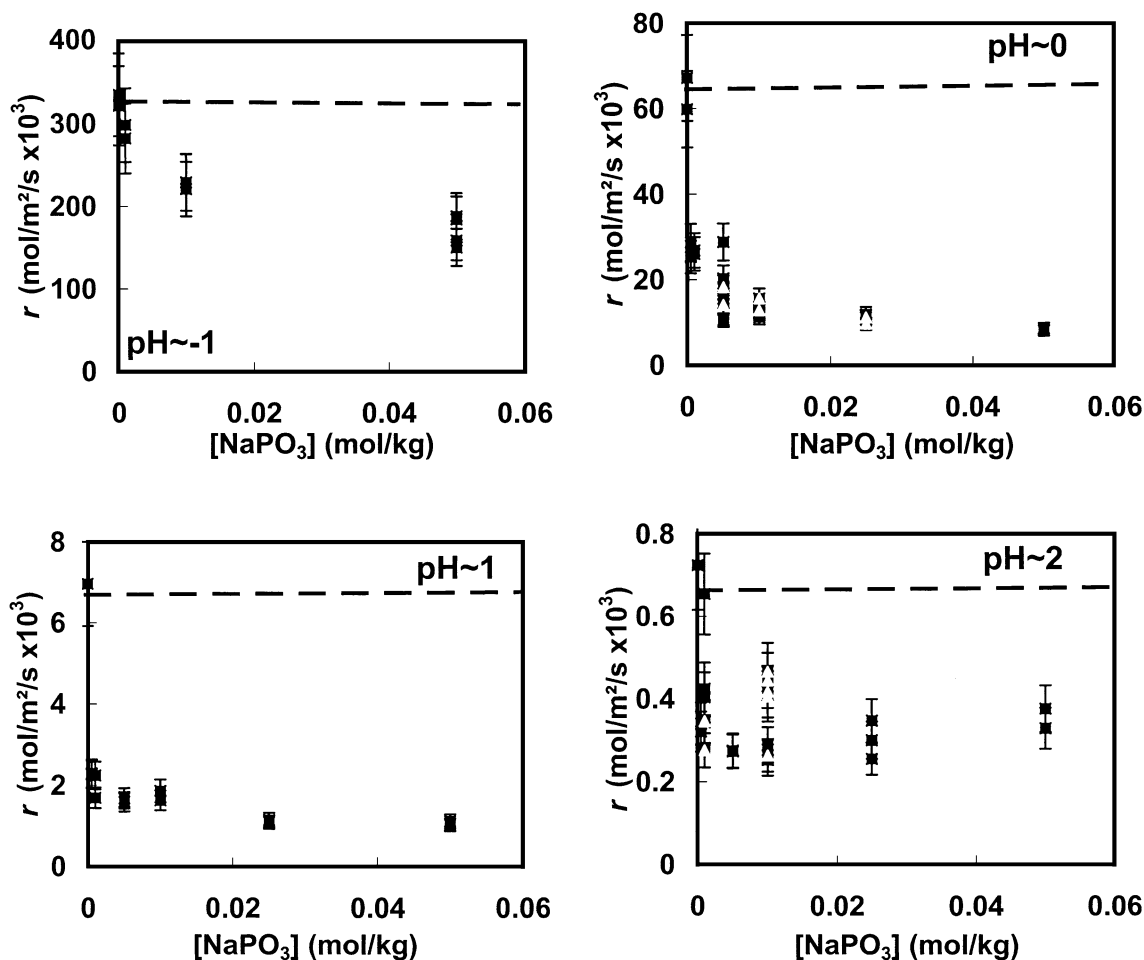


Fig. 2. Measured calcite dissolution rates at  $25^\circ\text{C}$  and  $\text{pH} \approx -1, 0, 1, 2$ , as a function of the aqueous  $\text{NaPO}_3$  concentration of the reactive fluid. The symbols represent measured rates; rates measured on samples oriented parallel to the cleavage plane are indicated by the open triangles, those oriented perpendicular to the  $c$ -crystallographic axis are shown as filled squares. Error bars correspond to a  $\pm 15\%$  uncertainty in the measured rates and the dashed lines denote calcite dissolution rates in the  $\text{NaPO}_3$ -free solutions. Note that  $\text{NaPO}_3$  dissociates in solution to  $\text{Na}^+$  and  $\text{H}_2\text{PO}_4^-$ .

Table 2

Measured calcite dissolution rates as a function of NaPO<sub>3</sub> concentration at a disk rotation speed of 340 min<sup>-1</sup>

Sample number	Mass dissolved (g)	Experiment duration (min)	Dissolution rate (mol/m <sup>2</sup> /s × 10 <sup>3</sup> )	pH	NaPO <sub>3</sub> concentration (mol/kg)	k <sub>2</sub> (mol/m <sup>2</sup> /s × 10 <sup>2</sup> )
<i>pH ~ -1</i>						
<b>679</b>	<b>0.8236</b>	<b>1</b>	<b>330</b>	<b>-0.96</b>	<b>0</b>	–
<b>687</b>	<b>0.8017</b>	<b>1</b>	<b>321</b>	<b>-0.96</b>	<b>0</b>	–
888	0.7026	1	282	-1.099	0.001	3.22
895	0.7429	1	298	-1.099	0.001	3.49
889	0.5499	1	221	-1.099	0.01	2.30
876	0.5702	1	229	-1.099	0.01	2.42
880	0.4593	1	184	-1.056	0.05	2.07
891	0.4586	1	184	-1.056	0.05	2.07
905	0.3951	1	159	-1.072	0.05	1.64
906	0.4678	1	188	-1.072	0.05	2.03
908	0.3746	1	150	-1.072	0.05	1.53
<i>pH ~ 0</i>						
<b>564</b>	<b>0.3347</b>	<b>2</b>	<b>67.1</b>	<b>0.09</b>	<b>0</b>	–
<b>538</b>	<b>0.2983</b>	<b>2</b>	<b>59.8</b>	<b>0.09</b>	<b>0</b>	–
875	0.1431	2	28.7	0.05	0.0005	5.70
874	0.1260	2	25.3	0.05	0.0005	4.60
825	0.1296	2	26.0	0.02	0.001	4.31
835	0.1337	2	26.8	0.02	0.001	4.53
873	0.1435	2	28.8	0.04	0.005	5.50
872	0.1011	2	20.3	0.05	0.005	3.29
885	0.0525	2	10.5	-0.02	0.005	1.17
887	0.0778	2	15.6	-0.02	0.005	1.86
838	0.0559	2	11.2	0.00	0.01	1.32
842	0.0619	2	12.4	0.00	0.01	1.49
871	0.0555	2	11.1	0.04	0.025	1.46
870	0.0590	2	11.8	0.04	0.025	1.57
864	0.0429	2	8.61	0.01	0.05	1.00
865	0.0404	2	8.11	0.01	0.05	0.93
696	0.0704	2	14.1	-0.02	0.005	1.65
713	0.0910	2	18.3	-0.02	0.005	2.28
694	0.0779	2	15.6	-0.02	0.01	1.87
706	0.0642	2	12.9	-0.02	0.01	1.48
942	0.0483	2	9.69	0.00	0.025	1.12
943	0.0556	2	11.2	0.00	0.025	1.31
<i>pH ~ 1</i>						
<b>510</b>	<b>1.0409</b>	<b>60</b>	<b>6.95</b>	<b>1.04</b>	<b>0</b>	–
843	0.1130	20	2.27	1.00	0.0005	3.27
828	0.1142	20	2.29	1.01	0.0005	3.43
811	0.0843	20	1.69	1.03	0.001	2.40
818	0.1117	20	2.24	1.01	0.001	3.23
837	0.0794	20	1.59	1.01	0.005	2.08
841	0.0837	20	1.68	1.01	0.005	2.23
815	0.0929	20	1.86	1.01	0.01	2.56
831	0.0812	20	1.63	1.01	0.01	2.15
869	0.0546	20	1.10	1.01	0.025	1.32
893	0.0573	20	1.15	1.00	0.025	1.36
862	0.0515	20	1.03	0.93	0.05	1.00
863	0.0558	20	1.12	0.94	0.05	1.12

Table 2 (continued)

Sample number	Mass dissolved (g)	Experiment duration (min)	Dissolution rate (mol/m <sup>2</sup> /s × 10 <sup>3</sup> )	pH	NaPO <sub>3</sub> concentration (mol/kg)	k <sub>2</sub> (mol/m <sup>2</sup> /s × 10 <sup>2</sup> )
<i>pH ~ 2</i>						
<b>689</b>	<b>0.16675</b>	<b>60</b>	<b>1.11</b>	<b>1.97</b>	<b>0</b>	–
<b>711</b>	<b>0.1083</b>	<b>60</b>	<b>0.724</b>	<b>2.03</b>	<b>0</b>	–
894	0.0960	120	0.321	2.05	0.0005	7.01
884	0.1016	120	0.340	2.00	0.0005	6.28
834	0.1956	120	0.654	2.07	0.001	–
813	0.1269	120	0.424	2.00	0.001	9.93
817	0.1028	120	0.344	2.04	0.001	7.67
814	0.1207	120	0.408	2.01	0.001	9.33
892	0.0823	120	0.275	2.028	0.005	4.86
879	0.0817	120	0.273	2.038	0.005	4.99
827	0.0755	120	0.253	2.04	0.01	4.42
822	0.0863	120	0.289	2.03	0.01	5.30
883	0.0764	120	0.255	2.016	0.025	4.13
886	0.0898	120	0.300	2.019	0.025	5.44
866	0.1039	120	0.348	2.03	0.025	7.49
867	0.0984	120	0.329	1.93	0.05	4.50
868	0.1125	120	0.376	1.97	0.05	6.67
692	<i>0.0825</i>	<i>120</i>	<i>0.276</i>	<i>2.041</i>	<i>0.001</i>	<i>5.13</i>
701	<i>0.1034</i>	<i>120</i>	<i>0.346</i>	<i>2.039</i>	<i>0.001</i>	<i>7.73</i>
705	<i>0.0217</i>	<i>33</i>	<i>0.264</i>	<i>2.018</i>	<i>0.01</i>	<i>4.38</i>
691	<i>0.1330</i>	<i>120</i>	<i>0.445</i>	<i>2.010</i>	<i>0.01</i>	<i>11.8</i>
697	<i>0.1393</i>	<i>120</i>	<i>0.466</i>	<i>2.030</i>	<i>0.01</i>	<i>15.3</i>
700	<i>0.1214</i>	<i>120</i>	<i>0.406</i>	<i>2.000</i>	<i>0.01</i>	<i>8.98</i>
704	<i>0.1249</i>	<i>120</i>	<i>0.418</i>	<i>2.010</i>	<i>0.01</i>	<i>10.1</i>

Those samples listed in bold font were previously reported by Alkattan et al. (1998); samples listed in italic font were performed using samples oriented such that the calcite face parallel to the cleavage plane was exposed to solution; all other disks were oriented such that the calcite face perpendicular to the *c*-crystallographic axis was exposed to solution. As it is not possible to obtain unambiguous *k*<sub>2</sub> values for experiments performed in NaPO<sub>3</sub>-free solutions, they are not provided in this table—see text.

face morphology, variations in crystal orientation, and the evolution of CO<sub>2</sub> bubbles at the calcite surface also add to the scatter apparent in the experimental data. Taking into account these factors, the overall uncertainty in the individual dissolution rates given in these tables is ~ 15%.

The variation of calcite dissolution rates as a function of dissolved MgCl<sub>2</sub> concentration is illustrated in Fig. 1. It can be seen in this figure that measured calcite dissolution rates are unaffected by the presence of dissolved MgCl<sub>2</sub> at pH 1 and 3. This observation is in contrast with the observations of Sjöberg (1978), who noted a strong decrease of calcite dissolution rates at 25 °C with increasing aqueous MgCl<sub>2</sub> concentration in neutral to basic pH. Sjöberg (1978) attributed calcite dissolution rate inhibition in response to increasing MgCl<sub>2</sub> concentration to aqueous Mg<sup>2+</sup> adsorption on the calcite surface. He successfully modeled his data by

assuming calcite dissolution rates were proportional to the fraction of the calcite surface that was Mg<sup>2+</sup>-free. The lack of calcite dissolution rate inhibition in the present study could possibly be attributed to the lack of Mg<sup>2+</sup> adsorption in acidic solutions, where calcite surfaces will be positively charged (Parks, 1975). Another possibility, discussed below, is that the effect of Mg<sup>2+</sup> on surface reaction rates is insufficiently strong to affect the overall calcite dissolution rate at acid conditions.

The variation of calcite dissolution rates as a function of dissolved NaPO<sub>3</sub> concentration is illustrated in Fig. 2. It can be seen in this figure that (1) calcite dissolution rates decrease significantly with increasing NaPO<sub>3</sub> concentration from pH –1 to 2 and (2) dissolution rates measured on samples oriented parallel to the cleavage plane are identical, within uncertainty, of those measured on crystals oriented perpendicular to

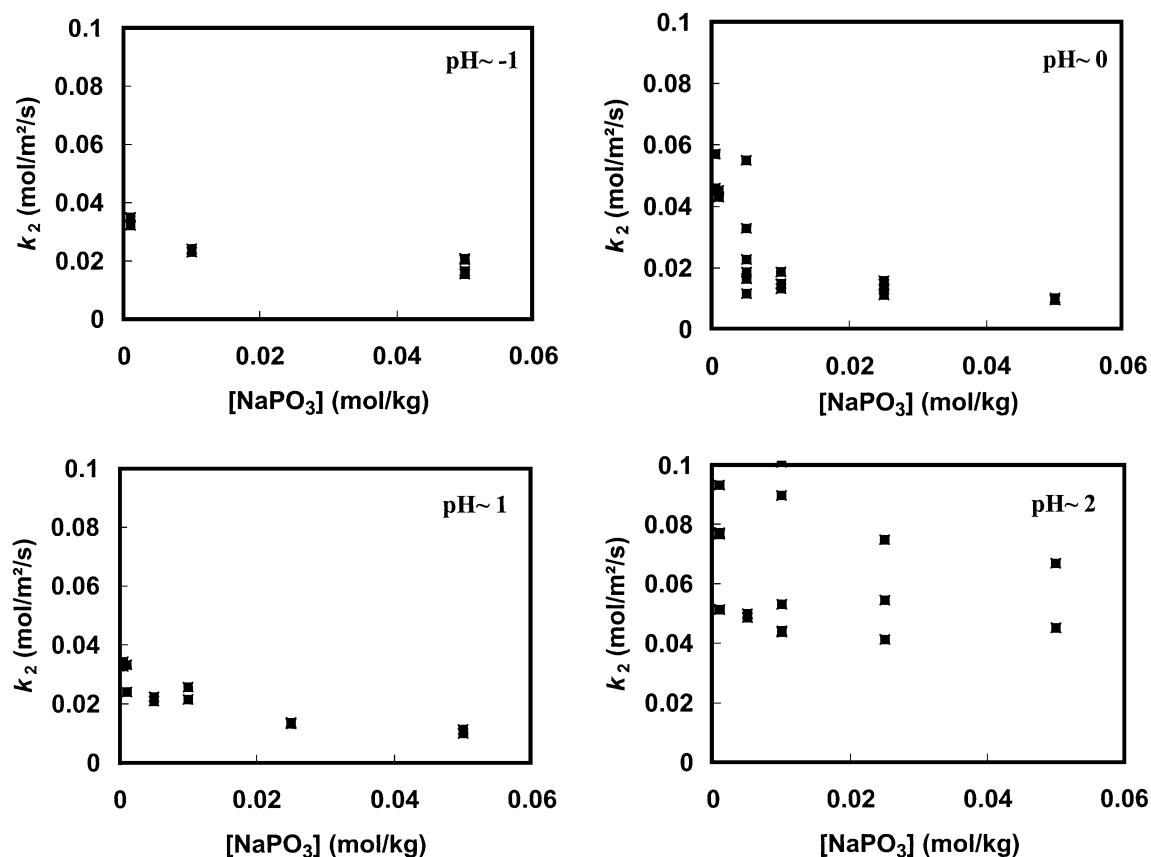


Fig. 3. Computed values of the chemical rate constant  $k_2$  as a function of the aqueous  $\text{NaPO}_3$  concentration of the reactive fluid. See caption of Fig. 2.

the  $c$ -crystallographic axis. Sjöberg (1978) observed a significant decrease in response to the presence of aqueous phosphate on 25 °C calcite dissolution rates measured from the quantity of acid consumed in pH stat reactors at pH 5 and 8.3. Aqueous phosphate inhibition of calcite dissolution rates neutral to basic pH was also discussed by Berner and Morse (1974), Morse (1974b), and Walter (1983). As was the case of Mg inhibition of calcite dissolution at this pH, rate inhibition was attributed to aqueous phosphate adsorption; calcite surfaces have been noted to be extremely favorable adsorption sites for aqueous phosphate (Raistrick, 1949; Stumm and Leckie, 1970; Griffin and Jurinak, 1973; DeKanel and Morse, 1978). It thus appears that aqueous phosphate, which is likely present as the anion  $\text{H}_2\text{PO}_4^-$  or the neutral species  $\text{H}_3\text{PO}_4^0$  at acidic con-

ditions can readily adsorb on the negatively charged calcite surfaces inhibiting calcite dissolution.

Assuming that the presence of trace quantities of aqueous  $\text{NaPO}_3$  in solution will negligibly affect the rates of aqueous  $\text{H}^+$  diffusion through the calcite surface boundary layer, values of the chemical rate constant,  $k_2$ , can be generated from these rate data using Eq. (9) together with a transport rate constant generated from parameters reported by Alkattan et al. (1998;  $k_t = 7.65 \times 10^{-5}$  m/s). This calculation was performed assuming  $\gamma_{\text{H}^+,s} = 1$  l/mol =  $1 \times 10^{-3}$  m<sup>3</sup>/mol,<sup>1</sup> and

<sup>1</sup> This assumption is only approximately correct. Aqueous HCl activity coefficients at 25 °C vary over the range 0.8–1 kg/mol with increasing HCl concentration from 0 to 1 mol/kg (Helgeson et al., 1981).



resulted in the values of  $k_2$  reported in Table 2 and illustrated in Fig. 3. Retrieved  $k_2$  values generally decrease with increasing aqueous  $\text{NaPO}_3$  concentration.  $k_2$  values at constant  $\text{NaPO}_3$  concentration are approximately pH independent for  $-1 \leq \text{pH} \leq 1$ ; at these pH values,  $k_2$  appears to attain a constant value of approximately  $0.02 \text{ mol/m}^2/\text{s}$  for aqueous  $\text{NaPO}_3$  concentrations in excess of  $0.01 \text{ mol/kg}$ . This observations suggests that (1) the calcite surfaces may be saturated with phosphate and (2) calcite surface speciation may be effectively constant in aqueous  $\text{NaPO}_3$  solutions when  $[\text{NaPO}_3] > 0.01 \text{ mol/kg}$  and  $\text{pH} \leq 1$ .  $k_2$  values at  $\text{pH} \sim 2$  are generally higher than those at lower pH and exhibit a somewhat scattered distribution. The source of this scatter is unclear, though the relatively high  $k_2$  values at  $\text{pH} \sim 2$  suggest that the capacity of  $\text{NaPO}_3$  to inhibit calcite dissolution is decreasing with increasing pH at  $\text{pH} > 1$ .

The ability to retrieve values of the chemical rate constant,  $k_2$ , from rates measured in  $\text{NaPO}_3$ -bearing aqueous solutions contrasts with that of  $\text{MgCl}_2$ -bearing solutions reported above and of  $\text{NaPO}_3/\text{MgCl}_2$ -free solutions originally reported by Alkattan et al. (1998). In the absence of substantial inhibition, the chemical rate constant,  $k_2$ , is so large compared to the transport rate that it negligibly affects the overall calcite dissolution rate, and thus cannot be unambiguously retrieved from these rotating disk experiments. Consequently, relatively small changes in the solute detachment rate from the calcite surface would not be observed in the experiments performed in the present study as the overall rates are dominated by the relatively slow solute transport rate. It is possible, therefore, that the presence of  $\text{MgCl}_2$  did inhibit somewhat solute detachment rates from the calcite surface, but this effect was too small to be observed. Based on the interpretation of their rate data, Alkattan et al. (1998) concluded that in the absence of inhibiting aqueous species,  $k_2$  values exceed  $0.4 \text{ mol/m}^2/\text{s}$ , which is an order of magnitude greater than most  $k_2$  values obtained from the interpretation of calcite dissolution rates measured in  $\text{NaPO}_3$ -bearing aqueous solutions and listed in Table 2. This comparison illustrates that although the presence of  $\text{NaPO}_3$  in solution decreases the overall calcite dissolution rate measured in the present study by as much as a factor of 6–7, the actual affect of aqueous  $\text{NaPO}_3$  on surface detachment rates may be far greater.

## 5. Conclusion

The results of this study illustrate the varying inhibition potential of aqueous species as a function of pH. Aqueous magnesium, which is known to be a strong inhibitor of calcite dissolution at neutral to basic conditions, has been found to have no affect on calcite dissolution rates at acidic conditions. In contrast, aqueous phosphate, which is also known to be a strong calcite dissolution rate inhibitor at neutral to basic pH, was found to also strongly inhibit calcite dissolution rates at acidic conditions. It should nevertheless be emphasized that the degree of inhibition on calcite dissolution rates due to the presence of aqueous phosphate is likely not sufficient to significantly affect most natural processes. The differing effects of aqueous magnesium and phosphate on calcite dissolution rates may be attributable to the different adsorption behaviors of these aqueous species. These results suggest the need to take account of the surface speciation of each aqueous species as a function of solution composition when attempting to deduce its potential inhibiting effects on a mineral's dissolution rate.

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