

Dissolution of forsteritic olivine at 65°C and $2 < \text{pH} < 5$

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Received 29 July 1998; accepted 12 August 1999

Abstract

Dissolution experiments with forsteritic olivine (Fo_{91}) were conducted in a batch reactor at a temperature of 65°C between pH 2 and 5. Constant pH was maintained by using a pH-stat technique. The following dissolution rate law for forsteritic olivine at 65°C and acid pH was derived based on the experimental results normalized to the initial surface area:

$$r = 10^{-8.51} (a_{\text{H}^+})^{0.70}$$

where r is rate in mol forsteritic olivine/cm²/s. Our results, combined with data from the literature for forsteritic olivine dissolution at 25°C, show that the pH-dependence of forsteritic olivine dissolution is temperature-dependent. As temperature increases, the dissolution rate of forsteritic olivine becomes more pH-dependent, which is consistent with a surface protonation model for dissolution at $\text{pH} < \text{pH}_{\text{pznpc}}$. The activation energy of dissolution, E_a , has been estimated based on our results and literature data at 30 ± 4 kcal/mol. We also observed that at pH between 2 and 4 and at 65°C, the release rates of Mg, Si and Fe were stoichiometric. However, at pH 5, the release rate of Fe was slower than that of Mg and Si, probably due to oxidation of the mineral surface. Results of several dissolution experiments in the presence of Al in solution (pH 3, 0.03–10 ppm Al) show that the dissolution rate of forsteritic olivine under the experimental conditions is independent of Al concentration within the experimental error. This result may indicate that Al does not form strong crosslinks to the unpolymerized surface of orthosilicates such as forsteritic olivine, and therefore does not retard the dissolution of this phase under the experimental conditions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Forsteritic olivine; Dissolution kinetics; Simple oxides

1. Introduction

Extensive research on dissolution kinetics shows that for simple oxides, dissolution is controlled by surface reaction at the oxide–water interface, where

the reactive solution species are H^+ , OH^- or other suitable ligands (e.g., Stumm and Furrer, 1987). The surface protonation behavior of simple oxides such as Al_2O_3 , TiO_2 and Fe_2O_3 as a function of pH and temperature have been constrained (e.g., Berube and DeBruyn, 1968; Furrer and Stumm, 1983; Carroll-Webb and Walther, 1988; Machesky, 1989; Brady and Walther, 1992). Dissolution behavior as a func-

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tion of pH is less well constrained for mixed oxides such as ortho-, ino-, phyllo-, and tectosilicates.

Several authors have argued that mineral dissolution will be pH-dependent for $\text{pH} < \text{pH}_{\text{pznpc}}$ or $\text{pH} > \text{pH}_{\text{pznpc}}$ (e.g., Furrer and Stumm, 1986). Here, pH_{pznpc} stands for pH of point of zero net proton charge, or the pH at which the concentration of positively charged surface sites equals the concentration of negatively charged surface sites of the mineral in the absence of specifically adsorbed cations or anions. In general, the pH dependence of silicates has been described by fitting the rate of dissolution for $\text{pH} < \text{pH}_{\text{pznpc}}$ to a simple rate equation for rate data at constant temperature:

$$\log r = \log k - n \text{pH} \quad (1)$$

where r is the dissolution rate, k is the apparent rate constant and n is the apparent reaction order with respect to activity of aqueous H^+ .

Brady and Walther (1992) and Casey and Sposito (1992) suggested, based on thermodynamic arguments, that the pH-dependence of mineral dissolution should increase with temperature at $\text{pH} < \text{pH}_{\text{pznpc}}$. However, the effects of temperature on the pH-dependence of silicate dissolution are not well-established. For example, Hellmann (1994) published data suggesting that n increased with increasing temperature (from 100 to 300°C) for albite; however, reanalysis of his data with our data suggested to us that n may remain constant from 5° to 300°C for dissolution of this phase (Chen and Brantley, 1997). In contrast, our experiments at $\text{pH} < \text{pH}_{\text{pznpc}}$ show that both diopside and anthophyllite dissolution become more pH-dependent at 90°C than at 25°C (Chen and Brantley, 1998). The increase in pH-dependence with temperature is greater for dissolution of diopside than anthophyllite over the same pH range (Chen and Brantley, 1998). If the effect of temperature on pH-dependence is related to the degree of polymerization of the silicate, we might expect to see an even stronger temperature effect on the dissolution of silicates that are even less polymerized, such as forsteritic olivine, at $\text{pH} < \text{pH}_{\text{pznpc}}$. For example, Westrich et al. (1993) report a strong change in pH dependence with temperature for several orthosilicates over the range $T = 25$ to 65°C.

Polymerization of the dissolving silicate phase may also be important with respect to inhibition by aluminum. Several workers have shown (Chou and Wollast, 1985; Casey et al., 1988; Oelkers et al., 1994; Chen and Brantley, 1997) that Al in solution affects dissolution of feldspar, perhaps because it repolymerizes the silica-rich feldspar surface. Fewer workers have investigated Al inhibition on less polymerized silicate phases. One of the purposes of this study was to look at the pH-dependence of a simple orthosilicate by conducting an experimental study of forsteritic olivine dissolution at an elevated temperature, and to compare the results with the literature data for dissolution of this phase at room temperature. The second purpose was to test whether dissolved Al inhibits olivine dissolution.

2. Dissolution of forsteritic olivine

The dissolution kinetics of forsteritic olivine at 25°C have been studied by many workers (e.g., Luce et al., 1972; Sanemasa et al., 1972; Siever and Woodford, 1979; Grandstaff, 1980, 1986; Siegel and Pfannkuch, 1984; Blum and Lasaga, 1988; van Herk et al., 1989; Sverdrup, 1990; Wogelius and Walther, 1991; Varadachran et al., 1994; Jonckbloedt, 1997; Rosso and Rimstidt, in press). Luce et al. (1972) reported no pH dependence for olivine dissolution, but his experimental protocol left ultrafine particles in the starting materials and, as a result, all dissolution was parabolic. Grandstaff (1980; 1986) dissolved forsteritic olivine (Fo_{83}) in HCl + KCl at pH 3 to 5 between 1° and 49°C. His results showed that, at 25°C, dissolution rate decreases from 10^{-14} to 10^{-16} mol/cm²/s as pH increases from 3 to 5, indicating a first order dependence of rate on $\{\text{H}^+\}$. He also determined that the activation energy of dissolution based on regression of log rate (at pH 3.25) vs. $1/T$ equals 9.1 kcal/mol. However, the rates reported by Grandstaff (1980; 1986) are 1–2 orders of magnitude lower than the rates reported later for forsteritic olivine and other orthosilicates at similar temperature and pH conditions (e.g., Blum and Lasaga, 1988; Sverdrup, 1990; Wogelius and Walther, 1991; Westrich et al., 1993). Some of this discrepancy may have been related to an erroneously

measured BET surface area (as suggested by Murphy, 1985; Wogelius and Walther, 1991, 1992).

Blum and Lasaga (1988) also reported a linear relationship between log dissolution rate and pH for dissolution of forsteritic olivine (Fo_{93}) ($n = 0.56$). Their results show that at 25°C, when pH increases from 2 to 4, dissolution rate decreases from 10^{-12} to 10^{-13} mol/cm²/s. Forsteritic olivine dissolution experiments at 25°C were also conducted by Sverdrup (1990). However, little information is given about the experiments and materials, and rates presented by this author are scattered.

Results similar to those of Blum and Lasaga (1988) were obtained for forsteritic olivine (Fo_{91}) dissolution at 25°C by Wogelius and Walther (1991). These workers measured rates of dissolution in excellent agreement with the results of Blum and Lasaga (1988). Using the results reported by both groups (without the data measured at pH 5.7), forsteritic olivine dissolution at 25°C and pH below neutral can be expressed using the equation:

$$r = 10^{-11.01} (a_{\text{H}^+})^{0.49} \quad (2)$$

where r is the rate, expressed in mol forsteritic olivine/cm²/s.

Westrich et al. (1993) show some dissolution data for forsteritic olivine (but without reporting rate values) and report a value of n based upon their own data and that of Wogelius and Walther (1991) of 0.54. Westrich et al. (1993) report that n varies from 0.4 to 0.6 for six different compositions of orthosilicate minerals.

Wogelius and Walther (1992) also conducted forsteritic olivine dissolution experiments at 65°C. Two experiments at pH below neutral were run at 65°C (pH 1.8 and 6 for up to 25 h). Their results show that between 25° and 65°C the pH-dependence of the rate does not change significantly, and they estimated the apparent activation energy for dissolution of forsteritic olivine (based on a plot of log rate vs. $1/T$) to be 19 ± 2.5 kcal/mol. (Because the pH-dependence did not change, this E_a is not pH-dependent.) However, dissolution at pH 6 was incongruent. The measured ratio of Mg/Si in solution at the end of their pH 6.0 experiment is 11.3, which is much higher than the stoichiometric ratio of 1.8

reported for the mineral composition. According to Wogelius (pers. comm.), the nonstoichiometry of the product solution at the end of the experiment might have been caused by precipitation.

In addition to surface protonation, other factors such as Al inhibition may also play an important role in controlling the dissolution of some aluminosilicates (Chou and Wollast, 1985; Oelkers et al., 1994; Chen and Brantley, 1997). However, it is unclear whether Al inhibition affects all silicate dissolution. According to Casey et al. (1988), Al inhibition of feldspar dissolution is the result of polymerization in which adsorbed Al^{3+} retards the dissolution by adding crosslinks to the silica network. No investigations of the effect of dissolved Al on olivine dissolution have been reported; therefore, it is not clear whether Al^{3+} in solution would also crosslink the unpolymerized surface and retard the dissolution of this phase.

3. Methods

Forsteritic olivine (Fo_{91}), from San Carlos, Arizona, was purchased from Ward's Natural Science Establishment (Table 1). The starting material (approximately $5 \times 5 \times 5$ mm), was hammer-crushed and ground using an agate mortar to a fine powder, and then dry-sieved to obtain a size fraction of 100–200 mesh (150 to 75 μm). The powder was then ultrasonically cleaned in ultrapure acetone, dried in an oven at 105°C, and stored in a desiccator before experiments. Surface area of the powder samples before and after experiments were measured using 3-point BET method with Kr as the adsorbent (Quantachrome Quantasorb Model OS-10). Observations by Wogelius and Walther (1992) and in our laboratory revealed no evidence for impurity phases.

Table 1
Sample Composition of San Carlos Olivine

MgO (wt.%)	SiO ₂ (wt.%)	FeO (wt.%)	NiO (wt.%)	Total (wt.%)	Mg/Si (mole ratio)	Fe/Si (mole ratio)
49.24	40.72	9.21	0.39	99.54	1.8	0.19

* Data from Wogelius and Walther (1992).

The reactor used in this study, a 2-l batch reactor made of polyethylene, is similar in design to those used by Casey et al. (1988). The lid of the reactor was made of a rubber stopper with holes for installation of the electrode, the tubing, the rod connector to the stirring bar, and a sampling vent (Fig. 1). The reactor was filled with 2 l of HCl + H₂O solution adjusted to run pH. One to six grams of powdered forsteritic olivine were then added to the reactor, which was immersed in a water bath to maintain a constant temperature of $65 \pm 1^\circ\text{C}$. The solution in the reactor was continuously stirred using a magnetic stir bar at either 200 or 350 rpm. To enhance the difference in stirring, a 3 cm long cylindrical stir bar was used for the first case, while a 5 cm cross stir bar was used for the second case. An ATI-Orion pH electrode combined with a temperature compensation

probe was inserted into the solution to monitor the change of pH resulting from dissolution (with an Orion Model 230A pH meter). The electrode was periodically calibrated against standard pH solutions at 25°C . No noticeable drift of the pH electrode in measuring buffers was observed for any experiments. The accuracy of pH measurements at 65°C was also checked before experiments. The results of the tests showed that the use of the temperature compensation probe associated with the pH meter effectively allowed measurement of the correct pH value at 65°C .

Some previous workers used buffer solutions or organic acids to maintain a constant pH during forsteritic olivine dissolution (e.g., Wogelius and Walther, 1991). However, buffers may promote or inhibit mineral dissolution (e.g., Dove and Crerar, 1990; Wogelius and Walther, 1991, 1992; Stillings

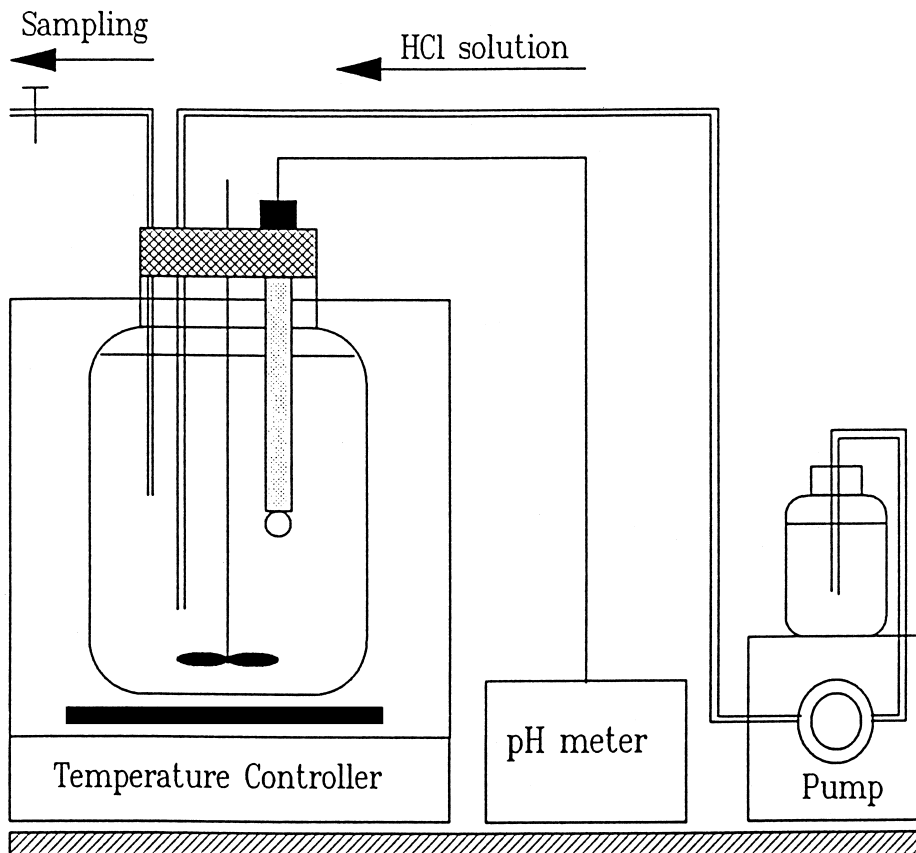


Fig. 1. Schematic presentation of the olivine dissolution experiments.

Table 2
Experimental conditions
na = none added.

RUN	Temperature (°C)	pH (65°C)	Al concentration (mmol/l)	Mass of forsterite (g)	Stirring rate	Duration (h)
OV-2	65	4.00	na	4.00	200	5
OV-3	65	2.95	na	2.00	200	5
OV-4	65	2.00	na	1.00	200	2
OV-5	65	5.00	na	6.00	200	5
OV-6	65	2.95	0.37 (10 ppm)	2.00	200	5
OV-7	65	2.95	0.1 (2.7 ppm)	2.00	200	5
OV-8	65	2.95	0.01 (.027 ppm)	2.00	200	5
OV-9	65	2.95	na	2.00	350	5

and Brantley, 1995). In this study, we therefore used pure HCl + H₂O. To maintain a constant value of pH during each experiment, a concentrated HCl solution was continuously pumped into the reactor by the operation of a peristaltic pump. The rate of HCl addition was manually adjusted depending on the rate of H⁺ consumption. The pH values of the solution were maintained within ±0.02 of run pH during the experiments. For experiments with added Al, an aluminum reference solution of 1000 ppm Al (Al dissolved in HCl solution, Fisher Scientific) was used to make solutions.

Solution samples were taken from the reactor at different intervals. Approximately 6 ml of sample was taken each time, and the maximum number of samples was 11 for any individual run. The total

volume of solution that was extracted for chemical analysis during the experiment was therefore relatively small (< 4%) compared to the initial volume of the solution (2 l). Also, removal of liquid was partially compensated by the addition of HCl solution used to maintain a constant pH (approximately 20–60 ml of solution was added over the entire experiment). Because of the minimal effect of aliquot removal, no attempt was made to adjust for the change in solution volume. Also, for each experiment, approximately 2% of the forsteritic olivine powder was dissolved. The change in sample weight was therefore ignored in estimating the dissolution rate. Finally, a small amount of water was lost by evaporation from the flask. However, the water loss by evaporation was very small (less than 2 ml out of

Table 3
Results of dissolution experiments

RUN	pH ^a	ΔG (kcal/mol)	Final area ^b (cm ² /g)	Dissolution rate ^c (mol forsteritic olivine/cm ² /s)	
				Based on Mg	Based on Si
OV-2	4.00	−32.4	560	2.56 ± 0.31 × 10 ^{−12}	2.50 ± 0.31 × 10 ^{−12}
OV-3	2.95	−36.9	510	1.75 ± 0.22 × 10 ^{−11}	1.74 ± 0.21 × 10 ^{−11}
OV-4	2.00	−43.2	450	8.17 ± 1.0 × 10 ^{−11}	8.09 ± 0.99 × 10 ^{−11}
OV-5	5.00	−27.3	570	1.1 × 10 ^{−12} –3.8 × 10 ^{−13d}	1.2 × 10 ^{−12} –5.6 × 10 ^{−13d}
OV-6	2.95	−36.6	660	1.52 ± 0.19 × 10 ^{−11}	1.47 ± 0.18 × 10 ^{−11}
OV-7	2.95	−36.8	700	1.39 ± 0.17 × 10 ^{−11}	1.42 ± 0.17 × 10 ^{−11}
OV-8	2.95	−36.7	630	1.57 ± 0.19 × 10 ^{−11}	1.53 ± 0.19 × 10 ^{−11}
OV-9	2.95	nc	540	1.95 ± 0.23 × 10 ^{−11}	2.08 ± 0.25 × 10 ^{−11}

^a The listed values are measured pH.

^b Initial specific surface area = 340 cm²/g.

^c Dissolution rate of forsteritic olivine, as mol Mg_{1.80}Fe_{0.20}SiO₄/cm²/s, normalized to final surface area.

^d See text and Fig. 4 for explanation.

2000 ml, or < 0.1% over a period of 5 h at 65°C), and therefore is ignored. The extracted solution was immediately filtered through a PTFE filter with pore size of 0.45 μm and acidified. Si, Mg, Fe and Al were analyzed with a PC3000 Leeman Labs ICP atomic emission spectrometer.

4. Experimental conditions

All experiments were conducted at 65°C in acid solutions. Four experiments, OV-2, OV-3, OV-4, and OV-5, were used to study the pH-dependence of

dissolution (the pH values vary from 2.00 to 5.00). Experiments OV-6, OV-7 and OV-8 were used to study the effect of Al on the dissolution of forsteritic olivine. The Al concentrations ranged from 0.27 to 10 ppm (or 0.01 to 0.37 mmol/l). One to six grams of forsteritic olivine powder were added to the reactor, depending on the solution pH. Except for the experiment at pH 2 (run for 2 h), all experiments were run for 5 h (Table 2). Experiments were run for durations of 2–5 h, based upon the linear Mg and Si release data reported throughout dissolution of olivine by Wogelius and Walther (1992) for up to 25 h at 65°C. All experiments were run at a stirring rate of

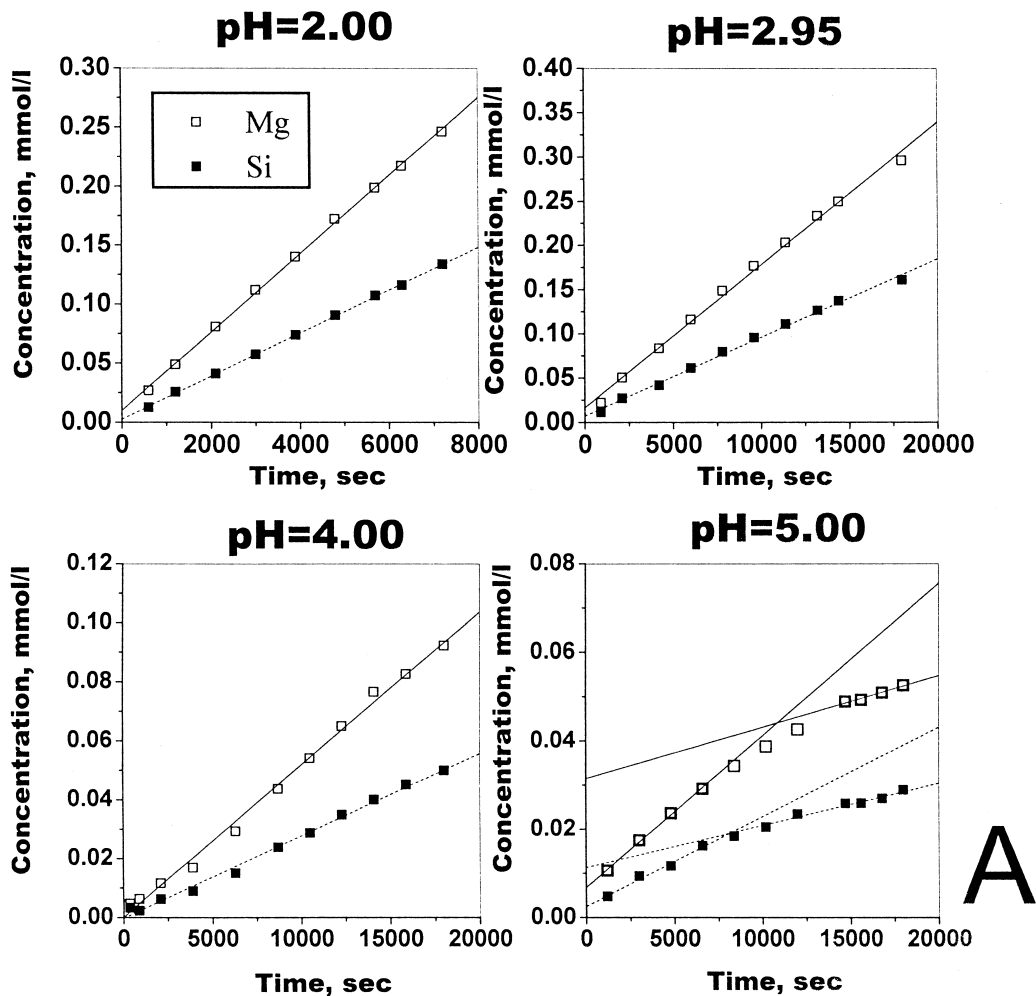


Fig. 2. (A) Changes in concentration of Mg and Si during dissolution of forsteritic olivine at varying pH. (B) Changes in concentration of Mg and Si at pH 2.95, with varying Al concentrations in solution.

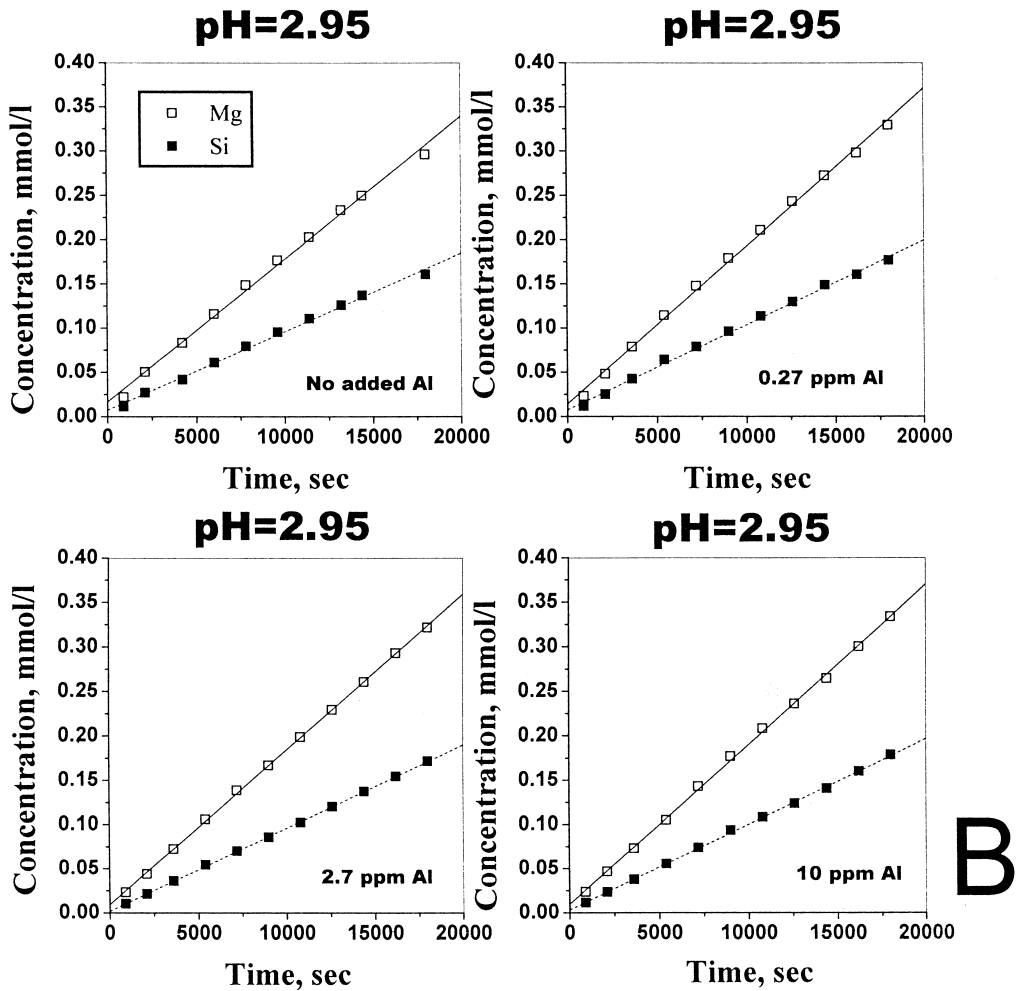


Fig. 2 (continued).

200 rpm, except for experiment OV65-9, which was run at 350 rpm.

5. Results

Concentrations of Al, Fe, Mg and Si in solutions of all experiments are summarized by Chen (1997). Table 3 lists the surface areas of forsteritic olivine powder samples before and after experiments and the dissolution rate, r , calculated based on the following equation:

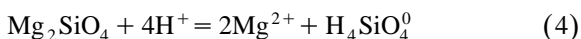
$$r = (dc/dt)V / (A_s gv) \quad (3)$$

where c (in mol/l) is the concentration, t is time (in sec), V is the volume of solution in the reactor (2 l), A_s (in cm^2/g) is the final specific surface area, g (in gram) is the mass of forsteritic olivine used, and v is the stoichiometric coefficient.

The term dc/dt in Eq. (3) is the slope of the plot of concentration vs. time, as depicted in Fig. 2 for Mg and Si. Notice that, except for the experiment at pH 5 (Run OV-5), all experiments show a very good linear relation between concentration and time. Therefore, slopes from Fig. 2 were used to calculate the dissolution rates (Table 3). These rates vary from 2.5×10^{-12} to 8.1×10^{-11} mol forsteritic

olivine/cm²/s. Good agreement was observed for the rates measured at pH 2.9 at two stirring speeds.

For experiment OV-5 at pH 5, dissolution rate changed over time. For this experiment, two regressions were made for each element released, one for initial dissolution from 20 to 110 min, and the other for late dissolution between 245 to 300 min. These rates are 1.12×10^{-12} and 3.77×10^{-13} mol forsteritic olivine/cm²/s based on Mg release, respectively. Table 3 also summarizes the values of the $\Delta G_{\text{reaction}}$ for all the experiments run at low stirring rate (-43.2 to -27.3 kcal/mol), as calculated by SOLMINEQ (Kharaka et al., 1988) for the following reaction at 65°C:



An error of about $\pm 12\%$ is estimated for the calculated dissolution rates. The error is estimated based on errors in rate of change in solution chemistry (including chemical analysis and regression, $\pm 5\%$),

solution volume change ($\pm 5\%$), and surface area measurement ($\pm 10\%$).

5.1. Dissolution stoichiometry

To investigate the stoichiometry of forsteritic olivine dissolution, Mg, Fe, and Si concentrations were monitored over time and the ratios of Mg/Si and Fe/Si are plotted in Fig. 3. Results show that, at all experimental conditions, the ratio of Mg/Si in solution was constant and equal to 1.9 ± 0.1 , indicating the congruent dissolution of Mg and Si (stoichiometric Mg/Si = 1.8). However, the release of Fe to the solution is pH-dependent. For pH below 4, we observed that release of Fe is stoichiometric. At pH greater than 4, the dissolution rate of forsteritic olivine estimated based on Fe release is smaller than those based on Mg and Si release, perhaps due to the precipitation of an iron-containing phase at higher pH. At pH = 4, Fe release is retarded for the first third of the experiment.

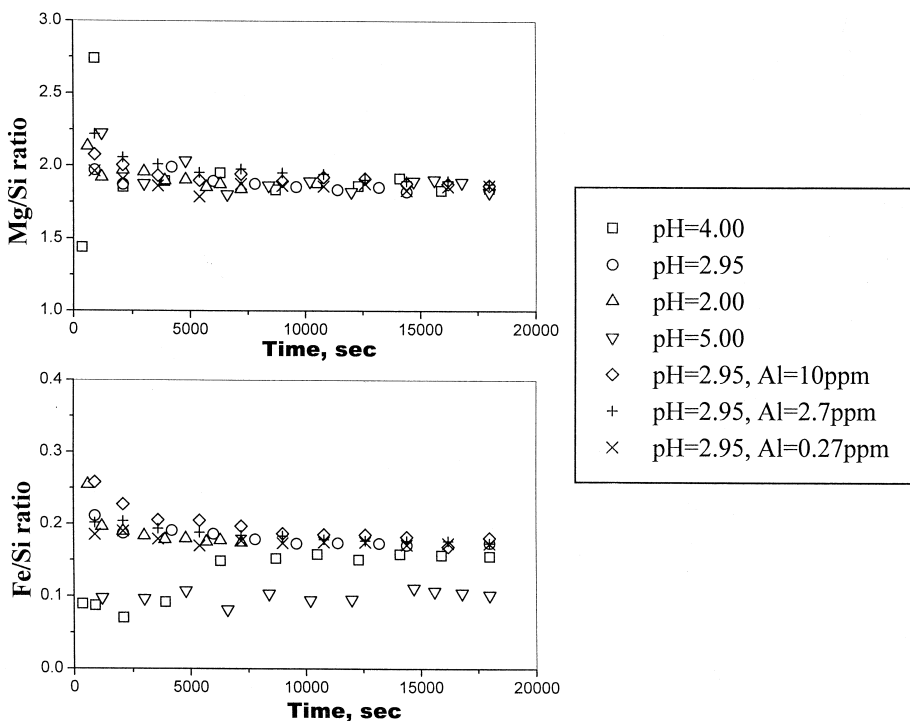


Fig. 3. Mg/Si and Fe/Si release rate ratios for experiments under conditions as indicated. The Mg/Si ratio of the forsteritic olivine was 1.8; Fe/Si was 0.19. All rates were normalized by final surface areas.

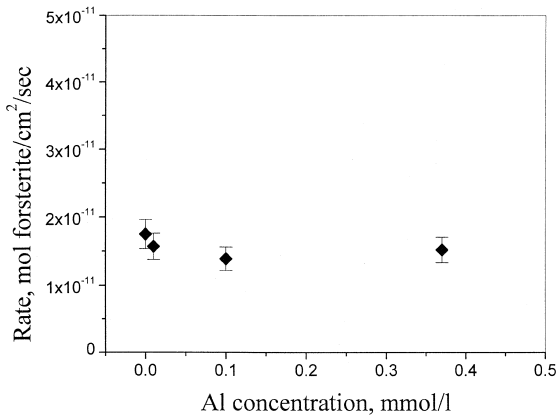


Fig. 4. Dependence of forsterite dissolution at pH 2.95 at 65°C on dissolved Al concentration. All rates were normalized by final surface areas.

5.2. Aluminum effect

Dissolution rates measured at pH 2.95 are plotted against the Al concentrations in Fig. 4. Under the given temperature and pH conditions, and for the range in concentration of Al (0–10 ppm or 0.37 mmol/l), the dissolution rate of forsteritic olivine is independent of Al.

6. Discussion

6.1. pH-dependence of forsteritic olivine dissolution at 65°C

The rates are plotted in Fig. 5 as log rate (normalized by final surface area) vs. pH for experiments performed in the absence of Al. As noted earlier, the dissolution at pH 5 is non-linear. Therefore, two dissolution rates are calculated for early and late dissolution which represent the upper and lower limits of dissolution rate for the time period between 1200 to 18,000 s at pH 5. These two rates are plotted using open diamonds in order to distinguish them from other rate measurements which represented linear release over the entire run duration.

Fig. 5 shows that log dissolution rate is a linear function of pH over the pH range of 2 to 4. The dissolution rate law for forsteritic olivine at 65°C and

acid pH can be represented using the following equation, using the final surface area:

$$r = 10^{-8.55} (a_{H^+})^{0.75} \quad (5)$$

The log of the rate constant ($= \log k = -8.51 \pm 0.16$, using one standard error in the regression of log rate vs. pH) calculated using the initial surface area does not differ significantly from the log k when calculating the rate using the final surface area ($\log k = -8.55 \pm 0.12$). Similarly, the value of n calculated from initial surface area normalization (0.70 ± 0.05) does not differ significantly from that calculated from using final surface area (0.75 ± 0.04). We present the rate constants normalized to both initial and final surface areas because most experimental rates are normalized by initial surface area, but field weathering rates must be normalized by final surface areas.

To study the temperature dependence of dissolution rate of forsteritic olivine, the results from this study are plotted on Fig. 6 (normalized by initial surface area as noted) together with data reported by Blum and Lasaga (1988) and Wogelius and Walther (1991) for dissolution of the same mineral run at 25°C. These last two sets of data represent rates normalized to initial surface area. Including errors in rate measurement ($\pm 12\%$), our log rate at pH 2

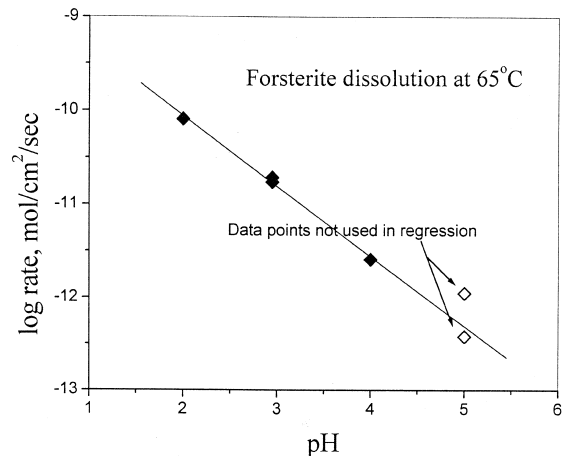


Fig. 5. pH-dependence of olivine dissolution at 65°C. Data plotted represents rates normalized to final surface area. Line represents linear regression of all data < pH 5. Rate is expressed as mol forsterite/cm² s.

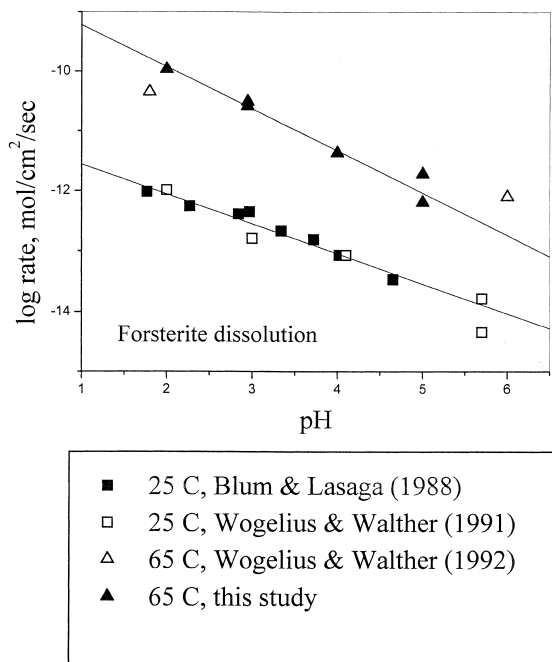


Fig. 6. pH-dependence of olivine dissolution at 25°C and 65°C. The line running through the 25°C data represents a linear regression of data by Blum and Lasaga (1988) and Wogelius and Walther (1991), without the data at pH 5.7. The line running through the 65°C data is the regression of the data from this work (without the data at pH 5) normalized to initial surface area (data points shown are also normalized to initial surface area).

(normalized by initial surface area) is constrained between -9.92 and -10.0 mol/cm²/s, while the log rate measured by Wogelius and Walther (1992) at pH 1.8 lies between -10.1 and -10.5 mol/cm²/s, assuming their error equalled the size of their symbols (Wogelius, pers. comm.). If we assume that error in measurement of surface area between laboratories may be larger than 10%, then these rate measurements may be well within error.

Comparison of data normalized to initial surface area obtained at the two temperatures (our data and data reported by Blum and Lasaga (1988) and Wogelius and Walther (1991)) suggests the pH-dependence of the dissolution rate, n , increases with temperature. At the 95% confidence level, n measured at 25°C (0.49 ± 0.095) differs from n measured at 65°C (0.70 ± 0.065). This observation is similar to that for pyroxene and amphibole dissolution for which we observed an increase in the pH-de-

pendence of dissolution rate with temperature (see Chen and Brantley, 1998) and is similar to the effect of temperature as observed on dissolution of three other orthosilicate minerals (Westrich et al., 1993). This result is also consistent with the model prediction of Casey and Sposito (1992) for dissolution at pH < pH_{pznpc}, assuming that the pH_{pznpc} of forsteritic olivine equals 10.5 ± 0.2 (Wogelius and Walther, 1991) or 9.1 (Sverjensky, 1994).

Our observation with respect to pH-dependence at 65°C differs from that of Wogelius and Walther (1992) who reported no significant change in the pH-dependence from 25° to 65°C based on a comparison between the low temperature data of Wogelius and Walther (1991) and the data they reported at 65°C. Their 65°C data are also plotted in Fig. 6 (open triangles). There are three possible reasons for the discrepancy between our results at the higher temperature and those obtained by Wogelius and Walther (1992). First, all of our experiments were conducted in solutions of HCl only, while in Wogelius and Walther's experiments, a buffer solution was used for one of their experiments (for pH = 1.8). Note, however, that they show evidence that the buffer solution has a very small effect on dissolution at pH 2. Second, all of our experiments except the one at pH 5 show stoichiometric release of Mg, Si and Fe, while in Wogelius and Walther's experiment at pH 6, dissolution was presumed incongruent. In our experiments, the data at pH 5, which show non-linear dissolution, were not used in determining the pH-dependence. Because few data points were used by Wogelius and Walther (1992) to determine the pH-dependence, an error in one data point would tremendously change the pH-dependence. Finally, it is possible that the rate at pH 6 used in the regression by Wogelius and Walther (1992) lies in the pH-independent part of the dissolution rate–pH curve. In support of this, we note that the rate we measured at pH 5 is consistent with the rate reported by Wogelius and Walther (1992) at pH 6 (suggesting that rates above pH 5 lie in the pH-independent part of the curve). For these reasons, in fitting data at both 25 and 65°C, we did not use the rates measured for pH > 5.

New data by Rosso and Rimstidt (in press) also are consistent with a model wherein n is constant with temperature for forsteritic olivine dissolution

below 45°C. We note that at a 99% confidence level for our data, we cannot reject the hypothesis that the slope at 65°C is equal to the slope at 25°C, as predicted by these workers and Wogelius and Walther (1992). More measurements over a broad range of temperature are needed to evaluate the temperature dependence.

Extrapolating the data of Rosso and Rimstidt (in press) to 65°C predicts rates slower than our rates by about a half order of magnitude (Rimstidt, D., pers. comm.). We infer that surface area measurements may be responsible for some of these discrepancies. For example, Rosso and Rimstidt (in press) used nitrogen for their BET measurements. In tests in our laboratory, using a Micromeritics ASAP 2010 Surface Area Analyzer on a Micromeritics aluminosilicate standard, surface area measured using N₂ as the adsorbate averaged ~35% higher than surface areas measured using Kr. Such an effect is also well-established in the surface area measurement literature. Since we used Kr, our surface areas would have been systematically smaller than those reported by Rosso and Rimstidt (i.e., if we had used the same grain size), and our rates would then have been systematically larger. In addition, the olivine used by Rosso and Rimstidt (in press) contained talc, and the surface area had to be corrected for this impurity. Therefore, the rate results from our group and their predictions for 65°C are probably equal within error. Note that Kr BET was used by both Blum and Lasaga (1988) and (1988, A. Blum, pers. comm.), and Wogelius and Walther (1991; 1992).

An activation energy (E_a) can be estimated based on the experimental data using the following equation:

$$\ln(r_1/r_2) = E_a/R(1/T_2 - 1/T_1) \quad (6)$$

where r_1 and r_2 are the dissolution rates at pH of interest and at temperatures T_1 and T_2 , respectively. R is the gas constant. We have previously referred to this as a pH-dependent activation energy (Chen and Brantley, 1998) because, when n changes as a function of temperature, E_a calculated in this way will also change with pH. In addition, this activation energy is an apparent activation energy calculated from two values of rates, rather than an activation energy calculated using rate constants determined at two or more temperatures.

To calculate the activation energy for the rate constant (Eq. (1)), we use a form of the Arrhenius equation:

$$E_a = \frac{2.303R}{\left[\frac{1}{T_2} - \frac{1}{T_1}\right]} \left(\log\left(\frac{k_1}{k_2}\right) \right) \quad (7)$$

We call this the pH-independent activation energy because it is calculated for the rate constant and not the rate.

The activation energy calculated from the rate constant of rate model Eq. (1) is 30 ± 4 kcal/mol. Because this value is equivalent to the value that would be calculated if an Arrhenius plot were completed using the rate constant defined in Eq. (1), we quote this value. However, this E_a , dependent upon n and the extrapolated value at pH = 0, incorporates extrapolation error. For this reason, we summarize (Table 4) the value of activation energy calculated at different pH values within the range of our experiments.

In comparing the low temperature data to our data, we note that a variety of different solutions were used for the low temperature experiments (e.g., see Wogelius and Walther (1991) for solution chemistry; Na perchlorate was used in the work of Blum and Lasaga (1988) and (1988, A. Blum, pers. comm.). Differences in solution chemistry presumably contribute to differences in measured rates. For example, Sanemasa et al. (1972) report that the dissolution of forsteritic olivine increases in solutions in the order of $\text{HClO}_4 < \text{HCl} < \text{H}_2\text{SO}_4$. Thus, our activation energy must be considered an estimate until more measurements are completed in constant solution chemistry.

The value of E_a calculated from the rate constant (i.e., at pH = 0) is larger than the E_a estimated by Wogelius and Walther (1992). These latter workers observed that n did not vary with T , and therefore, their activation energy would be identical regardless of whether it were calculated using Eq. (6) or Eq.

Table 4
Calculated activation energy for olivine dissolution

pH	0	1	2	3	4
E_a	30	27	25	22	20

(7). Note that this activation energy is not dependent upon pH because n does not vary with temperature.

Using Eq. (7) and calculating the E_a for our data between pH 2 and 4, the range (20–25 kcal/mol, see Table 4) compares well with the value reported by Wogelius and Walther (1992): 19 kcal \pm 2.5 kcal/mol. Both of these values are larger, however, than the value reported for pH 2.5 by Westrich et al. (1993) for six compositions of orthosilicate (= 12–16 kcal/mol), as measured for a temperature range from 25° to 45°C. Indeed, reported activation energies for olivine dissolution vary considerably. For example, E_a was reported to equal 14–16 kcal/mol at pH 1 (in HClO₄ and H₂SO₄ solutions respectively, Sanemasa et al. (1972)), 9.1 kcal/mol at pH 3.25 (in HCl + KCl, Grandstaff, 1980, 1986), 6.0–7.2 kcal/mol at pH 1 (in HCl and H₂SO₄ respectively, van Herk et al. (1989)), 16 kcal/mol (in H₂SO₄, Jonckbloedt, 1997), and 10.2 kcal/mol by Rosso and Rimstidt (in press). Differences in treatment of olivine powder, temperature range of measurements, experimental protocol, data analysis, and differences in solution chemistry may all contribute to these inconsistencies.

The value of E_a is consistent with a trend of decreasing activation energy of dissolution in HCl–H₂O with increasing connectedness of silicate tetrahedra (number of bridging oxygens per tetrahedron) as measured in our laboratory: the E_a for forsteritic olivine (30 \pm 4 kcal/mol, this study) > diopside (23 \pm 2 kcal/mol) > anthophyllite (19 \pm 1 kcal/mol, Chen and Brantley, 1998). In addition, as discussed in Brantley and Chen (1995), although there is no good measurement for the E_a of dissolution of enstatite available, an estimate is \sim 19 kcal/mol, showing that for the strict Mg endmembers, the measured E_a values also roughly decrease with connectedness. Furthermore, the activation energy for albite (15.6 \pm 0.8 kcal/mol, Chen and Brantley, 1997) is also lower than some of the less “connected” structures. This observation is surprising in that one would have a priori predicted that higher connectedness would correlate with higher E_a . The trend may be related to the observation that olivine dissolves stoichiometrically whereas the inosilicates first preferentially lose cations from the M1, M2, M3, or M4 sites. Similarly, the feldspars also lose cations from the surface during acid dissolution.

Without these cations, activation of the mineral surface may be easier (lower activation energy), even though the unaltered mineral was one of a class of more highly polymerized silicates. However, the extent of the data is limited for the full range of minerals, and mineral dissolution rates must be measured over wider ranges in temperature to test this trend.

The activation energy measured for olivine in this work is higher than the E_a of diffusion ($E_a \sim$ 5 kcal/mol), consistent with a surface-controlled model for dissolution. However, some of the activation energies previously cited in the literature for olivine are low enough that transport limitation may have occurred. The lack of dependence of dissolution rate on stirring rate (Table 3) in our experiments is, however, consistent with a surface-controlled mechanism for dissolution of olivine under these conditions.

6.2. Secondary phase precipitation

As noted earlier, dissolution of forsteritic olivine under the experimental conditions of this study is stoichiometric with respect to Mg/Si. In contrast, for dissolution at \sim pH 1, Seyama et al. (1996) report that X-ray photoelectron spectroscopy of the leached surface of forsteritic olivine reveals selective leaching of Mg²⁺ (and replacement by H⁺) and an unchanged silicate anion structure. In our experiments, we observe no such nonstoichiometric leaching of Mg. However, the release rate of Fe becomes nonstoichiometric at pH 5. It is possible that, because the reactor was open to the atmosphere, at higher pH values iron hydroxides precipitated or ferric iron adsorbed to the olivine surface. Following Wogelius and Walther (1992), we calculate the rate of Fe oxidation at atmospheric oxygen and pH 5 from the following equation (Davison and Seed, 1983; Millero et al., 1987; as cited by Wogelius and Walther, 1992):

$$R_{\text{ox}} (\text{mol/l s}) = 3.33 \times 10^{11} [\text{Fe(II)}] P_{\text{O}_2} (\text{OH}^-)^2$$

where [Fe(II)] is the molarity of ferrous iron, P_{O_2} is the partial pressure of oxygen in atm, and (OH⁻) is the activity of hydroxide in solution. As discussed by Wogelius and Walther, this equation was originally

proposed by Davison and Seed (1983), and then the (OH^-) dependence was extended to pH 5 by Millero et al. (1987). Although the rate model is quoted for 25°C, similar to the conclusions of Wogelius and Walther, we calculate that, during the 5 h duration of our experiment, only about 0.1% of the ferric iron released during dissolution would oxidize at pH 5. Therefore, we conclude that, even with a temperature enhancement of precipitation, after several hours, rather than a ferric precipitate forming, the mineral surface itself is probably oxidized, inhibiting the rate of dissolution.

The effect of Fe oxidation on olivine dissolution was also reported by Wogelius and Walther (1992). In their experiments on fayalite dissolution open to the atmosphere at 25°C at $2 < \text{pH} < 4.5$, Wogelius and Walther (1992) observed a continuous decrease in dissolution rate, which they attributed to oxidation or precipitation of surface Fe.

6.3. Effect of solution Al on dissolution rate of forsteritic olivine

Previous experiments on albite dissolution show that the rate of albite dissolution is dependent not only on temperature and solution pH, but also on the Al concentration in the solution (Chou and Wollast, 1985; Oelkers et al., 1994; Chen and Brantley, 1997). Dissolution rates of forsteritic olivine at 65°C and pH 2.95, measured with and without Al, are plotted vs. Al concentration in Fig. 4. (For the experiment with 10 ppm (0.37 mmol/l) of Al (Run OV-6 in Table 2), the solution was supersaturated with respect to boehmite ($\gamma\text{-AlO}(\text{OH})$) at 65°C based on thermodynamic calculations using SOLMINEQ). The result shows that over a wide range of Al concentration, the dissolution rate of forsteritic olivine is not significantly affected by Al. The observed Al-independent dissolution of forsteritic olivine may be related to the silicate structure. Adsorption of Al on the surface of forsteritic olivine, if it occurs, might not form stable crosslinks between the isolated silica tetrahedra, in contrast to the effect of Al on the dissolution of feldspars (Chou and Wollast, 1985; Casey et al., 1988; Oelkers et al., 1994; Chen and Brantley, 1997). Indeed, Fig. 4 is consistent with the suggestion that the structure and/or the surface charge of the hydrated olivine surface differs signifi-

cantly from the hydrated feldspar surface even when that feldspar surface has been leached of alkali, alkaline earth, and aluminum cations.

7. Conclusions

Eight experiments of forsteritic olivine dissolution using batch reactors were conducted at 65°C between pH 2 and 5. A strong pH-dependence of dissolution rate is observed under the experimental conditions. Comparing the literature data on forsteritic olivine dissolution at 25°C, we observed an increase in pH-dependence at higher temperature, which is consistent with the prediction of a surface protonation model (Brady and Walther, 1992; Casey and Sposito, 1992).

Based on literature data for forsteritic olivine dissolution at 25°C and our results at 65°C, we were able to estimate the pH-independent activation energy of forsteritic olivine dissolution (30 ± 4 kcal/mol). Because pH-dependence (n) changes with temperature, however, E_a at a given pH (for example the activation energy of weathering at a given pH) will decrease with increasing pH. Comparing this data with our previous data for inosilicate dissolution, values of the E_a calculated for rate Eq. (1) decreased from the Mg-endmember orthosilicate (forsteritic olivine, 30 ± 4 kcal/mol), to the Ca–Mg endmember pyroxene (diopside, 23 kcal/mol), to the Mg-endmember amphibole (anthophyllite, 19 kcal/mol).

Results also show that existence of Al in solution does not affect the rate of forsteritic olivine dissolution significantly under the experimental conditions. This result may indicate that Al does not form strong crosslinks to the unpolymerized surface of forsteritic olivine and thus does not retard the dissolution of this phase under the experimental conditions.

Acknowledgements

This research was funded through grants from the National Science Foundation (EAR 9305141) and from the David and Lucile Packard Foundation to S.L.B. We acknowledge help from D. Voigt, L.

Stillings, and S. Yau, and excellent reviews from P. Maurice and R. Wogelius. [J.D.]

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