Rate equations for sodium catalyzed amorphous silica dissolution

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Abstract—Newly measured amorphous silica dissolution rate data were combined with data from the literature to produce an equation that predicts the dissolution flux (J , mol/m²sec) of amorphous silica as a function of temperature (T , K), sodium concentration (m_{Na^+} , molal), and hydrogen ion activity (a_{H^+}).

$$J_{\text{Na}} = 14.62 \left(10^{-\left(\frac{77400}{2.303R}\right)\left(\frac{1}{T}\right)} \right) + 8.95 \left(10^{-\left(\frac{77700}{2.303R}\right)\left(\frac{1}{T}\right)} \right) \left(\frac{m_{\text{Na}^+}^{0.490}}{a_{\text{H}^+}^{0.377}} \right)$$

The same data fit equally well to an equation that expresses the dissolution flux as a function of temperature, sodium concentration, and hydroxide ion activity (a_{OH^-}).

$$J = 14.62 \left(10^{-\left(\frac{77400}{2.303R}\right)\left(\frac{1}{T}\right)} \right) + 1.73 \times 10^6 \left(10^{-\left(\frac{77700}{2.303R}\right)\left(\frac{1}{T}\right)} \right) m_{\text{Na}^+}^{0.490} a_{\text{OH}^-}^{0.377}$$

These equations have the same form as those for quartz (Rimstidt 2015) and show that sodium ions have the same catalytic effect on amorphous silica dissolution as they do for quartz.

1. Introduction

Amorphous silica phases, and closely related natural and synthetic glasses, are common in nature as well as in technology. These amorphous phases are more soluble than quartz so they dissolve more rapidly (Rimstidt and Barnes, 1980). Like quartz, amorphous silica dissolves faster at high pH

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by a process that is catalyzed by cations. This means that the weathering and diagenesis of opaline biogenic silica (*e.g.* phytoliths, diatoms, sponge spicules) is significantly affected by solution composition. In addition, it is possible that the weathering and transformation rates of natural and synthetic glasses are also catalyzed by dissolved cations. In this study we combined some newly measured amorphous silica dissolution rate data with data from the literature to develop rate equations for amorphous silica dissolution as a function of pH, sodium concentration (m_{Na}) and temperature (T). Although these rate equations are only valid for pure silica, they serve as a useful baseline to help us understand the dissolution rates of silica rich natural and synthetic phases.

Silica dissolves in water by releasing silicic acid into solution.

At high pH some of the silicic acid ionizes.

So there is a second dissolution reaction that occurs in parallel with reaction (1).

However, combining equation (3) with the equation for the ionization of water ($\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$) allows this reaction to also be written in terms of hydroxide ion.

Rimstidt (2015) found that quartz dissolution rates were fit equally well by a pH-based rate equation and a pOH-based rate equation. The pH-based equation implies that the reaction is inhibited by hydrogen ions. This is consistent with rate equations based on surface speciation such as those in Bickmore et al. (2008). The pOH-based equation suggests that hydroxide ions act as nucleophilic reagents attacking Si centers. Although the authors of this paper prefer this explanation because it is consistent with the Lewis acid base mechanism highlighted in the quantum mechanical model of Xiao and Lasaga (1996), we realize that it cannot be justified by the regression model alone. Appendix 2 in Rimstidt (2015) lists additional papers that discuss these and other ideas about silica dissolution reaction mechanisms.

2. Methods

Altogether 215 dissolution rate data were tabulated from three literature sources (Frayssé et al., 2006; Icenhower and Dove, 2000; Wirth, 1980). We did not use data from studies where the reacting solutions contained pH buffers (*e.g.* Mazer and Walther, 1994) nor did we use data from studies that used silica samples with surface coatings such as 'Monospher', which is coated with sulfonic acid functional groups (Seidel et al., 1997), or silica diatoms, which have natural organic coatings (Greenwood et al., 2005). The rate data that we used are listed in the Supplementary Information data table along with the temperature, pH and the sodium concentration for the experiments. All rates are normalized to BET surface area. Quench pH values (pH at room temperature) were used to develop the regression models. The actual pH of the solution at temperature was somewhat different. However, fits of data where the pH was adjusted for the effect of temperature produced regression parameters and R^2 values that were nearly the same as those based on quench pH. Therefore, we chose to fit the data using the quench pH in order to avoid introducing unnecessary complexity into the models.

There were very few rate measurements at high pH and moderate sodium concentration so 15 additional rate measurements were made in order to better constrain the rate model. These experiments were carried out at $0 \leq T \leq 50^\circ\text{C}$, $5.3 \leq \text{pH} \leq 10.4$ and $0 \leq m_{\text{Na}} \leq 1.0$. The experiments used fused quartz wool, which is pure SiO_2 glass (amorphous silica), from Technical Glass Product, Inc. The diameters of the quartz wool fibers ranged from 6 to 9 μm . The BET surface area of this material was $1.39 \text{ m}^2/\text{g}$ (measured by Micromeritics, Inc.). The geometric surface area was estimated to be $0.20 \text{ m}^2/\text{g}$. Solutions were prepared using reagent grade NaCl and the pH was adjusted using reagent grade Na_2CO_3 or HCl. The quartz dissolution rate studies listed in the Supplementary Information for Rimstidt (2015) shows good internal consistency among experiments conducted in chloride-, nitrate-, carbonate-, and sulfate-bearing solutions so we have assumed that silica dissolution rates are not affected by those anions.

The rates were measured using a mixed flow reactor with a recycle loop that ensured that the solution in the reactor was well mixed (Figure 1). Two reactor sizes were used. One with a length of 10.3 cm and a diameter of 1.9 cm (volume = 117 cm^3) was loosely packed with 5 g of quartz wool. The other, used for higher temperatures and sodium concentrations, with a length of 4.0 cm and a diameter of 1.9 cm (volume = 45 cm^3) was loosely packed with 0.5 g of

quartz wool. The fused quartz was used as obtained with no pretreatment. In order to ensure that this reactor behaved as an ideal mixed flow reactor, the feed pump was set to a low flow rate (3 to 50 mL/hr) and the recycle pump was set to a much higher flow rate (~ 1000 mL/hr) so that the solution passed over the glass wool many times during its residence in the reactor. Each experiment was run until the silica concentration varied by less than 10% from day to day. This typically occurred seven to ten days after the beginning of the experiment.

Figure 1. Schematic illustration of the externally recycled mixed-flow reactor used to measure the dissolution rate of the quartz wool.

Before each experiment, the column containing the fused quartz was partly filled with deionized water. It was then connected to the feed pump, which was operated at a slow flow rate until all of the air bubbles were forced from the reactor. Then the recycle pump was run in the reverse direction until air bubbles were cleared from the recycle loop. When the system was fully filled with water the recycle pump was turned on in the forward direction and the feed pump inlet was connected to the tank containing the experimental solution.

Once per day about 10 mL of effluent was collected into a weighed, acid-washed 15 mL centrifuge tube. The flow rate was determined from the change in mass of the tube and the time of sample

collection. The pH of the effluent was measured immediately after sample collection. Samples were stored at 4°C until analysis. The silicon concentration was determined using the silicon molybdate blue colorimetric method. There was no dissolved silica in the feed solution so the dissolution flux was found from the product of the effluent silica concentration and flow rate divided by the BET surface area of the quartz wool.

$$J = \frac{m_{Si} Q}{A} \quad (5)$$

Table 1 gives a summary of the notation and units used in this paper. The approach used to develop the rate equations the same as described in Rimstidt (2015). In the absence of sodium, the dissolution flux (J_o) from reaction (1) is only a function of temperature. A second reaction path is responsible for the sodium catalyzed dissolution flux (J_{Na}). The rate of this second reaction is a function of temperature, pH, and sodium concentration. The overall dissolution flux is the sum of these two parallel reactions.

$$J = J_o + J_{Na} \quad (6)$$

This required a two-step fitting process. First the logarithm of the dissolution flux of amorphous silica in sodium absent solutions ($\log J_o$) was fit as a function of $1/T$.

$$\log J_o = \log A + \frac{-E_a}{2.303R} \left(\frac{1}{T} \right) \quad (7)$$

Then the dissolution flux predicted by this rate equation was subtracted from the dissolution flux for experiments where the solutions contained dissolved sodium. The remaining flux (J_{Na}) was attributed to a reaction that involves the catalytic effect of sodium. The logarithm of this difference was fit as a function of pH (or pOH), m_{Na} , and $1/T$.

$$\log J_{Na} = \log A + \frac{-E_a}{2.303R} \left(\frac{1}{T} \right) + n_{H^+} pH + n_{Na^+} \log m_{Na^+} \quad (8)$$

or

$$\log J_{Na} = \log A + \frac{-E_a}{2.303R} \left(\frac{1}{T} \right) + n_{OH^-} pOH + n_{Na^+} \log m_{Na^+} \quad (9)$$

The antilog transforms of the two fitted equations (either (7) and (8) or (7) and (9)) were added to get an equation that predicts amorphous silica rates pH (or pOH), m_{Na} , and T

Table 1. Notation used in this paper. Because the rate that silica is released from the amorphous silica surface to the solution has units of flux that rate is called the dissolution flux (J , mol/m²sec).

A	pre-exponential in Arrhenius equation, mol/m ² sec
a_i	activity of species i
E_a	activation energy, kJ/mol
J	overall dissolution flux ($J = J_o + J_{Na}$), mol/m ² sec
J_{Na}	sodium catalyzed dissolution flux, mol/m ² sec
J_o	dissolution flux in sodium absent solutions, mol/m ² sec
m_i	concentration of species i , molal
n_i	reaction order for species i
pH	pH (= $-\log a_{H^+}$) at 25°C
pOH	pOH (= $-\log a_{OH^-}$) at 25°C
Q	flow rate, kg/sec
R	gas constant, 8.314 J/mol K
T	temperature, °C or K

The regression models were prepared using JMP10 (SAS Institute Inc.) statistical software. Partial regression plots (Moya-Laraño and Corcobado, 2008; Velleman and Welsch, 1981), which show the residuals of an independent variable versus the residuals of the dependent variable, were used to visualize the contribution of each independent variable to the overall fit. The slope of the line shown on those plots equals the regression coefficient for that variable. A steep slope means that the independent variable strongly influences the dependent variable.

3. Results

The dissolution flux data from the experiments are listed in Table 2. These data were combined with the literature data (see Supplemental Information) to produce a rate equation for amorphous silica as a function of pH, sodium concentration and temperature. During the modeling it was discovered that the data from Table 4 in Icenhower and Dove (2000) (low temperature externally recycled reactor experiments) consistently fell below the best-fit line, some by as much as one log unit. We interpreted this to mean that there was a systematic problem with those data so we removed them from the regression model. This left us with 36 data for the sodium-absent model and 164 data for the sodium-present model.

137 Table 2. Amorphous silica dissolution flux values determined in this study.

experiment	$T, ^\circ\text{C}$	pH	$m_{\text{Na}}, \text{molal}$	$\log J$
QW1	22	5.23	0.000	-12.00
QW2	22	7.74	0.001	-11.96
QW3	50	5.24	0.000	-11.19
QW5	22	9.80	0.001	-10.40
QW6	22	9.85	0.010	-10.09
QW7	22	10.04	0.100	-10.00
QW8	22	9.97	1.000	-9.98
QW9	50	9.92	0.001	-9.37
QW10	50	9.96	0.010	-9.31
QW11	50	10.00	0.100	-9.15
QW12	50	9.72	0.100	-9.15
QW13	0	9.81	0.001	-11.36
QW14	0	9.69	0.010	-10.79
QW15	0	9.54	0.100	-11.72
QW16	0	9.54	1.000	-11.61

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139 Regression of all the data for the sodium absent experiments (Figure 2) produced the following
140 equation.

141
$$\log J_o = 1.165(0.171) - \frac{4042(65)}{T} \quad (10)$$

$$R^2 = 0.991 \quad n = 36$$

142 The numbers in parentheses following the fitted parameter represent one standard error for that
143 parameter. The activation energy derived from this fit is 77.4 kJ/mol. The antilog of this expression
144 gives an equation that predicts the amorphous silica dissolution flux as a function of temperature.

145
$$J_o = 14.62 \left(10^{-\left(\frac{77400}{2.303R}\right)\left(\frac{1}{T}\right)} \right) \quad (11)$$

Figure 2. Graph of $\log J_o$ versus $1/T$ for experiments with no dissolved sodium.

The value of J_o predicted by equation (11) was subtracted from the observed dissolution flux for solutions that contained sodium to get the dissolution flux for the sodium catalyzed reaction. The values of $\log J_{Na}$ were then regressed against $1/T$, pH , and $\log m_{Na}$ (Figure 3) to produce an equation that describes the rate for the sodium catalyzed reaction.

$$\log J_{Na} = 0.952(0.129) + \frac{-4057(51)}{T} + 0.377(0.015)pH + 0.490(0.030)\log m_{Na^+} \quad (12)$$

$R^2 = 0.978 \quad n = 164$

The numbers in parentheses following the fitted parameter represent one standard error for that parameter. The antilog of this expression predicts the rate of the sodium-catalyzed reaction. The activation energy for this reaction is 77.7 kJ/mol.

$$J_{Na} = 8.95 \left(10^{-\left(\frac{77700}{2.303R}\right)\left(\frac{1}{T}\right)} \right) \left(\frac{m_{Na^+}^{0.490}}{a_{H^+}^{0.377}} \right) \quad (13)$$

Combining equation (12) with (13) gives an equation that predicts the overall amorphous silica dissolution flux.

$$J = 14.62 \left(10^{-\left(\frac{77400}{2.303R}\right)\left(\frac{1}{T}\right)} \right) + 8.95 \left(10^{-\left(\frac{77700}{2.303R}\right)\left(\frac{1}{T}\right)} \right) \left(\frac{m_{Na^+}^{0.490}}{a_{H^+}^{0.377}} \right) \quad (14)$$

Figure 3. Fit of $\log J_{Na}$ as a function of pH, $\log m_{Na}$, and $1/T$. (a) Observed values of $\log J_{Na}$ versus predicted values of $\log J_{Na}$. (b) Partial regression leverage plot for $1/T$. (c) Partial regression leverage plot for pH. (d) Partial regression leverage plot for $\log m_{Na}$.

Equation (14) predicts that rate of the sodium-catalyzed reaction is inversely proportional to the hydrogen ion activity, which implies that hydrogen ions inhibit the sodium catalyzed dissolution reaction. An alternative explanation is that hydroxide ions participate in the activated complex making the rate directly proportional to the hydroxide ion activity. We tested this possibility by regressing $\log J_{Na}$ against $1/T$, pOH , and $\log m_{Na}$.

$$\log J_{Na} = 6.237(0.231) + \frac{-4057(51)}{T} + 0.490(0.030)\log m_{Na} - 0.377(0.015)pOH \quad (15)$$

$$R^2 = 0.978 \quad n = 164$$

The numbers in parentheses represent one standard error of the fitted parameter. The patterns found in the graphs for this regression model are identical to those for the pH-based model based except the slope on the pOH partial regression plot is reversed. Because equations (13) and (15) fit the data equally well, we cannot use the fitted rate equation to eliminate either hypothesis.

Taking the antilog of equation (15) and combining with equation (11) gives an equation that predicts the overall amorphous silica dissolution flux in terms temperature, sodium concentration and hydroxide activity.

$$J = 14.62 \left(10^{-\left(\frac{77400}{2.303R}\right)\left(\frac{1}{T}\right)} \right) + 1.73 \times 10^6 \left(10^{-\left(\frac{77700}{2.303R}\right)\left(\frac{1}{T}\right)} \right) m_{\text{Na}^+}^{0.490} a_{\text{OH}^-}^{0.377} \quad (16)$$

4. Discussion and Conclusions

The rate equations given in this paper are suitable for modeling geochemical processes but they are nothing more than empirical interpolations between the existing data. Because they are not based on a fundamental model of the reaction mechanism we do not recommend extrapolating them much beyond the experimental conditions. Furthermore, the fitting process may have been biased by the clumped distribution of experimental conditions. The new experimental data reported in this paper helps this problem somewhat by anchoring the data at high pH and low temperatures but the model would be improved by data taken from a wider range of conditions. For example, there is considerable evidence that amorphous silica and quartz dissolution rates increase below pH 3 but we have not included any of those data in our model. As a result we recommend that the rate equations be used only for $3 < \text{pH} < 11$. Finally, our models are based on total sodium concentrations and do not account for speciation effects or for the effects of other cations (*e.g.* K^+ , Ca^{2+} , Mg^{2+} , *etc.*). The dissolution flux values used to create the rate equations in this paper and in Rimstidt (2015) are normalized to BET surface area measurements. Multiplying those values $\sim \times 5$ should give reasonable estimates of these dissolution flux values based on geometric surface area (see the discussion about geometric and BET surface areas in Rimstidt et al., 2012).

Rimstidt (2015) showed that the effect of sodium concentration and pH on quartz dissolution rates could be modeled equally well by multiple rate equations because of correlations among independent variables used to construct those equations. In this study we showed that the rate

equations based on pH and pOH fit the data equally well and we expect that rate equations based on surface speciation, like those in Bickmore et al. (2008), would also fit the data quite well. As a result it is not possible to infer a reaction mechanism from these rate equations alone.

The dissolution flux of amorphous silica as a function of pH, contoured in sodium concentrations (Figure 4) is essentially identical to the diagram for quartz (see Figure 7 in Rimstidt, 2015) except that the contours are displaced to a higher value by about 1 log unit because amorphous silica solubility is about ten times higher than for quartz. This is consistent with the idea that the reaction mechanism is the same for both phases as assumed in the rate equations in Rimstidt and Barnes (1980).

The rate equations in this paper provide a good baseline for understanding the dissolution rates of related materials. The data used to produce the rate equations are from experiments that used crushed fused quartz (Icenhower and Dove, 2000; Wirth and Gieskes, 1979), pyrolyzed silica (Icenhower and Dove, 2000), plant phytoliths (Frayssé et al., 2006), and quartz wool (this study). The dissolution rates of all of these materials appear to be concordant. The dissolution rates for diatoms in seawater reported in Rickert et al. (2002) are somewhat scattered, no doubt because of the challenge of obtaining reliable surface area values, but they are reasonably consistent with the rate predicted for seawater sodium concentrations. Also, the rates for true seawater compositions should be higher than the seawater sodium point on this figure due to the additional catalytic effects of other cations. Figure 4 shows dissolution rates of nepheline, jadite, and albite glasses at pH 4, 6, 9, and 12 reported by Hamilton et al. (2001). At pH > 8, the slopes of the log J versus pH graphs are parallel to the sodium isopleths, which suggests that the bond breaking reactions that release silica from these glasses might be the same as those that are responsible for amorphous silica dissolution.

Figure 4. Predicted logarithm of the amorphous silica dissolution flux at 25°C as a function of pH contoured in Na^+ concentration, based on equation (14). The shaded area represents hydroxide activities that are not attainable because sodium must be added to the solution along with the hydroxide. Note that when no Na^+ is present the dissolution flux is independent of pH. The star symbols represent cleaned diatom dissolution rates in seawater reported by Rickert et al. (2002). The other symbols show dissolution rates for nepheline, jadite, and albite glasses at pH 4, 6, 9, and 12 reported by Hamilton et al. (2001).

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