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ABSTRACT: We measured labradorite ($Ca_{0.6}Na_{0.4}Al_{1.6}Si_{2.4}O_8$) dissolution rates using a mixed flow reactor from 30 to 130ºC as a function of CO_2 (3 x 10^{-3} and 0.6 M), and aluminum (10^{-6} to 10^{-3}M) at pH 3.2. Over these conditions, labradorite dissolution can be described with a single rate expression that accounts for observed increases in dissolution rate with temperature and decreases in dissolution rate with dissolved aluminum:

$$\text{Rate}_{\text{Si}}\ (\text{mol Labradorite cm}^{-2}\text{s}^{-1}) = k'' \times 10^{-Ea/2.303RT}\ [(a^{3n}_{H+}/a^{n}_{Al3+})K_T/(1+K_T\ (a^{3n}_{H+}/a^{n}_{Al3+}))]. \qquad \text{A1.}$$

where the apparent dissolution rate constant, $k'' = 10^{-5.69}$ (mol Labradorite $cm^{-2}s^{-1}$); the net activation energy, E_a = 10.06 (kcal mol^{-1}); H^+-Al^{3+} exchange coeffiecient, n = 0.31; and silica rich surface complex formation constant, K_T = 4.5 to 5.6 from 30 to 130ºC. The effect of CO_2(aq) on mineral dissolution is accounted for by changes in solution pH. At temperatures below 60ºC, labradorite dissolves incongruently with preferential dissolution of Na, Ca and Al over Si.

1 INTRODUCTION

Geologic sequestration of CO_2 in sedimentary basins or in saline aquifers appears to be a promising method for disposal, because the reaction of CO_2, water, and primary silicate minerals produces more stable secondary silicates, hydroxides, and carbonates. Measurement of mineral dissolution and precipitation rates is fundamental to the successful disposal of greenhouse CO_2-rich gases in aquifers, because reservoir storage capacity is related to the conversion of CO_2(g) to carbonate minerals, and because secondary mineral precipitation will alter reservoir porosity and permeability. Our interest in quantifying labradorite ($Ca_{0.6}Na_{0.4}Al_{1.6}Si_{2.4}O_8$) dissolution rates with a single rate equation as a function of pCO_2, dissolved Al, and temperature was motivated by the need to understand the source term for secondary mineral precipitation caused by the neutralization of injected acid CO_2 by rock-water interactions. Labradorite dissolution rates were measured in acidic waters saturated with supercritical CO_2 or with atmospheric CO_2 as a function of dissolved Al (10^{-6} to 10^{-3} M) and temperature (30 to 130°C). The resulting rate equation can be directly incorporated into reactive transport codes to better evaluate geologic storage of CO_2.

2 EXPERIMENTAL METHODS

Ground labradorite ($Ca_{0.6}Na_{0.4}Al_{1.6}Si_{2.4}O_8$) phenocrysts from a weathered basalt flow near Pueblo Park, was the feldspar used in this study (Casey et al., 1988). Waters saturated with supercritical CO_2 were made by reacting pressurized liquid CO_2 at 165°C. All other solutions were reagent grade HCl and $Al(Cl)_3nH_2O$. We used a titanium mixed flow reactor to measure the effects of dissolved CO_2 and Al on labradorite dissolution kinetics in several stacked experiments. The net rate of reaction was calculated from changes in inflow and outflow solution composition, flow rate, and mineral surface area (0.03 m^2/g as determined by nitrogen adsorption BET method).

3 RESULTS AND DISCUSSION

3.1 *Incongruent labradorite dissolution*

In our study we observe incongruent dissolution at 60˚C and below, with enhanced release of sodium, calcium and aluminum over silica in solutions equilibrated with either laboratory air, $CO_{2(aq)} \approx 3\times10^{-3}$M, or equilibrated with supercritical CO_2, ≈ 0.6 M (Fig. 1). Labradorite dissolution is congruent above 100°C. At 130°C we clearly see evidence for precipitation of an aluminum-bearing mineral from the aluminum-normalized dissolution rate, which is more than 25 times lower than the silica-normalized dissolution rate. This suggests that the secondary precipitate is an Al-hydroxide, which exhibits retrograde solubility in acid solutions, due to the temperature dependence of aluminum hydrolysis (Bourcier et al, 1993). Although these waters were also supersaturated with respect to kaolinite ($Al_2Si_2O_5(OH)_4$), congruent calcium, sodium, and silica release as well as systematic increase of the silica dissolution rates with temperature (log Rate vs. T^{-1}) shown in Figure 1 suggest no precipitation of a silica bearing solid.

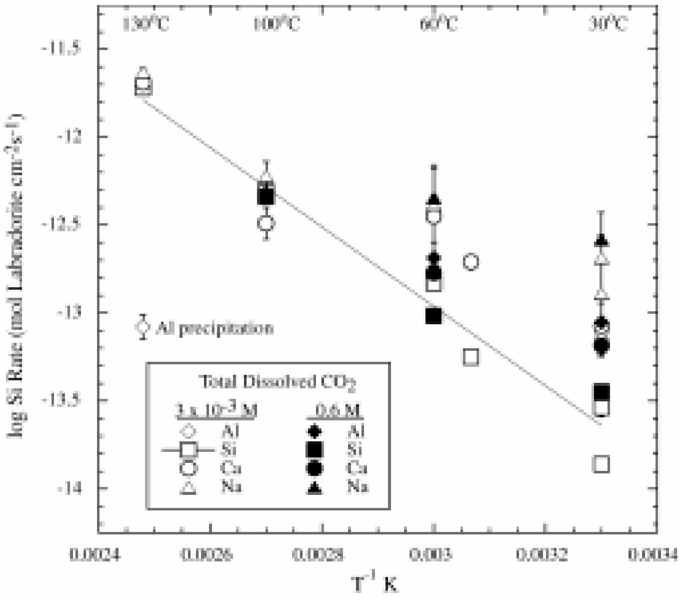

Figure 1. Comparison of labradorite dissolution rates at pH 3.2 in waters equilibrated with atmospheric CO_2 (open symbols) and equilibrated with supercritical CO_2 (filled symbols, 0.6 M CO_2) as function of temperature and release of Na, Ca, Al, and Si. All rates are normalized to their mole fraction concentrations in labradorite at a constant flow rate to normalize effect of dissolved Al on dissolution rate.

Several other studies have shown that anorthitic feldspars similar in composition to labradorite used in this study dissolve incongruently for long periods of time (as much as 3000 hours) at 25ºC (Stillings & Brantley 1995; Casey et al. 1989a, b; Nesbitt et al. 1991, Shotyk & Nesbitt 1990, Taylor et al. 2000) and one study at 45ºC (Casey et al. 1988). The temperature dependence suggests that congruent dissolution occurs when the hydrolysis rate of the Al-O-Si bridging bonds exceeds the effect of H^+ exchange for Na^+, Ca^{2+} and some Al^{3+} on dissolution. This interpretation is consistent with other studies. Nesbitt et al. (1991) concluded that incongruent dissolution was a product of ion exchange, because they observed congruent labradorite dissolution in electrolyte solutions and incongruent dissolution in pure HCl-H_2O solutions. Similarly, Brantley & Stillings (1996) and Stillings & Brantley (1995) found that in dilute solutions ion exchange enhances dissolution.

3.2 *Effect of $CO_2(aq)$*

We observed no direct effect of dissolved CO_2 on labradorite dissolution from 30 to 130˚C (Fig. 1). Labradorite dissolution rates measured at pH 3.2 with much lower dissolved CO_2 (~3×10^{-3} M in dilute HCl solutions saturated with laboratory air) are within experimental uncertainty of those reacted in waters equilibrated with supercritical CO_2 containing about 0.6 M dissolved CO_2 and the same pH. These results agree with labradorite dissolution at much lower concentrations of CO_2 (Brady & Carroll 1994). Any effect of high levels of CO_2 in sequestration schemes on mineral dissolution rates can be accounted for by CO_2 solubility and the resulting acidity in the formation waters, greatly simplifying the dissolution rate equation. As the formation waters are neutralized downstream from the injection well, CO_2 may have a slight impact on silicate dissolution kinetics. Berg & Banwart (2000) show that Ca-feldspar dissolution rates are slightly enhanced at near neutral pH by dissolved CO_3^{2-} (Rate = $k_{diss}[CO_3^{2-}]^{0.24}$).

3.3 *Effect of dissolved aluminum and temperature*

Oelkers & co-workers (Gautier et al. 1994; Oelkers et al. 1994; Oelkers & Schott, 1995; Devidal et al. 1997) account for the decrease in silicate dissolution with increasing dissolved aluminum by the formation of rate-limiting silica rich surface complexes. In this model, the concentration of these complexes is dependent on the dissolved aluminum concentration according to the following mass balance equation:

$$\text{M-AlSiO} + 3nH^+ = \text{M-SiO} + nAl^{3+}, \qquad 1.$$

where M-AlSiO represents an Al-filled mineral surface site, n is a stoichiometric exchange coefficient for H^+ and Al^{3+}, and M-SiO is the silica rich complex at the mineral surface. At conditions far from equilibrium this rate expression is independent of reaction affinity.

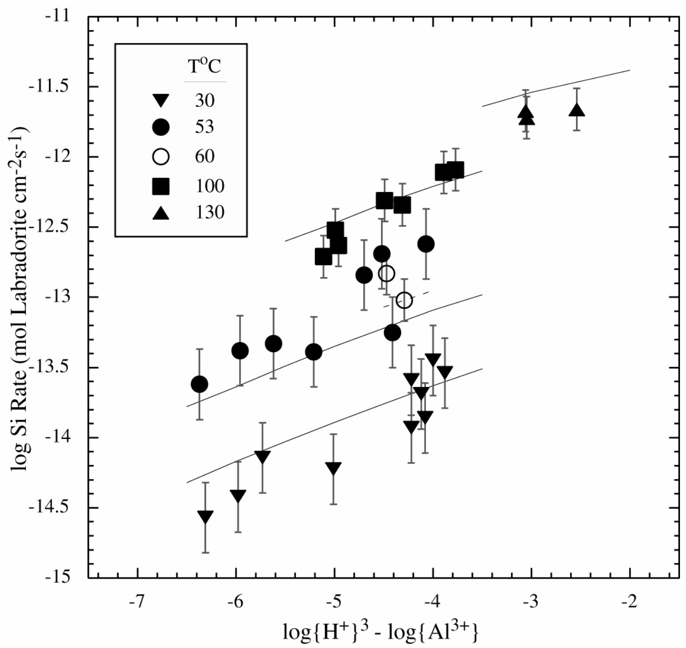

Figure 2. Temperature and aluminum dependence of labradorite dissolution plotted as log Si rate (mol Labradorite cm^{-2} s^{-1}) versus $\log\{H^+\}^3/\{Al^{3+}\}$.

We extend this rate model to account for the effect of temperature as well as the effect of aluminum on labradorite dissolution using the following equation:

$$Rate_{Si}\ (\text{mol Labradorite } cm^{-2}s^{-1}) = k'' \times 10^{-Ea/2.303RT}$$
$$[(a^{3n}_{H+}/a^{n}_{Al3+})K_T/(1+K_T\ (a^{3n}_{H+}/a^{n}_{Al3+}))]. \qquad 2.$$

where k'' is the apparent dissolution rate constant, E_a is the activation energy. In Equation 2, the temperature dependence of the formation constant, K_T, can be estimated from the van't Hoff equation:

$$\text{Log}\ (K_1/K_2) = \Delta H/2.303R(T_2^{-1}-T_1^{-1}). \qquad 3.$$

Using Equations 2 and 3 we derive k'', E_a, and n, K_T, and ΔH, the respective stoichiometric exchange coefficient, formation constant at temperature, and the enthalpy of reaction for H^+ - Al^{3+} exchange to form the silica-rich surface complex from a non-linear multiple regression of rate data from 30 to 130°C. The fit to the data are shown in Figure 2 and correspond to log k'' = -5.69 (mol Labradorite cm^{-2} s^{-1}), E_a = 10.06 (kcal/mol), ΔH = 0.54 (kcal/mol) and n = 0.31. Regressed values for K_T are 4.5, 4.8, 4.9, 5.3, and 5.6 for 30, 53, 60, 100, and 130°C, respectively. We normalize the rate data to the stoichiometric release of dissolved silica, because decomposition of the Al-O-Si bridging bonds is believed to control feldspar dissolution. Equation 2 does not account for the incongruent dissolution observed at lower temperatures.

4 SUMMARY

The focus of this work is to measure mineral dissolution rates needed to predict changes in reservoir storage capacity due to injection of supercritical CO_2 in the subsurface where it will react with aquifer water and rock. We describe labradorite ($Ca_{0.6}Na_{0.4}Al_{1.6}Si_{2.4}O_8$) dissolution with a single rate equation as a function of pCO_2 (3×10^{-3} and 0.6 M), dissolved Al (10^{-6} to 10^{-3}M), and temperature (30 to 130°C). The resulting temperature dependent rate equation is an extension of the model proposed by Oelkers and co-workers in which the dependence of silicate dissolution rates on dissolved aluminum is attributed to the formation of rate-limiting silica rich surface complexes. This study adds to a growing body of literature that shows increasing concentrations of dissolved aluminum inhibit alumino-silicate dissolution rates. Although the effect of dissolved aluminum on dissolution rates is real, it's effect on rates is secondary compared to that of temperature. Any enhanced dissolution rates in solutions with high dissolved CO_2 are due to the increase in acidity from the solubility of CO_2 and can be modeled with a rate equation that accounts for solution pH and dissolved aluminum. At 60°C and below, labradorite dissolution is incongruent with calcium rates as high as three times the silica rates. These rates appear to persist for long periods of time, and may need to be incorporated in CO_2 sequestration simulations to accurately predict the storage of CO_2 in carbonate minerals.

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