Chemical affinity and pH effects on chlorite dissolution kinetics under geological CO₂ sequestration related conditions

Shuo Zhang^{1,2*}, Li Yang², Donald J. DePaolo^{1,2} and Carl I. Steefel²

¹University of California Berkeley, Earth and Planetary Science, shuozhang@berkeley.edu

²Lawrence Berkeley National Laboratory, Earth Sciences, lyang@lbl.gov, djdepaolo@lbl.gov, cisteeefel@lbl.gov

Abstract

The kinetic dissolution of Flagstaff Hill chlorite (CCa-2 from Clay Minerals Society), $(Mg_{4.55}Al_{1.23}Fe_{0.12})(Al_{1.04}Si_{2.96})O_{10}(OH)_8$, was investigated using a well-mixed flow-through reactor at 100 °C, pH values ranging from 3.0 to 7.5, and variable saturation states. The objective was to measure the dependence of chlorite dissolution rate on pH as well as on degree of undersaturation under conditions applicable to geologic carbon storage. A batch experiment was conducted to determine the equilibrium constant of the dissolution reaction at 100 °C for the chlorite mineral phase used in this study. A series of experiments was run at varying CO₂ partial pressures (0-60bars) and different flow rates (0.01-0.25ml/min). We use our experimental results in conjunction with previously published data to separate the effects of pH and solution saturation state. At constant pH, the chlorite dissolution rate decreases slowly as a function of the Gibbs free energy of reaction (ΔG_r), which is a quantitative measure of the degree of undersaturation. The undersaturation required ($-\Delta G_r > 100$ kJ/mol) to reach a limiting far-from-equilibrium rate (the “dissolution plateau”) is roughly an order of magnitude larger than expected from transition state theory, but similar to that determined for smectite ($-\Delta G_r > 130$ kJ/mol) (Cama et al., 2000). Hence, chlorite dissolution behaves as if the chlorite were close to equilibrium even in solutions that are strongly undersaturated. The chlorite dissolution rate (R) as a function of pH and chemical affinity (ΔG_r) at 100 °C can be fit reasonably well with the following expression:

$$R = (10^{-7.64} a_H^{1.05} + 10^{-11.56}) \{1 - \exp[-0.01677(\frac{|\Delta G_r|}{RT})^{1.3}]\}$$

The rate law obtained in this study provides a basis for modeling chlorite mineral dissolution over a range of pH and saturation conditions, which is essential in applications such as subsurface CO₂ sequestration.

1. Introduction

Injection of CO₂ into deep saline aquifers is one means of sequestering CO₂ released from the burning of fossil fuels in power generation facilities (IPCC, 2005). Injected CO₂ dissolves into the native formation brine, making the brine corrosive and aggressively reactive toward the native minerals (Xu et al., 2004). Minerals that

contain cations such as Mg, Ca, and Fe dissolve in the CO₂ affected brine and release cations for CO₂ carbonation if the alkalinity increases as well (Steefel et al., 2013). The permanent fixation of CO₂ in the solid phases (calcite, magnesite, and ankerite) by combining these cations with CO₂ is referred to as mineral trapping (IPCC, 2005). Minerals that are sources of divalent cations and common in impure sandstones are biotite, chlorite, glauconite, amphibole, epidote, and montmorillonite. Chlorite (sheet-structured aluminosilicates containing variable amounts of magnesium and iron) is found to be the most abundant and reactive mineral that contains the cations in one of the CO₂ sequestration pilot sites in Cranfield, Mississippi (Landrot et al., 2012). Chlorite minerals are also common constituents of numerous formations and typically occur as grain-coating or pore-filling growths in sedimentary sandstones, alteration products of mafic minerals in basaltic units, or as products of low-grade metamorphism of many prior assemblages. Although chlorite dissolution rates are not as high as those of mafic minerals such as pyroxene and olivine, the extent of water-chlorite reaction is expected to be significant because (1) the brine in contact with rocks will be acidified with dissolved CO₂, (2) the time scale for safe storage of CO₂ in a sequestration site may be of order thousands of years, and (3) the reactive surface area of chlorite-rich sandstones is relatively large ($11.62 \times 10^{-2} \text{ m}^2/\text{g}$ for the Cranfield sandstone (Landrot et al., 2012)).

Geochemical reactive transport simulations are currently used to model the reaction and evolution of CO₂ containing fluids with bedrock minerals during CO₂ sequestration. In order to make accurate predictions of the evolution of such subsurface systems with modeling, it is critical to know the mineral/fluid reaction kinetics for the relevant phases. Most of the geochemical transport simulation codes available now include the ability to treat the kinetics of mineral dissolution/precipitation reactions coupled to the transport equations (see for example (Steefel and Lasaga, 1994)). Most treatments of mineral dissolution and precipitation reaction kinetics in the reactive transport simulators, however, have relied on rate laws based on linear transition state theory formulations (Aagaard and Helgeson, 1982; Lasaga, 1984). For the purposes of modeling CO₂ injection and sequestration and its effects on geochemistry and mineral evolution, it is critical to provide the experimentally verified kinetic rate equations over the full range of relevant conditions. Some studies of chlorite mineral dissolution kinetics have been published (Brandt et al., 2003; Lowson et al., 2007; Malmström et al., 1996; Rochelle et al., 1994; Smith et al., 2013), although none of these have explored the dependence of chlorite dissolution kinetics on the departure from equilibrium (or chemical affinity), despite the demonstrated importance of this effect in natural systems (Maher et al., 2009; Steefel et al., 2005). The dependence of the rate on the chemical affinity becomes particularly important if the transition to the maximum far from equilibrium rate (the so-called “dissolution plateau”) is broad, i.e., it does not show a linear dependence on the departure from equilibrium (Maher et al., 2009).

In the present work, laboratory experiments were conducted to understand the dissolution rate dependence of chlorite with respect to the chemical affinity or Gibbs free energy of the reaction. We used well-stirred flow-through reaction vessels in which steady-state rates were determined at specific solution saturation states, and at elevated temperature and pressure relevant for CO₂ sequestration. Our two major objectives are: 1) to examine the effect of chemical affinity on chlorite dissolution rate within the framework of transition state theory, and 2) to obtain a complete kinetic dissolution rate equation on mineral chlorite that is applicable for subsurface CO₂ sequestration modeling.

1.1. Previous studies

Most previous studies of chlorite dissolution have been conducted at room temperature and pressure, although at various pH values (Banfield and Murakami, 1998; Brandt et al., 2003; Hayashi and Yamada, 1990; Lowson et al., 2007; Lowson et al., 2005; Malmström et al., 1996; Rochelle et al., 1994). Lowson et al. (2005) summarized results reported in the literature and concluded that the dissolution of chlorite is enhanced in acidic solutions and alkaline solutions and is independent of pH in the neutral pH region. In CO₂ saturated water with a pH of 3-4, these studies suggest the dissolution rate of chlorite would be 10⁻¹²-10⁻¹¹ mol/m²/s at 25 °C assuming that the effect of CO₂ on dissolution kinetics is only via its effect on pH.

Smith et al. (2013) measured chlorite ((Mg_{4.29}Al_{1.48}Fe_{0.10})(Al_{1.22}Si_{2.78})O₁₀(OH)₈) dissolution kinetics under far from equilibrium conditions using a mixed-flow reactor over temperatures of 100-275 °C at pH values of 3.0-5.7 in a background solution matrix of 0.05 m NaCl. Over the investigated range of far-from-equilibrium experimental conditions, the surface area normalized rate of Mg-rich chlorite dissolution was described as (Smith et al., 2013):

$$rate = k_{acid} \exp\left[\left(\frac{-E_{acid}}{R}\right)\left(\frac{1}{T} - \frac{1}{298K}\right)\right] a_{H^+}^n \quad (1)$$

where the apparent acid rate constant at 25 °C is $k_{acid} = 10^{-9.91}$ mol/m²/s, the reaction order n with respect to H⁺(aq) is 0.49, and the activation energy for the acid mechanism is $E_{acid} = 25.1$ kJ/mol.

Lowson et al (2007) measured dissolution rates of an iron rich chlorite (Mg_{2.76}Fe(II)_{1.90}Fe(III)_{0.07}Al_{0.97})[Si_{2.48}Al_{1.52}O₁₀](OH)₈ as a function of pH over the range from 3.0 to 10.5 and at temperatures between 25 and 95°C. They fitted their dissolution rates as a function of pH at room temperature as

$$R = 10^{-9.79} a_{H^+}^{0.49} + 10^{-13.00} + 10^{-16.79} / a_{H^+}^{0.43} \quad (2)$$

To date, no experiments have been reported that determine the chlorite dissolution rate under near equilibrium conditions. However in natural systems, close-to-equilibrium conditions are prevalent, so it is critical to investigate the effect of chemical affinity in order to have a dissolution rate law that is applicable over the full range of conditions. In this study, we conducted experiments under both far-from-equilibrium and near-equilibrium conditions, and observed significantly different behavior of chlorite dissolution under these two conditions. Measured dissolution rates are expressed in terms of both a pH and a chemical affinity term, thus providing a complete kinetic expression of chlorite dissolution kinetics at 100 °C.

1.2. Effect of environmental variables on mineral dissolution kinetics

A general rate law for dissolution and precipitation can be written as (Lasaga, 1995):

$$rate = k_0 \exp\left(\frac{-E_{app}}{RT}\right) a_{H^+}^{n_{H^+}} \prod a_i^{n_i} g(I) f(\Delta G_r) \quad (3)$$

where k_0 is a constant, E_{app} is the apparent activation energy of the overall reaction, R is the gas constant, T is the absolute temperature, a_i and a_{H^+} are the activities in solution of species i and H^+ respectively, n_i and n_{H^+} are the orders of the reaction with respect to these species, $g(I)$ is a function of the ionic strength(I) and $f(\Delta G_r)$ is a function of the Gibbs free energy to account for the chemical affinity effect. This formulation is semi-empirical, and its primary usefulness is to remind the user that mineral-fluid reaction rates are complicated, and are typically affected by several environmental variables. A quantitative understanding of the effects of all the above variables is needed to accurately model the geochemical reactions resulting from CO₂ sequestration via a coupled reaction-transport model.

The dependence of $f(\Delta G_r)$ is often presented in a generalized form derived from transition state theory(TST) (Lasaga, 1998):

$$f(\Delta G_r) = 1 - \exp\left(\frac{\Delta G_r}{RT}\right) \quad (4)$$

where R is the gas constant and T is the absolute temperature. This expression is based on the assumption of detailed balance (or reversibility) and for mineral-fluid reactions

is difficult to predict *a priori* (or to justify). The equation may be generalized to (Aagaard and Helgeson, 1982):

$$f(\Delta G_r) = 1 - \exp\left(\frac{\Delta G_r}{\sigma RT}\right) \quad (5)$$

where σ is a coefficient that is not necessarily equal to 1. Usually this is considered as the Temkin coefficient that relates the stoichiometry of the rate-limiting step to the stoichiometry of the mineral-water reaction. For small deviations from equilibrium, i.e., $|\Delta G_r| \ll \sigma RT$, a Taylor series expansion of the exponential term leads to a linear relation between rate and ΔG_r

$$f(\Delta G_r) = \frac{\Delta G_r}{\sigma RT} \quad (6)$$

However, experiments have shown that dissolution is not a linear function of the Gibbs free energy in many cases. (Burch et al., 1993; Cama et al., 2000; Carroll et al., 1998; Hellmann and Tisserand, 2006; Nagy et al., 1999; Nagy and Lasaga, 1992). Nagy and Lasaga (1992) proposed to use the following equation to describe gibbsite dissolution rate as a function of ΔG_r :

$$f(\Delta G_r) = 1 - \exp\left[m\left(\frac{\Delta G_r}{\sigma RT}\right)^n\right] \quad (7)$$

where m and n are experimentally determined coefficients.

In this study, a series of experiments was conducted at different CO_2 partial pressures (0-60 bars) and different flow rates (0.01-0.25 ml/min) to control the departures of the experimental system from equilibrium and study the effects of Gibbs free energy on mineral chlorite dissolution kinetics. We show that the chemical affinity effect on the kinetics of chlorite dissolution cannot be described by a simple linear TST rate law, but can be fitted with an empirical TST based equation such as Equation 7 from Nagy and Lasaga (1992).

2. Experimental methods

2.1. Sample

Chlorite schist from Flagstaff Hill, California, the standard Mg-rich chlorite source mineral (CCa-2) from the Clay Minerals Society, was used in this experimental study. The average chlorite composition based on electron microprobe analysis was $(\text{Mg}_{4.55}\text{Al}_{1.23}\text{Fe}_{0.12})(\text{Al}_{1.04}\text{Si}_{2.96})\text{O}_{10}(\text{OH})_8$, derived by distributing aluminum first in the

tetrahedral site and the remainder in octahedral sites, and assuming all iron as ferrous, following the recommendations and observations of Foster (1962).

The chlorite sample was mechanically broken into pieces of cm-range and then grounded and sieved to a particle size of 90 to 105 micron. Samples were then rinsed clean of small particle debris prior to dissolution experiments by washing with ultra-pure H₂O and vacuum filtration through 0.1 micron polycarbonate membrane filter. The cleaned samples were dried at 50 °C in an oven, gently crushed and stored in a HDPE bottle for experimental use. The BET surface area determined for the chlorite samples prepared in this way was 8.44 m²/g, as measured on a Quantachrome Autosorb-1 surface area analyzer with N₂ as absorption gas.

2.2. Flow through experiments

Figure 1 is a schematic illustration of the experimental system that was used to investigate chlorite dissolution kinetics when reacting with CO₂ saturated fluids under high-temperature and high-pressure conditions. A mixed flow-through reactor (Series 4560 Mini Reactor 300 mL) manufactured by Parr Instruments Company was used in the study. All parts of the reactors that were in contact with the high temperature aqueous solution are made of Hastelloy or 316 Stainless Steel. Flow rates were controlled by a HPLC pump (labeled 'brine pump' in Figure 1) and were varied from 0.25 ml/min to 0.01 ml/min, yielding a residence time within the stirred flow-through reactor of 20 h to 20 days. A few hundred hours are usually maintained for each experiment, corresponding to 6 to 1 residence volumes. Stirring of chlorite and the reacting fluids was through a mechanically driven stirrer placed inside the Parr reactor. CO₂ in the experiment study was injected through a supercritical CO₂ pump at a flow rate of 0.01 to 0.1 ml/min so as to obtain the desired *p*CO₂ conditions. Total DIC measurement was used to verify that desired *p*CO₂ is achieved. The experimental system pressure was kept constant with a Jasco BP-2080 adjustable automatic back pressure regulator at given pressures. The temperature was controlled in the experiments using an automatic temperature controller supplied with the Parr reactor.

During each of the experiments, one gram of the sieved chlorite sample was transferred into the reactor. CO₂ and saline water (0.01 M NaCl) were first pumped into a mixing tee where they were mixed and brought to the experimental temperature of 100 °C. The mixing tee has a volume of ~10 ml, while CO₂ and saline water are pumped through it at a rate of 0.01 ml/min to 0.25 ml/min, yielding a residence time of 1000 minutes to 40 minutes. For experiments with low partial pressure of CO₂ (0~0.1 bar), high purity CO₂ gas was purged directly into the reaction stock solutions through a two stage regulator and allowed to equilibrate overnight before injections into the experiment reactor. The brine saturated with CO₂ was then pumped into the reactor while maintaining the experimental system at the designated pressures. The solution inside the reactor chamber was constantly stirred during the experiment.

2.3. Solutions and analyses

Solutions were filtered through a 10 micron Hastelloy filter on the effluent port of the Parr reactor and passed through the automatic back pressure regulator before dripping into the sample collection vials. Filtered effluents were collected in clean low-density polyethylene bottles or polypropylene vials. The solutions collected were analyzed for Mg, Fe, Al and Si by a Perkin Elmer DRCII inductively coupled plasma mass spectroscopy (ICP-MS) after acidification with 2% ultra-pure HNO₃. The solution pH was measured with an Acute pH electrode with a reported accuracy of 0.02 pH units. The solution pH was then corrected to experimental conditions at high temperature and high pressure using the modeling code PHREEQC.

3. Dissolution reaction and equilibrium constant

The chemical reaction describing dissolution of the Clay Minerals Society chlorite used in this study under acidic conditions can be expressed as:

The equilibrium constant for this reaction is given by:

$$K_{eq} = \frac{(a_{Al^{3+}})^{2.27} (a_{Fe^{2+}})^{0.12} (a_{Mg^{2+}})^{4.5} (a_{SiO_2})^{2.96} (a_{H_2O})^{12.075}}{(a_{H^+})^{16.15}} \quad (9)$$

where a_i represents the thermodynamic activity of the dissolved species.

Based on mass balance, the surface area normalized mineral dissolution rate is calculated from the measured difference between the outflow and injection solution concentration of element i , ΔC_i (mol/g solution) according to the expression:

$$R_i^d = \frac{Q \Delta C_i}{m A v_i} \quad (10)$$

where R_i^d = reaction rate (mol/m²/s); Q = flow rate (g/s); m = mass of mineral (g); A = specific surface area (m²/g); and v_i is the stoichiometric factor (moles of element/moles of mineral). This is valid when steady state is reached, i.e., the concentration in the output solution reaches a constant value.

The solution saturation state with respect to chlorite is expressed in terms of the Gibbs free energy of reaction,

$$\Delta G_r = RT \ln\left[\frac{IAP}{K_{eq}}\right] = RT \ln[\Omega] \quad (11)$$

where R is the gas constant, T is the absolute temperature (K), IAP and K_{eq} are the ion activity product and the equilibrium constant respectively, and $\Omega = IAP/K_{eq}$. The geochemical computer code PHREEQC (Parkhurst, 1999) was used to calculate the activities of solution species and the corresponding ion activity product at experimental conditions.

4. Results

A series of experiments was run at different CO₂ partial pressures (0bar, 0.1bar, 20bar, and 60bar) and different flow rates (0.25ml/min, 0.05ml/min and 0.01 ml/min) to study the Gibbs free energy effect on the chlorite dissolution kinetics. All experimental conditions, measured concentrations of solution specie, corrected pH values, the Gibbs free energies and dissolution rates obtained are summarized in Table 1. Reaction rates are calculated from the steady state concentration profiles of Si.

4.1. Equilibrium constant of chlorite dissolution reaction

In order to determine the effect of solution chemical affinity on chlorite dissolution kinetics, an accurate value of the equilibrium constant on the chlorite sample studied is required. For this purpose, we have run a batch experiment to determine an apparent equilibrium constant as a proxy for the required thermodynamic constant. The batch experiment reactor was stirred for two months at constant temperature to determine the equilibrium constant for the chlorite mineral used in the study. According to the corresponding fluid chemistry analyzed by ICP-MS, the ion activity product obtained from the batch experiment was calculated and used as the equilibrium constant for the chlorite dissolution reaction at 100°C. The K_{eq} obtained from our batch experiments was determined to be $10^{-45.57}$. In the PHREEQC LLNL database, the end-member of the chlorite mineral group that has the closest composition to our sample is Clinocllore-14A, which contains no Fe. Using the analytic equation for K_{eq} of Clinocllore-14A, the equilibrium constant at 100°C is $10^{-45.27}$, which is quite close to the measured K_{eq} from our experiments. Also, as pointed out by Burch et al. (1993), substituting apparent equilibrium constant K_{eq}^* for K_{eq} would only shift the values of the Gibbs free energy, but would not affect the functional dependence of rate on the degree of saturation. Thus the measured equilibrium constant should be a good reference number for calculating chemical affinities of all the kinetic dissolution experiments conducted.

4.2. Congruency of chlorite dissolution

Congruent dissolution of chlorite is indicated if the reaction rate calculated from Equation 10 is identical using the outflow concentrations of magnesium, aluminum, iron, or silica. Nonstoichiometric dissolution, if it occurs, may reflect chemical zonation within the mineral, e.g., the development of a leached layer or the presence of non-homogenous defects or impurities, such that the stoichiometry of the dissolving surface regions is different from the average composition of the mineral. Nonstoichiometric dissolution may also be the result of precipitation of secondary phases during the experiment. To ascertain that the dissolution rate obtained is reliable, it is important to show that the rate calculated from equation 10 reflects the destruction of the whole crystallographic framework of the chlorite. Chlorite dissolution rates were calculated based on the release of silicon, aluminum, iron and magnesium at steady state, for each of the flow-through experiments. Figure 2 plots the dissolution rates evaluated based on the release of Al and Mg versus those obtained based on the release of Si. The solid line in Figure 2 is the 1/1 diagonal.

Taking into account of the uncertainties in the rates obtained, Figure 2 shows a good agreement between dissolution rates calculated from the effluent concentrations of Mg and Si. The calculated dissolution rates based on the concentrations of Al and Fe are substantially lower. This discrepancy indicates that either the release rates of Fe and Al are less than the stoichiometric or that the Fe and Al are reprecipitated in another phase. Taking into account the low solubility of Fe and Al phases in solution, the latter explanation seems to be most probable. To evaluate this, the saturation index for relevant phases that might precipitate during the mixed-flow reactor experiments was calculated for each experimental condition using the speciation program PHREEQC(Parkhurst, 1999). Calculated saturation index values for possible secondary phases in Table 2 indicate that the experiment was supersaturated or close to saturated with respect to several hydrous Al phases. Based on the calculations, it appears likely that the low Al concentrations may be controlled by equilibrium with gibbsite. Since the release of Mg and Si appeared to be stoichiometric, we assume that the release of Fe and Al was stoichiometric as well. In addition, brown-colored Fe-bearing secondary mineral phases were observed in the vessel after the experiment. However, based on SEM images of chlorite particles before and after reaction, there was no detectable secondary mineral precipitation on the surface of the sample and there was no distinguishable alteration of the chlorite mineral surface. Mass balance calculation indicates that only about 1% of the chlorite sample was dissolved during the experiment. Since Al and Fe was minor constituents of the chlorite mineral, the volume fraction of secondary minerals precipitated from the Al and Fe released in solution during the experiment would be much less than 1% of the volume of the original chlorite. Such a small amount of precipitate is difficult to detect with Scanning Electron Microscopy. So the precipitated secondary phases should not block the primary mineral surface or affect the chlorite dissolution kinetics during the

experiment.

4.3. Differing effluent concentrations under far from and near equilibrium conditions.

According to linear transition state theory, the chemical affinity term $f(\Delta G_r)$ is 1 minus an exponential term that has a value between 0 to 1 (Equation 4). When $|\Delta G_r|$ is large (which indicates far-from-equilibrium conditions), the exponential term is close to zero, and the chemical affinity $f(\Delta G_r)$ is approximately equal to 1. In the linear TST formulation, the chemical affinity term begins to decrease toward zero (chemical equilibrium) when $|\Delta G_r|$ decreases to a value of about $4RT$, which under our experimental conditions is about 12.4 kJ/mol. The value of $f(\Delta G_r)$ approaches zero only when ΔG_r is less than about $0.1RT$, which corresponds to about 0.31 kJ/mol. Consequently, the chemical affinity term takes effect only when Ω is barely distinguishable from unity.

To investigate the effects of chemical affinity on chlorite dissolution rates, our approach was to increase the dissolved species concentrations (and hence IAP) systematically in a continuous set of experiments while keeping pH and other variables constant. The increase in concentrations of dissolved species were achieved either by decreasing flow rate or by adding additional Mg to the injection solution. Under far-from-equilibrium conditions where the dissolution rate is insensitive to ΔG_r , a decrease in flow rate, thus increasing the residence time in the reactor, should result in a proportional increase in Mg and Si concentrations according to Equation 10. Figure 3 and Figure 4 show the behavior of solution chemistry and calculated dissolution rates in the first experiment set carried out at low pH and without any cations added to the injection solution. The effluent Mg and Si concentrations initially reached steady state in about 100 hours at a high flow rate of 0.25 ml/min. The concentrations increased when the flow rate was decreased to 0.05 ml/min, finally reaching new steady state values about 5 times higher than in the fast flow rate (short residence time) case. The saturation index of chlorite was thus higher in the slow flow rate condition than in the high flow rate condition, but the measured dissolution rate remained unchanged. The transition from 0.05 ml/min to 0.01 ml/min showed similar behavior. This was consistent with transition state theory where mineral dissolution rate is constant at far from equilibrium conditions, and therefore not sensitive to the thermodynamic driving force (chemical affinity) of the system. The ΔG_r value was -227 kJ/mol at 0.25 ml/min flow rate, -197 kJ/mol at 0.05 ml/min, and -162 kJ/mol at 0.01 ml/min. The wide range of ΔG and near-constant dissolution rate indicated that all of these experiments were conducted under far-from-equilibrium conditions.

Figure 5 shows the measured effluent concentrations of elements in pH ~7 water with no added CO₂. Satisfactory steady state dissolution conditions were reached under both 0.05 ml/min and 0.01 ml/min flow rates. In comparison with the experiments

described above carried out at low pH, the effluent elemental concentrations increased only by about 1.25 times, corresponding to a dissolution rate decrease of a factor of 4, rather than the 5 times predicted by the change in flow rate and far-from-equilibrium conditions. This result indicates that the solution was in the “near equilibrium” regime where a change in ΔG_r has caused a change in dissolution rate. The calculated ΔG_r is -46.5 kJ/mol at 0.05 ml/min and -15.1 kJ/mol at 0.01 ml/min. These values were much lower than those at the low-pH conditions, but still large relative to RT (≈ 3.1 kJ/mol).

Figure 6 showed the results from another set of experiments where the solution chemical affinity was changed by adding additional Mg^{2+} in brine saturated with CO_2 at 0.1 bar pressure. After completion of the experiment with 0.01M NaCl brine solution only, the injection solution was switched to a new composition consisting of 0.1M MgCl_2 and 0.01M NaCl to drive the solution closer to equilibrium with mineral chlorite. If the experiment were still at far from equilibrium conditions after addition of Mg, change of chemical affinity would not affect the dissolution rate of chlorite. However, we observed a decrease in the effluent Si concentration, indicating a decrease of the dissolution rate of chlorite under near-equilibrium-conditions. Calculated ΔG_r values were -113.94kJ/mol and -68.00kJ/mol before and after switching to injecting stock solutions with added Mg^{2+} .

In summary, we controlled the chemical affinity of the experiment system by changing flow rates in both acidic and neutral brines, and by adding dissolved Mg^{2+} to near-neutral brine. With those approaches, we were able to measure the chlorite dissolution rate at ΔG_r values varying from -227 to -15 kJ/mol. We observed that the chlorite dissolution rate was insensitive to changes of ΔG_r when the value was larger than -100 kJ/mol, but showed variation with ΔG_r when the value was lower than -100 kJ/mol. This observation suggests that chlorite dissolution exhibits “near equilibrium” behavior when ΔG_r is between -100 and 0 kJ/mol.

4.4. Dependence of dissolution rate on pH

Since the pH and Gibbs free energy effects are intertwined in the overall kinetic rate expression, in order to evaluate the effect of Gibbs free energy on chlorite dissolution kinetics, we need to first determine the dependence of dissolution rate on pH so as to normalize and isolate its effects. Similarly, the effects of Gibbs free energy have to be isolated during pH dependence determination. For this purpose, we used experimental data that were all at far-from-equilibrium conditions, where the Gibbs free energy terms $f(\Delta G_r)$ were all at one, to obtain the pH dependence. Following Chou and Wollast (1985), the relationship between the rate and pH can be described by:

$$R_d = k_H a_H^n + k_{H_2O} + k_{OH} a_{OH}^m = k_H a_H^n + k_{H_2O} + k_{OH}^* / a_H^m \quad (12)$$

where R_d is the overall dissolution rate of chlorite [$\text{mol}(\text{mineral})/\text{m}^2/\text{s}$], k_H , k_{OH} and k_{H_2O} are the acid enhanced, hydroxide enhanced and water hydrolysis dissolution rate constants with k_{OH}^* representing the hydroxide-enhanced dissolution rate constant expressed in terms of hydrogen ion. The terms a_H and a_{OH} are the activities for the hydrogen and hydroxide ions, respectively, and n and m are the reaction orders with respect to the hydrogen and hydroxide ions.

As shown above (Equation 2), Lowson et al. (2005) fitted their dissolution rates as a function of pH at room temperature with the equation:

$$R_d = 10^{-9.79} a_H^{0.49} + 10^{-13.00} + 10^{-16.79} / a_{H^+}^{0.43}$$

Smith et al. (2013) expanded the equation to high temperature, but only within the acidic region, where they found (Equation 1)

$$\text{rate} = k_{acid} \exp\left[\left(\frac{-E_{acid}}{R}\right)\left(\frac{1}{T} - \frac{1}{298K}\right)\right] a_{H^+}^n$$

$$\log k_{acid,298K} = -9.91 \text{ mol/m}^2/\text{s}, E_{acid} = 25.1 \text{ kJ/mol}, n = 0.488$$

In fitting the measured dissolution rates as a function of pH, the assumption is that all rates are at far-from-equilibrium conditions and hence there are no chemical affinity effects. However, if the dissolution rates do not correspond to far-from-equilibrium conditions, the pH effects are intertwined with the chemical affinity effects. After careful examination, we found that the experiments of Smith et al (2013) were indeed at far-from-equilibrium conditions. The values of ΔG_r in Smith et al. (2013) are estimated using their reported dissolution rates, and assuming that all the other elements are released congruently. This might overestimate the concentrations of Al and Fe in the solution, but since the results are already far from equilibrium, and lower concentrations of Al and Fe would only result in larger undersaturation, which would not affect the conclusion of this study.

However, not all of the experiments from Lowson et al. (2007) were at far-from equilibrium conditions, even though the saturation index $\log(IAP/K)$ in their experiments at 95 °C were thought to be in the range -13.5 to -55.0. Although these values would correspond to far-from-equilibrium conditions according to the standard linear form of the transition state theory rate formulation, our results and the following considerations suggest that these ΔG_r values are not on the dissolution plateau and therefore not far from equilibrium.

(1) Studies of the dependence of the dissolution rate of clay minerals on chemical affinity have shown that dissolution begins to be slowed at values of $\Delta G_r \approx -125.5$

kJ/mol for both smectite and montmorillonite (Cama et al., 2000). This corresponds to a saturation index of approximately $\log(IAP/K) \approx -17$. Since chlorite, smectite and montmorillonite are all phyllosilicates (or sheet silicates), it is possible that chlorite dissolution could behave in a similar way.

(2) The reaction equilibrium constant K_{eq} was not well defined in previous studies, especially for intermediate Mg, Fe chlorite compositions used in the study of Lawson et al. (2007). Lawson et al. (2007) used the data from Kittrick (1982) who measured the solubility of two chlorites and determined that $\log K_{eq}=42.3$ at 25 °C. However, the chlorite composition in Lawson et al. (2007) is

while none of the samples in Kittrick (1982) has a composition close to this. For example, the stoichiometric number of Fe^{2+} in Lawson et al. (2007) is 1.90, while the samples in Kittrick (1982) have Fe^{2+} of 0.99, 0.57, 3.29, 2.61 respectively. There are only a few measured thermodynamic data available for chlorite minerals to our knowledge. The structural formulas of chlorite reported in available thermodynamic studies are listed in Table 3 . Among them, Gailhanou et al (2009) used a chlorite that has the closest composition to that from Lawson et al. (2007)

Gailhanou et al.(2007) obtained a Gibbs free energy of formation for chlorite to be -7607.1 kJ/mol at room temperature and pressure based on corresponding enthalpy and entropy of formation (-8253.70kJ/mol and -2170J/mol/K respectively).

Thermodynamic parameters of this chlorite are listed in Table 4 together with those for aqueous species from Anderson(2005). The dissolution Gibbs free energy of the chlorite used in the study of Lawson et al. (2007) is calculated to be -310.2 kJ/mol at standard state using those parameters. This corresponds to $\log K_{eq}=52.3$ at 25°C. The corresponding equilibrium constant at 95°C is calculated to be $\log K_{eq}(95^{\circ}C)=33.6$ using the Van't Hoff equation.

We used this lower value of the equilibrium constant at 95°C to recalculate the chemical affinity of the experiments in the Lawson et al. (2007) study. Table 5 listed all the experimental runs in Lawson et al. (2007) that were carried out under acidic to neutral pH values at 95°C. The first two runs at pH 3.26 and 4.21 in acid solutions were indeed quite far from equilibrium ($\log Q/K=-55.0$ and -45.2 respectively). The experimental run at pH 6.59 was not recalculated due to lack of stability constant values for the buffer phthalate. The experiments at pH 5.56 and 6.9 were recalculated using the same PHREEQC code and database as in Lawson et al. (2007) and the new $\log K_{eq}(95^{\circ}C)$ of 33.6. The new saturation indices with respect to chlorite were

calculated to be -3.74 and -0.92 respectively, which were actually closer to equilibrium. Under these conditions, one expects a dependence of the rate on chemical affinity.

To summarize, after a careful review of our experimental results and available literature data, only those data at far from equilibrium condition were used to determine the pH dependent dissolution rate expression. The data used for this purpose include all of those measured at acidic conditions ($pH < 4$), two at $pH = 4.16$ and 5.69 from Smith et al. (2013), one at $pH = 4.21$ from Lowson et al. (2007), and two from our current study at $pH = 4.89$ and 6.43 (squares in Figure 7). Using the equation in Chou and Wollast (1985), parameters k_H , n and k_{OH} are determined using a least square method. According to these data, the pH dependence of the rate of chlorite dissolution under far from equilibrium conditions can be expressed as

$$R = 10^{-7.64} a_{H^+}^{1.05} + 10^{-11.56} \quad (13)$$

at 100 °C in acidic to neutral conditions.

4.5. Dependence of chlorite dissolution rate on Gibbs free energy

The effect of Gibbs free energy (chemical affinity) on the chlorite dissolution kinetic rate equation ($f(\Delta G_r)$ term in Equation 3) was evaluated by isolating the corresponding pH effects first and then compared and fitted within the framework of general transition state theory. To do this, the experiment dissolution rates measured were normalized first by dividing against the calculated rates at corresponding pH values from far-from-equilibrium conditions (with chemical affinity term, $f(\Delta G_r)$, as 1) according to the pH effect equation obtained above (Equation 14). The results obtained then were the pure $f(\Delta G_r)$ effect term in the rate equation with its value close to 1 representing the far-from-equilibrium condition and a value less than 1 showing the corrections from Gibbs free energy effects (the departure from equilibrium). The ΔG_r values were calculated for each experiment using PHREEQC considering the same species as in Table 3 of Lowson et al. (2007). The corrected pH under experimental conditions is used in the calculation of ΔG_r . The chemical affinity term $f(\Delta G_r)$ and the corresponding Gibbs free energies of reaction for the steady state of each experiment are listed in Table 6 and plotted in Figure 8.

The $f(\Delta G_r)$ determined in this way (Figure 8) decreased gradually from 1 to 0 between $\Delta G_r = 0$ and $\Delta G_r \approx -100$ kJ/mol. This behavior contrasts with that expected from a linear transition state theory (red curve in Figure 8). Following the approach by Nagy and Lasaga (1992), we described the chlorite rate dependence on the degree of undersaturation by fitting the experimental data to Equation 14.

$$f(\Delta G_r) = 1 - \exp\left[m\left(\frac{\Delta G_r}{RT}\right)^n\right] \quad (14)$$

The coefficients: m , and n were calculated from a nonlinear least square regression fitting. The regression coefficient $R^2=0.83$ and the resulting coefficients are $m=-0.01677$ and $n=1.3$. Substituting the resulting coefficients gives

$$f(\Delta G_r) = 1 - \exp\left[-0.01677\left(\frac{|\Delta G_r|}{RT}\right)^{1.3}\right] \quad (15)$$

The good comparison of the prediction from Equation (15) and the experimental data is shown in Figure 8 . The shape of the curve and the critical free energy where dissolution rate starts to decrease (the edge of the dissolution plateau) were determined primarily by the data at near equilibrium conditions. In Figure 8, those data include 5 points from our current experiment study and two experimental points from Lowson et al. (2007) at close to equilibrium conditions ($\Delta G_r=-6.63\text{kJ/mol}$, and -26.77kJ/mol). Figure 8 shows that the chemical affinity term starts to show significant effects when the reaction Gibbs free energy, $|\Delta G_r|$, falls less than 100kJ/mol .

Combining the effects of Gibbs free energy and pH, we obtained a general rate law for chlorite dissolution at 100°C in acidic to neutral conditions as:

$$R = (10^{-7.64} a_H^{1.05} + 10^{-11.56}) \{1 - \exp[-0.01677\left(\frac{|\Delta G_r|}{RT}\right)^{1.3}]\} \quad (16)$$

The comparison of measured dissolution rates and predicted rates using both the current rate law and the rate law from Smith et al (2013) are plotted in Figure 9 . Since the rate law in Smith et al (2013) is for far-from-equilibrium dissolution of chlorite, the predicted rates are larger than the experimental rates. The addition of the modeled $f(\Delta G_r)$ term in the current rate law improves the predicted dissolution rates for the near-equilibrium data.

The general rate equation on the chlorite dissolution kinetics obtained in this study showed large deviations from the predictions by simple linear rate laws from transition state theory. Linear rate laws only apply when the mineral-fluids reactions are controlled by one rate-limiting elementary reaction. However, as pointed out by Burch et al. (1993), minerals dissolutions often proceed with multiple parallel reactions on different energetic reactive sites, such as local surface defects and dislocations, on mineral surfaces. The non-linear dependence of ΔG_r on chlorite dissolution rates obtained in this study revealed that the dissolution reactions were not controlled by a single mechanism during the whole range of solution undersaturation

states studied. It is likely the surface dislocation-assisted dissolution and etch pit formations played an important role in controlling the reaction rates in near equilibrium conditions and gave rise to such a highly non-linear behavior with respect to ΔG_r , as pointed out by Nagy and Lasaga (1992). However, it is difficult to postulate the detailed reaction mechanisms involved under different undersaturation states and link them to the corresponding parameters in the overall empirical rate equation currently without further microscopic molecular observations. The experiment studies here further emphasized caution against practices of a simple extrapolation on mineral dissolution rates from only far from equilibrium data based on transition state theory.

4.6. Implications for CO₂ mineral sequestration

Chlorite is a common divalent cation-bearing mineral in sedimentary rocks and hence its dissolution kinetics is important for understanding the fate of trapped CO₂ in the context of geologic carbon storage. The measured dissolution rate of chlorite in our study is about 10^{-11} mole/m²/sec at $pH=3.3-3.4$, which is the pH for CO₂ saturated brine. If we consider 1 m³ of chlorite-bearing sands with a rock density of 2800 kg/m³, Landrot et al. (2012) measured that 8.3% of the rock is chlorite, and 31.8% of chlorite is accessible, then the mass of accessible chlorite in 1 m³ of rock $m_0=73.9\text{kg}$. Using the reactive surface area of chlorite measured by Landrot et al.(2012) ($A_0=11.62 \times 10^{-2}\text{m}^2/\text{g}$), on a time scale of 1000 years, the amount of dissolved chlorite would be about 115 moles, and the total amount of released Mg and Fe would be 575 moles. Assuming 10% of the rock volume is filled with capillary-trapped supercritical CO₂ which has a density of 600 kg/m³, the total amount of CO₂ in 1 m³ rock is 1364 moles. Therefore, the released Mg from chlorite in such sandstones could provide enough cations to potentially mineralize about half the stored CO₂ in this volume within 1000 years.

The above calculation is important because it shows that mineralization of CO₂ could be substantial in a long term, contrary to the common view that only minor chemical reactions will happen for CO₂ sequestration. The calculation is based on the assumption that $pH \approx 3.3-3.4$, and that brine is far from equilibrium with respect to chlorite. The dissolution rate of chlorite would be inhibited if pH is increased or if brine is concentrated and close to equilibrium for chlorite. The general rate law in this study provides inputs for reactive transport simulation to calculate the amount of mineral dissolution under these circumstances.

5. Conclusions

The dissolution rate of Flagstaff Hill chlorite (CCa-2) was examined using a well-mixed flow-through reactor. The experiments were conducted at 100 °C, pH from 3-7.5 and a range of pCO₂ from 0 to 60 bars, and variable degree of saturation

state. The average Mg/Si ratio in outflow samples is in good agreement with the molar ratio in the mineral, indicating stoichiometric dissolution of chlorite.

Chlorite dissolution rates were analyzed and fitted as functions of pH and chemical affinity (ΔG_r). Only the data that were under far from equilibrium conditions are used in fitting the relationship between dissolution rate and pH so as to ensure that the near equilibrium (ΔG_r) effects were not included. Using this approach, the effects of chemical affinity on the dissolution rate of chlorite have been determined for the first time. Results show that the experimental data can be fitted by an empirical nonlinear rate law within the framework of transition state theory as shown in Nagy and Lasaga (1992). The chlorite dissolution rate varied as a function of the Gibbs free energy over a larger range ($-\Delta G_r > 100$ kJ/mol) than expected from a linear TST rate law, and was similar to the dissolution rate formulation determined for smectite ($-\Delta G_r > 130$ kJ/mol) (Cama et al., 2000). Our results indicate that chlorite dissolution is inhibited under a wide range of saturation conditions and might explain the fact that a low reactivity of Cranfield rock was measured by Lu et al. (2012) in batch experiments even though a high reactive surface area was determined by Landrot et al. (2012).

6. Acknowledgements

The work was supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy as part of the Energy Frontier Research *Center Nanoscale Controls on Geologic CO₂* under Contract No. DE-AC02-CH11231.

References

- Aagaard, P., Helgeson, H.C., 1982. Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions; I, Theoretical considerations. *American Journal of Science*, 282(3): 237-285.
- Aja, S.U., 2002. THE STABILITY OF Fe-Mg CHLORITES IN HYDROTHERMAL SOLUTIONS: II. THERMODYNAMIC PROPERTIES. *Clays and Clay Minerals*, 50(5): 591-600.
- Anderson, G., 2005. *Thermodynamics of Natural Systems*.
- Banfield, J.F., Murakami, T., 1998. Atomic-resolution transmission electron microscope evidence for the mechanism by which chlorite weathers to 1 : 1 semi-regular chlorite-vermiculite. *American Mineralogist*, 83(3-4): 348-357.
- Brandt, F., Bosbach, D., Krawczyk-Bärsch, E., Arnold, T., Bernhard, G., 2003. Chlorite dissolution in the acid pH-range: a combined microscopic and macroscopic approach. *Geochimica Et Cosmochimica Acta*, 67(8): 1451-1461.
- Burch, T.E., Nagy, K.L., Lasaga, A.C., 1993. Free energy dependence of albite dissolution kinetics at 80 °C and pH 8.8. *Chemical Geology*, 105: 137-162.
- Cama, J., Ganor, J., Ayora, C., Lasaga, C.A., 2000. Smectite dissolution kinetics at 80 °C and pH 8.8. *Geochimica Et Cosmochimica Acta*, 64(15): 2701-2717.
- Carroll, S., Mroczek, E., Alai, M., Ebert, M., 1998. Amorphous silica precipitation (60 to 120 °C): comparison of laboratory and field rates. *Geochimica Et Cosmochimica Acta*, 62(8): 1379-1396.
- Foster, D.A., 1962. Interpretation of the composition and a classification of the chlorites. *Geological Survey Professional Paper 414-A*. U.S. Geological Survey, Washington, D.C (38 pp.).
- Gailhanou, H. et al., 2009. Thermodynamic properties of chlorite CCa-2. Heat capacities, heat contents and entropies. *Geochimica Et Cosmochimica Acta*, 73(16): 4738-4749.
- Gailhanou, H. et al., 2007. Experimental determination of thermodynamic properties of a chlorite. *INTERNATIONAL MEETING, SEPTEMBER 17-18, 2007, LILLE, FRANCE* Page 355. *CLAYS IN NATURAL & ENGINEERED BARRIERS FOR RADIOACTIVE WASTE CONFINEMENT*.
- Hayashi, H., Yamada, M., 1990. Kinetics of dissolution of noncrystalline oxides and crystalline clay minerals in a basic tiron solution. *Clays and Clay Minerals*, 38(3): 308-314.
- Hellmann, R., Tisserand, D., 2006. Dissolution kinetics as a function of the Gibbs free energy of reaction: An experimental study based on albite feldspar. *Geochimica Et Cosmochimica Acta*, 70(2): 364-383.
- IPCC, 2005. IPCC special report on carbon dioxide capture and storage : summary for policymakers. IPCC, S.I.
- Kittrick, 1982. Solubility of two high-Mg and two high-Fe chloites using multiple equilibria. *Clay Clay Miner.* 30(3), 167– 179.

- Landrot, G., Ajo-Franklin, J.B., Yang, L., Cabrini, S., Steefel, C.I., 2012. Measurement of accessible reactive surface area in a sandstone, with application to CO₂ mineralization. *Chemical Geology*, 318–319(0): 113-125.
- Lasaga, A.C., 1984. Chemical kinetics of water-rock interactions. *Journal of Geophysical Research: Solid Earth*, 89(B6): 4009-4025.
- Lasaga, A.C., 1995. Fundamental approaches in describing mineral dissolution and precipitation rates. *Reviews in Mineralogy and Geochemistry*, 31(1): 23-86.
- Lasaga, A.C., 1998. *Kinetic theory in the earth sciences*. Princeton University Press, Princeton, N.J.
- Lowson, R.T., Brown, P.L., Comarmond, M.C.J., Rajaratnam, G., 2007. The kinetics of chlorite dissolution. *Geochimica Et Cosmochimica Acta*, 71(6): 1431-1447.
- Lowson, R.T., Comarmond, M.C.J., Rajaratnam, G., Brown, P.L., 2005. The kinetics of the dissolution of chlorite as a function of pH and at 25°C. *Geochimica Et Cosmochimica Acta*, 69(7): 1687-1699.
- Lu, J. et al., 2012. CO₂-rock-brine interactions in Lower Tuscaloosa Formation at Cranfield CO₂ sequestration site, Mississippi, U.S.A. *Chemical Geology*, 291: 269-277.
- Maher, K., Steefel, C.I., White, A.F., Stonestrom, D.A., 2009. The role of reaction affinity and secondary minerals in regulating chemical weathering rates at the Santa Cruz Soil Chronosequence, California. *Geochimica Et Cosmochimica Acta*, 73(10): 2804-2831.
- Malmström, M., Banwart, S., Lewenhagen, J., Duro, L., Bruno, J., 1996. The dissolution of biotite and chlorite at 25°C in the near-neutral pH region. *Journal of Contaminant Hydrology*, 21(1-4): 201-213.
- Nagy, K.L., Cygan, R.T., Hanchar, J.M., Sturchio, N.C., 1999. Gibbsite growth kinetics on gibbsite, kaolinite, and muscovite substrates: atomic force microscopy evidence for epitaxy and an assessment of reactive surface area. *Geochimica Et Cosmochimica Acta*, 63(16): 2337-2351.
- Nagy, K.L., Lasaga, A.C., 1992. Dissolution and precipitation kinetics of gibbsite at 80 °C and pH 3: The dependence on solution saturation state. *Geochimica Et Cosmochimica Acta*, 56(8): 3093-3111.
- Parkhurst, D.L., 1999. User's guide to PHREEQC (version 2) [microform] : a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations / by David L. Parkhurst and C.A.J. Appelo. Water-resources investigations report ; 99-4259. U.S. Geological Survey : Earth Science Information Center, Open-File Reports Section [distributor], Denver, Colo. :.
- Rochelle, C.A. et al., 1994. Experimental Determination of Chlorite Dissolution Rates. . *MRS Proceedings*, 353(149).
- Saccoccia, P.J., Seyfried Jr, W.E., 1994. The solubility of chlorite solid solutions in 3.2 wt% NaCl fluids from 300–400°C, 500 bars. *Geochimica Et Cosmochimica Acta*, 58(2): 567-585.

- Smith, M.M., Wolery, T.J., Carroll, S.A., 2013. Kinetics of chlorite dissolution at elevated temperatures and CO₂ conditions. *Chemical Geology*, 347(0): 1-8.
- Steefel, C.I., DePaolo, D.J., Lichtner, P.C., 2005. Reactive transport modeling: An essential tool and a new research approach for the Earth sciences. *Earth and Planetary Science Letters*, 240(3,Äì4): 539-558.
- Steefel, C.I., Lasaga, A.C., 1994. A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. *American Journal of Science*, 294(5): 529-592.
- Steefel, C.I., Molins, S., Trebotich, D., 2013. Pore Scale Processes Associated with Subsurface CO₂ Injection and Sequestration. *Reviews in Mineralogy and Geochemistry*, 77(1): 259-303.
- Wollast, R., Chou, L., 1985. Kinetic Study of The Dissolution of Albite with a Continuous Flow-Through Fluidized Bed Reactor. In: Drever, J. (Ed.), *The Chemistry of Weathering*. Nato ASI Series. Springer Netherlands, pp. 75-96.
- Xu, T.F., Apps, J.A., Pruess, K., 2004. Numerical simulation of CO₂ disposal by mineral trapping in deep aquifers. *Applied Geochemistry*, 19(6): 917-936.

Figure 1 Schematic drawing of the flow-through batch experiment setup. The CO₂ and saline water are first pumped into a tee where they are mixed and brought to experimental temperature. The CO₂ saturated brine is then pumped into the reactor and mixed with chlorite particles, while continuously stirring the reactor volume. Samples are collected after the back pressure regulator and their elemental concentrations are measured using ICP-MS.

Figure 2 Comparison of the chlorite dissolution rates calculated from the release of Si, Mg, and Al compared to the 1/1 diagonal. The dissolution rates calculated from the effluent concentrations of Mg and Si show good agreement, while the calculated dissolution rates using Al are substantially lower. The most likely explanation is that low Al concentrations reflect reprecipitation of secondary hydrous Al phases, such as gibbsite.

Figure 3 Concentrations of effluent elements for chlorite dissolution in 60 bar CO₂-saturated water at 100 °C. Steady states are achieved under three flow rates, 0.25ml/min, 0.05ml/min, and 0.01ml/min. Steady state concentrations of Mg and Si are inversely proportional to flow rates.

Figure 4 Dissolution rates determined by individual elements in 60 bar CO₂- saturated water at 100 °C. The calculated dissolution rates generally remain unchanged at steady states, despite the saturation index of chlorite being larger in the slow flow rate condition than in the high flow rate condition. This indicates that the mineral is at far from equilibrium conditions at all three flow rates, and the dissolution rate is not sensitive to the thermodynamic driving force for the conditions of these experiments.

Figure 5 Concentrations of effluent elements for chlorite dissolution in DI water at pH ~7 and 100 °C. In comparison with Figure 3, the concentration profiles of Mg and Si at steady states showed an increase of 1.25 rather than the proportional increase of 5 expected from the decrease in flow rate expected if far from equilibrium conditions applied.

Figure 6 Change of effluent concentrations in experiments where extra MgCl_2 is added after near-steady state conditions are achieved. Decreased outflow Si concentrations at steady state are observed, which indicates a decrease of the dissolution rate of chlorite due to the increase in the saturation index of chlorite generated by the added Mg^{2+} .

Figure 7 Fitting of chlorite dissolution rates as a function of pH. Only experimental data at far from equilibrium conditions (solid squares) are used for the fitting purpose to make sure that the equilibrium effects are not intertwined. Dissolution rates under near equilibrium conditions are smaller than expected from the pure pH curve.

Figure 8 Fitting of rate reduction factor as a function of ΔG determined from the present study using the empirical law of Nagy and Lasaga (1992) compared with the linear transition state theory kinetic law. The chlorite dissolution rate increases as a function of the Gibbs free energy over a larger range than expected from linear TST.

Figure 9 Comparison of measured dissolution rates and predicted rates using both the current model and the model from Smith et al (2013). Since the model in Smith et al (2013) is for far-from-equilibrium dissolution of chlorite, the predicted rates are larger than the experimental rates. The addition of the $f(\Delta G_r)$ term in the current model improves the predicted dissolution rates for the near-equilibrium data.

Table 1 Corrected pH under experimental conditions, flow rates, measured steady state concentrations and calculated ΔG_r values and chlorite dissolution rates

CO ₂ pressure	pH	flow rate (ml/min)	Mg (10 ⁻⁵ mol/L)	Al (10 ⁻⁵ mol/L)	Si (10 ⁻⁵ mol/L)	Fe (10 ⁻⁵ mol/L)	ΔG (kJ/mol)	Rate(Si) (10 ⁻¹² mol/m ² /s)
0bar	6.427	0.05	8.41	0.03	6.45	0.09	-90.72	3.70
0bar	6.402	0.01	10.10	0.32	8.89	1.31	-28.36	1.02
20bar	3.606	0.25	3.44	1.89	3.51	1.79	-155.44	10.10
60bar	3.321	0.25	4.89	0.17	3.04	0.01	-226.66	8.77
60bar	3.433	0.05	19.80	0.06	9.98	0.01	-197.37	5.77
60bar	3.756	0.01	78.20	0.06	29.50	0.01	-161.87	3.41
0bar	6.842	0.25	7.32	0.07	0.38	0.32	-78.15	1.25
0bar	7.257	0.05	8.45	0.34	0.98	0.70	-46.50	0.64
0bar	7.508	0.01	12.20	0.03	1.81	2.90	-15.07	0.24
0.1bar	4.885	0.25	1.09	0.06	1.11	0.28	-113.94	3.21
0.1bar+Mg	5.186	0.25	11300.00	0.14	0.56	0.26	-68.00	1.60

Table 2 Saturation index for possible secondary minerals for chlorite dissolution experiments

	0bar	0bar	0bar	20bar	60bar	60bar	60bar	chemical
SI	0.25ml/min	0.05ml/min	0.01ml/min	0.25ml/min	0.25ml/min	0.05ml/min	0.01ml/min	formula
Diaspore	0.23	-0.13	0.31	0.76	1.02	-0.06	0.57	AlHO ₂
Boehmite	-0.06	-0.43	0.01	0.47	0.73	-0.36	0.28	AlO ₂ H
Gibbsite	-0.53	-0.90	-0.46	0	0.25	-0.83	-0.19	Al(OH) ₃
Kaolinite	-4.89	-4.84	-3.44	-2.07	-1.4	-2.66	-0.45	Al ₂ Si ₂ O ₅ (OH) ₄

Table 3 Structural formula of chlorite reported from other kinetic and thermodynamic studies compared with the one in the current study

	Current study	(Smith et al., 2013)	(Lowson et al., 2007)	(Gailhanou et al., 2009)	(Saccocia and Seyfried)								
					(Kittrick, 1982)				Jr, 1994)		(Aja, 2002)		
Si	2.96	2.78	2.48	2.633	2.97	2.99	2.47	2.84	2.945	2.56	2.83	2.815	2.63
Al	2.27	2.7	2.49	2.483	2.47	2.4	3.13	2.91	2.058	2.642	2.335	2.675	2.34
Fe ²⁺	0.12	0.1	1.9	1.712	0.99	0.57	3.29	2.61	0.454	2.297	0.5	0.3	3.08
Fe ³⁺	0	0	0.07	0.215	0.07	0.21	0	0.12	0.131	0.277	0.07	2.715	0.28
Mg	4.45	4.29	2.76	2.952	3.24	3.52	1.05	1.16	4.357	2.162	4.2	1.15	1.025
Mn	0	0	0	0.012	0	0	0	0	0.009	0.033	0.005	0.025	0.025
Ca	0	0	0	0.011	0	0	0	0	0	0	0.01	0.015	0.155

Table 4 Thermodynamic calculations of the ΔG_r value at 25 °C of the chlorite sample from Lawson et al. (2007)*

	Chlorite	H ⁺	SiO ₂ (aq)	Al ³⁺	Mg ²⁺	Fe ²⁺	Fe ³⁺	Mn ²⁺	Ca ²⁺	H ₂ O	SUM
stoichiometric	-1	-17.468	2.633	2.483	2.952	1.712	0.215	0.012	0.011	12.734	
S ₀ (J/mol)	468.4	0.0	75.3	-321.7	-138.1	-137.7	-315.9	-73.6	-53.1	69.9	
ΔrS_0 (J/mol)	-468.4	0.0	198.3	-798.8	-407.7	-235.7	-67.9	-0.9	-0.6	890.2	-891.5
ΔfH_0 (kJ/mol)	-8253.7	0.0	-877.7	-531.0	-466.9	-89.1	-48.5	-220.8	-542.8	-285.8	
ΔrH_0 (kJ/mol)	8253.7	0.0	-2311.0	-1318.5	-1378.1	-152.5	-10.4	-2.6	-6.0	-3639.8	-565.2
ΔfG_0 (kJ/mol)	-7607.1	0.0	-833.4	-485.0	-454.8	-78.9	-4.7	-228.1	-553.6	-237.1	
ΔrG_0 (kJ/mol)	7607.1	0.0	-2194.4	-1204.3	-1342.6	-135.1	-1.0	-2.7	-6.1	-3019.6	-298.6

*Based on thermodynamic data from Gailhanou et al.(2007) for chlorite and Anderson(2005) for aqueous species.

Table 5 Recalculation of saturation indices for experiments in Lawson et al. (2007)

Buffer	Al	Fe	Mg	Si	log R	Log(Q/K)	Log(Q/K)	
concentration	pH	(mg/L)	(mg/L)	(mg/L)	(mol/m ² /s)	Lowson et al.	current	
0.05M KHPhth	3.26	3.6	9.18	6.08	6.84	-10.9	-54.99	N/A
0.05M KHPhth	4.21	1.79	1.79	1.93	2.53	-11.49	-45.2	N/A
0.1 M H ₃ BO ₃	5.56	0.03	0.03	0.32	0.58	-11.905	-18.72	-3.75
0.05M KHPhth, 0.02M NaOH	6.59	0.06	0.06	0.25	0.58	-12.123	-32.14	N/A
0.025M KH ₂ PO ₄ , 0.025M Na ₂ HPO ₄	6.9	0.11	0.02	0.34	0.93	-12.171	-17.34	-0.93

Table 6 Data used to determine the relationship between f(ΔG_r) and ΔG_r in Figure 8

	pH	ΔG_r (kJ/mol)	Measured rate (10 ⁻¹² mol/m ² /s)	Corresponding far-from-equilibrium rate (10 ⁻¹² mol/m ² /s)	f(ΔG_r)
0bar0.25ml/min	6.842	-78.15	1.25	2.77	0.45
0bar0.05ml/min	7.257	-46.50	0.64	2.77	0.23
0bar0.01ml/min	7.508	-15.07	0.24	2.77	0.084
0.1bar0.25ml/min	4.89	-113.94	3.19	2.94	1.08
0.1bar0.25ml/min(MgCl ₂)	5.19	-68.00	1.59	2.85	0.56
0bar0.01ml/min	6.402	-28.36	1.02	2.78	0.37
Lowson et al (2007)	5.56	-26.77	1.24	2.81	0.44
Lowson et al (2007)	6.90	-6.63	0.68	2.77	0.24
Smith et al (2013)	4.16	-139.15	3.19	3.75	0.85
Smith et al (2013)	3.70	-174.87	6.60	5.76	1.15
Smith et al (2013)	3.57	-181.80	6.84	6.86	1.00
Smith et al (2013)	3.02	-200.37	18.60	18.2	1.02