Chlorite dissolution kinetics at pH 3-10 and temperature to 275 °C

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Abstract

Sheet silicates and clays are ubiquitous in geothermal environments. Their dissolution is of interest because this process contributes to scaling reactions along fluid pathways and alteration of fracture surfaces which could affect reservoir permeability. In order to better predict the geochemical impacts on long-term performance of engineered geothermal systems, we have measured chlorite dissolution and developed a generalized kinetic rate law applicable over an expanded range of solution pH and temperature. Chlorite, $(\text{Mg,Al,Fe})_{12}(\text{Si,Al})_8\text{O}_{20}(\text{OH})_{16}$, commonly occurs in many geothermal host rocks as either a primary mineral or alteration product. A combination of new rate data from this study (collected using an Mg-rich chlorite variety, at 100-275 °C and pH > 5.5) as well as all available published chlorite dissolution datasets results in a kinetic rate equation that is valid over temperatures of 25-275 °C and $3 \leq \text{pH} \leq 10$:

$$R = \left(\left[1 \cdot 10^{-4} \cdot e^{-30/RT} \cdot a_{H^+}^{0.74} \right] + \left[4.7 \cdot 10^{-11} \cdot e^{-13/RT} \right] + \left[1.5 \cdot 10^{-9} \cdot e^{-15/RT} \cdot a_{OH^-}^{0.43} \right] \right) \cdot \left(1 - e^{\Delta G_r/RT} \right)$$

The form of this equation, which includes a reaction affinity term to slow reaction as equilibrium is approached, can be incorporated into most existing reactive transport codes for use in prediction of rock-water interactions in engineered geothermal systems.

Keywords: chlorite, clinochlore, sheet silicate, phyllosilicate, dissolution, kinetics, reaction affinity, geothermal

Introduction

Production of energy from engineered geothermal systems (EGS) requires sustained permeability for approximately 30 years, and one potential method of procuring sufficient fluid flow is through the reactivation of pre-existing fractures in deep hot rock. Chemical reactions pose an important but poorly understood threat to long-term EGS success because the necessary kinetic data for modeling the reactivity of common fracture-associated minerals are lacking at target temperature conditions. This lack of kinetic data hinders our ability to accurately simulate and predict the impact of water-rock disequilibrium and reaction on the evolution of fracture pathways, partially filled veins, fracture asperities, and fracture/matrix exchange.

Our poor understanding of the effects of these rock-water interactions on fracture (and overall reservoir) permeability is demonstrated by the variable results obtained through experimental laboratory studies on fractured rock cores. Some data suggest that chemical reactions can significantly reduce fracture permeability even at temperatures much lower than EGS target zones (≥ 200 °C, e.g., Morrow et al., 1981, 2001; Polak et al, 2003; Carlson et al, 2005; Viani et al, 2005; Yasuhara and Elsworth, 2008; Yasuhara et al., 2011), while dissolution in CO₂-rich high-temperature environments can lead to prolonged increases in fractured greywacke permeability (200 °C, Smith et al., 2013a). Other experimental work has noted switching between permeability increases and decreases in fractured limestones (Polak et al., 2004;

Singurindy and Berkowitz, 2005) and quartz-rich rocks (Yasuhara et al., 2006). An improved ability to assess the magnitude of chemical reaction on longer-term geothermal sustainability is crucial to mitigating detrimental heat transfer effects that may arise from reductions in fracture network permeability throughout the subsurface resource.

In principle the role of geochemistry could be assessed primarily through modeling, but kinetic data and rate equations are currently lacking for many prevalent fracture-associated minerals at EGS temperatures (~200 to 400 °C). Even though clays and sheet silicate minerals can comprise up to 40% of target EGS zones (Lutz et al., 2010), kinetic data for such minerals are rare even to 100°C (e.g., smectite up to 80 °C, Cama et al, 2000; illite to 50 °C, Köhler et al., 2003; chlorite to 95 °C, Lowson et al., 2007; biotite to 95 °C, Hu and Jun, 2012; chlorite to 275 °C, Smith et al., 2013b). Extrapolation of rate equations derived from low-temperature weathering studies should thus be viewed with caution, because this practice has been shown to overestimate chlorite dissolution rates at typical EGS conditions by up to four orders of magnitude (Smith et al., 2013b).

We focus in this study on the dissolution kinetics of the phyllosilicate mineral chlorite. Chlorite occurs in sedimentary rocks as either an allogenic detrital phase or an authigenic pore-filling phase, in igneous rocks as a common secondary replacement mineral; and in low- to mid-grade metamorphics and in hydrothermally altered rocks. Its potential use as a geothermometer and geobarometer has been reviewed by De Caritat et al. (1993) and by Laird (1991). Experimental measurements of kinetic chlorite dissolution rates have, until recently, been confined to low-

temperature studies, as a result of focus on weathering reactions and clay-lined nuclear waste repositories.

On the whole, more data are available for chlorite dissolution under low-pH (acid) conditions. Ross (1967) published the first kinetic chlorite dissolution data in acid media (2.0 N HCl), and estimated an activation energy of $\sim 88 \text{ kJ mol}^{-1}$ for a low-iron chlorite from 25-60 °C data. To determine the order of kinetic reaction with respect to proton activity (a_{H^+}), Hamer et al. (2003) observed 25 °C chlorite dissolution in several organic and inorganic acids and derived a range for this parameter (referred to as n) of 0.45-0.70. Enhanced release rates of octahedrally-located cations (e.g., Mg, Fe, and Al) were noted by Kodama and Schnitzer (1973) in 25 °C fulvic acid compared to hydrochloric. Observations from atomic force microscopy of 25 °C dissolution at acid conditions led Brandt et al. (2003) to propose that chlorite dissolution is limited to basal sheet layers and occurs over only a limited proportion of mineral surfaces, leading to significantly faster “reactive”-surface normalized rates. Kameda et al. (2009), however, observed the formation of an amorphous leached layer at chlorite grain edges after similar 25 °C acid pH dissolution, indicating reactivity at those sites as well.

In contrast to 25 °C chlorite dissolution rates on the order of $\sim 10^{-10}$, $10^{-11} \text{ mole m}^{-2} \text{ s}^{-1}$ observed at acid pH, both Gustaffson and Puigdomenech (2003) and May et al. (2003) noted slower rates at near-neutral pH 5-7.5 conditions (10^{-12} , and $10^{-13} \text{ mole m}^{-2} \text{ s}^{-1}$, respectively). At highly alkaline (pH>10) conditions, rates have been observed to increase again slightly, up to $10^{-11.2}$ (Lowson et al., 2005, Figure 3).

It is somewhat unclear what effect Mg/Fe substitution has on chlorite rates; at highly alkaline pH Rochelle et al.'s (1996) high-Fe chlorite rates ($\sim 10^{-11}$) were nearly one order of magnitude faster than rates measured by Gustaffson and Puigdomenech (2003; 10^{-12}) from a relatively Mg-rich chlorite, but Malmstrom et al. (1996) published a significantly faster Mg-rich chlorite rate obtained at pH 8 compared to other available data. Only Gustaffson and Puigdomenech (2003; Mg-rich pennite variety) and Lowson et al. (2005; higher-Fe ripidolite variety) each collected sufficient 25 °C rate data to produce a rate equation spanning the pH range of 3-10; the difference in rates observed from the different chlorite varieties at a given pH is on the order of 0-0.75 log units. However, this magnitude is also on a par with the total variation in rates from different studies conducted at the same pH.

Lowson et al. (2005) provided an extensive review of 25 °C chlorite studies, and demonstrated a parabolic relationship of dissolution rate magnitude with pH (faster rates at acid and alkaline pH; slowing rates at neutral pH). In deriving a kinetic rate expression with three individual rate mechanisms corresponding with these three pH regions, Lowson et al. (2005) published 25 °C rate constants of $\log k_{\text{acid}} = -9.8$, $\log k_{\text{neutral}} = -13$, and $\log k_{\text{basic}} = -16.8$. Interestingly, chlorite dissolution rates extracted from a 25 °C whole-rock metabasalt dissolution study at neutral pH (Critelli et al., 2014) fall within one order of magnitude of the rate observed by Lowson et al. (2005) at corresponding pH. Although individual rate measurements were relatively similar, the rate constants determined by Gustaffson and Puigdomenech (2003) to describe their data are lower for the acid regime ($\log k_{\text{acid}} = -10.4$), similar for the neutral regime ($\log k_{\text{neutral}} = -13.5$), and much higher for the basic regime ($\log k_{\text{basic}} = -11.3$). It should be noted both that fewer data points exist with which to constrain rates at alkaline pH, and also that fluids at these pH

conditions appear to be much closer to equilibrium with respect to chlorite (i.e., observed rates may have been affected by the approach of fluid-mineral equilibrium; Lowson et al., 2007, Table 5).

Lowson et al. (2007) extended the temperature range of available chlorite dissolution data up to 95 °C using the same Fe-rich chlorite material and described the measured rates as a function of [Al] species. Smith et al. (2013b) measured the first chlorite acid dissolution rates at temperatures ≥ 100 °C, both with and without dissolved $\text{CO}_{2(\text{aq})}$, and provided an activation energy value of 25 kJ mol⁻¹ in contrast to the much higher value generated by Ross (1967). Black and Haese (2014) subsequently published additional chlorite dissolution rates obtained under CO_2 -saturated conditions at 50, 80, and 120 °C, yielding a similar acid rate constant and a slightly lower activation energy (16 kJ mol⁻¹). To date, only one study has examined the role of reaction affinity, at 100 °C and pH 3-7.5; these authors concluded that a nonlinear reaction affinity term was appropriate to describe reaction rates as fluid-chlorite equilibrium is approached (Zhang et al., 2015).

We present here a dataset of 20 new high-temperature (100-275 °C) chlorite rates obtained at neutral to alkaline pH conditions. This work builds on our previous study of chlorite dissolution for CO_2 -EGS applications at acid pH by extending the solution pH range to capture a wider range of reactive conditions at higher temperatures. These new rate data are combined with previously published data to derive a single rate equation that describes chlorite dissolution from 25 to 275°C and pH 3 to 10. The resulting rate equation can be directly incorporated into larger-

scale reactive transport simulations to assess the impact of geochemical reactions on fracture shear zone and reservoir permeability.

Materials & Methods

Chlorite characterization – Chlorite (Mg-rich variety, clinochlore), identical to that used in previous work (Smith et al., 2013b) and purchased from the Source Clays Repository (Flagstaff Hills “CCa-2” chlorite, El Dorado County, California; described by Post and Plummer, 1972), was used in these experiments. Mineral dissolution rates reported in Table 1 were calculated from dissolved silica concentrations using the stoichiometry determined by Smith et al. (2013b) of $(\text{Mg}_{4.29}\text{Al}_{1.48}\text{Fe}_{0.10})(\text{Al}_{1.22}\text{Si}_{2.78})\text{O}_{10}(\text{OH})_8$. The low iron content and initial surface area differed from values reported for this mineral by the Clay Minerals Society, but have been independently replicated by another research group (Black and Haese, 2014). The bulk specimen was crushed to pea-size and then mechanically milled to the 150-250 μm size fraction used in the experiments.

Multi-point N_2 -BET surface area measurements of the bulk, unreacted micro-mill-ground “CCa-2” chlorite grains provided a value of $4.9 \pm 0.3 \text{ m}^2 \text{ g}^{-1}$, similar to the estimate of $5.1 \pm 0.4 \text{ m}^2 \text{ g}^{-1}$ for the hand-crushed “CCa-2” chlorite used in Smith et al. (2013b). Chlorite samples reacted in neutral and basic solution pH experiments displayed post-reaction surface area values that ranged from unchanged to at most three times lower than initial unreacted values. To calculate chlorite dissolution rates, we use the average specific surface area value measured prior to reaction, to remain consistent with rates calculated in our previous study (Smith et al., 2013b) and in other

previously published chlorite studies. The differences in rate values resulting from this assumption are smaller than the total uncertainty reported for each rate (Table 1).

Scanning electron microscopy (SEM) confirmed the presence of trace rutile (TiO_2) within the original chlorite solid. Thin sub-sections prepared with a focused ion beam were subjected to high resolution transmission electron microscopy (TEM) which confirmed the chlorite structure including characteristic 14.2 Å spacing. SEM, TEM and electron dispersive spectrometry were also used to search for evidence of secondary mineral precipitation in select samples.

Flow-through reactors and experimental methods – All experiments were performed in a background matrix of reagent-grade 0.05m NaCl and distilled deionized water initially purged with N_2 gas to remove atmospheric oxygen. Reagent-grade hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the pH of individual solutions to desired levels. Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) and (NaHBO_3) were also used as buffering agents in certain high pH experiments. Total chloride (Cl^-) levels in the experimental solutions were maintained at a constant value of 0.05m, but sodium levels ranged up to 0.075m as a result of added buffers and/or pH adjustment by sodium hydroxide. Experimental solution compositions are listed in Table 1.

Titanium single-pass mixed-flow reactors (e.g., Dove and Crerar, 1990) were used to conduct chlorite dissolution experiments over a temperature range of 100-275 °C and a pH range of 3-10. See Smith et al. (2013b, Figure 1) for a schematic of the experimental set-up. Room temperature solutions were pumped into the experimental reactors to pressurize each system, and then the

reactors were brought to temperature over a period of several hours while influent solution continued to flow at a constant flowrate of 0.5 mL min^{-1} . Time $t = 0$ in Figure 1 represents the time when reactor systems achieved target temperature. Chlorite grains ($\sim 1 \text{ g}$ per experiment) were suspended between two sheets of fine titanium mesh in a sample holder within each reactor vessel, to avoid abrasion during stirring.

Reactor system pressures were maintained well above boiling-point pressures by the use of back-pressure regulators installed at the reactor outlet. All wetted reactor surfaces (including pumps and back-pressure regulators) were made of C-276 alloy, passivated grade-4 titanium, or PEEK. At the conclusion of each experiment, sample holders were removed from each reactor as soon as liquid temperatures decreased below $100 \text{ }^{\circ}\text{C}$, and samples were dried overnight at $60 \text{ }^{\circ}\text{C}$.

Solution chemistry and derivation of rate values – Fluid samples were collected directly downstream of the back-pressure regulator using disposable luer-lock syringes. Effluent samples were split into three aliquots: 15 mLs were filtered ($0.2 \text{ }\mu\text{m}$) and acidified for dissolved silica, magnesium, aluminum, iron, calcium and other trace metal analyses by inductively-coupled plasma mass spectrometry (ICP-MS); 1 mL was filtered and 10x diluted with distilled water for ion chromatography to confirm consistent background sodium (Na^{+}) and chloride (Cl^{-}) solution concentrations; and 3-5 mLs were reserved, unfiltered, for $21 \text{ }^{\circ}\text{C}$ pH measurement. Samples from selected experiments were also re-analyzed for dissolved silica by UV spectrophotometry to confirm the low values measured with ICP-MS.

Net chlorite dissolution rates, R_{chl} [$\text{mol m}^{-2} \text{s}^{-1}$], were derived from steady-state solution chemistry data according to:

$$R_{\text{chl}} = \frac{C_i \cdot v}{\sigma_i \cdot m_{\text{chl}} \cdot \text{SSA}_{\text{chl}}} \quad (1)$$

using steady-state dissolved concentrations, C_i , corrected for any background detection of element i ; stoichiometry of the measured dissolved species within the mineral solid phase, σ_i ; flowrate, v ; and chlorite mass and specific surface area, m_{chl} and SSA_{chl} . Silica-derived rate values are reported in Table 1. Figure 1 shows typical examples of changes in solute concentrations over time and illustrates the longer timeframe necessary to reach steady-state conditions in neutral to basic solutions compared to previous experiments performed in acidic solutions (Smith et al., 2013b).

The geochemical code EQ3/6 (<https://missions.llnl.gov/energy/technologies/geochemistry>; accessed May 2015; Wolery, 1992) and the *data0.shv.V8.R6* database (Johnson and Lundeen, 1994) were used to calculate solution pH at experimental temperatures in addition to mineral-specific fluid saturation indices (SI) and Gibbs free energy of reaction (ΔG_r) relative to dissolution of the phase clinocllore-14A. To avoid propagating relatively large errors from IC measurements into the calculation of solution pH, each solution chemistry dataset was first charge-balanced on chloride at 21 °C using measured solution pH values, and then modeled at the experimental temperature for determination of *in situ* solution pH. Changes in chloride concentration resulting from charge balances were always less than $\pm 3\%$.

Saturation indices (SI) represent the chemical “distance” from equilibrium of a given fluid composition with respect to a mineral of interest, and are defined as:

$$SI = \log \frac{Q}{K_{eq}} \quad (2)$$

This comparison of the ion activity product, Q , and the equilibrium constant of the mineral of interest, K_{eq} , leads to positive SI values for supersaturated fluids and negative values for undersaturated fluids. Comparison of saturation indices among different experimental datasets must take into account the variability in available chlorite K_{eq} values. The K_{eq} value for clinocllore-14A, the closest analogue in the *data0.shv.V8.R6* database to our low-iron chlorite material, was $10^{-67.2}$ at 25 °C and $10^{-45.2}$ at 100 °C. These values are within one log unit of other database values used by previous researchers (Table SI-1), and the 100 °C value falls within 0.5 log units of the value measured by batch solubility experiment by Zhang et al. (2015). However, the 25 °C K_{eq} value used by Lawson et al. (2005; 2007) is significantly larger than other published values. These authors estimated this value using the experimentally-derived framework set forth by Kittrick (1982) to account for the higher iron content of their ripidolite chlorite variety. The impact of this difference in K_{eq} is that SI values reported by Lawson et al. (2005, 2007) are generally more undersaturated compared to values published by other researchers at comparable temperatures and pH. Zhang et al. (2015) recalculated the SI values of Lawson et al. (2007) with the objective of determining the appropriate form of a reaction affinity term; however, in this work we use Lawson et al.'s (2005, 2007) rates and modeled saturation indices as published, noting that rate measurements and corresponding stability may well vary with differing chlorite compositions and Mg/Fe substitution.

Treatment of experimental errors – Errors associated with the rates in Table 1 represent propagation of individual errors from the five components of equation (1). Errors in measured dissolved silica concentrations equal one standard deviation of the steady-state concentration,

while constant errors in the remaining four parameters (flowrate, mineral weight, final reactive surface area, and stoichiometric coefficient for silica) reflect instrumental and measurement accuracy. We note that reported errors in Table 1 are approximately twice as large as errors associated with previously published chlorite dissolution data.

Data fitting and parameter estimation methods – Dissolution rate models for fitting the combined rate datasets were evaluated using graphical and computational methods (**Parameter ESTimation** tool, PEST; Doherty, 2005). This combined approach was taken because optimization of the generalized kinetic rate model

$$R = \left(\left[A_A \cdot e^{-E_A/RT} \cdot a_{H^+}^n \right] + \left[A_N \cdot e^{-E_N/RT} \right] + \left[A_B \cdot e^{-E_B/RT} \cdot a_{OH^-}^m \right] \right) \cdot f(\Delta G_r), \quad (3)$$

against the dataset yielded highly correlated mechanism-specific parameter values (e.g., A_A , E_A , and n all strongly correlated). Given this non-uniqueness (also noted by Cama et al., 2000) graphical methods of independently estimating E_i (activation energies) and n (rate dependence on a_{H^+}) were utilized to reduce the number of unknown model parameters.

To derive E_i estimates from Arrhenius treatments, we defined far-from-equilibrium (FFE) rates as those with $\Delta G_r \leq -65 \text{ kJ mol}^{-1}$ (Figure SI-1). This threshold, although higher than the -130 kJ mol^{-1} proposed for smectite by Cama et al. (2000), was required to supply enough data to define a hydroxide-catalyzed basic mechanism. Activation energies for individual acid, neutral, and basic (alkaline) rate mechanisms were then estimated from the slopes of lines fit to natural log FFE rate data versus inverse temperature. An initial value for n (the order of reaction with respect to hydrogen activity) was estimated from log FFE rate data versus solution pH at 100°C , while Lowson et al.'s (2005) value of m (reaction order with respect to hydroxide activity) was

used. During remaining parameter optimization with PEST, each rate was weighted with a factor inversely related to its magnitude. We stress that optimization of the remaining Arrhenius pre-factor A_i [$\text{mol m}^{-2} \text{s}^{-1}$] values in the final kinetic equation is conditional to the graphically derived parameter values, given the high level of correlation. While these pre-factors can be recast as 25 °C rate constants, this comparison may not be valid unless activation energies are similar among individual studies.

Results & Discussion

In this section we discuss the dependence of chlorite dissolution on pH, temperature, and reaction affinity and derive a dissolution rate equation applicable over pH 3-10 and 25 to 275 °C. Rate equations were derived using new data from 100-275 °C collected in this study and previously published experiments using low-iron chlorite (Zhang et al., 2015; Black and Haese, 2014; Smith et al., 2013b) and chlorite with slightly higher iron contents (Lowson et al., 2007, 2005; Brandt et al., 2003). Aluminum and silica stoichiometry were similar among all studies, with $\text{Al:Si} \approx 1$. Possible implications of the observed pH dependence of non-stoichiometric dissolution, diffusive transport, and reaction affinity are discussed.

A generalized kinetic rate law which takes into account pH-mediated dissolution mechanisms and potential effects of fluid approach to mineral saturation is:

$$R = \left(\left[A_A \cdot e^{-E_A/RT} \cdot a_{\text{H}^+}^n \right] + \left[A_N \cdot e^{-E_N/RT} \right] + \left[A_B \cdot e^{-E_B/RT} \cdot a_{\text{OH}^-}^m \right] \right) \cdot f(\Delta G_r) \quad (4)$$

In Equation 4, the dissolution rate R [$\text{mol m}^{-2} \text{s}^{-1}$] is dependent upon several parameters: A_i [$\text{mol m}^{-2} \text{s}^{-1}$] represents a pre-exponential constant for a particular rate mechanism (Acid-, Neutral-, or

Basic-catalyzed); E_i represents corresponding activation energies [kJ mol^{-1}] describing the dependence of the particular rate mechanism on temperature, T ; a_i represents the activity of an aqueous species, here, H^+ and OH^- ions, with the dependence of the rate on these activities given by coefficients n and m . The final term represents some functional dependence of the overall rate on the Gibbs free energy of reaction, ΔG_r , to slow the reaction rate as equilibrium is approached. We note that chlorite dissolution has previously been described in terms of its dependence on Al^{3+} concentrations (Lowson et al., 2007) as well as its inhibition by HCO_3^- ions (Black and Haese, 2014). We focus here on a rate form similar to equation (4), because we did not conduct rate experiments with variable concentrations of these species.

pH and temperature dependence – We use dissolved silica concentrations to monitor chlorite dissolution because silica concentrations should not be altered by secondary mineral precipitation (with the possible exception of three experiments supersaturated with respect to chlorite at $\text{pH} > 9$; see Table 1). Figure 2 shows net observed chlorite dissolution rates from our work at higher temperature (100 to 275 °C), as well as selected data (75, 45 °C; Lowson et al., 2007) to represent lower-temperature trends. For temperatures greater than or equal to 100 °C, measured chlorite dissolution rates are fastest in acid pH solutions, and decrease to nearly constant values over the near-neutral to alkaline pH range (5-10), similar to behavior observed for diopside (Knauss et al., 1993; Daval et al., 2010) and talc (Saldi et al., 2007). This trend is distinct from the U-shaped (parabolic) behavior indicated by equation (4) and observed for many aluminosilicate minerals, including chlorite, at lower temperatures (White and Brantley, 1995; Lowson et al., 2005). A second observation is that above 100 °C, rates are not strongly

dependent on temperature, with the exception of rates measured at $\text{pH} < 4$. At 250 and 275 °C, no temperature dependence is observed over the entire pH range.

Congruent/incongruent dissolution – Figures 3a,b plot the ratios of steady-state aqueous Mg/Si and Al/Si concentrations measured in this study and Smith et al (2013b), where the dashed line in each plot indicates stoichiometric dissolution as defined by the elemental masses measured in the unreacted chlorite solid. We do not discuss Fe/Si ratios because iron is only a minor constituent of this chlorite variety and the value of this ratio showed no distinct trends with respect to pH or temperature. Magnesium and aluminum displayed opposite behavior in stoichiometric release rates over pH 3 to 10; trends in these elemental ratios relative to pH suggest that precipitation of magnesium-bearing phases may occur at $\text{pH} > 6$ and aluminum-bearing phases at $\text{pH} < 6$. Geochemical modeling suggests that aluminum- or magnesium- (oxy)hydroxides are the most likely precipitates rather than magnesium- or aluminosilicates; note the overlap of regions of nonstoichiometric dissolution with brucite and diasporite saturation in Figures 3c,d. Silica-bearing minerals such as kaolinite, talc, and antigorite remain undersaturated over the experimental pH and temperature ranges. Mineral grains were examined with transmission electron microscopy after reaction in both acidic (Smith et al., 2013b) and alkaline media (this study) for evidence of possible precipitates, but no changes from the initial chlorite structure and texture were noted.

Diffusion versus kinetic control of dissolution rates – The relatively low dependence of chlorite dissolution on temperature (Figure 2) in comparison with previous estimates cannot be attributed to diffusion-limited transport, because aqueous diffusion is estimated to occur at a faster rate (1-3

orders of magnitude) than measured mineral reactions for all experimental conditions. We illustrate this by focusing on the rates obtained from the highest temperature and lowest pH experiments, where the effects of diffusion are likely to be most prevalent (e.g., Lasaga, 1984; Casey, 1987; Murphy et al., 1989). Even in well-mixed reactors, a fluid boundary layer exists at the mineral surface across which dissolved reactants must diffuse toward the solid phase and reaction products must diffuse through to the bulk aqueous phase. Sampled bulk aqueous compositions are indicative of the kinetic dissolution rate occurring at the mineral surface only if diffusion across the boundary layer does not limit transport to the bulk solution.

The steady-state diffusive flux, J_i [mole m⁻² s⁻¹], of an aqueous species of interest i across the boundary layer is:

$$J_i = \frac{D_i}{\varepsilon} \cdot \Delta C_i = \frac{D_i}{\varepsilon} \cdot (C_{\text{surf},i} - C_{\text{bulk},i}), \quad (5)$$

where ε is the thickness of the boundary layer [m]; ΔC_i refers to the concentration gradient of species i from the mineral surface to the bulk aqueous phase [mol m⁻³]; and D_i is the diffusion coefficient for the aqueous species at the temperature of interest (here, 275 °C) [m² s⁻¹]. We make the assumption that chlorite grains (likely tabular geometry) can be treated as spherical particles in order to apply the approach of Jeschke and Dreybrodt (2002) to estimate an approximate layer thickness of $\varepsilon = 1 \cdot 10^{-5}$ m for the 150-250 μm size fraction solids. We estimate SiO_{2(aq)} diffusion coefficients at elevated temperature of $\sim 50 \cdot 10^{-9}$ m² s⁻¹ using 25 °C values ($1 \cdot 2 \cdot 10^{-9}$ m² s⁻¹; Wollast and Garrels, 1971; Applin, 1987), assuming a similar temperature dependence for aqueous diffusion coefficients of 1.5 orders of magnitude between 0-300 °C (Oelkers and Helgeson, 1988). C_{surf} was calculated assuming equilibrium for the specific temperature and pH of the experiment. This method yields a diffusive flux of $\sim 6 \cdot 10^{-3}$ mole m⁻² s⁻¹

at 275 °C and pH 4.34, many orders of magnitude faster than the observed dissolution rate from bulk solution composition at these conditions.

Effect of approach to equilibrium on rate magnitudes – It is possible that some measured rates depend on reaction affinity because the solutions approach equilibrium with chlorite with increasing pH. Figure 4 shows saturation index, *SI*, versus pH for all high-temperature data collected in this work and Smith et al. (2013b), as well as results from Brandt et al., (2003) Lowson et al. (2005, 2007), Black and Haese (2013), and Zhang et al. (2015) from similar pH conditions at lower temperatures. Supersaturated rates shown in Figure 4 represent those experiments (this study; Lowson et al., 2007) for which net silica concentrations remained positive and yet no evidence for chlorite reprecipitation or secondary precipitation was noted. These “supersaturated” dissolution rates may reflect some mixed combination of reaction affinity, bulk versus localized geochemical conditions, and potential analytical error. We show them in Figure 4 and elsewhere only to demonstrate trends in rate datasets; they are not used to derive the dissolution rate equation.

The combined dataset demonstrates that chlorite equilibrium is favored with increasing solution pH over the full temperature range of 25-275 °C, and suggests that the use of a term incorporating the effect of fluid approach to chlorite equilibrium may be needed to model the observed dissolution rates, especially at alkaline pH conditions.

Derivation and comparison of rate models – We evaluate both far-from-equilibrium (FFE) and near-equilibrium variations of the generalized kinetic dissolution rate equation (equation 4,

without and with an $f(\Delta G_r)$ term) to model the higher-temperature data collected in this work and Smith et al. (2013b), as well as the larger dataset incorporating all additional published chlorite dissolution rates with fluid saturation data (Brandt et al., 2003; Lowson et al., 2005, 2007; Black and Haese, 2013; Zhang et al., 2015; see Table SI-2) using a combination of graphical and PEST parameter optimization. The rate equation that best fits the data includes acid, neutral, and alkaline pH mechanisms, and a simple linear form of the reaction affinity term:

$$R = \left(\left[A_A \cdot e^{-E_A/RT} \cdot a_{H^+}^n \right] + \left[A_N \cdot e^{-E_N/RT} \right] + \left[A_B \cdot e^{-E_B/RT} \cdot a_{OH^-}^m \right] \right) \cdot \left(1 - e^{\Delta G_r/RT} \right). \quad (6)$$

Despite the minimal dependence of the rates on pH in alkaline solutions (non-parabolic rate/pH behavior), we find that a separate alkaline rate mechanism is necessary to prevent FFE rate models from underpredicting rates for unsaturated rates at high pH, and so we include it despite the lack of good constraints on A_B .

Far-from equilibrium – Rates from far-from-equilibrium conditions ($\Delta G_r \leq -65 \text{ kJ mol}^{-1}$) were used in Arrhenius treatments to determine best-fit apparent activation energies (E_A , E_N , E_B) for FFE dissolution models for two temperature regimes: $T \geq 100 \text{ }^\circ\text{C}$, and $25 \leq T \leq 275 \text{ }^\circ\text{C}$. The acid-promoted activation energy was first estimated as 41 kJ mol^{-1} from $T \geq 100 \text{ }^\circ\text{C}$ data, and 19 kJ mol^{-1} from data spanning $25 \text{ }^\circ\text{C} \leq T \leq 275 \text{ }^\circ\text{C}$ (Figure 5a). For the neutral mechanism, $T \geq 100 \text{ }^\circ\text{C}$ data yielded an E_N estimate of 13 kJ mol^{-1} , and 24 kJ mol^{-1} from 25-275 $^\circ\text{C}$ data (Figure 5c). These estimated energies are relatively low compared to the reported range for layered silicate minerals ($\sim 20\text{-}90 \text{ kJ mol}^{-1}$) and are 3-4 times lower than previously estimated values for chlorite dissolution (Nagy, 1995; Palandri and Kharaka, 2004), but are consistent with values previously reported by Smith et al. (2013b) and Black and Haese (2014). Deriving an activation energy estimate for the hydroxide-catalyzed mechanism is problematic because few rates at high pH in

the collective dataset are sufficiently far from equilibrium (e.g., Daval et al., 2010). The best constraints we can extract from the FFE dataset (Figure 5d) are $E_B = 15 \text{ kJ mol}^{-1}$, determined from rates collected at 65-275 °C and pH > 9 (this study, Lowson et al., 2007).

The reaction order for the acid-promoted mechanism, n , was graphically estimated from 100 °C, $\Delta G_r \leq -65 \text{ kJ mol}^{-1}$ data as 0.74 (Figure 5b). In the absence of a rate dataset at any given temperature spanning a sufficient range of alkaline pH, we fix the reaction order of the hydroxide-promoted mechanism, m , at the 0.43 value determined at 25 °C by Lowson et al. (2005).

Considering only rates obtained at $T \geq 100 \text{ °C}$ and $\Delta G_r \leq -65 \text{ kJ mol}^{-1}$ and honoring the graphically-derived parameter values for that temperature range leads to a best-fit FFE rate equation:

$$R_{\text{chl}, T \geq 100^\circ\text{C}} = \left(\left[1.1 \cdot 10^{-3} \cdot e^{-41/R \cdot T} \cdot a_{\text{H}^+}^{0.74} \right] + \left[8 \cdot 10^{-11} \cdot e^{-13/R \cdot T} \right] + \left[1.5 \cdot 10^{-9} \cdot e^{-15/R \cdot T} \cdot a_{\text{OH}^-}^{0.43} \right] \right). \quad (7)$$

Alternatively, to satisfactorily represent the trends in rate data over the entire temperature range (25-275 °C), the FFE rate equation can be expressed as:

$$R_{\text{chl}, 25-275^\circ\text{C}} = \left(\left[1 \cdot 10^{-4} \cdot e^{-30/R \cdot T} \cdot a_{\text{H}^+}^{0.74} \right] + \left[4.7 \cdot 10^{-11} \cdot e^{-13/R \cdot T} \right] + \left[1.5 \cdot 10^{-9} \cdot e^{-15/R \cdot T} \cdot a_{\text{OH}^-}^{0.43} \right] \right). \quad (8)$$

The E_A and E_N values in equation (8) represent a compromise from the values derived from the full temperature dataset (Figures 5a,c) in order to better fit this larger dataset. The value of n in equations (7-8) is relatively high compared to the values obtained by Hamer et al. (2003), but it adequately captures the trends of rate with acid pH over a large range of temperature. The resulting A_A and A_N values are strongly dependent on the choice of E_A/n and E_N values. Modeled

uncertainties in A_A and A_N in both equations (7-8) are on the order of ~ 0.5 log units, but uncertainty in A_B is extremely large (up to 2 log units), indicating the less constrained nature of this term due to the scarcity of undersaturated high pH rates needed to define this alkaline/basic mechanism (see also Lawson et al., 2005, p1696). The combination of $A_B/E_B/m$ values in equations (7-8) should be thought of as lower bounds to the “true” description of the alkaline rate mechanism, because further reductions in these parameter values reduce the magnitude of the alkaline mechanism such that the neutral mechanism dominates even at high pH conditions.

The fits of both far-from-equilibrium rate equations (7-8) are shown relative to rate data in Figure 6. The higher-temperature equation (7) displays an increasingly broader plateau in predicted rate values at neutral pH compared to the full-temperature equation (8). The full-temperature 25-275 °C model fits the majority of rate data to within 0.5 log units, though the alkaline portion of this rate model is admittedly not well-constrained by existing data.

Reaction affinity – The inclusion of a reaction affinity term, $f(\Delta G_r)$, is crucial to any dissolution rate expression, because it allows for slowing of reaction in response to fluid-mineral approach to equilibrium. Several theoretically based and empirical forms of this term have been proposed in the literature. The most common forms of $f(\Delta G_r)$ are:

$$f(\Delta G_r) = 1 - \frac{Q}{K_{eq}} = 1 - e\left(\frac{\Delta G_r}{RT}\right), \quad (9)$$

or

$$f(\Delta G_r) = \left(1 - \left(\frac{Q}{K_{eq}}\right)^p\right), \text{ or } \left(1 - e\left(\frac{p \cdot \Delta G_r}{RT}\right)\right), \quad (10)$$

where p is a coefficient sometimes referred to as the Temkin coefficient σ ($\sigma = p^{-1}$), often invoked to represent an average stoichiometric number for the overall reaction (e.g., Helgeson et

al., 1984) and which could be approximated as 0.36 for the chlorite used in this study (e.g., Nagy and Lasaga, 1992). Recently, Zhang et al. (2015) had success fitting chlorite dissolution rates in the $-80 \leq \Delta G_r \leq -15 \text{ kJ mol}^{-1}$ range using a nonlinear reaction affinity term:

$$f(\Delta G_r) = \left(1 - e \left(p \cdot \left(\frac{|\Delta G_r|}{RT} \right)^q \right) \right), \quad (11)$$

with p and q fitted to values of -0.01677 and 1.3, respectively, based on 11 measurements at pH 3.3-7.5 and 100 °C. Equation (11) is an empirical $f(\Delta G_r)$ relationship; equations (9-10) are derived from theoretical considerations but the definition of the p coefficient is not always straightforward in multi-oxide systems (e.g., Gin et al., 2008). Figure 7 illustrates the impact of these reaction affinity terms on predicted rates, showing an increased slowing of dissolution rate with increasing complexity of the reaction affinity term (equations 9-11).

Those rates with $0 \geq \Delta G_r \geq -65 \text{ kJ mol}^{-1}$ (rates *closer* to equilibrium, $n = 58$) were used to assess the appropriateness of various reaction affinity terms $f(\Delta G_r)$ (equations 9-11) in conjunction with the $25 \leq T \leq 275 \text{ °C}$ far-from-equilibrium rate equation (8). We find that chlorite dissolution is best described by a reaction affinity term based on transition-state theory where $p = 1$ (i.e., equation 9), suggesting that the approach to equilibrium should lower the rate only when solutions are very close to equilibrium, i.e., rates with $\Delta G_r \geq -2 \text{ kJ mol}^{-1}$ ($SI > -0.5$). Inclusion of additional fitting parameters required by equations (10,11) overemphasizes the importance of the reaction affinity effect and results in poor fits for solutions farther from equilibrium or those already underpredicted by the FFE equation. Figure 8 shows the impact of the various reaction affinity forms on predicted versus observed dissolution rates for those rates defined here as near-equilibrium ($0 \geq \Delta G_r \geq -65 \text{ kJ mol}^{-1}$) as well as the larger subset of rates with $0 \geq \Delta G_r \geq -130 \text{ kJ mol}^{-1}$ (the near-equilibrium range proposed by Cama et al., (2000) for another sheet silicate). The

near-equilibrium models are defined in Figure 8 with $p = 1$ (equation 9); $p = 0.36$ (equation 10); and $p = -0.01677$, $q = 1.3$ after Zhang et al. (2015; equation (11)).

Fitting the reaction affinity term is limited by the available data. The use of $\Delta G_r \leq -65 \text{ kJ mol}^{-1}$ rates to extract the far-from-equilibrium parameters in the alkaline pH mechanism necessitates a reaction affinity term that lowers rates only at conditions very near equilibrium. Likewise, the lack of near-equilibrium data at acidic pH (excepting the 100 °C data collected by Zhang et al., 2015) prevents the testing of more complex forms of reaction affinity term over the full range of expected pH conditions. Given these current limitations, as well as the fact that parameters p and q in equation (11) are strongly correlated, we recommend that the reaction affinity term be described as simply as possible, i.e., equation (9). Chlorite dissolution over the temperature range of 25-275 °C is thus described as:

$$R_{25-275^\circ\text{C}} = \left(\left[1 \cdot 10^{-4} \cdot e^{-30/R \cdot T} \cdot a_{\text{H}^+}^{0.74} \right] + \left[4.7 \cdot 10^{-11} \cdot e^{-13/R \cdot T} \right] + \left[1.5 \cdot 10^{-9} \cdot e^{-15/R \cdot T} \cdot a_{\text{OH}^-}^{0.43} \right] \right) \cdot \left(1 - e^{\Delta G_r/RT} \right). \quad (12)$$

Conclusions and Implication for EGS

The objective of this suite of experiments was to develop a useful kinetic dissolution expression for chlorite that would be applicable over a wide range of solution pH and temperature conditions representative of subsurface conditions, particularly for natural and/or engineered geothermal reservoirs. The recommended rate equation is dependent on both pH and temperature and utilizes three different dissolution mechanisms (acid, neutral, and basic), and was derived from 100-275 °C rate data collected in this study and the companion work (Smith et al., 2013b) as well as available published data from other sources from 25-120 °C (Brandt et al., 2003;

Lowson et al., 2005, 2007; Black and Haese, 2014; Zhang et al., 2015). The rate data were fit to a generalized rate model,

$$R_{\text{chl}} = \left(\left[1 \cdot 10^{-4} \cdot e^{-30/R \cdot T} \cdot a_{\text{H}^+}^{0.74} \right] + \left[4.7 \cdot 10^{-11} \cdot e^{-13/R \cdot T} \right] + \left[1.5 \cdot 10^{-9} \cdot e^{-15/R \cdot T} \cdot a_{\text{OH}^-}^{0.43} \right] \right) \cdot \left(1 - e^{\Delta G_r / RT} \right),$$

which should be easily incorporated into most existing reactive transport codes for use in prediction of rock-water interactions in geothermal systems. The use of a reaction affinity term in the rate model did not provide significantly better fits to the dataset considered here because the majority of observed rates were obtained at relatively far-from-equilibrium conditions.

However, the use of such a term is recommended for geochemical predictions of chlorite dissolution in natural systems, including hydrothermal and geothermal reservoirs, where flow rates and/or high residence times will likely lead to near-equilibrium fluid conditions.

Specifically, we find that the dissolution of chlorite, a sheet silicate, is relatively slow at elevated temperatures (100-275 °C), compared to other common tectosilicate minerals for which higher-temperature kinetic data are available (e.g., one to three orders of magnitude slower than quartz and feldspars, Palandri and Kharaka, 2004). In comparison to other Mg-silicate minerals, measured chlorite rates are roughly similar to anthophyllite rates, about one order of magnitude slower than talc rates, and considerably slower than Mg-rich serpentine rates (Chen and Brantley, 1998; Saldi et al., 2007; Daval et al., 2013). These relatively slow chlorite rates and the overall variation of only ~2 orders of magnitude difference in rate values measured over 25 to 275 °C provide the basis for relatively lower activation energies for specific rate mechanisms, in conflict with previously reported higher values based on extrapolation of low-temperature experimental data to higher temperatures. Additionally, we note that the dissolution rate of chlorite does not increase in alkaline pH conditions but rather remains at the same level as that

noted for neutral conditions, with only a weak dependence on temperature. The available rate data at high pH cannot differentiate whether this lack of rate dependence at alkaline pH is due to decreased effects of hydroxide-catalyzed reaction or increased effects of fluid saturation under these conditions.

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Figure 1: Typical experimental solution concentrations [mmol/L] versus time [hrs] for chlorite dissolution experiments conducted at elevated temperature under a) basic and b) acidic pH conditions. Note the longer time required for concentrations to reach steady-state levels at basic pH conditions.

Figure 2: Observed dissolution rates versus solution pH, from this work and Smith et al., 2013, ($\square$); and Lowson et al., 2007 (Δ). Solid lines represent fitted rates at corresponding temperatures calculated from 25-275 °C equation (8). Smaller symbols represent rates measured at $\Delta G_r \geq -65$ kJ mol⁻¹ conditions.

Figure 3: Ratios of steady-state release rates of a) Mg:Si, and b) Al:Si versus steady-state modeled solution pH at experimental temperatures. Also shown are modeled fluid saturation indices, SI , with respect to c) brucite, $Mg(OH)_2$; and d) diasporite, $\alpha-AlO(OH)$, versus steady-state solution. All data from this work and from Smith et al., 2013b. Dashed horizontal lines in a,b represent ratios present in unreacted chlorite material; dashed lines in c,d represent fluid equilibrium with respect to brucite and diasporite. Symbols overlain by heavy crosses indicate experiments in which fluids were supersaturated with respect to chlorite (clinochlore-14A).

Figure 4: Modeled fluid saturation indices versus solution pH for temperatures of a) 100-275 °C (this work), and b) 25-120 °C. Data are as follows: this work and Smith et al., 2013b ($\square$); Black and Haese, 2014 ($\diamond$); Zhang et al., 2015 ($\circ$); Lowson et al., 2005, 2007 (Δ); and Brandt et al., 2003 (—).

Figure 5: Estimates of apparent activation energies (a, c, d) and n coefficient (b) derived from far-from-equilibrium (i.e., $\Delta G_r \leq -65\text{ kJ mol}^{-1}$) rate data (this work, Zhang et al., 2015; Black and Haese, 2014; Smith et al., 2013b; Lowson et al., 2005, 2007; Brandt et al., 2003; see Table SI-2). Error bars represent either uncertainty in single rate values or the range of rates available at given temperatures. Solid lines represent best-fit slopes to all data, while dashed lines represent slopes for $T \geq 100\text{ °C}$ data. Data defining the acid mechanism were confined to $\text{pH} \leq 3.7$; for the neutral mechanism, $5.5 \leq \text{pH} \leq 6.5$; for the basic/alkaline mechanism $\text{pH} \geq 8.9$.

Figure 6: Dissolution rate data versus solution pH at various temperatures from 25 to 275 °C. Black solid lines represent 25-275 °C far-from-equilibrium rate equation (8); red dashed lines represent far-from-equilibrium rate equation (7) derived for $T \geq 100$ °C. Data symbols are as follows: from this work and Smith et al., 2013b ($\square$); Black and Haese, 2014 ($\diamond$); Zhang et al., 2015 ($\circ$); Lawson et al., 2005, 2007 (Δ); Brandt et al., 2003 (—). Gray shaded symbols represent far-from-equilibrium rates ($\Delta G_r \leq -65$ kJ mol⁻¹); white symbols represent near-equilibrium rates ($-65 \leq \Delta G_r \leq 0$); red symbols represent supersaturated rates ($\Delta G_r \geq 0$).

Figure 7: Normalized rate (R_{NE}/R_{FFE}) versus Gibbs free energy of reaction, ΔG_r (kJ mol^{-1}). Reaction affinity terms, equations 9-11 with coefficients as defined in the text, are shown as lines.

Figure 8: Comparison of predicted rates (including reaction affinity terms) versus measured rates, mol m⁻² s⁻¹ (data include rates from this study; Zhang et al., 2015; Black and Haese, 2014; Smith et al., 2013b; Lowson et al., 2005, 2007; see Table SI-2). Solid symbols indicate rates with modeled $\Delta G_r \geq -130$ kJ mol⁻¹; outlined symbols indicate the subset of rates with modeled $\Delta G_r = -65$ kJ mol⁻¹. Dashed lines indicates 1:1 agreement between predicted and observed rates.

Table 1: Experimental conditions, Si-derived chlorite dissolution rates, steady-state dissolved silica, magnesium, and aluminum concentrations, modeled saturation indices/Gibbs free energy of reaction (with respect to clinocllore-14A), and pH adjustments for experiments conducted at primarily neutral and alkaline solution pH. Rates are normalized to average initial chlorite surface area, $5.0 \text{ m}^2 \text{ g}^{-1}$. See Table SI-1 for additional chlorite rate data from other sources used in rate derivation. *n.d.* = not detected.

T, °C	pH (at T)	Dissolution Rate $\times 10^{12}$, $\text{mol m}^{-2} \text{ s}^{-1}$	$[\text{SiO}_{2(\text{aq})}]$ $\times 10^6$, mol L^{-1}	$[\text{Mg}]$ $\times 10^6$, mol L^{-1}	$[\text{Al}]$ $\times 10^6$, mol L^{-1}	Log (Q/K_{eq})	ΔG_r , kJ mole^{-1}	Solution Additions
100	6.01	1.39 ± 0.74	3.45 ± 0.14	3.29 ± 0.06	0.35 ± 0.01	-22.7	-162	NaOH
100	6.08	2.76 ± 1.5	4.69 ± 0.25	5.17 ± 0.16	1.99 ± 0.07	-19.3	-138	NaOH
100	7.95	1.60 ± 1.0	2.76 ± 1.0	0.51 ± 0.02	5.36 ± 0.15	-8.46	-60.4	$\text{Na}_2\text{B}_4\text{O}_7$, NaOH
100	9.38	1.02 ± 0.54	1.80 ± 0.02	0.21 ± 0.01	1.68 ± 0.03	-2.09	-14.9	$\text{Na}_2\text{B}_4\text{O}_7$, NaOH
150	5.48	4.03 ± 2.1	11.0 ± 0.2	11.0 ± 0.2	7.63 ± 0.15	-16.0	-130	NaOH
150	5.76	3.16 ± 1.7	5.40 ± 0.32	3.66 ± 0.08	4.23 ± 0.11	-17.7	-143	NaOH
150	7.32	1.87 ± 1.0	3.20 ± 0.18	0.27 ± 0.02	21 ± 0.5	-10.0	-81.0	$\text{Na}_2\text{B}_4\text{O}_7$, NaOH
150	8.89	1.48 ± 0.78	2.55 ± 0.09	0.19 ± 0.02	1.11 ± 0.01	0.554	4.46	NaOH
200	5.37	3.91 ± 2.1	10.0 ± 0.4	10.2 ± 0.2	14.8 ± 0.3	-13.3	-120	NaOH
200	6.80	3.33 ± 1.8	5.67 ± 0.11	0.18 ± 0.004	6.03 ± 0.11	-11.2	-101	$\text{Na}_2\text{B}_4\text{O}_7$, NaOH
200	7.18	1.48 ± 0.78	2.56 ± 0.04	2.14 ± 0.02	2.70 ± 0.04	-5.29	-47.9	NaOH
200	8.97	0.25 ± 0.14	0.48 ± 0.08	0.057 ± 0.027	4.07 ± 0.09	4.07	37.4	NaOH
250	3.72	358 ± 190	662 ± 10	686 ± 18	$0.76(\pm 0.02)$	-13.6	-136	HCl
250	5.53	4.57 ± 2.4	7.77 ± 0.31	5.28 ± 0.15	$6.20(\pm 0.18)$	-12.4	-124	NaOH
250	7.41	3.45 ± 1.8	6.88 ± 0.11	0.093 ± 0.006	5.38 ± 0.15	-4.80	-48.1	$\text{Na}_2\text{B}_4\text{O}_7$, NaOH
250	9.05	6.92 ± 0.37	1.20 ± 0.14	0.021 ± 0.004	2.40 ± 0.04	7.63	76.4	NaOH
275	5.52	6.52 ± 3.4	11.1 ± 0.4	1.46 ± 0.04	1.82 ± 0.07	-15.2	-160	NaOH
275	5.61	3.29 ± 1.7	5.64 ± 0.12	0.67 ± 0.005	3.68 ± 0.07	-16.2	-170	NaHBO_3 , NaOH
275	7.77	4.32 ± 2.3	7.55 ± 0.12	0.058 ± 0.008	5.03 ± 0.06	-2.03	-21.3	NaOH
275	9.12	6.74 ± 3.6	11.9 ± 0.2	<i>n.d.</i>	14.2 ± 0.1	-6.46	-67.8	NaOH

Smith and Carroll, Chlorite dissolution kinetics at pH 3-10 and temperature to 275 °C

Equation (1):

$$R_{\text{chl}} = \frac{C_i \cdot v}{\sigma_i \cdot m_{\text{chl}} \cdot SSA_{\text{chl}}}$$

Equation (2):

$$SI = \log \frac{Q}{K_{\text{eq}}}$$

Equations (3,4):

$$R = \left(\left[A_A \cdot e^{-E_A/RT} \cdot a_{\text{H}^+}^n \right] + \left[A_N \cdot e^{-E_N/RT} \right] + \left[A_B \cdot e^{-E_B/RT} \cdot a_{\text{OH}^-}^m \right] \right) \cdot f(\Delta G_r)$$

Equation (5):

$$J_i = \frac{D_i}{\varepsilon} \cdot \Delta C_i = \frac{D_i}{\varepsilon} \cdot (C_{\text{surf},i} - C_{\text{bulk},i})$$

Equation (6):

$$R = \left(\left[A_A \cdot e^{-E_A/RT} \cdot a_{\text{H}^+}^n \right] + \left[A_N \cdot e^{-E_N/RT} \right] + \left[A_B \cdot e^{-E_B/RT} \cdot a_{\text{OH}^-}^m \right] \right) \cdot \left(1 - e^{\Delta G_r/RT} \right)$$

Equation (7):

$$R_{\text{chl}, T \geq 100^\circ\text{C}} = \left(\left[1.1 \cdot 10^{-3} \cdot e^{-41/RT} \cdot a_{\text{H}^+}^{0.74} \right] + \left[8 \cdot 10^{-11} \cdot e^{-13/RT} \right] + \left[1.5 \cdot 10^{-9} \cdot e^{-15/RT} \cdot a_{\text{OH}^-}^{0.43} \right] \right)$$

Equation (8):

$$R_{\text{chl}, 25-275^\circ\text{C}} = \left(\left[1 \cdot 10^{-4} \cdot e^{-30/RT} \cdot a_{\text{H}^+}^{0.74} \right] + \left[4.7 \cdot 10^{-11} \cdot e^{-13/RT} \right] + \left[1.5 \cdot 10^{-9} \cdot e^{-15/RT} \cdot a_{\text{OH}^-}^{0.43} \right] \right)$$

Equation (9):

$$f(\Delta G_r) = 1 - \frac{Q}{K_{\text{eq}}} = 1 - e^{\left(\frac{\Delta G_r}{RT} \right)}$$

Equation (10):

$$f(\Delta G_r) = \left(1 - \left(\frac{Q}{K_{\text{eq}}} \right)^p \right), \text{ or } \left(1 - e^{\left(\frac{p \cdot \Delta G_r}{RT} \right)} \right)$$

Equation (11):

$$f(\Delta G_r) = \left(1 - e^{\left(p \cdot \left(\frac{|\Delta G_r|}{RT} \right)^q \right)} \right)$$

Equation (12):

$$R_{25-275^{\circ}\text{C}} = \left(\left[1 \cdot 10^{-4} \cdot e^{-30/\text{R}\cdot\text{T}} \cdot a_{\text{H}^{+}}^{0.74} \right] + \left[4.7 \cdot 10^{-11} \cdot e^{-13/\text{R}\cdot\text{T}} \right] + \left[1.5 \cdot 10^{-9} \cdot e^{-15/\text{R}\cdot\text{T}} \cdot a_{\text{OH}^{-}}^{0.43} \right] \right) \cdot \left(1 - e^{\Delta G_{\text{r}}/\text{RT}} \right)$$