

## Chlorite Kinetics and Impact on EGS-CO<sub>2</sub>

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### Keywords

*Engineered geothermal systems-CO<sub>2</sub> (EGS-CO<sub>2</sub>), geothermal mineral kinetics, chlorite kinetics, scaling, mineral alteration*

### ABSTRACT

Although CO<sub>2</sub> has been identified as a possible option for use in enhanced geothermal systems (Pruess, 2006), its effect on mineral alteration reactions and/or scaling in these systems is not currently well-constrained. Model results investigating a CO<sub>2</sub>-rich natural analog site (the Ohaaki-Broadlands system, New Zealand) suggest that elevated levels of aqueous CO<sub>2</sub> cause relatively rapid and extensive dissolution of chlorite (and other sheet silicate minerals), accompanied by recrystallization of carbonates. These simulations were performed using available low-temperature kinetic data for chlorite (Palandri & Kharaka, 2004) which were then extrapolated to the higher temperatures of the geothermal system. However, our experiments have shown that measured chlorite dissolution rates at higher temperatures (100-280°C) and CO<sub>2</sub> concentrations are several orders of magnitude slower than the extrapolated rates. A larger experimental dataset is being collected to quantify the exact mechanisms influencing chlorite dissolution rates, but we currently find that the use of low-temperature kinetics data for chlorite (and possibly other sheet silicates for which higher-temperature dissolution data are lacking) may result in significantly higher predictions of mineral alteration.

### Introduction

The use of supercritical CO<sub>2</sub> as a working fluid for enhanced geothermal systems (EGS) has been previously evaluated by others (Brown, 2000; Pruess, 2006) who concluded that the lower viscosity and increased buoyancy of CO<sub>2</sub> make it an appealing choice as a heat-exchange fluid in EGS. Especially in arid regions such as the western United States, the substitution of supercritical CO<sub>2</sub> as a heat transmission fluid in place of water could provide an attractive method for developing geothermal energy prospects. In such projects, any operational losses of CO<sub>2</sub> could potentially be

captured in the short-term as a dissolved phase in deeper groundwaters, or even sequestered as a solid mineral phase. A more thorough understanding of the geochemical behavior of supercritical CO<sub>2</sub>-rock-water interactions will be crucial for predicting the storage or transport of CO<sub>2</sub> in EGS reservoirs and the resulting porosity evolution over longer timespans. However, as noted by Pruess (2006), significant gaps exist in our knowledge of relevant mineral kinetics under the expected pressure, temperature, and geochemical conditions of CO<sub>2</sub>-EGS sites. Accordingly, we have initiated experimental studies, coupled with and informed by concurrent modeling efforts (see Wolery & Carroll, 2010) with the goal of describing the dissolution rate and kinetics of chlorite, a Mg- and Fe-bearing sheet silicate present in many geothermal reservoirs.

Modeling work by Xu et al. (2005) and Wolery & Carroll (2010), as well as more recent work involving CO<sub>2</sub>-sandstone-shale-water reactive experiments (Carroll et al., in review) strongly suggest that chlorite minerals are among the phases most susceptible to CO<sub>2</sub>-driven dissolution, and that this process is an important source of metal ions which may form secondary carbonate minerals, potentially affecting resulting reservoir performance via generation of scale minerals. Although some kinetic data exist for chlorite at sub-100°C temperatures (e.g., Palandri & Kharaka, 2004, and references therein), our experiments encompass a wider and more applicable range of temperatures (100-280°C) and pCO<sub>2</sub> conditions (up to supercritical CO<sub>2</sub> saturation at each temperature) for geothermal environments. In this work, we aim to identify and model relevant consequences of CO<sub>2</sub>-rock-water interactions in a hypothetical EGS-CO<sub>2</sub> scenario using existing kinetic data, and to simultaneously develop and constrain a chlorite dissolution rate equation (dependent on pCO<sub>2</sub>, pH, and temperature) to further hone predictive capabilities.

### Modeling Efforts

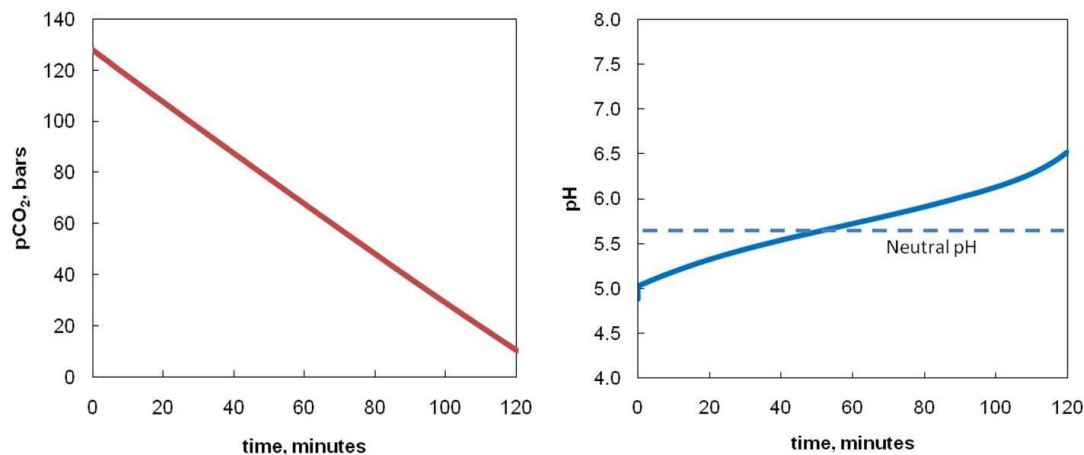
Wolery and Carroll (2010) conducted a series of thermodynamic calculations examining the stability of major minerals representing the greywacke basement of the Ohaaki Broadlands geothermal field, New Zealand, as a natural analog for a CO<sub>2</sub>-enriched or potential CO<sub>2</sub>/EGS environment. Various mineral

assemblages were equilibrated with reconstructed deep basement water containing 0.6m CO<sub>2</sub>, 0.004m H<sub>2</sub>S, and roughly 0.05m NaCl salinity, following Hedenquist (1990). A primary conclusion of this modeling study was that the mineral assemblage quartz-albite-K-feldspar-pyrite was largely unreactive up to 300°C in the presence of the high CO<sub>2</sub> water, and remained close to calcite equilibrium. However, the addition of a chlorite or mica mineral to the assemblage initiated extensive reaction and formation of smectite and/or illite clays. In general, CO<sub>2</sub> was not consumed in these reactions, and carbonate mineral formation was absent. The pH generally remained above neutral pH for this temperature, though it was reduced slightly by the addition of CO<sub>2</sub> (a weak acid at 300°C).

New efforts have expanded these models to take into account representative mineral proportions, and to include mineral kinetics to reconstruct a time scale over which reaction might occur. To obtain a better sense of the reaction of high CO<sub>2</sub> water with these constitutive greywacke minerals (quartz, albite, muscovite, K-feldspar, chlorite, biotite, pyrite, and calcite), we performed kinetic simulations over 100-300°C and up to 400 days using EQ3/6 software (version 8.0b), the same thermodynamic database used by Wolery and Carroll (2010), and kinetic rate law data drawn from Palandri and Kharaka (2004). The CO<sub>2</sub> level was deliberately doubled to 1.2m (a high value likely to bound results expected in an EGS-CO<sub>2</sub> system).

These new simulations were made for temperatures of 100, 200, and 300°C. Only partial results (200°C simulations) are presented here, and they are mainly intended to illustrate the effect of chlorite (ripidolite) as a key reactive phase.

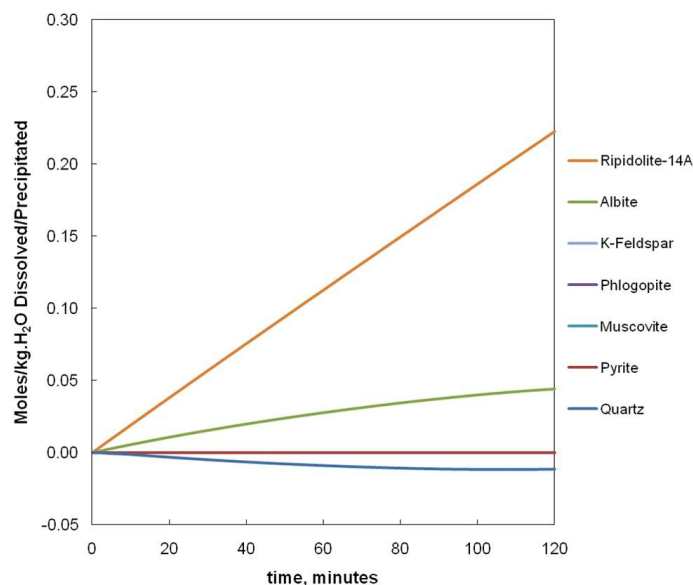
We caution that the results of these runs should not be interpreted overly quantitatively; instead, they are useful mainly for recognition of important reactions and identification of potentially influential data gaps. The kinetic data inputs summarized by Palandri and Kharaka (2004) represent only a “best available” understanding of dissolution rates. For most minerals (including chlorite), they are calibrated against experimental data for temperatures below 100°C. Kinetic data for mineral precipitation are mostly lacking, and precipitation therefore is controlled by partial equilibrium in the simulations. We note that there are also issues with the thermodynamic data, notably how accurate they are at high temperature for smectite clays (see Wolery and Carroll, 2010).



**Figure 1.** pCO<sub>2</sub> (left) and pH (right) in the first 120 minutes of reaction at 200°C. The decrease in pCO<sub>2</sub> correlates with the consumption of CO<sub>2</sub> in reaction.

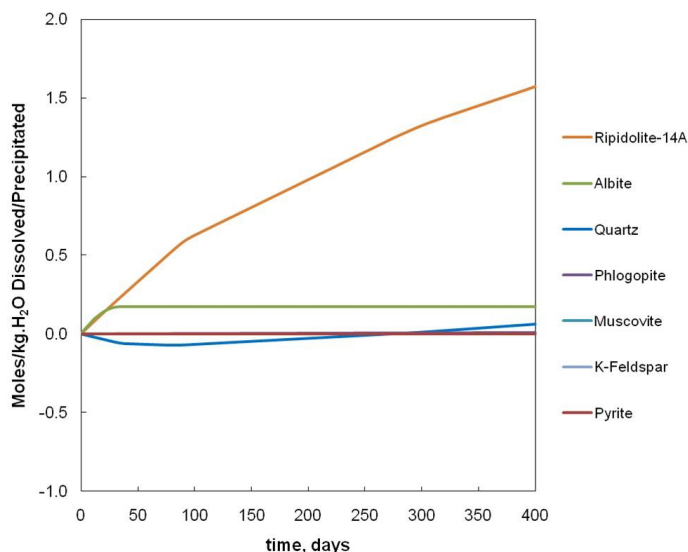
A major feature in these simulations is increase in pH and decrease in pCO<sub>2</sub> (proportional to CO<sub>2(aq)</sub>) as CO<sub>2</sub> reacts with minerals. This is shown in Figure 1 for the 200°C simulation; changes occur more slowly at 100°C and faster at 300°C. At 200°C, CO<sub>2</sub> consumption is largely complete with 120 minutes.

A major mineralogical consequence of CO<sub>2</sub> addition is the rapid (~200 minute) recrystallization of the original pure calcite to impure calcite ((Ca,Mg,Fe)CO<sub>3</sub>). In these simulations, there is a net gain in total solid carbonate owing to the release of Mg and Fe from dissolving silicates, notably ripidolite and phlogopite (biotite). Figure 2 shows the cumulative dissolution/growth of original minerals (excluding calcite) in the first 120 minutes at 200°C. For all minerals shown in this figure, rate law control applies. Dissolution of original calcite is the most rapid, but this is not shown as it is of much greater magnitude (and it is balanced by the formation of “new” impure calcite). Of the remaining minerals, ripidolite is dissolving the most quickly, followed by albite. Quartz precipitates due to a supersaturation caused by the addition of CO<sub>2</sub>, while other minerals behave inertly by comparison.



**Figure 2.** Starting mineral dissolution according to rate law control in the first 120 minutes of the 200°C simulation. Calcite dissolution/precipitation not shown here (see text).

Figure 3 demonstrates dissolution/growth of the starting minerals under rate law control over a longer timescale of 400 days (at 100°C, as opposed to the earlier plots). Albite saturates early (resulting in the flattened curve), while ripidolite dissolution is prominent, extending over the full time period shown. Original calcite



**Figure 3.** Dissolution/growth of minerals under rate law control for the first 400 days at 100°C. Calcite dissolution/recrystallization is again omitted (see text).

rapidly dissolves and is also rapidly reprecipitated (or as we interpret, recrystallized) into a less pure,  $\text{Ca}(\text{Mg,Fe})\text{CO}_3$  form, thus its transformation is not shown in Figure 3.

These selected results illustrate that the reaction of high  $\text{CO}_2$  water with common reservoir is a complex process, with different time scales applying to different minerals. Using existing kinetic data, however, it is clear that geochemical modeling predicts ripidolite dissolution to be a major (even dominant) factor that could compromise a  $\text{CO}_2/\text{EGS}$ . Given these results, we emphasize the need for reliable sheet silicate kinetic data obtained at relevant geothermal temperatures in order to make more confident predictions of mineral reactivity and porosity evolution. The experiments discussed below are designed to fill an existing data gap for chlorite, a common secondary mineral often identified in geothermal systems.

## Materials & Methods

Bulk chlorite samples (CCa-2) from Flagstaff Hill, El Dorado County, California, were obtained from the Source Clays Repository (Purdue University, IN). These samples were crushed and sieved to obtain the 150-250 micron fraction. Triple-point BET surface area analyses using  $\text{N}_2$  gas provided a specific surface area estimate of  $5.462 \pm 0.092 \text{ m}^2/\text{g}$ . Several splits were analyzed by x-ray diffraction to confirm the sample was a nearly pure chlorite most closely described as a clinocllore (a Mg-rich  $(\text{Mg,Fe,Mn})_5\text{Al}(\text{Al,Si})_3\text{O}_{10}(\text{OH})_8$  variety).

Sodium chloride ( $\text{NaCl}$ , 99.5% purity; EMD Chemicals) was used to prepare 0.05M  $\text{NaCl}$  solutions in water for all experiments. Solution aliquots were collected prior to and after each experiment to provide blank corrections for experimental samples. Both liquid and gaseous  $\text{CO}_2$  were used under pressure to force supercritical  $\text{CO}_2$  equilibrium with the prepared  $\text{NaCl}$  solutions over experimental temperatures of 100-280°C.

The experimental systems utilized ~300mL titanium mixed-flow reactors (e.g., Dove & Crerar, 1990) containing at least

one gram of chlorite solids. The reactor vessels were fed  $\text{CO}_2$ -equilibrated aqueous solutions through Hastelloy C276 tubing and fittings at a constant 0.5mL/min flowrate by pulseless dual-piston pumps drawing fluid from separate static titanium reactor vessels where 0.05M  $\text{NaCl}$  solutions were maintained at equilibrium with supercritical  $\text{CO}_2$  at desired pressures and temperatures. The volume of the static system determined the maximum length of the experiment (approximately 75 hours). Reactor vessel pressure was maintained using a back-pressure regulator from which aqueous fluids were extracted through a sampling port. Reactor vessels were always maintained at equal or lower temperatures and equal or greater pressures than the static vessels, to ensure that no  $\text{CO}_2$  degassing en route to the chlorite solids. Through manipulation of pressure and temperature in the static vessel (containing the  $\text{NaCl}$  solution and supercritical  $\text{CO}_2$ ), we were able to produce input solutions containing up to 0.52M  $\text{CO}_{2(\text{aq})}$ ; however, at higher temperatures,  $\text{CO}_{2(\text{aq})}$  content was limited to lower concentrations by experimental constraints.

Degassed samples were analyzed for Al, Ca, Mg, Mn, Ni, Si, and other elements by ICP-AES, and samples collected in 1N  $\text{NaOH}$  with gas-tight syringes were analyzed by infrared carbon analyzer to determine carbon content of the solutions. Additional  $\text{NaOH}$ -extracted samples were also collected from a sampling port upstream of the reactor vessel to confirm  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibrium and monitor  $\text{CO}_2$  input over the duration of each experiment. Speciation, saturation indices, and pH of these samples were calculated using EQ3/6 and the expanded “geo” database including data for a wide variety of sheet silicates including several clays (Wolery & Jarek, 2003; Wolery & Jove-Colon, 2007).

## Experimental Results & Discussion

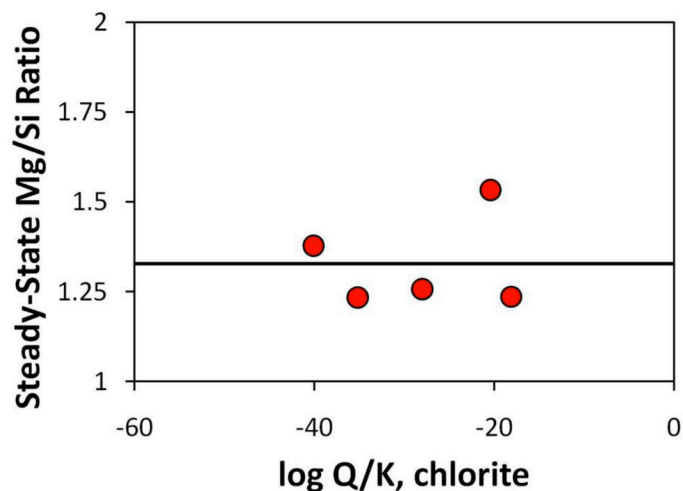
At present, complete datasets are available for only 5 of the total planned kinetics experiments; these current datasets encompass  $\text{CO}_{2(\text{aq})}$  concentrations up to 0.55M and temperatures up to 200°C. A large range of experimental conditions are needed to accurately quantify the interrelationship of temperature,  $\text{CO}_2$  concentrations, and pH (affected by both  $\text{CO}_2$  and temperature) to the dissolution rate. Our completed experimental studies will span temperatures from 100-280°C and  $\text{CO}_{2(\text{aq})}$  concentrations up to ~0.6M. At this point we hypothesize, based on kinetic studies of other silicates (e.g., Carroll & Knauss, 2005; Gustafsson & Puigdomenech, 2003; Oelkers, 2001), that the rate equation under far-from-equilibrium conditions may take the simplified form:

$$\text{Rate} [\text{mol s}^{-1}] = k \times [\exp(-E_a/RT)] \times (a_{\text{H}^+})^n$$

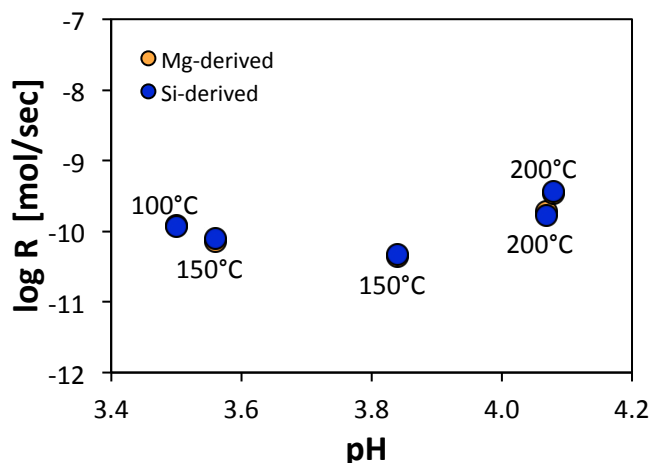
where  $k$ , the reaction rate constant, depends on both the temperature  $T$  and the pH of the system to some degree  $n$ .  $R$  represents the universal gas constant. As more experimental data is collected, additional terms may be required to describe relevant phenomena. At the present time, we are able to calculate only preliminary rates based on the available data, but comparison of these initial values with previously published low-temperatures already reveals discrepancies.

Steady-state elemental release rates of both Mg (assumed to occupy primarily octahedral sites in the chlorite structure) and Si (assumed to occupy tetrahedral sites) were observed from between 30 and 40 hours of reaction to the end of each experiment. As a

result, 3-5 data points per experiment were available for use in dissolution rate calculations. Figure 4 demonstrates that the stoichiometric ratio of Mg/Si remained relatively constant (average = 1.33) over all currently analyzed experiments conducted at far-from-equilibrium conditions, demonstrating congruent dissolution of chlorite. This Mg/Si ratio was then used in conjunction with XRF data to normalize elemental release rates to moles of chlorite solid.

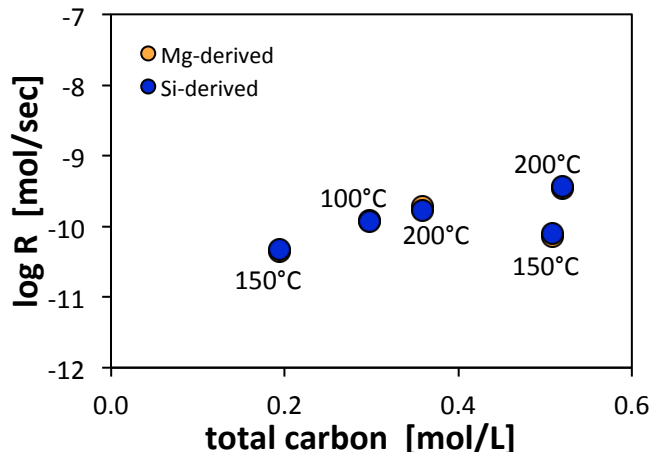


**Figure 4.** Ratio of Mg to Si steady-state molar concentrations versus log (Q/K) chlorite (negative values indicate increasing distance from thermodynamic equilibrium) for 5 completed experiments (1 experiment at 100°C, and 2 each at 150°C and 200°C). The average ratio of 1.33 is shown as a bold line.



**Figure 5.** Log chlorite dissolution rate [mol/sec] versus steady-state pH, for five completed experiments.

Solution chemistry and total carbon data were used to calculate corresponding solution pH values at the *in situ* pressures and temperatures of the reactors. Chlorite dissolution rates obtained from Mg and Si data are displayed versus estimated *in situ* pH (Figure 5), and versus total dissolved carbon content (Figure 6). As noted in our model simulations, acidity increases with decreasing temperature, but the overall relationship among temperature, pH,  $[\text{CO}_2]$ , and dissolution rate cannot be fully elucidated with this partial dataset. Our efforts are currently focused on obtaining rate data under conditions of various  $\text{CO}_{2(\text{aq})}$  concentrations at the



**Figure 6.** Log chlorite dissolution rate [mol/sec] versus steady-state measured total carbon, for five completed experiments.

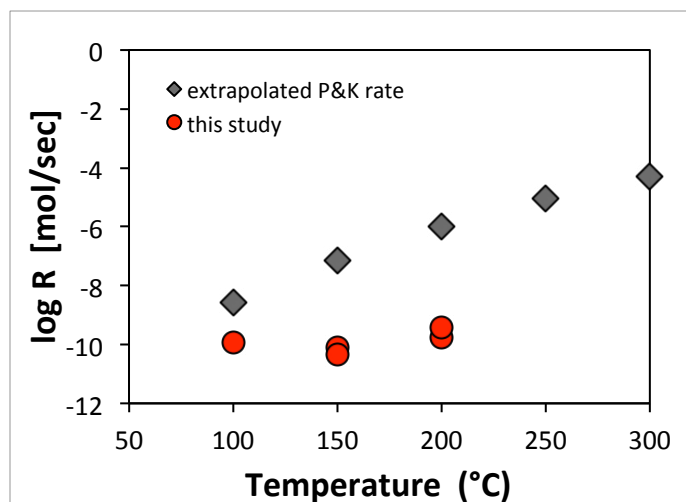
temperatures shown in Figures 5 and 6, as well as data at higher temperatures (up to 280°C).

Using the available data from our chlorite characterization and kinetic experiments, as well as the constants compiled by Palandri and Kharaka (2004) from studies conducted at 25-90°C (see Table 1), we show in Figure 7 that the extrapolation of the existing low-temperature data to our experimental temperatures and pH values tends to overestimate the rate of chlorite dissolution

**Table 1.** Values for chlorite rate extrapolation.

Parameter	Value	Reference
Specific surface area	5.492 m <sup>2</sup> /g	this study
Steady-state pH	3.5-4.2	this study
Activation energy	88 kJ/mol*	Palandri & Kharaka, 2004
Log k, acid mechanism	-11.1	Palandri & Kharaka, 2004
n, acid mechanism	0.5	Palandri & Kharaka, 2004
Log k, neutral mechanism	-12.52	Palandri & Kharaka, 2004

\*The activation energy is equal for both acid and neutral mechanisms.



**Figure 7.** Log chlorite dissolution rates (mol/sec) versus temperature. Extrapolated data were obtained by applying our experiment-specific parameters (surface area and pH) to the rate formulation obtained from Palandri & Kharaka's (2004) compilation. Differences in rates resulting from variation in pH or surface area are smaller than the symbols.

by 2-4 orders of magnitude. Our earlier modeling efforts (using this same kinetic data) linked the extensive recrystallization of existing calcite to the production of Mg and Fe ions produced through chlorite and other sheet silicate dissolution. If in fact the rate of Mg/Fe cation release is slower than predicted at these typical geothermal reservoir temperatures, then impacts of mineral alteration on geothermal performance could be significantly less than predicted using current kinetic data.

## Conclusions

Current experimental results suggest that mineral alteration will play a much smaller role in the EGS-CO<sub>2</sub> environment than suggested when low temperature-derived mineral rate equations are used in simulations. Chlorite dissolution is predicted to drive the alteration of greywacke rocks in the Broadlands-Ohaaki, New Zealand geothermal system. However, new dissolution data from this study at conditions representative of EGS-CO<sub>2</sub> environments show that the rates are orders of magnitude slower. The much slower chlorite dissolution rates should lead to less mineral alteration and lower the probability of mineral scaling in water-dominated regions. Additional experiments are underway to develop a robust rate equation to be applied to EGS-CO<sub>2</sub> simulations to more fully understand the role that mineral alteration will play in these environments.

Significantly lower chlorite dissolution rates measured in this study also call into question the suitability of using rate data for other sheet silicates that have also been largely derived from low temperature data.

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