Rates of Mineral Dissolution under CO₂ Storage Conditions

Jay R. Black^{a,b*}, Susan A. Carroll^c and Ralf R. Haese^{a,b}

^aCooperative Research Centre for Greenhouse Gas Technologies, CO2CRC

^bPeter Cook Centre for CCS Research, School of Earth Sciences, The University of Melbourne, VIC 3010, Australia

^cLawrence Livermore National Laboratory; Livermore, CA 94550 USA

* corresponding author:

Email: jay.black@unimelb.edu.au

Phone: +61 3 90355218

Abstract (217 words)

Evaluating the potential of a sedimentary basin reservoir to securely store CO₂ benefits from a comprehensive understanding of the geochemical reactions that take place once CO₂ is injected into a formation. In particular, models that predict the transport and reaction of CO₂ within a reservoir require a definition of the types of reactions affected by enhanced levels of CO₂ and how the kinetics of these reactions will affect a heterogeneous mineralogy and formation waters within a reservoir over time. In this review we evaluate rate models used to describe mineral dissolution kinetics and compare the range in values reported for the kinetic parameters used to describe the reactivity of various minerals relevant to mainly siliciclastic reservoirs. Parameters that have a significant impact on model results include the reactive surface area of a mineral, the apparent activation energies used to extrapolate reaction rates to the temperatures of potential storage reservoirs (c. 50-125°C) and the in-situ pH of formation waters with elevated concentrations of dissolved CO₂. The variation in reported values for these parameters can lead to predicted rates that span many orders of magnitude for a given mineral. Despite these uncertainties recent success with geochemical models has been made by applying a Monte Carlo approach to optimise the kinetic parameters for minerals where robust thermodynamic and kinetic data do not exist.

1. Introduction

Major changes to current energy technologies are required to mitigate rising CO₂ levels in the atmosphere. Carbon capture and storage (CCS) has been identified as a key technology to reduce CO₂ emissions which are estimated as c. 30 gigatonnes of CO₂ per year through the burning of fossil fuels (IEA, 2012). CCS can be implemented at a scale suitable for reducing the emissions of large point sources such as power plants, but high costs and concerns about the long-term containment of CO₂ in the storage reservoir have limited the global deployment of CCS (GCCSI, 2012).

The geologic storage of CO₂ occurs naturally during the process of chemical weathering of surface terrains and influences rates of erosion and element fluxes in the environment (Navarre-Sitchler and Thyne, 2007), but this occurs on a slow time scale compared to anthropogenic emission rates and is balanced by other geologic processes that influence the C-cycle and atmospheric CO₂ concentrations (Torres et al., 2014). Storage of CO₂ by burial, through injection into deep (> 800 m depth) reservoirs, offers in principle an effective means for offsetting emissions of CO₂. A range of assessments are required to develop a detailed understanding of subsurface conditions at basin, sub-basin and site specific scale and to evaluate the suitability for CO₂ storage (Carpenter et al., 2011). Safe long-term containment of CO₂ in targeted subsurface reservoirs is a critical objective and is partly tested through predictive modelling simulating the mobility and reactivity of CO₂.

Changes to the geochemistry of a saline reservoir upon injection of supercritical CO₂ for storage purposes include: 1) acidification of formation waters due to CO₂ dissolution; 2) buffering of formation water pH by carbonate and silicate mineral dissolution; 3) precipitation of secondary mineral phases, including secondary carbonates that contribute to the long-term storage of CO₂ in a formation. The effect of mineral dissolution and precipitation on the properties of a reservoir, the overlying caprock and wellbore integrity are some of the key questions that need to be addressed when assessing the integrity and mineral trapping potential of a reservoir, and thus in part the capacity to securely store CO₂. Central to understanding the geochemical

1 response are the development of kinetic rate laws that tie mineral dissolution to solution
2 composition, temperature, and mineral solubility.

3
4 In this manuscript we present some of the key points on the use of kinetic data
5 for geochemical modelling purposes for the broad audience working in this field, and
6 plot some of the range in uncertainty in kinetic input parameters used for predicting
7 mineral dissolution rates under CO₂ storage conditions. The following section
8 summarises the principle CO₂-fluid-rock/mineral interactions in a reservoir to place the
9 importance of modelling mineral dissolution in the context of CO₂ storage.

10 11 *1.1 Processes controlling the chemistry at CO₂-water-rock interfaces*

12 The injection of supercritical CO₂ (sc-CO₂) into the pore space of a target storage
13 reservoir will lead to a range of chemical and physical processes changing the fluid
14 chemistry and the mineralogy of the reservoir. The following zones within a reservoir
15 and the associated processes have received particular attention and are illustrated in
16 Figure 1:

- 17
18 1) Near the point of injection of dry sc-CO₂, pore space is dehydrated due to the
19 slight solubility of H₂O in the sc-CO₂ plume (c. 0.5% at 60°C and 100 bar,
20 (Spycher et al., 2003)). Dehydration of saline groundwater leads to an increase in
21 the dissolved solid concentration and may cause the precipitation of salts and
22 other minerals near a well-head (Kim et al., 2013; Zeidouni et al., 2009).
- 23
24 2) Following the injection of CO₂ into a water saturated reservoir, water re-invades
25 the pore space within the plume footprint. The pore space is filled with residually
26 trapped sc-CO₂ surrounded by CO₂-saturated water forming a low-pH
27 environment. The magnitude of carbonate mineral trapping capacity is dependent
28 on the formation water composition and the variety of reactive minerals within a
29 reservoir (Gilfillan et al., 2009; Xu et al., 2005; Yang et al., 2014).

- 1 3) The direct contact of wet sc-CO₂ with mineral interfaces may lead to mineral
2 replacement reactions (Kwak et al., 2011) or corrosion and replacement
3 reactions within wellbore cements (Kutchko et al., 2007; Mason et al., 2013).
4 Kaolinite has been observed to be enriched in the gas leg of a natural gas
5 accumulation with intermediate (29-56 mol%) CO₂ concentrations compared to
6 the zone below the gas-water interface (Higgs et al., submitted). As sc-CO₂ acts
7 as a non-polar solvent the sc-CO₂ plume can be enriched in compounds such as
8 residual hydrocarbons (Monin et al., 1988). It may also contain trace levels of gas
9 impurities (e.g. SO_x, NO_x and O₂), if they were not fully removed during the
10 capture process (Ellis et al., 2010).
11
- 12 4) At the sc-CO₂-water interface CO₂ is continuously dissolving in formation waters
13 through a diffusive boundary layer (Riaz et al., 2006). The density of formation
14 waters increases as the water becomes enriched in CO₂, leading to an inverse
15 density stratification that will destabilise over time (Riaz et al., 2006). The CO₂-
16 enriched water sinks and sustains convective mixing in the reservoir (Ennis-King
17 and Paterson, 2007). Importantly for the water composition and respective fluid-
18 rock reactions, due to mixing CO₂ only reaches a concentration of about 2 wt%
19 as compared to a CO₂ solubility of 4 to 5 wt% (Gasda et al., 2011). The CO₂
20 dissolution flux after boundary layer destabilisation has been estimated to be
21 about 10% of the CO₂ injection rate at the Sleipner injection site (Neufeld et al.,
22 2010). Dissolution of the impurity SO₂ at the sc-CO₂-water interface has also
23 been shown to be diffusion-limited, thus enhanced acidification of formation
24 waters due to SO₂ hydrolysis to form sulphurous acid or oxidation to form
25 sulphuric acid may be restricted to the diffusive boundary layer (Ellis et al., 2010).
26
- 27 5) Fluid-rock reactions driven by the acidification of formation waters enriched in
28 CO₂ may occur within the zones of downward advecting fingers. Contrary to the
29 plume forefront (zone 2, Figure 1), the maximum CO₂ enrichment is only around
30 half the CO₂-saturated water zone (see above) and it is temporally and spatially
31 dynamic. Flushing of pore space with fresh fluids may drive mineral

dissolution/precipitation processes, which are controlled by surface reaction kinetics rather than fluid transport processes. Lithological heterogeneity, specifically the variability in permeability and mineralogy greatly affects reservoir hydrodynamics and thus the spread of a plume and subsequent geochemical reactions. Interbedded baffles typically contain a larger fraction of reactive clay minerals and represent significant zones involving carbonate mineral precipitation (Carroll et al., 2011; Higgs et al., 2013).

In this review we focus on interactions between CO₂-enriched fluids and siliciclastic reservoir minerals, and some mafic minerals relevant to different CO₂ storage scenarios, and aim to present an overview of studies investigating the rates and mechanisms governing these processes. Our goal is to highlight the important implications arising from these studies towards integrating geochemical kinetics into predictive geochemical models.

2. Modelling mineral dissolution rates

The connection between the dissolution of minerals in a storage reservoir supplying cations for the precipitation of secondary carbonate phases over time has been clearly demonstrated in a number of modelling studies (Gaus et al., 2005; Hellevang et al., 2013; Pham et al., 2011; Xu et al., 2004). Predicting the effective mineral trapping capacity of a reservoir requires an adequate description of the reaction kinetics of various mineral phases, as different analytical descriptions of dissolution and precipitation mechanisms can lead to dramatic changes in the onset of mineral precipitation and the rate of mineral dissolution (Hellevang et al., 2013). Hellevang et al. (2013) review reaction-path modelling approaches using various assumptions regarding equilibrium and kinetic regimes and recommend that dissolution and precipitation reactions should be decoupled, because the mechanisms are inherently different and that simple first-order decay equations should be used to describe the dissolution of undersaturated minerals where these minerals are dissolving within a far-from-equilibrium regime.

A potential problem arising from these recommendations is that the reaction rates are no longer tied to mineral equilibrium and simple decay equations neglect potential catalytic/inhibitory effects on the dissolution rates of undersaturated mineral phases, complicating the dissolution mechanism. Many studies have shown that dissolution rates are dependent upon a solutions saturation state relative to a dissolving phase, with various empirical rate laws being proposed to describe the decrease in dissolution rate closer to equilibrium conditions (Burch et al., 1993; Nagy et al., 1991; Oelkers et al., 1994; Palandri and Kharaka, 2004). These effects are illustrated in a general rate law (Equation 1) for heterogeneous mineral dissolution (Lasaga, 1998):

$$\text{Rate} = \text{RSA} \cdot k^0 \cdot e^{-E_A/RT} \cdot \prod_i a_i^{n_i} \cdot f(\Delta G) \quad (1)$$

Where, RSA = reactive surface area

k^0 = standard rate constant

E_A / RT = apparent activation energy divided by gas constant and temperature

$a_i^{n_i}$ = activity of aqueous species, i, to the power of n

$f(\Delta G)$ = function of the thermodynamic potential or driving force

The development of this general rate law from transition state theory (TST) is reliant on an accurate description of the elementary processes underlying the dissolution mechanism and a statistical mechanical treatment of activated complex formation and destruction (Aagaard and Helgeson, 1982; Lasaga, 1981). Assumptions about this underlying mechanism lead to the general form presented (Equation 1) and relate the thermodynamic driving force for an overall reaction (incorporated in the $f(\Delta G)$ function) to one or more parallel elementary processes, either at steady state or with a single rate determining step, describing a reaction mechanism. Reaction mechanisms where multiple elementary processes simultaneously affect the observed rate can lead to more complex rate laws (Equation 2, (Nagy et al., 1991)):

$$Rate_{overall} = -k_+^2 \cdot [D] \cdot [E] \cdot \frac{1+\gamma}{2\gamma} \left(1 - \left(1 - \frac{4\gamma}{(1+\gamma)^2} \cdot [1 - \exp(\Delta G_r^o / R \cdot T)] \right)^{1/2} \right)$$

$$\text{where, } \gamma \equiv \frac{k_+^2 \cdot [D] \cdot [E]}{k_+^1 \cdot [A] \cdot [B]} \quad (2)$$

Add to this the complexity needed to describe the density of specific adsorbed species to reactive surface sites, thus replacing the activity term in Equation 1 with an adsorption isotherm (Ganor and Lasaga, 1998; Stillings and Brantley, 1995), and developing a detailed description of mineral dissolution, in the heterogeneous mineral assemblage of a storage reservoir, becomes an enormous task. Much of the experimental data and a fundamental understanding of specific reaction mechanisms are incomplete or inadequate to accurately describe the long-term evolution of the geochemistry in a storage reservoir. In particular very few studies have investigated the potential for direct mineral carbonation taking place via replacement reactions where the wet sc-CO₂ phase contacts a mineral interface. All this being said, great progress has been made towards understanding some of the most fundamental water-rock interactions (Brantley et al., 2008; Lasaga, 1998; Oelkers and Schott, 2009; Ohlin et al., 2010) and theoretical methods utilising computational approaches for studying interface problems are becoming a standard in geochemical modelling (Lasaga and Luttge, 2001; Nielsen et al., 2012; Rustad and Casey, 2012).

In the following sections we review the effect of various parameters describing mineral dissolution rates as described by dissolution mechanisms arising from the standard form of the rate equation (Equation 1). The specific example of chlorite dissolution is used to highlight issues that may arise from the arbitrary choice of kinetic parameters from multiple sources, and the complication of modelling dissolution where multiple surface mechanisms affect rates. Precipitation rates and nucleation processes pose even more complex mechanisms (Burton et al., 1951; Lasaga, 1998; Morse and Casey, 1988) and a review of these processes is beyond the scope of the discussion here, but important for determining mineral trapping capacity and precipitation rates under CO₂ storage conditions (Hellevang et al., 2013; Pham et al., 2011).

2.1 Effect of pressure and temperature

There are a number of parameters in the general rate law describing mineral dissolution rates (Equation 1) that are dependent on the sub-surface conditions of a target storage reservoir. Rate constants are pressure and temperature dependent, as are the equilibria describing species activities that may be important to a specific dissolution mechanism.

The rate constant as defined in Equation 1, k^0 , is specified for some standard state (e.g. pressure = 1 bar; temperature = 0°C). Extrapolation of the rate constant to the appropriate temperature in a reservoir is done via an Arrhenius relationship with the apparent activation energy for the process (E_A) in the exponential term, thus leading to dissolution rates increasing with increasing temperature. This is illustrated in Figure 2, which plots calculated rates at three different temperatures relevant to CO₂ storage reservoirs relative to predicted rates at 25°C as a function of apparent activation energy. Most sedimentary storage reservoirs range between 50 to 125°C, and as Figure 2 shows the larger the apparent activation energy for a dissolution process is, the larger the predicted rate once extrapolated to higher temperatures. The apparent activation energy for a dissolution process, far from equilibrium, is also dependent upon the specific dissolution mechanism as will be elaborated on in Section 2.3. Figure 3 plots the range of reported apparent activation energies determined for minerals relevant to primarily siliciclastic reservoirs, showing a significant range of uncertainty for specific acid or neutral dissolution mechanisms (see Section 2.3 for discussion on the effect of pH). For the purpose of illustration we consider the range of apparent activation energies reported for layered silicate minerals. Apparent activation energies for the acid mechanism tend to cluster around 20 kJ/mol, but are also reported at much higher values near 60-80 kJ/mol (Figure 3). Such variance in the apparent activation energy could lead to rates that differ by more than 10 to 100 times when extrapolated to 60 and 125°C (Figure 2).

Pressure may also have an effect on rate constants where formation of an activated complex is associated with a large change in activation volume. However, for aqueous kinetics over a pressure range of a few kilobars (greater than the variation in

target reservoirs) this leads to less than an order of magnitude difference in the rate constant (Lasaga, 1998; Schott et al., 2009). This is further supported by the concluding remarks of Aagaard and Helgeson (1982) stating that the volume of activation and standard molal heat capacity for the formation of activated complexes is likely to be negligible. Thus, pressure effects are largely absorbed by other uncertainties and various studies have shown that $p\text{CO}_2$ (over a 200 bar range) has little effect on dissolution rates beyond the associated shift due to changes in solution chemistry (Black and Haese, 2014; Smith et al., 2013b).

2.2 Effect of reactive surface area on mineral dissolution rates

The general rate law presented in Equation 1 is directly proportional to the reactive surface area (RSA) of a mineral exposed to fluid. Thus most rate data are reported normalised to a measured surface area, generally the specific surface area as measured by methods of BET analysis (Brunauer et al., 1938). Other methods, such as estimating specific surface area using geometric techniques, yield results for the specific surface area of a mineral sample that may be orders of magnitude different (Black and Haese, 2014; Golubev et al., 2009; Pokrovsky et al., 2005). However, specific surface areas, as reported by BET analysis, may not be the best representation of reactive surface area, and normalising rates to a specific surface area can also be complicated by changes to this property over the course of experiments (Metz et al., 2005; Stillings and Brantley, 1995), and by freshly ground versus weathered mineral surfaces (Anbeek, 1992a; Anbeek, 1992b). For example, Metz et al. (2005) demonstrate that the measured specific surface area of smectites can vary significantly before and after conducting dissolution experiments, and that the effective reactive surface area may be better described as the specific surface area relating to exposed edge sites upon which dissolution proceeds. These complications are discussed in detail by Brantley and Chen (1995) who present a review of pyroxene and amphibole weathering rates. Brantley and Chen show that the widely used assumption that rate scales proportionally with surface area, as indicated by Equation 1, is not always implicitly tested in experimental studies, and in some cases this assumption is invalidated when put to the test (e.g. Zhang et al. (1993)). Thus, whether or not

dissolution rates scale proportionally with surface area should be evaluated on a case-by-case basis for different mineral phases and adds significant uncertainty to any description of mineral dissolution rates. For modelling purposes the sources used for specific surface areas (measured by BET or geometric methods) or adjustments made to describe the reactive surface area of a mineral should be detailed, so that estimates of surface area normalised rates between studies can be compared unambiguously.

A range of surface areas for different mineral phases of relevance to mainly siliciclastic storage reservoirs, are plotted in Figure 4. Measured specific surface areas (blue bars, Figure 4) are compared to reactive surface areas (green bars, Figure 4) reported in modelling studies used to adjust mineral reaction rates. The range of reactive surface areas reported vary by many orders of magnitude, in some cases encompassing measured specific surface areas for minerals, but often reactive surface areas are used that are orders of magnitude lower than the specific surfaces areas used to normalise dissolution rates in experiments. The RSA used in modelling is often a fraction of measured BET to account for observed discrepancies between the weathering rates of minerals in natural systems and laboratory experiments using processed mineral specimens (Brantley, 2003; Lüttge, 2005; White and Brantley, 2003), as highlighted in Figure 4. In some cases the definition for reactive surface area varies to that of the measured specific surface area, trying to account for the actual exposure of mineral surfaces within a fractured pore space (Sonnenthal and Spycher, 2001). Other experimental studies try to account for the actual reactive surface area by examining the role crystal structure plays in how dissolution proceeds on mineral surfaces (e.g. step-wave models, (Lasaga and Luttge, 2001)). As will be highlighted later (Section 4) the choice of an appropriate RSA for modelling purposes can be aided by an uncertainty analysis built into the modelling approach.

2.3 Effect of pH on mineral dissolution

The majority of reactive-transport studies for CO₂ storage cite Palandri and Kharaka (2004) as the main source for kinetic parameters used in a general rate law incorporating an acidic, neutral and alkali mechanism for dissolution (Equation 3):

$$Rate = -RSA \cdot \left[k_{H^+}^0 \cdot \exp\left(\frac{-E_{H^+}}{RT}\right) + k_{H_2O}^0 \cdot \exp\left(\frac{-E_{H_2O}}{RT}\right) + k_{OH^-}^0 \cdot \exp\left(\frac{-E_{OH^-}}{RT}\right) \right] \cdot f(DG_r)_i \quad (3)$$

Where there are three standard rate constants ($k_{H^+}^0$, $k_{H_2O}^0$, $k_{OH^-}^0$) and associated apparent activation energies (E_{H^+} , E_{H_2O} , E_{OH^-}) for proton enhanced, hydrolysis and hydroxyl enhanced dissolution mechanisms, each of which is modified by a different functional dependence as the dissolution reaction approaches equilibrium ($f(\Delta G_r)_i$, discussed in Section 2.5). For the purposes of modelling a CO₂ storage scenario parameters for the acid and neutral mechanisms may be the most pertinent given that pH under elevated CO₂ conditions will range anywhere from 3.5 to 6 depending upon the pressure, temperature and other dissolved solutes present.

Palandri and Kharaka (2004) provide an excellent resource of compiled kinetic parameters for use with Equation 3 for a range of minerals, and it is often used by modellers as an initial point of reference for kinetic parameters to incorporate into geochemical models (E.g. Xu et al. (2007)). For many minerals Palandri and Kharaka's (2004) compilation provides a robust description of dissolution rates under the acidic conditions most relevant to a CO₂ storage scenario, with chlorite being a notable exception. Detailed studies of chlorite dissolution over a broad range of pH by Lawson et al. (2007; 2005) led to kinetic parameters for an acidic, neutral and alkali mechanism being reported at 25°C, and the description of an underlying surface complex model describing a reaction mechanism controlled by the dissolved Al speciation. Marini (2006) compiles Lawson et al.'s (2005) reported rate constants with the apparent activation energy of 88 kJ mol⁻¹ from an acidic dissolution study by Ross (1967). However, plotting the results (Figure 5A) of combining this apparent activation energy with Lawson et al.'s (2005) reported rate constants shows that the model predicts chlorite dissolution rates orders of magnitude faster at higher temperatures (> 25°C) than experimentally observed (Lawson et al., 2007; Smith et al., 2013b). Kinetic parameters relevant to CO₂ storage conditions have been revised by Smith et al. (2013b) and Black and Haese (2014) to show that a much smaller apparent activation

energy adequately fits specific experimental studies (model by Smith and Carroll (2014) plotted in Figure 5B) in the acidic-neutral regime.

Care must also be taken when defining the standard states used when reporting parameters. Palandri and Kharaka (2004) report rate constants at 25°C and a pH = 0, whereas, in developing rate laws from TST the intrinsic rate constant or frequency factor (A) is extrapolated to a specific temperature and pH depending upon the form of the rate law (e.g., Equation 3). The magnitude of E_A (apparent activation energy) and A are correlated by the form of the rate law, and Figure 5 illustrates that the correction to the apparent activation energy for chlorite dissolution from 88 kJ mol⁻¹ to 24.9 kJ mol⁻¹ made by Smith and Carroll (2014) has also changed the optimised value of log₁₀(k_{H+}^0) from 5.63 to -5.52. Thus arbitrarily mixing kinetic parameters from various sources could lead to dramatic differences in calculated rates of dissolution, as illustrated in Figure 5A.

2.4 Surface complex phenomena and effects on mineral dissolution properties

Developing rate laws further to account for underlying reaction mechanisms often involves some description of the surface chemistry and a surface complex model to describe the formation and interaction of dissolved components with reactive surface sites (Blum and Lasaga, 1988; Ganor et al., 1999; Oelkers et al., 1994).

The influence of dissolved species on mineral dissolution can lead to enhancement or inhibition of dissolution rates (activity terms in Equation 1). Again, this is nicely illustrated with the case of chlorite dissolution. Hamer et al. (2003) measured the dissolution rate of a chlorite mineral as a function of pH by varying pH with various inorganic and organic acids. Figure 6 shows the relative chlorite dissolution rate dependence on various acids, with the organic acids (oxalic and citric) showing a stronger dependence on pH. These differences were interpreted by Hamer et al. (2003) as representing ligand promoted dissolution, and assuming chloride does not have an effect, a relative enhancement factor (in parentheses) that specific ligands have on the chlorite dissolution rate follow the order (Hamer et al., 2003):

nitrate	≡	chloride	≡	acetate	<	sulphate	<	citrate	<	oxalate
(0.97)		(1.00)		(1.01)		(1.19)		(2.70)		(3.27)

1
2 Brandt et al. (2003) also measured the dissolution of chlorite at 25°C as a
3 function of pH in solutions of HCl and their results plot with a shallower slope as a
4 function of pH than those of Hamer et al. (2003). These observations have important
5 implications to modelling dissolution rates in general as can be seen by the 2.5 log unit
6 difference in dissolution rate at pH 2 (Figure 6). Black and Haese (2014) expanded on
7 these observations to suggest that bicarbonate inhibits the rate of chlorite dissolution
8 and proposed a surface complex model whereby bicarbonate adsorbs to protonated
9 surface sites. The inhibition of the rate of chlorite dissolution in bicarbonate buffered
10 solutions is highlighted in Figure 6, where the measured rates by Black and Haese
11 (2014) at 80°C are slower or comparable to other experimental studies at 25°C and
12 have a weaker pH dependence than other anions. Some of the difference in dissolution
13 rates plotted in Figure 6 between separate studies may be explained by differences in
14 the BET surface area of processed mineral specimens used, Figure 4 illustrates the
15 range in reported BET surface area for chlorite.

16 These observations have important implications for modelling geochemical
17 kinetics under CO₂ storage conditions. For instance, if CO₂ is being injected with co-
18 contaminants such as NO_x or SO_x gases, disproportionation and/or oxidation may lead
19 to the formation of nitric and sulphuric acid, respectively. Nitric acid may not have an
20 appreciable effect on chlorite dissolution rates other than enhancing dissolution rate
21 with decreasing pH, whereas, dissolution rates may be enhanced to a greater extent by
22 the formation of sulphuric acid according to the above estimated relative enhancement
23 factor. However, if local formation waters have appreciable amounts of dissolved
24 bicarbonate buffering pH this may lead to chlorite having decreased reactivity. Building
25 these observations into a comprehensive rate model to describe the dissolution
26 properties of chlorite over a wide range of reservoir conditions would require
27 comprehensive data sets and rate laws describing the competition between proton and
28 ligand promoted dissolution. In Section 3.1 we discuss some relevant reaction
29 mechanisms proposed for specific mineral phases in cases where dissolved inorganic
30 carbon species play a role in the dissolution mechanism.

2.5 Saturation state effects on mineral dissolution rates

The importance of reaction mechanism/s can be further highlighted in considering the free energy dependence of reactions. Many studies have shown that minerals dissolve with a linear dependence on the $f(\Delta G_r)$ function (Equation 1) near equilibrium for specific mineral phases (Aagaard and Helgeson, 1982; Nagy et al., 1991; Rimstidt and Barnes, 1980). However, some minerals exhibit non-linear dependencies on the $f(\Delta G_r)$ term (Burch et al., 1993; Cama et al., 2000; Nagy and Lasaga, 1992). The nature of this dependence is controlled by the underlying reaction mechanism/s, and where non-linear effects are observed it is an indication of a changing reaction mechanism as a function of saturation state (Nagy and Lasaga, 1992). While non-linear effects have been modelled empirically using different functional dependencies of $f(\Delta G_r)$ (Hellmann and Tisserand, 2006), the parameters of these fits will only be valid for the conditions that the experiments were conducted. In order to describe how rates will vary under different conditions (pH, temperature) a description of the underlying reaction mechanism/s is needed and care should be taken in implementing these empirical rate laws in geochemical models. That being said it is often easier and more computationally efficient to describe dissolution rates with empirical fits to extensive data sets. Modified rate laws, to account for the discrepancy between dissolution rates observed in the field and rates measured in laboratory studies, using the $f(\Delta G_r)$ term are discussed in length by Ganor et al. (2007). Further insights into the relation of mineral dissolution and precipitation reaction mechanism/s to solution saturation state are being made through experimental advances in studying microscopic surface processes (Dove and Han, 2007).

2.6 Mineral replacement reactions – direct sc-CO₂ interactions

The kinetics of mineral carbonation in siliciclastic reservoirs through direct contact with a sc-CO₂ fluid phase has not received much attention in the geochemical community. Experiments by Lin et al. (2008) showed that dry sc-CO₂ is unreactive with minerals relevant to a siliciclastic reservoir, but as some water is soluble in the sc-CO₂ plume forming a wet sc-CO₂ phase Lin et al. (2008) suggested that this water forms a thin film on mineral surfaces mediating and enhancing mineral replacement reactions.

Shao et al. (2011) observed similar reactions taking place in experiments looking at wet sc-CO₂ interactions with phlogopite. Similarly, in experiments on a mafic mineral relevant to other CO₂ storage scenarios, Kwak et al. (2011) showed that water acts as a catalyst for converting forsterite to magnesite and amorphous silicate phases. These studies, however, were not conducted as kinetic experiments necessary to fit rate constants to experimental data, and were focussed on the types of mineral alteration taking place. Incorporating these types of reactions and rates into geochemical models may be a difficult task given a general lack of data and the non-ideal behaviour of the high ionic strength fluids resulting from mineral dissolution in a small amount of water.

3. Mineral dissolution rate comparisons

Figure 7 summarizes the pH dependence for mineral dissolution rates. As has been known for some time, decreasing the pH from near neutral waters to those saturated with respect to supercritical CO₂ has a marked effect on mineral dissolution rates. Reaction rates may increase by as much as 2 orders of magnitude with a decrease in pH from 8 to 4 for many mineral phases. Figure 7 compares the relative reactivity of a number of mineral phases relevant to CO₂ storage in a reservoir at 60°C and at a pH = 4, which may be a representative pH for fluids containing elevated levels of CO_{2(aq)}. Blue bars represent extrapolations of measurements made without elevated CO₂ present (low CO₂) and red bars represent measurements where elevated CO₂ was used. Green bars in Figure 7 are calculated rates for a low CO₂ water at a pH of 8, which may be typical of the initial pH of formation waters in target formations buffered by the presence of carbonates. Extrapolating rates to the reported conditions (60°C and pH = 4 and 8) is inherently difficult given most studies focus on one temperature (often 25°C) or specific solution compositions. Most of the rates plotted in Figure 7 under low CO₂ conditions are extrapolated using the kinetic parameters reported by Palandri and Kharaka (2004) for an acidic, neutral and alkali dissolution mechanism (Equation 3), but other sources are cited in the caption giving a range of reported rates. In general, the effect of elevated CO₂ concentration (red bars) is comparable to predictions of the pH effect alone under low-CO₂ (ambient) conditions.

1 The following section discusses studies specific to different mineral phases under
2 elevated CO₂ conditions, and the underlying mechanisms that have been identified that
3 may help explain these general observations made in Figure 7.

4 5 *3.1 Effect of CO₂ on relative mineral reaction rates*

6 Carbonates represent some of the most reactive phases in natural systems, with
7 dissolution and precipitation rates approaching diffusion limits, which leads to complex
8 reaction mechanisms straddling transport-limited and surface-kinetically controlled
9 regimes (Casey, 1987; Plummer and Wigley, 1976). Given the relationship between the
10 saturation state of carbonates in the environment and levels of $p\text{CO}_2$ (Stumm and
11 Morgan, 1996), saturating reservoirs with CO₂ is likely to have a significant impact on
12 carbonate mineralogy. Saturating waters with CO₂ leads to a shift in the dissolved
13 carbonate speciation and a subsequent decrease in pH, and the thermodynamic
14 properties for the CO₂-H₂O-x system are constantly under review and being refined for
15 various PVTx conditions (where x may represent various dissolved components) in
16 order to accurately model these properties (Duan and Mao, 2006; Duan and Sun, 2003;
17 Hu et al., 2007; Mao et al., 2010; Mao et al., 2013; Span and Wagner, 1996; Spycher
18 and Pruess, 2005; Spycher et al., 2003).

19 Most studies relevant to CO₂ storage will be concerned with precipitation rates
20 and nucleation mechanisms for carbonates as they serve as the primary phase for long-
21 term mineral trapping within a reservoir. These processes are beyond the scope of
22 discussion here, however, injection of CO₂ and shifting of groundwater pH may actually
23 lead to the dissolution of carbonate phases initially present in an aquifer. Thus providing
24 a source of cations and dissolved carbonate species for buffering pH and eventually
25 leading to the precipitation of new mineral phases (Hellevang et al., 2013). The timing of
26 these processes is highly dependent upon characterising the amount of reactive
27 carbonate phase initially present in a reservoir and whether or not these phases will
28 remain supersaturated relative to groundwaters once they are concentrated with
29 CO_{2(aq)}, which is unlikely due to acidification of waters by increasing $p\text{CO}_2$. Geochemical
30 modelling studies often represent the reactivity of multiple carbonate phases using the
31 same set of kinetic parameters (Xu et al., 2007) due to a lack of data on specific mineral

phases. However, Figure 7 shows that the reactivity of different carbonate phases vary over many log orders of magnitude and this may have a significant impact on the long-term carbonate mineralogy in a reservoir. Recent reactive-transport experiments show that proton-enhanced dissolution rate equations for calcite and dolomite (Palandri and Kharaka, 2004) adequately capture dissolution in limestone and dolostone CO₂ storage reservoirs when calibrated for reactive surface area (Carroll et al., 2013a; Hao et al., 2013; Smith et al., 2013a).

Pokrovsky et al. (2009) present a detailed discussion of metal-carbonate dissolution processes and extend experimental work on calcite, dolomite and magnesite to pH and elevated *p*CO₂ conditions. The surface complex models presented describe two parallel dissolution pathways where the far-from-equilibrium rate is controlled by the formation of the surface species >CO₃H⁰ and >MeOH₂⁺ (Equation 4):

$$Rate = k_{CO_3} \times \frac{[>CO_3H^0]}{[H^+]}^m + k_{Me} \times \frac{[>MeOH_2^+]}{[H^+]}^n \quad (4)$$

where, m and n are reaction order with respect to the surface sites >CO₃H⁰ and >MeOH₂⁺, respectively. Pokrovsky et al. (2009) found a complex response of the dissolution rate of calcite, magnesite and dolomite to *p*CO₂, which changed with temperature and pH. However, they found the effect of *p*CO₂ itself was negligible compared to the effect of proton enhanced dissolution or inhibition by dissolved bicarbonate/carbonate species that are involved in the formation of the rate controlling surface complexes illustrated in Equation 4.

In contrast, silicate and aluminosilicate mineral phases exhibit much slower reaction rates when compared to the carbonate phases (Figure 7). Dissolution studies using forsterite (Hänchen et al., 2006; Wang and Giammar, 2013) and aluminosilicate phases (Carroll and Knauss, 2005; Smith et al., 2013b) have found elevated *p*CO₂ to have a negligible effect on observed dissolution rates under acid conditions (pH < 5). However, some studies have found that as pH increases, to circumneutral conditions, rising levels of dissolved carbonate lead to new surface complexes forming and enhanced rates of dissolution (Berg and Banwart, 2000; Utsunomiya et al., 1999).

Others have reported adsorbed bicarbonate having an inhibiting effect on dissolution rates (Black and Haese, 2014).

Clays and other aluminosilicate phases effectively become rate-limiting for the formation of new mineral phases, such as secondary carbonates, when they act as the source and supply of cations through dissolution (Hellevang et al., 2013). These mineral phases often occur as pore filling or grain coating phases in reservoirs, and thus their reactivity may also be rate-limiting if they act as barriers to exposing more reactive minerals to elevated CO₂ fluids or precipitate as secondary phases themselves (Hangx and Spiers, 2009).

4. Implications and recommendations for geochemical modelling of carbon storage

Geochemical models used to assess the impact of CO₂ storage on reservoir performance typically adopt a building block approach, using site mineralogy, published thermodynamic and kinetic data, and expert opinion. However, this approach can be quite uncertain based on the variability and co-dependence of kinetic parameters. This is especially true for apparent activation energies and reactive surface areas where variability can lead to rates that differ by several orders of magnitude (Figures 2, 3 and 4). Another hurdle to developing robust rock-water models is the poor match between actual mineral stoichiometry found in rock and that found in thermodynamic databases, along with uncertainty in the value of some equilibrium constants. This is especially problematic for clay minerals found in siliciclastic storage reservoirs.

One way to constrain model parameters is to assess parameter uncertainty against experimental data from a specific storage site. Carroll et al. (2013b) developed a geochemical model that describes the geochemical response of the Mt. Simon sandstone and the Eau Claire shale, the target CO₂ storage reservoir and caprock for the Archer Daniels Midland demonstration site in Illinois, using a modified Monte Carlo method to sample rate constants, reactive surface areas, initial mineral mass fractions, equilibrium solubility products, and non-stoichiometric dissolution of clay minerals. The geochemical model consisted of quartz, microcline, illite, and annite dissolution coincident with montmorillonite, kaolinite and amorphous silica precipitation. About 3000

forward geochemical calculations were conducted for each experimental data set to converge on the optimal geochemical model for the storage reservoir and the caprock. The approach used a Metropolis-Hastings algorithm to generate small perturbations to the initial parameter set for each realization. This process repeats itself with improved goodness of fit to the experimental data between realizations.

Carroll et al. (2013b) found that most of the parameters needed only modest adjustments to published kinetic and thermodynamic constants to fit the experimental data using the modified Monte Carlo approach for calibration. They found that multiple simulations converged on values that were within 0.8 ± 0.7 log units for rate constants, 3 ± 0.4 kJ/mol for activation energies, 0.1 ± 0.01 for pH exponent n , and 2.75 ± 0.02 for illite and montmorillonite $\log(IAP/K_{sp})$ when compared to values predicted using the tabulated kinetic parameters in Palandri and Kharaka (2004). Modelling the iron-rich clay was a notable exception, requiring an apparent activation energy more similar to those reported for biotite (22 kJ/mol) than for chlorite (88 kJ/mol). The use of annite, an iron-rich biotite, required an offset of about 17 to 19 $\log(IAP/K_{sp})$. In addition to the significant adjustments to the thermodynamic constants for the iron-clay model, incongruent reaction terms were needed to capture the change in solution composition under acid CO_2 conditions. Additionally the simulations converged on mineral mass fractions (± 0.03) and surface areas (± 0.08 log units) within narrow distributions compared to the wider search range used. The approach is especially useful for estimating parameters for iron clay minerals because robust thermodynamic and kinetic data are lacking.

5. Conclusions

Geochemical models for CO_2 storage benefit from a description of mineral dissolution rates under the elevated pressure, temperature and dissolved CO_2 conditions of storage reservoirs in order to describe changes to the mineralogy, and dissolved solute load of formation waters. Rate laws used to describe rates of mineral dissolution are dependent on a number of physical and chemical properties, including:

- The reactive surface area (RSA) of a mineral exposed to fluids, which can be gauged as a fraction of the specific surface area as measured by various

1 analytical methods and thus estimates used for modelling purposes can vary by
2 1 to 4 orders of magnitude. Detailing what values are used for the RSA of a
3 mineral should be standard practice in modelling studies.

- 4 • The elevated temperatures of CO₂ storage reservoirs (50-125°C), necessitates
5 the use of apparent activation energies for mineral dissolution processes to
6 extrapolate rate constants to higher temperatures. Reported apparent activation
7 energies for various layered silicate minerals vary anywhere from 20-90 kJ/mol,
8 with larger apparent activation energies leading to larger uncertainty in predicting
9 rates at higher temperatures.
- 10 • The pH of formation waters has a significant impact on mineral dissolution rates,
11 with rates potentially increasing by 0.5 a log order of magnitude for every unit
12 change in pH. Other dissolved species can also affect dissolution rates leading to
13 an uncertainty in the effect of pH of 1 to 2 orders of magnitude.

14
15 Given the uncertainties in kinetic parameters used in rate laws, such as those
16 presented in Equations 1-3, care should be taken not to mix-and-match optimised
17 parameters from various sources. The kinetic parameters of a rate law should be
18 optimised and tested against experimental data sets before implementation in
19 modelling, and deterministic modelling for optimising these parameters to experiments
20 has proven to be an effective approach. Such models help test and validate the kinetic
21 parameters used and describe the degree of uncertainty for specific mineral phases and
22 reactions.

23 24 25 **Acknowledgements**

26 The authors thank the Cooperative Research Centre for Greenhouse Gas
27 Technologies, CO2CRC, for sponsoring this research and acknowledge the funding
28 provided by the Commonwealth of Australia, State governments, industry and academic
29 partners through the CO2CRC Program. Thanks to members of the CO2CRC for
30 scientific discussions.

1 Carroll acknowledges support from the US DOE Fossil Energy Carbon Storage
2 Program. This work was performed under the auspices of the U.S. Department of
3 Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-
4 07NA27344.

5

6

7

Figures Captions

Figure 1. Zones of geochemical importance within a CO₂ storage reservoir: 1. CO₂ hydration with potential salting-out of formation waters; 2. Post-injection CO₂ plume footprint with residual CO₂ and CO₂-saturated water; 3. Wet sc-CO₂-rock reactions; 4. CO₂ dissolution into formation water; 5. Fluid-rock reactions in downward advecting part of convection cells.

Figure 2. Effect of apparent activation energy on predicted dissolution rates at three temperatures relative to 25°C.

Figure 3. Range of apparent activation energies reported for rate constants from various dissolution mechanisms: blue bars: proton enhanced dissolution under low-CO₂ conditions; red bars: proton enhanced mechanism under elevated CO₂ conditions; green bars: neutral mechanism under low-CO₂ conditions; orange bars: neutral mechanism under elevated CO₂ conditions. [1] (Palandri and Kharaka, 2004); [2] (Pokrovsky et al., 2009); [3] (Golubev et al., 2009); [4] (Testemale et al., 2009); [5] (Hellevang et al., 2010); [6] (Hellevang et al., 2011); [7] (Rosso and Rimstidt, 2000); [8] (Hänchen et al., 2006); [9] (Wang and Giammar, 2013); [10] (Marini, 2006); [11] (Rimstidt and Barnes, 1980); [12] (Carroll and Knauss, 2005); [13] (Li et al., 2006); [14] (Oelkers and Schott, 1995); [15] (Carroll et al., 2013b); [16] (Smith et al., 2013b); [17] (Black and Haese, 2014); [18] (Cama et al., 2002); [19] (Ganor et al., 1995). [20] (Ross, 1967); [21] (Brandt et al., 2003); [22] (Smith and Carroll, 2014); [23] (Carroll and Walther, 1990).

Figure 4. A range of reported surface areas (cm² g⁻¹) for minerals relevant to siliclastic reservoirs. Blue bars (refs 7-39): experimentally measured specific surface areas by BET methods; Green bars (refs 1-6): reactive surface areas reported and used in reaction-path and reactive-transport modelling studies. Refs: [1] (Sonnenthal and Spycher, 2001); [2] (Xu et al., 2005); [3] (Xu et al., 2007); [4] (Maher et al., 2009); [5] (Carroll et al., 2013b); [6] (Hellevang et al., 2013); [7] (Pokrovsky et al., 2005); [8] (Plummer and Busenberg, 1982); [9] (Gautelier et al., 2007); [10] (Pokrovsky and Schott, 2002); [11] (Golubev et al., 2009); [12] (Jordan et al., 2007); [13] (Hellevang et al., 2005); [14] (Hellevang et al., 2010); [15] (Giammar et al., 2005); [16] (Wang and Giammar, 2013); [17] (Knauss and Wolery, 1988); [18] (Rimstidt and Barnes, 1980); [19] (Oelkers and Schott, 1995); [20] (Berg and Banwart, 2000); [21] (Allan et al., 2011);

[22] (Carroll and Knauss, 2005); [23] (Burch et al., 1993); [24] (Wollast and Chou, 1992); [25] (Stillings and Brantley, 1995); [26] (Gautier et al., 1994); [27] (Malmström et al., 1996); [28] (Acker and Bricker, 1992); [29] (Brandt et al., 2003); [30] (Lowson et al., 2005); [31] (Black and Haese, 2014); [32] (Smith and Carroll, 2014); [33] (Köhler et al., 2003); [34] (Kaufhold and Dohrmann, 2012); [35] (Golubev et al., 2006); [36] (Marty et al., 2011); [37] (Wieland and Stumm, 1992); [38] (Carroll and Walther, 1990); [39] (Nagy et al., 1991).

Figure 5. Effect of temperature (shades) and pH on chlorite dissolution rates experimentally measured, squares: Brandt et al. (2003); stars: Lowson et al. (2007; 2005); triangles: Smith et al. (2013b); and modelled using A) a mixture of kinetic parameters compiled in Marini (2006) for Eq. 3 B) kinetic parameters reported by Smith and Carroll (2014) for the acidic and neutral components of Eq. 3.

Figure 6. Chlorite dissolution rate as a function of pH in different acidic electrolyte solutions (Black and Haese, 2014; Brandt et al., 2003; Hamer et al., 2003; Lowson et al., 2005). Black lines – 25°C; Gray line – 80°C.

Figure 7. Ranges of reported mineral reactivity extrapolated to 60°C at pH = 8 under low-CO₂ (green bars); pH = 4 under low-CO₂ (blue bars), and pH = 4 under elevated-CO₂ conditions (red bars). See caption to Figure 3 for [references].

References:

- Aagaard, P., Helgeson, H.C., 1982. Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions: I. Theoretical considerations. *Am J Sci*, 282(3): 237-285.
- Acker, J.G., Bricker, O.P., 1992. The influence of pH on biotite dissolution and alteration kinetics at low temperature. *Geochimica et Cosmochimica Acta*, 56(8): 3073-3092.
- Allan, M.M., Turner, A., Yardley, B.W.D., 2011. Relation between the dissolution rates of single minerals and reservoir rocks in acidified pore waters. *Applied Geochemistry*, 26(8): 1289-1301.
- Anbeek, C., 1992a. The dependence of dissolution rates on grain size for some fresh and weathered feldspars. *Geochimica et Cosmochimica Acta*, 56(11): 3957-3970.
- Anbeek, C., 1992b. Surface roughness of minerals and implications for dissolution studies. *Geochimica et Cosmochimica Acta*, 56(4): 1461-1469.
- Berg, A., Banwart, S.A., 2000. Carbon dioxide mediated dissolution of Ca-feldspar: implications for silicate weathering. *Chemical Geology*, 163(1-4): 25-42.
- Black, J.R., Haese, R.R., 2014. Chlorite Dissolution Rates Under CO₂ Saturated Conditions at 50 to 120°C and 120 to 200 bar CO₂. *Geochimica et Cosmochimica Acta*, 125: 225-240.
- Blum, A.E., Lasaga, A.C., 1988. Role of surface speciation in the low-temperature dissolution of minerals. *Nature*, 331(6155): 431-433.
- 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.
- Brantley, S.L., 2003. 5.03 - Reaction Kinetics of Primary Rock-Forming Minerals under Ambient Conditions. In: Drever, J.I. (Ed.), *Treatise on Geochemistry*. Elsevier Pergamon, Oxford, pp. 73-117.
- Brantley, S.L., Chen, Y., 1995. Chemical weathering rates of pyroxenes and amphiboles. *Reviews in Mineralogy and Geochemistry*, 31(1): 119-172.
- Brantley, S.L., Kubicki, J., White, A.F., 2008. *Kinetics of Water-Rock Interaction*. Springer, New York.
- Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*, 60(2): 309-319.
- 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(1-3): 137-162.
- Burton, W.K., Cabrera, N., Frank, F.C., 1951. The Growth of Crystals and the Equilibrium Structure of their Surfaces. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 243(866): 299-358.
- 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.

- 1 Cama, J., Metz, V., Ganor, J., 2002. The effect of pH and temperature on kaolinite
2 dissolution rate under acidic conditions. *Geochimica et Cosmochimica Acta*,
3 66(22): 3913-3926.
- 4 Carpenter, M., Kvien, K., Aarnes, J., 2011. The CO2QUALSTORE guideline for
5 selection, characterisation and qualification of sites and projects for geological
6 storage of CO2. *International Journal of Greenhouse Gas Control*, 5(4): 942-951.
- 7 Carroll, S., Hao, Y., Smith, M., Sholokhova, Y., 2013a. Development of scaling
8 parameters to describe CO₂–rock interactions within Weyburn-Midale carbonate
9 flow units. *International Journal of Greenhouse Gas Control*, 16, Supplement
10 1(0): S185-S193.
- 11 Carroll, S.A., Knauss, K.G., 2005. Dependence of labradorite dissolution kinetics on
12 CO_{2(aq)}, Al_(aq), and temperature. *Chemical Geology*, 217(3-4): 213-225.
- 13 Carroll, S.A., McNab, W.W., Dai, Z., Torres, S.C., 2013b. Reactivity of Mount Simon
14 Sandstone and the Eau Claire Shale Under CO₂ Storage Conditions.
15 *Environmental Science & Technology*, 47(1): 252-261.
- 16 Carroll, S.A., McNab, W.W., Torres, S.C., 2011. Experimental study of cement-
17 sandstone/shale-brine-CO₂ interactions. *Geochemical Transactions*, 12(9).
- 18 Carroll, S.A., Walther, J.V., 1990. Kaolinite dissolution at 25°C, 60°C, and 80°C.
19 *American Journal of Science*, 290(7): 797-810.
- 20 Casey, W.H., 1987. Heterogeneous kinetics and diffusion boundary layers: The
21 example of reaction in a fracture. *Journal of Geophysical Research: Solid Earth*,
22 92(B8): 8007-8013.
- 23 Dove, P.M., Han, N., 2007. Kinetics of mineral dissolution and growth as reciprocal
24 microscopic surface processes across chemical driving force, AIP Conference
25 Proceedings. IOP INSTITUTE OF PHYSICS PUBLISHING LTD, pp. 215.
- 26 Duan, Z., Mao, S., 2006. A thermodynamic model for calculating methane solubility,
27 density and gas phase composition of methane-bearing aqueous fluids from 273
28 to 523 K and from 1 to 2000 bar. *Geochimica et Cosmochimica Acta*, 70(13):
29 3369-3386.
- 30 Duan, Z., Sun, R., 2003. An improved model calculating CO₂ solubility in pure water and
31 aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chemical*
32 *Geology*, 193(3-4): 257-271.
- 33 Ellis, B.R., Crandell, L.E., Peters, C.A., 2010. Limitations for brine acidification due to
34 SO₂ co-injection in geologic carbon sequestration. *International Journal of*
35 *Greenhouse Gas Control*, 4(3): 575-582.
- 36 Ennis-King, J., Paterson, L., 2007. Coupling of geochemical reactions and convective
37 mixing in the long-term geological storage of carbon dioxide. *International*
38 *Journal of Greenhouse Gas Control*, 1(1): 86-93.
- 39 Ganor, J., Lasaga, A.C., 1998. Simple mechanistic models for inhibition of a dissolution
40 reaction. *Geochimica et Cosmochimica Acta*, 62(8): 1295-1306.
- 41 Ganor, J., Lu, P., Zheng, Z., Zhu, C., 2007. Bridging the gap between laboratory
42 measurements and field estimations of silicate weathering using simple
43 calculations. *Environmental Geology*, 53(3): 599-610.
- 44 Ganor, J., Mogollón, J.L., Lasaga, A.C., 1995. The effect of pH on kaolinite dissolution
45 rates and on activation energy. *Geochimica et Cosmochimica Acta*, 59(6): 1037-
46 1052.

- 1 Ganor, J., Mogollón, J.L., Lasaga, A.C., 1999. Kinetics of gibbsite dissolution under low
2 ionic strength conditions. *Geochimica et Cosmochimica Acta*, 63(11/12): 1635-
3 1651.
- 4 Gasda, S.E., Nordbotten, J.M., Celia, M.A., 2011. Vertically averaged approaches for
5 CO₂ migration with solubility trapping. *Water Resources Research*, 47(5):
6 W05528.
- 7 Gaus, I., Azaroual, M., Czernichowski-Lauriol, I., 2005. Reactive transport modelling of
8 the impact of CO₂ injection on the clayey cap rock at Sleipner (North Sea).
9 *Chemical Geology*, 217(3-4): 319-337.
- 10 Gautelier, M., Schott, J., Oelkers, E.H., 2007. An experimental study of dolomite
11 dissolution rates at 80°C as a function of chemical affinity and solution
12 composition. *Chemical Geology*, 242(3-4): 509-517.
- 13 Gautier, J.-M., Oelkers, E.H., Schott, J., 1994. Experimental study of K-feldspar
14 dissolution rates as a function of chemical affinity at 150°C and pH 9.
15 *Geochimica et Cosmochimica Acta*, 58(21): 4549-4560.
- 16 GCCSI, 2012. The Global Status of CCS : 2012, Global CCS Institute, Canberra,
17 Australia.
- 18 Giammar, D.E., Bruant Jr, R.G., Peters, C.A., 2005. Forsterite dissolution and
19 magnesite precipitation at conditions relevant for deep saline aquifer storage and
20 sequestration of carbon dioxide. *Chemical Geology*, 217(3-4): 257-276.
- 21 Gilfillan, S.M.V., Lollar, B.S., Holland, G., Blagburn, D., Stevens, S., Schoell, M.,
22 Cassidy, M., Ding, Z., Zhou, Z., Lacrampe-Couloume, G., Ballentine, C.J., 2009.
23 Solubility trapping in formation water as dominant CO₂ sink in natural gas fields.
24 *Nature*, 458(7238): 614-618.
- 25 Golubev, S.V., Bauer, A., Pokrovsky, O.S., 2006. Effect of pH and organic ligands on
26 the kinetics of smectite dissolution at 25°C. *Geochimica et Cosmochimica Acta*,
27 70(17): 4436-4451.
- 28 Golubev, S.V., Bénézech, P., Schott, J., Dandurand, J.L., Castillo, A., 2009. Siderite
29 dissolution kinetics in acidic aqueous solutions from 25 to 100°C and 0 to 50 atm
30 pCO₂. *Chemical Geology*, 265(1-2): 13-19.
- 31 Hamer, M., Graham, R.C., Amrhein, C., Bozhilov, K.N., 2003. Dissolution of Ripidolite
32 (Mg, Fe-Chlorite) in Organic and Inorganic Acid Solutions. *Soil Sci. Soc. Am. J.*,
33 67(2): 654-661.
- 34 Hänchen, M., Prigiobbe, V., Storti, G., Seward, T.M., Mazzotti, M., 2006. Dissolution
35 kinetics of forsteritic olivine at 90°C including effects of the presence of CO₂.
36 *Geochimica et Cosmochimica Acta*, 70(17): 4403-4416.
- 37 Hangx, S.J.T., Spiers, C.J., 2009. Reaction of plagioclase feldspars with CO₂ under
38 hydrothermal conditions. *Chemical Geology*, 265(1-2): 88-98.
- 39 Hao, Y., Smith, M., Sholokhova, Y., Carroll, S., 2013. CO₂-induced dissolution of low
40 permeability carbonates. Part II: Numerical modeling of experiments. *Advances*
41 *in Water Resources*, 62C(0): 388-408.
- 42 Hellevang, H., Aagaard, P., Oelkers, E.H., Kvamme, B., 2005. Can Dawsonite
43 Permanently Trap CO₂? *Environmental Science & Technology*, 39(21): 8281-
44 8287.

- 1 Hellevang, H., Declercq, J., Aagaard, P., 2011. Why is Dawsonite Absent in CO₂
2 Charged Reservoirs? *Oil Gas Sci. Technol. - Rev. IFP Energies nouvelles*, 66(1):
3 119-135.
- 4 Hellevang, H., Declercq, J., Kvamme, B., Aagaard, P., 2010. The dissolution rates of
5 dawsonite at pH 0.9 to 5 and temperatures of 22, 60 and 77°C. *Applied*
6 *Geochemistry*, 25(10): 1575-1586.
- 7 Hellevang, H., Pham, V.T.H., Aagaard, P., 2013. Kinetic modelling of CO₂–water–rock
8 interactions. *International Journal of Greenhouse Gas Control*, 15(0): 3-15.
- 9 Hellmann, R., Tisserand, D., 2006. Dissolution kinetics as a function of the Gibbs free
10 energy of reaction: An experimental study based on albite feldspar. *Geochimica*
11 *et Cosmochimica Acta*, 70(2): 364-383.
- 12 Higgs, K.E., Funnell, R.H., Reyes, A.G., 2013. Changes in reservoir heterogeneity and
13 quality as a response to high partial pressures of CO₂ in a gas reservoir, New
14 Zealand. *Marine and Petroleum Geology*, 48(0): 293-322.
- 15 Higgs, K.E., Haese, R.R., Golding, S., Schacht, U., Watson, M., submitted. The Pretty
16 Hill Formation as a natural analogue for CO₂ storage; an investigation of
17 mineralogical and isotopic changes associated with sandstones exposed to low,
18 intermediate and high CO₂ concentrations over geological time.
- 19 Hu, J., Duan, Z., Zhu, C., Chou, I.M., 2007. PVTx properties of the CO₂-H₂O and CO₂-
20 H₂O-NaCl systems below 647 K: Assessment of experimental data and
21 thermodynamic models. *Chemical Geology*, 238(3-4): 249-267.
- 22 IEA, 2012. IEA Statistics. CO₂ Emissions from Fuel Combustion: Highlights, OECD/IEA,
23 Paris, France.
- 24 Jordan, G., Pokrovsky, O.S., Guichet, X., Schmahl, W.W., 2007. Organic and inorganic
25 ligand effects on magnesite dissolution at 100°C and pH = 5 to 10. *Chemical*
26 *Geology*, 242(3-4): 484-496.
- 27 Kaufhold, S., Dohrmann, R., 2012. Mineral standards for the COORAL project: #C007
28 "Illite", Technical report for Federal Institute for Geosciences and Natural
29 Resources, BGR, Hannover, Germany.
- 30 Kim, M., Sell, A., Sinton, D., 2013. Aquifer-on-a-Chip: understanding pore-scale salt
31 precipitation dynamics during CO₂ sequestration. *Lab on a Chip*, 13: 2508-2518.
- 32 Knauss, K.G., Wolery, T.J., 1988. The dissolution kinetics of quartz as a function of pH
33 and time at 70°C. *Geochimica et Cosmochimica Acta*, 52(1): 43-53.
- 34 Köhler, S.J., Dufaud, F., Oelkers, E.H., 2003. An experimental study of illite dissolution
35 kinetics as a function of pH from 1.4 to 12.4 and temperature from 5 to 50°C.
36 *Geochimica et Cosmochimica Acta*, 67(19): 3583-3594.
- 37 Kutchko, B.G., Strazisar, B.R., Dzombak, D.A., Lowry, G.V., Thaulow, N., 2007.
38 Degradation of Well Cement by CO₂ under Geologic Sequestration Conditions.
39 *Environmental Science & Technology*, 41(13): 4787-4792.
- 40 Kwak, J.H., Hu, J.Z., Turcu, R.V.F., Rosso, K.M., Ilton, E.S., Wang, C., Sears, J.A.,
41 Engelhard, M.H., Felmy, A.R., Hoyt, D.W., 2011. The role of H₂O in the
42 carbonation of forsterite in supercritical CO₂. *International Journal of Greenhouse*
43 *Gas Control*, 5(4): 1081-1092.
- 44 Lasaga, A.C., 1981. Transition state theory. In: Lasaga, A.C., Kirkpatrick, R.J. (Eds.),
45 *Kinetics of Geochemical Processes. Reviews in Mineralogy. Mineralogical*
46 *Society of America, Washington, D.C.*, pp. 135-169.

- 1 Lasaga, A.C., 1998. Kinetic Theory in the Earth Sciences. Princeton University Press,
2 Princeton, NJ.
- 3 Lasaga, A.C., Luttge, A., 2001. Variation of Crystal Dissolution Rate Based on a
4 Dissolution Stepwave Model. *Science*, 291(5512): 2400-2404.
- 5 Li, L., Peters, C.A., Celia, M.A., 2006. Upscaling geochemical reaction rates using pore-
6 scale network modeling. *Advances in Water Resources*, 29(9): 1351-1370.
- 7 Lin, H., Fujii, T., Takisawa, R., Takahashi, T., Hashida, T., 2008. Experimental
8 evaluation of interactions in supercritical CO₂/water/rock minerals system under
9 geologic CO₂ sequestration conditions. *Journal of Materials Science*, 43(7):
10 2307-2315.
- 11 Lowson, R.T., Brown, P.L., Comarmond, M.C.J., Rajaratnam, G., 2007. The kinetics of
12 chlorite dissolution. *Geochimica et Cosmochimica Acta*, 71(6): 1431-1447.
- 13 Lowson, R.T., Comarmond, M.C.J., Rajaratnam, G., Brown, P.L., 2005. The kinetics of
14 the dissolution of chlorite as a function of pH and at 25°C. *Geochimica et*
15 *Cosmochimica Acta*, 69(7): 1687-1699.
- 16 Lüttge, A., 2005. Etch pit coalescence, surface area, and overall mineral dissolution
17 rates. *American Mineralogist*, 90(11-12): 1776-1783.
- 18 Maher, K., Steefel, C.I., White, A.F., Stonestrom, D.A., 2009. The role of reaction affinity
19 and secondary minerals in regulating chemical weathering rates at the Santa
20 Cruz Soil Chronosequence, California. *Geochimica et Cosmochimica Acta*,
21 73(10): 2804-2831.
- 22 Malmström, M., Banwart, S., Lewenhagen, J., Duro, L., Bruno, J., 1996. The dissolution
23 of biotite and chlorite at 25°C in the near-neutral pH region. *Journal of*
24 *Contaminant Hydrology*, 21(1-4): 201-213.
- 25 Mao, S., Duan, Z., Hu, J., Zhang, D., 2010. A model for single-phase PVTx properties of
26 CO₂-CH₄-C₂H₆-N₂-H₂O-NaCl fluid mixtures from 273 to 1273 K and from 1 to
27 5000 bar. *Chemical Geology*, 275(3-4): 148-160.
- 28 Mao, S., Zhang, D., Li, Y., Liu, N., 2013. An improved model for calculating CO₂
29 solubility in aqueous NaCl solutions and the application to CO₂-H₂O-NaCl fluid
30 inclusions. *Chemical Geology*, 347(0): 43-58.
- 31 Marini, L., 2006. Geological Sequestration of Carbon Dioxide: Thermodynamics,
32 kinetics and reaction path modeling. *Developments in Geochemistry*, 11.
33 Elsevier, The Netherlands, 453 pp.
- 34 Marty, N.C.M., Cama, J., Sato, T., Chino, D., Villiéras, F., Razafitianamaharavo, A.,
35 Brendlé, J., Giffaut, E., Soler, J.M., Gaucher, E.C., Tournassat, C., 2011.
36 Dissolution kinetics of synthetic Na-smectite. An integrated experimental
37 approach. *Geochimica et Cosmochimica Acta*, 75(20): 5849-5864.
- 38 Mason, H.E., Du Frane, W.L., Walsh, S.D.C., Dai, Z., Charnvanichborikarn, S., Carroll,
39 S.A., 2013. Chemical and Mechanical Properties of Wellbore Cement Altered by
40 CO₂-Rich Brine Using a Multianalytical Approach. *Environmental Science &*
41 *Technology*, 47(3): 1745-1752.
- 42 Metz, V., Raanan, H., Pieper, H., Bosbach, D., Ganor, J., 2005. Towards the
43 establishment of a reliable proxy for the reactive surface area of smectite.
44 *Geochimica et Cosmochimica Acta*, 69(10): 2581-2591.

- 1 Monin, J.C., Barth, D., Perrut, M., Espitalié, M., Durand, B., 1988. Extraction of
2 hydrocarbons from sedimentary rocks by supercritical carbon dioxide. *Organic*
3 *Geochemistry*, 13(4–6): 1079-1086.
- 4 Morse, J.W., Casey, W.H., 1988. Ostwald processes and mineral paragenesis in
5 sediments. *American Journal of Science*, 288(6): 537-560.
- 6 Nagy, K.L., Blum, A.E., Lasaga, A.C., 1991. Dissolution and precipitation kinetics of
7 kaolinite at 80 degrees C and pH 3; the dependence on solution saturation state.
8 *Am J Sci*, 291(7): 649-686.
- 9 Nagy, K.L., Lasaga, A.C., 1992. Dissolution and precipitation kinetics of gibbsite at 80°C
10 and pH 3: The dependence on solution saturation state. *Geochimica et*
11 *Cosmochimica Acta*, 56(8): 3093-3111.
- 12 Navarre-Sitchler, A., Thyne, G., 2007. Effects of carbon dioxide on mineral weathering
13 rates at earth surface conditions. *Chemical Geology*, 243(1–2): 53-63.
- 14 Neufeld, J.A., Hesse, M.A., Riaz, A., Hallworth, M.A., Tchelepi, H.A., Huppert, H.E.,
15 2010. Convective dissolution of carbon dioxide in saline aquifers. *Geophysical*
16 *Research Letters*, 37(22): L22404.
- 17 Nielsen, L.C., Bourg, I.C., Sposito, G., 2012. Predicting CO₂-water interfacial tension
18 under pressure and temperature conditions of geologic CO₂ storage. *Geochimica*
19 *et Cosmochimica Acta*, 81(0): 28-38.
- 20 Oelkers, E.H., Schott, J., 1995. Experimental study of anorthite dissolution and the
21 relative mechanism of feldspar hydrolysis. *Geochimica et Cosmochimica Acta*,
22 59(24): 5039-5053.
- 23 Oelkers, E.H., Schott, J., 2009. Thermodynamics and Kinetics of Water-Rock
24 Interaction. *Reviews in Mineralogy & Geochemistry*. Mineralogical Society of
25 America.
- 26 Oelkers, E.H., Schott, J., Devidal, J.-L., 1994. The effect of aluminum, pH, and chemical
27 affinity on the rates of aluminosilicate dissolution reactions. *Geochimica et*
28 *Cosmochimica Acta*, 58(9): 2011-2024.
- 29 Ohlin, C.A., Villa, E.M., Rustad, J.R., Casey, W.H., 2010. Dissolution of insulating oxide
30 materials at the molecular scale. *Nat Mater*, 9(1): 11-19.
- 31 Palandri, J.L., Kharaka, Y.K., 2004. A compilation of rate parameters of water–mineral
32 interaction kinetics for application to geochemical modeling, U.S. Geological
33 Survey, Menlo Park, California.
- 34 Pham, V.T.H., Lu, P., Aagaard, P., Zhu, C., Hellevang, H., 2011. On the potential of
35 CO₂-water-rock interactions for CO₂ storage using a modified kinetic model.
36 *International Journal of Greenhouse Gas Control*, 5(4): 1002-1015.
- 37 Plummer, L.N., Busenberg, E., 1982. The solubilities of calcite, aragonite and vaterite in
38 CO₂-H₂O solutions between 0 and 90°C, and an evaluation of the aqueous model
39 for the system CaCO₃-CO₂-H₂O. *Geochimica et Cosmochimica Acta*, 46(6):
40 1011-1040.
- 41 Plummer, L.N., Wigley, T.M.L., 1976. The dissolution of calcite in CO₂-saturated
42 solutions at 25°C and 1 atmosphere total pressure. *Geochimica et*
43 *Cosmochimica Acta*, 40(2): 191-202.
- 44 Pokrovsky, O.S., Golubev, S.V., Schott, J., 2005. Dissolution kinetics of calcite,
45 dolomite and magnesite at 25°C and 0 to 50 atm pCO₂. *Chemical Geology*,
46 217(3-4): 239-255.

- 1 Pokrovsky, O.S., Golubev, S.V., Schott, J., Castillo, A., 2009. Calcite, dolomite and
2 magnesite dissolution kinetics in aqueous solutions at acid to circumneutral pH,
3 25 to 150°C and 1 to 55 atm pCO₂: New constraints on CO₂ sequestration in
4 sedimentary basins. *Chemical Geology*, 265(1-2): 20-32.
- 5 Pokrovsky, O.S., Schott, J., 2002. Surface Chemistry and Dissolution Kinetics of
6 Divalent Metal Carbonates. *Environmental Science & Technology*, 36(3): 426-
7 432.
- 8 Riaz, A., Hesse, M., Tchelepi, H.A., Orr, F.M., 2006. Onset of convection in a
9 gravitationally unstable diffusive boundary layer in porous media. *Journal of Fluid*
10 *Mechanics*, 548: 87-111.
- 11 Rimstidt, J.D., Barnes, H.L., 1980. The kinetics of silica-water reactions. *Geochimica et*
12 *Cosmochimica Acta*, 44(11): 1683-1699.
- 13 Ross, G.J., 1967. Kinetics of acid dissolution of an orthochlorite mineral. *Canadian*
14 *Journal of Chemistry*, 45(24): 3031-3034.
- 15 Rosso, J.J., Rimstidt, J.D., 2000. A high resolution study of forsterite dissolution rates.
16 *Geochimica et Cosmochimica Acta*, 64(5): 797-811.
- 17 Rustad, J.R., Casey, W.H., 2012. Metastable structures and isotope exchange reactions
18 in polyoxometalate ions provide a molecular view of oxide dissolution. *Nat Mater*,
19 11(3): 223-226.
- 20 Schott, J., Pokrovsky, O.S., Oelkers, E.H., 2009. The Link Between Mineral
21 Dissolution/Precipitation Kinetics and Solution Chemistry. *Reviews in Mineralogy*
22 *and Geochemistry*, 70(1): 207-258.
- 23 Shao, H., Ray, J.R., Jun, Y.-S., 2011. Effects of Salinity and the Extent of Water on
24 Supercritical CO₂-Induced Phlogopite Dissolution and Secondary Mineral
25 Formation. *Environmental Science & Technology*, 45(4): 1737-1743.
- 26 Smith, M.M., Carroll, S.A., 2014. Experimental Determination of Chlorite Kinetics at
27 Geothermal Conditions, Thirty-Ninth Workshop on Geothermal Reservoir
28 Engineering, Stanford University, Stanford, California.
- 29 Smith, M.M., Sholokhova, Y., Hao, Y., Carroll, S.A., 2013a. CO₂-induced dissolution of
30 low permeability carbonates. Part I: Characterization and experiments. *Advances*
31 *in Water Resources*, 62C(0): 370-387.
- 32 Smith, M.M., Wolery, T.J., Carroll, S.A., 2013b. Kinetics of chlorite dissolution at
33 elevated temperatures and CO₂ conditions. *Chemical Geology*, 347: 1-8.
- 34 Sonnenthal, E., Spycher, N., 2001, Drift-Scale Coupled Processes (DST and THC
35 Seepage) Models. Lawrence Berkeley National Laboratory, Berkeley, CA.
- 36 Span, R., Wagner, W., 1996. A new equation of state for carbon dioxide covering the
37 fluid region from the triple-point temperature to 1100 K at pressures up to 800
38 MPa. *Journal of Physical and Chemical Reference Data*, 25(6): 1509-1596.
- 39 Spycher, N., Pruess, K., 2005. CO₂-H₂O mixtures in the geological sequestration of
40 CO₂. II. Partitioning in chloride brines at 12-100°C and up to 600 bar. *Geochimica*
41 *et Cosmochimica Acta*, 69(13): 3309-3320.
- 42 Spycher, N., Pruess, K., Ennis-King, J., 2003. CO₂-H₂O mixtures in the geological
43 sequestration of CO₂. I. Assessment and calculation of mutual solubilities from 12
44 to 100°C and up to 600 bar. *Geochimica et Cosmochimica Acta*, 67(16): 3015-
45 3031.

- 1 Stillings, L.L., Brantley, S.L., 1995. Feldspar dissolution at 25°C and pH 3: Reaction
2 stoichiometry and the effect of cations. *Geochimica et Cosmochimica Acta*,
3 59(8): 1483-1496.
- 4 Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry: Chemical equilibria and rates in*
5 *natural waters*. Wiley-Interscience, New York.
- 6 Testemale, D., Dufaud, F., Martinez, I., Bénézeth, P., Hazemann, J.-L., Schott, J.,
7 Guyot, F., 2009. An X-ray absorption study of the dissolution of siderite at 300
8 bar between 50°C and 100°C. *Chemical Geology*, 259(1-2): 8-16.
- 9 Torres, M.A., West, A.J., Li, G., 2014. Sulphide oxidation and carbonate dissolution as a
10 source of CO₂ over geological timescales. *Nature*, 507(7492): 346-349.
- 11 Utsunomiya, S., Murakami, T., Kadohara, H., Tsukimura, K., 1999. The effect of partial
12 pressure of carbon dioxide on anorthite dissolution. *Mineralogical journal*, 21(1):
13 1-8.
- 14 Wang, F., Giammar, D.E., 2013. Forsterite Dissolution in Saline Water at Elevated
15 Temperature and High CO₂ Pressure. *Environmental Science & Technology*,
16 47(1): 168-173.
- 17 White, A.F., Brantley, S.L., 2003. The effect of time on the weathering of silicate
18 minerals: why do weathering rates differ in the laboratory and field? *Chemical*
19 *Geology*, 202(3-4): 479-506.
- 20 Wieland, E., Stumm, W., 1992. Dissolution kinetics of kaolinite in acidic aqueous
21 solutions at 25°C. *Geochimica et Cosmochimica Acta*, 56(9): 3339-3355.
- 22 Wollast, R., Chou, L., 1992. Surface reactions during the early stages of weathering of
23 albite. *Geochimica et Cosmochimica Acta*, 56(8): 3113-3121.
- 24 Xu, T., Apps, J.A., Pruess, K., 2004. Numerical simulation of CO₂ disposal by mineral
25 trapping in deep aquifers. *Applied Geochemistry*, 19(6): 917-936.
- 26 Xu, T., Apps, J.A., Pruess, K., 2005. Mineral sequestration of carbon dioxide in a
27 sandstone-shale system. *Chemical Geology*, 217(3-4): 295-318.
- 28 Xu, T., Apps, J.A., Pruess, K., Yamamoto, H., 2007. Numerical modeling of injection
29 and mineral trapping of CO₂ with H₂S and SO₂ in a sandstone formation.
30 *Chemical Geology*, 242(3-4): 319-346.
- 31 Yang, L., Xu, T., Yang, B., Tian, H., Lei, H., 2014. Effects of mineral composition and
32 heterogeneity on the reservoir quality evolution with CO₂ intrusion. *Geochemistry,*
33 *Geophysics, Geosystems*, 15(3): 605-618.
- 34 Zeidouni, M., Pooladi-Darvish, M., Keith, D., 2009. Analytical solution to evaluate salt
35 precipitation during CO₂ injection in saline aquifers. *International Journal of*
36 *Greenhouse Gas Control*, 3(5): 600-611.
- 37 Zhang, H., Bloom, P.R., Nater, E.A., 1993. Change in surface area and dissolution rates
38 during hornblende dissolution at pH 4.0. *Geochimica et Cosmochimica Acta*,
39 57(8): 1681-1689.

1 Figures.

Figure 1. Zones of geochemical importance within a CO₂ storage reservoir: 1. CO₂ hydration with potential salting-out of formation waters; 2. Post-injection CO₂ plume footprint with residual CO₂ and CO₂-saturated water; 3. Wet sc-CO₂-rock reactions; 4. CO₂ dissolution into formation water; 5. Fluid-rock reactions in downward advecting part of convection cells.

Figure 2. Effect of apparent activation energy on predicted dissolution rates at three temperatures relative to 25°C.

Figure 3. Range of apparent activation energies reported for rate constants from various dissolution mechanisms: **blue bars:** proton enhanced dissolution under low-CO₂ conditions; **red bars:** proton enhanced mechanism under elevated CO₂ conditions; **green bars:** neutral mechanism under low-CO₂ conditions; **orange bars:** neutral mechanism under elevated CO₂ conditions. [1] (Palandri and Kharaka, 2004); [2] (Pokrovsky et al., 2009); [3] (Golubev et al., 2009); [4] (Testemale et al., 2009); [5] (Hellevang et al., 2010); [6] (Hellevang et al., 2011); [7] (Rosso and Rimstidt, 2000); [8] (Hänchen et al., 2006); [9] (Wang and Giammar, 2013); [10] (Marini, 2006); [11] (Rimstidt and Barnes, 1980); [12] (Carroll and Knauss, 2005); [13] (Li et al., 2006); [14] (Oelkers and Schott, 1995); [15] (Carroll et al., 2013b); [16] (Smith et al., 2013b); [17] (Black and Haese, 2014); [18] (Cama et al., 2002); [19] (Ganor et al., 1995). [20] (Ross, 1967); [21] (Brandt et al., 2003); [22] (Smith and Carroll, 2014); [23] (Carroll and Walther, 1990).

Figure 4. A range of reported surface areas (cm² g⁻¹) for minerals relevant to siliclastic reservoirs. **Blue bars (refs 7-39):** experimentally measured specific surface areas by BET methods; **Green bars (refs 1-6):** reactive surface areas reported and used in reaction-path and reactive-transport modelling studies. **Refs:** [1] (Sonnenthal and Spycher, 2001); [2] (Xu et al., 2005); [3] (Xu et al., 2007); [4] (Maher et al., 2009); [5] (Carroll et al., 2013b); [6] (Hellevang et al., 2013); [7] (Pokrovsky et al., 2005); [8] (Plummer and Busenberg, 1982); [9] (Gautelier et al., 2007); [10] (Pokrovsky and Schott, 2002); [11] (Golubev et al., 2009); [12] (Jordan et al., 2007); [13] (Hellevang et al., 2005); [14] (Hellevang et al., 2010); [15] (Giammar et al., 2005); [16] (Wang and Giammar, 2013); [17] (Knauss and Wolery, 1988); [18] (Rimstidt and Barnes, 1980); [19] (Oelkers and Schott, 1995); [20] (Berg and Banwart, 2000); [21] (Allan et al., 2011); [22] (Carroll and Knauss, 2005); [23] (Burch et al., 1993); [24] (Wollast and Chou, 1992); [25] (Stillings and Brantley, 1995); [26] (Gautier et al., 1994); [27] (Malmström et al., 1996); [28] (Acker and Bricker, 1992); [29] (Brandt et al., 2003); [30] (Lowson et al.,

2005); [31] (Black and Haese, 2014); [32] (Smith and Carroll, 2014); [33] (Köhler et al., 2003); [34] (Kaufhold and Dohrmann, 2012); [35] (Golubev et al., 2006); [36] (Marty et al., 2011); [37] (Wieland and Stumm, 1992); [38] (Carroll and Walther, 1990); [39] (Nagy et al., 1991).

Figure 5. Effect of temperature (shades) and pH on chlorite dissolution rates experimentally measured, squares: Brandt et al. (2003); stars: Lowson et al. (2007; 2005); triangles: Smith et al. (2013b); and modelled using **A**) a mixture of kinetic parameters compiled in Marini (2006) for Eq. 3 **B**) kinetic parameters reported by Smith and Carroll (2014) for the acidic and neutral components of Eq. 3.

Figure 6. Chlorite dissolution rate as a function of pH in different acidic electrolyte solutions (Black and Haese, 2014; Brandt et al., 2003; Hamer et al., 2003; Lowson et al., 2005). Black lines – 25°C; Gray line – 80°C.

Figure 7. Ranges of reported mineral reactivity extrapolated to 60°C at pH = 8 under low-CO₂ (green bars); pH = 4 under low-CO₂ (blue bars), and pH = 4 under elevated-CO₂ conditions (red bars). See caption to **Figure 3** for [references].