Chrysotile dissolution rates: Implications for carbon sequestration

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ABSTRACT

Serpentine minerals (e.g., chrysotile) are a potentially important medium for sequestration of CO_2 via carbonation reactions. The goals of this study are to report a steady-state, far from equilibrium chrysotile dissolution rate law and to better define what role serpentine dissolution kinetics will have in constraining rates of carbon sequestration via serpentine carbonation. The steady-state dissolution rate of chrysotile in 0.1 m NaCl solutions was measured at 22 °C and pH ranging from 2 to 8. Dissolution experiments were performed in a continuously stirred flow-through reactor with the input solutions pre-equilibrated with atmospheric CO_2. Both Mg and Si steady-state fluxes from the chrysotile surface, and the overall chrysotile flux were regressed and the following empirical relationships were obtained:
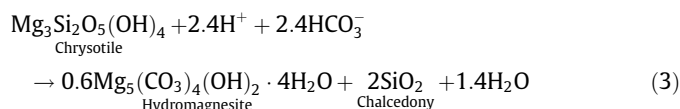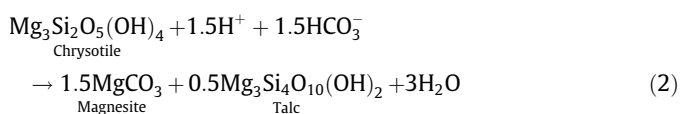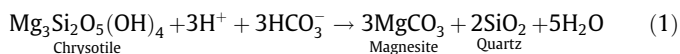
$$F_{Mg} = -0.22pH - 10.02; \quad F_{Si} = -0.19pH - 10.37; \quad F_{chrysotile} = -0.21pH - 10.57$$

where F_{Mg}, F_{Si}, and $F_{chrysotile}$ are the $\log_{10}$ Mg, Si, and molar chrysotile fluxes in mol/m^2/s, respectively. Element fluxes were used in reaction-path calculations to constrain the rate of CO_2 sequestration in two geological environments that have been proposed as potential sinks for anthropogenic CO_2. Carbon sequestration in chrysotile tailings at 10 °C is approximately an order of magnitude faster than carbon sequestration in a serpentinite-hosted aquifer at 60 °C on a per kilogram of water basis. A serpentinite-hosted aquifer, however, provides a larger sequestration capacity. The chrysotile dissolution rate law determined in this study has important implications for constraining potential rates of sequestration in serpentinite-hosted aquifers and under accelerated sequestration scenarios in mine tailings.

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1. Introduction

Mineral surface reactions in aqueous solutions operate in the nanoscale environment yet these reactions can dramatically control bulk chemical properties. Serpentine (e.g., chrysotile) surface reactions with CO_2-rich solutions can lead to carbonate mineral precipitation (Eqs. (1)–(3)). As a result, serpentine is being investigated as a medium for geological sequestration of CO_2 via chemical weathering reactions (Guthrie et al., 2001; Lackner, 2003; Cipolli et al., 2004; Park and Fan, 2004; Marini, 2006; Wilson et al., 2006, 2009a; Alexander et al., 2007; Gerdemann et al., 2007; Teir et al., 2007, 2009; Larachi et al., 2010; Power et al., 2010, 2011, 2013; Krevor and Lackner, 2011; Orlando et al., 2011; Pronost et al., 2011; Wang and Maroto-Valer, 2011; Bea et al., 2012).

$$\underset{\text{Chrysotile}}{Mg_3Si_2O_5(OH)_4} + 3H^+ + 3HCO_3^- \rightarrow 3\underset{\text{Magnesite}}{MgCO_3} + 2\underset{\text{Quartz}}{SiO_2} + 5H_2O \qquad (1)$$

$$\underset{\text{Chrysotile}}{Mg_3Si_2O_5(OH)_4} + 1.5H^+ + 1.5HCO_3^-$$
$$\rightarrow 1.5\underset{\text{Magnesite}}{MgCO_3} + 0.5\underset{\text{Talc}}{Mg_3Si_4O_{10}(OH)_2} + 3H_2O \qquad (2)$$

$$\underset{\text{Chrysotile}}{Mg_3Si_2O_5(OH)_4} + 2.4H^+ + 2.4HCO_3^-$$
$$\rightarrow 0.6\underset{\text{Hydromagnesite}}{Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O} + 2\underset{\text{Chalcedony}}{SiO_2} + 1.4H_2O \qquad (3)$$

At near-surface, low temperature conditions the formation of hydrated Mg-carbonate minerals (e.g., hydromagnesite) rather than magnesite is favored and has been documented in both artificial (e.g., mine sites) and natural environments (e.g., hydromagnesite playas) (Sherlock et al., 1993; Hansen et al., 2005; Power et al., 2009; Wilson et al., 2006, 2011).

In low temperature environments, the serpentine dissolution rate is kinetically limited and not well known. Reaction-path and reaction-transport modeling within these environments are correspondingly hindered (Cipolli et al., 2004; Marini, 2006). Understanding the factors that control the rate of serpentine dissolution is essential to predicting the extent to which CO_2 mineralization may proceed. Many experimental studies of serpentine dissolution kinetics have focused on chrysotile. These experiments have investigated a restricted chemical solution space, either dictated to resemble the conditions in the human lung, under pH drift conditions, and/or at limited run duration (Choi and Smith, 1972; Thomassin et al., 1977; Verlinden et al., 1984; Bales and Morgan, 1985; Swenters et al., 1985; Gronow, 1987; Hume and Rimstidt, 1992; Allen and Smith, 1994; Morgan, 1997; Morgan and Talbot,

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1997; Bonifacio et al., 2001). As a result it is difficult to extract steady-state dissolution rates as a function of bulk solution chemistry from previous experimental investigations.

Chrysotile dissolution reaction rates were measured as a function of pH from 2 to 8 at low temperatures (20–22 °C). These rates were used to define a chrysotile dissolution rate law, which was extended to pH 10 using data from Bales and Morgan (1985). In order to apply the laboratory determined dissolution rate law to field situations, it is important to understand the effect of dissolution history on the steady-state rate. That is, the rate law can only be applied with confidence if the steady-state chrysotile dissolution rate is not path-dependent. To determine the effect of rapid changes in bulk water chemistry (i.e., dissolution history) on steady-state dissolution rates, 'pH-jump' experiments were also conducted. The aim of this study is (1) to report a steady-state, far from equilibrium chrysotile dissolution rate law, (2) to determine the effect of dissolution history on steady-state reaction rates, and (3) to better define what role chrysotile dissolution kinetics will have in constraining rates of geological sequestration of CO_2.

2. Steady-state mineral dissolution

Chrysotile dissolution experiments were designed to determine steady-state magnesium and silicon fluxes (F_{Mg} and F_{Si}) from the mineral surface as a function of bulk solution chemistry. A single pass, continuously stirred tank reactor (CSTR) was used to measure the flux of dissolved mineral elements under transient and steady-state conditions. Steady-state fluxes were inferred when the effluent chemistry of a CSTR did not change over five fluid residence times. CSTRs are commonly used to understand kinetic reactions at the mineral–solution interface (Samson et al., 2000; Pokrovsky and Schott, 2000, 2004; Golubev et al., 2005) as they allow direct measurement of fluxes:

$$F_i^j = \frac{[C_i^{out} - C_i^{in}]}{\tau A_v} \quad (4)$$

In this expression, F_i^j is the flux of element 'i' from dissolution of mineral 'j' (mol/m²/s), τ is the average residence time of fluid in the reactor (s) and is equal to the ratio of the fluid volume to the flow rate, C_i is the concentration of element 'i' (mol/L) in the input and output solution, and A_v is the reactive surface area of the solid phases to volume of solution ratio (m²/L). A_v can be calculated as:

$$A_v = \frac{A_s m}{V_w} = \frac{A_s \rho V_s (1 - \Phi)}{V_{wc} 1000} \quad (5)$$

where A_s is the specific surface area of the mineral (m²/g), m is the mass of the mineral (g), V_w is the volume of water in contact with the mineral (L), ρ is the density of the mineral (g/m³), V_s is the volume fraction of the mineral of interest (volume of mineral/total solid volume), V_{wc} is the volumetric water content (volume of water/total volume), and Φ is the porosity of the material. The far right-hand side of Eq. (5) (($A_s \rho V_s (1 - \Phi)/(V_{wc} 1000)$)) would be used to calculate the mineral surface area to water volume ratio in a solid-dominated system. It is assumed that reactive surface area is equivalent to BET surface area, although this is not always the case (Lee et al., 1998; Gautier et al., 2001; Hodson, 2006). Direct measurement of reaction rate is determined in a CSTR under the assumption of a uniform fluid composition throughout the reaction vessel, and at steady-state the extent of reaction is measured at constant chemical affinity. Eq. (4) describes the element flux from the mineral surface. Element flux and mineral dissolution rates are related through the stoichiometric coefficient for the element of interest.

3. Methodology

3.1. Materials

For the starting material, a bulk sample of natural chrysotile was obtained from the Cassiar Mine, British Columbia, Canada. The sample was high-grade fibrous-matted ore. X-ray diffraction (XRD) analysis revealed the presence of chrysotile, talc, magnetite, quartz, and clay minerals (palygorskite and sepiolite). The ore was hand sorted to remove obvious impurities. The sample was then suspended in distilled water and ultrasonically cleaned and stirred with a magnetic stir bar. The solution was decanted and the process continued until the solution was free from fine-grained particulates and the magnetic stir bar did not collect any magnetite. The suspension was then centrifuged to separate the supernatant from the chrysotile. The resulting chrysotile was further washed with distilled water and repeatedly centrifuged until the supernatant reached a constant electrical conductivity. The moist chrysotile fibers were then dried under a heat lamp. XRD analysis revealed that magnetite was successfully removed; however, minor amounts of talc, quartz, and clay minerals remained. The contribution of these excess phases to the flux of Mg and Si is thought to be small due to their negligible abundance and the comparatively large surface area of chrysotile. For example, although talc [$Mg_3Si_4O_{10}(OH)_2$] may have similar surface area normalized dissolution rates, it has a considerably lower surface area (0.603 ± 0.009 m²/g) even when ground to a grain size of between 50 and 200 μm (Saldi et al., 2007).

The specific surface area of chrysotile was measured before and after each experiment with a Quantachrome-1A system using the N_2 (gas)-BET method (Barrett et al., 1951). The initial specific surface area was 17.60 ± 0.08 m²/g ($n = 2$). Final surface areas ranged from 23.35 to 52.03 m²/g. No changes in mineral surface morphology were recognizable with field emission scanning electron microscopy with a resolution of 5 nm. The increase in final surface area is likely due to mechanical breakdown of fiber bundles in the CSTR. Chemical composition of chrysotile was determined by a commercial analytical laboratory, ALS Chemex, using a Li metaborate fusion technique and X-ray fluorescence analysis (Table 1). Due to the elastic nature of the chrysotile fibers, the sample sent for analysis could not be powdered without being ashed first at 1000 °C. The bound water was determined to be 13.5 ± 0.2% from ashing three separate chrysotile samples. The ashed samples were then crushed and sent to ALS Chemex for analysis. Loss on ignition (LOI) reported by ALS Chemex indicated that the ashed samples absorbed water. The analytical data gives a Mg to Si molar ratio that was very close to the ideal ratio of 1.5 for chrysotile, confirming that the abundance of talc and clay phases was very minor.

3.2. Chrysotile dissolution experiments

Dissolution experiments were carried out in a 1 L polypropylene vessel containing chrysotile and solution in a solid to liquid mass ratio of about 1:1000 (Fig. 1). The reactor was immersed in a water bath at room temperature (20–22 °C) for most experiments to

Table 1
Chemical composition of anhydrous chrysotile[a].

Major oxides	wt%	Minor oxides	wt%
SiO_2	46.29	CaO	0.44
MgO	45.60	Na_2O	0.29
Fe_2O_3	3.59	K_2O	0.17
Al_2O_3	1.32	Cr_2O_3	0.11

[a] Approximately 3% H_2O had reabsorbed into the ashed sample by the time it was sent for analysis.