



# Rate equations for modeling carbon dioxide sequestration in basalt



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## ARTICLE INFO

### Article history:

Received 23 November 2016

Received in revised form

30 March 2017

Accepted 31 March 2017

Available online 2 April 2017

Editorial handling by Prof. M. Kersten.

### Keywords:

CO<sub>2</sub> sequestration

TOUGHREACT models

Glassy basalt rate equation

Crystalline basalt rate equation

## ABSTRACT

Dissolution rate equations are developed from published data for glassy and crystalline basalt to predict the silica release flux ( $J_{Si}$ ) as a function of hydrogen ion activity ( $2 < \text{pH} < 12$ ) and temperature ( $0^\circ < T < 100^\circ \text{C}$ ). For glassy basalt the silica flux is

$$J_{Si} = (5.00 \times 10^2) e^{\left(\frac{-39700}{R}\right) \frac{1}{T}} a_{\text{H}^+}^{1.01} + (5.26 \times 10^{-5}) e^{\left(\frac{-38400}{R}\right) \frac{1}{T}} a_{\text{H}^+}^{-0.258}$$

and for crystalline basalt the silica flux is

$$J_{Si} = (7.40) e^{\left(\frac{-40100}{R}\right) \frac{1}{T}} a_{\text{H}^+}^{0.680} + (8.67 \times 10^{-7}) e^{\left(\frac{-32900}{R}\right) \frac{1}{T}} a_{\text{H}^+}^{-0.286}.$$

These rate equations are implemented in TOUGHREACT to simulate a CO<sub>2</sub> saturated solution reacting with glassy and crystalline basalt in batch and semibatch reactors. The crystalline basalt models are compared with a more complex basalt representation comprising a composite mixture of olivine, plagioclase and pyroxene dissolution rates. Results show that numerical models based on the newly developed rate equations make reasonable predictions. Batch reactor models initially contained a solution spiked with CO<sub>2</sub>. These models showed relatively rapid CO<sub>2</sub> consumption followed by cessation of the reaction with the glassy and crystalline basalt after the CO<sub>2</sub> was exhausted and a terminal pH near eight. The composite basalt model was less successful because the plagioclase continued to react after the CO<sub>2</sub> was exhausted causing the pH to rise to an unreasonably high value near 12. Semibatch reactor models containing a solution continuously supplied with CO<sub>2</sub> showed relatively rapid CO<sub>2</sub> consumption until all basalt was consumed. Complete semibatch reaction produced a sodium and bicarbonate rich solution with a pH near eight for all three basalt compositions.

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## 1. Introduction

The suitability of basalt reservoirs for carbon capture and sequestration (CCS) is being tested on the basis of favorable CO<sub>2</sub>-water-rock geochemical reactions that result in permanent CO<sub>2</sub> isolation through mineral trapping (Matter et al., 2016; Bacon et al., 2014; Schaef et al., 2013; Gysi and Stefánsson, 2011; Matter and Kelemen, 2009; McGrail et al., 2017). The motivation for CCS in basalt is largely attributable to the relatively high CO<sub>2</sub> storage potential within both onshore and offshore basalt formations. For example, McGrail et al. (2006) estimate CO<sub>2</sub> storage potential in the Columbia River Basalt Group in the northwestern United States to be as high as 100 Gt CO<sub>2</sub>, and studies by Goldberg et al. (2008, 2010) suggest that offshore basalt formations within the Juan de Fuca plate and Central Atlantic Magmatic Province hold potential for CO<sub>2</sub>

disposal on comparable scales. On a global basis, perhaps the most significant opportunity for CCS in mafic reservoirs is within India's Deccan Traps, where CO<sub>2</sub> storage estimates are on the order of 150 Gt (Jayaraman, 2007), and the demand for coal-fired electricity is driven by rapid economic growth.

The premise motivating CCS in mafic reservoirs is that CO<sub>2</sub> dissolution in water produces carbonic acid, which provides hydrogen ions for basalt dissolution and bicarbonate ions for carbonate precipitation. The overall dissolution rate of the basalt governs cation availability and pH in the CO<sub>2</sub>-water-basalt system and exerts first-order control on the mineral trapping potential of the reservoir. The first step in this process involves CO<sub>2</sub> dissolution to produce carbonic acid, which dissociates to bicarbonate and hydrogen ions:

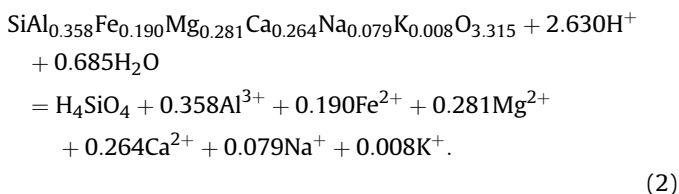


In the next step, the hydrogen ions promote the dissolution of the basalt. For Icelandic basalts considered in this paper, the

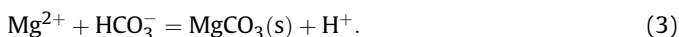
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generalized reaction based on the basalt composition from Oelkers and Gislason (2001) and Gudbrandsson et al. (2011) is:



At higher pH the aluminum hydrolyzes to form hydroxy species resulting in a proportionally lower consumption of hydrogen ions. In the final step, the divalent cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{2+}$ ) from the dissolved basalt combine with bicarbonate and carbonate ions to precipitate carbonate minerals and release additional hydrogen ions into solution, e.g.,



In addition, the Si and Al from the basalt precipitates into clay minerals (e.g., illite and montmorillonite) and these reactions also produce hydrogen ions, which contribute to further basalt dissolution (Gysi and Stefánsson, 2012).

In recent years, several modeling studies and small-scale field experiments have shown that  $\text{CO}_2$  sequestration in basalt reservoirs may be feasible despite significant levels of reservoir heterogeneity. For example, industrial-scale  $\text{CO}_2$  sequestration has been tested in low-volume basalt reservoirs using Monte Carlo numerical modeling methods, which show that permeability heterogeneity strongly influences reservoir injectivity; however, the confinement potential is favorable over time-scales needed for mineralization (Pollyea et al., 2014; Pollyea and Fairley, 2012). Additionally, small-scale basalt sequestration field experiments have been undertaken at the Wallula Basalt Sequestration Pilot Project in southeastern Washington, USA (McGrail et al., 2017), and the CarbFix Project at Hellisheidi geothermal power plant in southwest Iceland (Matter et al., 2016; Gislason et al., 2010). While these projects are similar in their approach to carbon isolation through  $\text{CO}_2$ -water-rock mineralization reactions, the field implementation in each project differs in the delivery of  $\text{CO}_2$ . At the Wallula site, 1000 metric tons of  $\text{CO}_2$  was injected in the supercritical (sc) phase in August 2013, and analysis of post-injection sidewall cores indicate that carbonate mineral precipitation was widespread in the injection zone (McGrail et al., 2017). At the CarbFix field site, two  $\text{CO}_2$  injections were undertaken in 2012 (175 tons and 73 tons) to test the novel  $\text{CO}_2$  delivery mechanism in which  $\text{CO}_2$  and water are co-injected while keeping  $\text{CO}_2$  concentration in the injected fluid below the solubility limit (Matter et al., 2016). This injection approach minimizes both degassing potential and buoyancy driven fluid flow, thus permitting  $\text{CO}_2$  injections at moderate depths (400–800 m), where pure  $\text{CO}_2$  would be subcritical (Sigfusson et al., 2015). During the CarbFix injections, the  $\text{CO}_2$  was spiked with radioactive  $^{14}\text{C}$  to quantify the *in situ* mass conversion of  $\text{CO}_2$  to carbonate minerals, and results indicate that over 95% of the injected  $\text{CO}_2$  mass was isolated within 2 years of the injections (Matter et al., 2016).

The promising results from the Wallula and CarbFix demonstration sites strongly motivate continued research towards understanding the  $\text{CO}_2$ -water-basalt system for CCS applications. Consequently, there is increasing demand for simulation tools that can be readily implemented for modeling the behavior of high  $P_{\text{CO}_2}$  systems. As a result, the purpose of this paper is to report rate equations that can be used to predict rates of  $\text{CO}_2$  consumption by reactions with crystalline or glassy basalt. We fit published silica release rates for glassy and crystalline Icelandic basalt to equations

that predict dissolution rates as a function of pH and temperature. The application of these glassy and crystalline basalt dissolution equations is illustrated in batch (closed) and semibatch (fixed  $P_{\text{CO}_2}$ ) reactor simulations using the TOUGHREACT numerical simulator for non-isothermal multi-phase reactive transport (Xu et al., 2014). Input records for the implementation of these rate models are presented as Supplemental Information (Tables S1–S2).

## 2. Methods

### 2.1. Rate equations

Published experimental values of the silica release flux ( $J_{\text{Si}}$ ) from crystalline and glassy Icelandic basalt samples were tabulated along with temperature and pH (Supplemental Information, Tables S3 and S4). For glassy basalt, there are 135 data (Flaathen et al., 2010; Gislason and Oelkers, 2003; Oelkers and Gislason, 2001; Wolff-Boenisch et al., 2004a) and for crystalline basalt there are 26 data (Gudbrandsson et al., 2011).

The silica release flux from dissolving basalt is primarily controlled by pH and temperature.

$$J_{\text{Si}} = k a_{\text{H}^+}^n = \left( A e^{-1000E_a/RT} \right) a_{\text{H}^+}^n. \quad (4)$$

In Equation (4), the activation energy ( $E_a$ ) is commonly reported in  $\text{kJ mol}^{-1}$ , and we retain this unit convention here. As a result,  $E_a$  is scaled by the conversion factor 1000 J per kJ in order to maintain internal consistency with the gas constant ( $R$ ), which has units of  $\text{J mol}^{-1} \text{K}^{-1}$ . See Table 1 for an explanation of the notation used in this paper. This equation can be linearized by a log transformation.

$$\log J_{\text{Si}} = \log k + n \log a_{\text{H}^+} = \log A - \frac{1000E_a}{2.303R} \left( \frac{1}{T} \right) - npH \quad (5)$$

The generalized form of this equation has three fitting parameters ( $a$ ,  $b$  and  $c$ ).

$$\log J_{\text{Si}} = a + \frac{b}{T} + cpH \quad (6)$$

Multiple linear regression modeling, using the JMP10 (SAS Institute Inc.) program, was applied to each data set to obtain values for  $a$ ,  $b$  and  $c$ . Prior to regression analysis, the datasets were normalized to geometric surface area. Partial regression graphs, shown in Supplemental Information (Figs. S1–S4), were used to visualize the contribution of each independent variable to the overall fit (Moya-Laraño and Corcobado, 2008; Velleman and Welsch, 1981). These graphs plot the residuals of the dependent variable versus the residuals of each independent variable. The slope of the line on each graph equals the regression coefficient for that variable so that a steep slope means that the independent variable strongly influences the dependent variable. Inspection of the data showed a minimum in  $\log J_{\text{Si}}$  near pH 6 for both glassy and crystalline basalt but no evidence for a rate plateau in the near neutral pH region. As a result, the data sets were divided at pH 6 fit to separate equations to get the dissolution flux for  $\text{pH} < 6$  ( $J_{<6\text{Si}}$ ) and for  $\text{pH} > 6$  ( $J_{>6\text{Si}}$ ). The rate equation for the entire pH range ( $2 < \text{pH} < 12$ ) was constructed by summing the antilog transformation of the low and high pH equations ( $J_{\text{Si}} = J_{<6\text{Si}} + J_{>6\text{Si}}$ ).

For use in TOUGHREACT, the rate equations from the regression models must be recast into the format used in Palandri and Kharaka (2004). This format is based on the idea that the overall rate is the sum of parallel, independent reaction rates. For reactions affected by only pH and temperature, the overall rate constant is calculated by summing the terms of following equation:

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