Dissolution kinetics of anorthite in a supercritical CO$_2$–water system

MASAO SORAI* AND MUNETAKE SASAKI

Institute for Geo-Resources and Environment, National Institute of Advanced Industrial Science and Technology (AIST), Central 7, Higashi 1-1-1, Tsukuba, Ibaraki 305-8567, Japan

ABSTRACT

The Gibbs free energy change, $\Delta G_r$, dependence of the anorthite dissolution rate in a supercritical CO$_2$–water system was measured as part of a geochemical assessment of CO$_2$ geological sequestration. Being bounded at $\Delta G_r^{\text{crit}}$, the critical $\Delta G_r$ required for an opening of the etch pit at a screw dislocation, it has been accepted that mineral dissolution follows etch pit formation assisted by dislocations below $\Delta G_r^{\text{crit}}$, whereas the horizontal step retreats without the etch pit above $\Delta G_r^{\text{crit}}$. The experiment described herein, however, revealed that another mode of dissolution occurs more distant from equilibrium by spontaneous formation of the etch pit over the entire surface, as observed on calcite. The dissolution rate is higher by more than one order of magnitude than that in the dislocation-assisted mode. Therefore, including the rate gap at $\Delta G_r^{\text{crit}}$, a nonlinear curve with three steps instead of a sigmoidal curve is proposed for the $\Delta G_r$ dependence of the anorthite dissolution rate. Extremely slow rates were observed depending on observed points for the same $\Delta G_r$ condition. Although the reason for such a rate difference remains unknown, it is likely related to the defect density on the crystal surface. It is possible that initial spreading of the dissolved surface attributable to the etch pit formation assisted by defects provides some trigger for subsequent explosive etch pit formation. These findings suggest that the initial transient process can strongly influence the kinetics of geochemical reactions that occur during CO$_2$ geological sequestration.

Keywords: CO$_2$ geological sequestration, phase-shift interferometry, dissolution rate, Gibbs free energy, anorthite, feldspar

INTRODUCTION

Recently, carbon dioxide (CO$_2$) geological sequestration (CGS) has received attention as a global warming countermeasure (e.g., IPCC 2005). Typical concepts of CGS include injecting anthropogenic CO$_2$ captured from power plants into underground aquifers at 1000 m depth without direct emission to the atmosphere. However, CGS demands safety assessments based on the prediction of CO$_2$ behaviors. Such assessments must include geochemical processes with long timescales up to several thousand years plus geophysical assessments starting immediately after CO$_2$ injection. Among the former processes, the initial dissolution of reservoir minerals in the pore water acidified by dissolved CO$_2$ is most important because it becomes an origin of subsequent reactions. As such, feldspar, which has high reactivity, is a target mineral because it is the most abundant mineral in the upper crust (Nesbitt and Young 1984).

Highly reliable dissolution rate data of feldspar are necessary for improved prediction of the timescale of geochemical processes. It is expected that the dissolution rate of feldspar in pore water is lower than that in pure water because pore water that is stagnant over a geological timescale must be much closer to equilibrium. Moreover, the saturation state of pore water varies with dissolution progress. The variation in saturation state can further decrease the dissolution rate. Therefore, it is important to know the saturation dependence of the dissolution rate, at least in the variation range of the degree of saturation of pore water from immediately after CO$_2$ injection to attainment of system equilibrium.

Generally, the rate formula for a mineral reaction is expressed as the following Equation 1 (e.g., Lasaga 1998):

$$\text{Rate} = k \exp \left( \frac{E}{RT} \right) \Pi^n \left( f(G_r) \right)$$  \hspace{1cm} (1)

where $k$ is the rate constant, $A$ signifies the reactive surface area, $E$ is the activation energy, $R$ denotes the gas constant, $T$ is the absolute temperature, $a_i$ is the activity of chemical species $i$, and $n_i$ stands for the reaction order for $a_i$. The last term $f(G_r)$ corresponds to a function related to the Gibbs free energy change, which is expressed as a function of the degree of saturation:

$$\Delta G_r = RT \ln \left( \frac{Q}{K_{eq}} \right)$$  \hspace{1cm} (2)

where $Q$ signifies the activity product and $K_{eq}$ is the equilibrium constant. In Equation 2, $\Delta G_r$, which is zero at equilibrium, takes a positive value in a supersaturated state, although it is negative in an undersaturated state. In either case, the absolute value of $\Delta G_r$ becomes greater according to its difference from equilibrium.

Many efforts have been undertaken to validate various effects on feldspar dissolution rate including pH and temperature (Chou and Wollast 1985; Holdren and Speyer 1985a; Knauss and Wolery 1986; Hellmann 1994, 1995; Chen and Brantley 1997; Welch and Ullman 2000), reactive surface area (Holdren and Speyer 1985b, 1987; Hodson 2006), various solution compositions (Amrhein and Suarez 1988; Stillings and Brantley 1995; Blake and Walter 1999), and their combinations (Oelkers and Schott 1995; Brantley and Stillings 1996; Welch and Ullman 1996; Stillings et al. 1996). With respect to feldspar dissolution in carbonic acid systems, previous researchers measured the rate as a function of the partial pressure of CO$_2$ and concentra-