

Dissolution kinetics of diopside as a function of the Gibbs free energy of reaction

R. HELLMANN¹, D. DAVAL^{1,2,3}, D. TISSERAND¹,
I. MARTINEZ², J. CORVISIER³ AND F. GUYOT²

¹LGIT-CNRS, Grenoble, France

(*correspondence: hellmann@obs.ujf-grenoble.fr)

²IPGP, Paris, France (daval@ipgp.jussieu.fr)

³Laboratoire de Géologie, ENS, CNRS, Paris, France

In natural environments, the dissolution of silicates occurs over a wide range of saturation states. The effect of how far from equilibrium the reaction takes place (i.e. $f(\Delta G_r)$) on the dissolution rate of silicates is thus a crucial parameter that needs to be determined in order to accurately model mass transfer due to fluid-rock interactions. The present study aims at investigating the relation between the dissolution rate of diopside, a common pyroxene in (ultra)basic rocks, and the Gibbs free energy of reaction, ΔG_r . The experiments were carried out in a continuously stirred flow-through reactor at 90°C and $\text{pH}_{(90^\circ\text{C})}$ 5.0 (\pm 0.1). The overall relation between ΔG_r and the rate R was determined over an extended free energy range of $-130 < \Delta G_r < -45 \text{ kJ mol}^{-1}$. The data define a highly non-linear relation between R and ΔG_r . At far from equilibrium conditions ($\Delta G_r < -72 \text{ kJ mol}^{-1}$), a rate plateau is observed. A sharp decrease of the dissolution rate (\sim 1 order of magnitude) occurs over the range $-72 \leq \Delta G_r \leq -60 \text{ kJ mol}^{-1}$. Dissolution closer to equilibrium ($-60 \leq \Delta G_r \leq -45 \text{ kJ mol}^{-1}$, and ongoing measurements) is characterized by a much weaker dependence of the rates on ΔG_r . A comparison of the experimental R - ΔG_r data with a theoretical R - ΔG_r curve based on transition state theory (TST) reveals complete incompatibility, in particular at near-equilibrium conditions. Instead, we fit our data with an overall rate law based on two parallel dissolution mechanisms, adapted from Burch *et al.* [1] and originally based on BCF theory (e.g., see similar modeling in Hellmann and Tisserand [2]). To highlight the danger of using geochemical codes that use TST-rate laws, we have developed a kinetic module implementing both types of $f(\Delta G_r)$ functions to model diopside carbonation reactions. Our results show that the use of TST-rate laws can result in a significant overestimation of the carbonation rate, an important effect if accurate amounts of conversion of CO_2 into carbonates in (ultra)basic rocks have to be estimated.

[1] Burch T.E., Nagy K.L. and Lasaga A.C. (1993) *Chem. Geol.* **105**, 137-162. [2] Hellmann, R. and Tisserand, D. (2006) *GCA* **70**, 364-383.

Time-resolved oxalate speciation at the surface of gibbsite (α -Al(OH)₃) using infrared spectroscopy

A. HELLSTRÖM*, J.S. LORING AND P. PERSSON

Department of Chemistry, Umeå University, 901 87 Umeå, Sweden

(*correspondence: Anneli.Hellstrom@chem.umu.se)

Numerous studies have investigated the interactions between carboxylate ligands and mineral surfaces. Carboxylate ligands form both inner- and outer-sphere complexes and play a role in the dissolution of minerals [1]. Spectroscopic information about the surface complexes is useful for determining the coordination geometries of the adsorbed ligands, and this can lead to a better understanding of how the ligands cause dissolution. It is known that oxalate, as an example of a ligand forming bidentate mononuclear structures, has a significant effect on the dissolution of certain minerals [2].

The aim of this project was to gain further information regarding the interactions of oxalate at the water-gibbsite (α -Al(OH)₃) interface using a combination of potentiometric titrations and IR spectroscopy [3]. For the experiments, an overlayer of gibbsite was evaporated onto a ZnSe ATR crystal. A gibbsite suspension was flowed over this overlayer, and its pH was maintained at 6 by additions of dilute hydrochloric acid or sodium hydroxide.

Oxalate was added to the suspension, and spectra were recorded as a function of time. Initially, both inner- and outer-sphere complexes were observed in the spectra, but within the first hour the outer-sphere complexes were replaced by inner-sphere complexes. The subsequent addition of the siderophore desferrioxamine-B to the mineral suspension resulted in a decrease in surface concentration of inner-sphere complexes and an increase in outer-sphere complexes. These results indicate that the oxalate-gibbsite system might exhibit similarities with a dissolution-readsorption process previously observed in the corresponding oxalate-goethite (α -FeOOH) system [3]. The relative concentrations of the inner- and outer-sphere complexes do however differ, probably as a consequence of the different stabilities of their respective surface- and solution species.

[1] Axe & Persson (2001) *Geochimica et Cosmochimica acta* **65** 4481-4492 [2] Zitic & Stumm (1984) *Geochimica et Cosmochimica acta* **48** 1493-1503 [3] Loring *et al.* (2008) *Langmuir* **24** 7054-7057