

## Quantum mechanical modeling of hydrolysis and H<sub>2</sub>O-exchange in Mg-, Ca-, and Ni-silicate clusters: Implications for dissolution mechanisms of olivine minerals

CHRISTIN P. MORROW,<sup>1,\*</sup> AMANDA A. OLSEN<sup>2</sup> AND JAMES D. KUBICKI<sup>3</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019, U.S.A.

<sup>2</sup>School of Earth and Climate Sciences, The University of Maine, Orono, Maine 04469, U.S.A.

<sup>3</sup>Department of Geosciences and the Earth and Environmental Systems Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

### ABSTRACT

Barrier heights (BHs) for hydrolysis and H<sub>2</sub>O exchange reactions at M-O-Si (M = Ni<sup>2+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) linkages on olivine (M<sub>2</sub>SiO<sub>4</sub>) mineral surfaces were determined via DFT calculations. BHs for hydrolysis of protonated Ni-O-Si, Mg-O-Si, and Ca-O-Si sites are 76, 54, and 27 kJ/mol, respectively, and are 69 and 24 kJ/mol for H<sub>2</sub>O exchange reactions of protonated Mg-O-Si and Ca-O-Si sites, respectively. Rate constants were calculated via classical transition state theory (TST) using these BHs. For protonated Ni-O-Si, Mg-O-Si, and Ca-O-Si sites, these are  $7.2 \times 10^{-1}$ ,  $4.7 \times 10^4$ , and  $1.5 \times 10^9$  s<sup>-1</sup> [pseudo-first-order where (H<sub>2</sub>O) is assumed to be constant], respectively, and for H<sub>2</sub>O exchange at protonated Mg-O-Si and Ca-O-Si sites are  $2.6 \times 10^1$  and  $3.7 \times 10^9$  s<sup>-1</sup> [pseudo-first-order where (H<sub>2</sub>O) is assumed to be constant], respectively. Approach of an H<sub>2</sub>O molecule from the second hydration sphere toward a protonated Ni-O-Si site leads to breakage of the Ni-O bond and subsequent release of Ni<sup>2+</sup> to solution. For protonated Mg-O-Si sites, however, H<sub>2</sub>O exchange does not lead to rupture of the Mg-O bond and would not be a step toward dissolution of the mineral. Potential energy surface (PES) scans of H<sub>2</sub>O exchange indicated formation of a hepta-coordinated Ca<sup>2+</sup>, so neither H<sub>2</sub>O exchange nor hydrolysis of the Ca-O-Si linkage occurred in this case. Calculated rate constants are consistent with experimental data for end-member composition olivine minerals where observed rates of dissolution increase in the order Ni<sup>2+</sup> < Mg<sup>2+</sup> < Ca<sup>2+</sup>.

**Keywords:** Dissolution, silicate, reaction mechanism, density functional theory (DFT), quantum mechanical (QM), rate constant, H<sub>2</sub>O exchange, hydrolysis, olivine