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Quantum mechanical modeling of hydrolysis and H_2O-exchange in Mg-, Ca-, and Ni-silicate clusters: Implications for dissolution mechanisms of olivine minerals

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ABSTRACT

Barrier heights (BHs) for hydrolysis and H_2O exchange reactions at M-O-Si (M = Ni^{2+}, Mg^{2+}, and Ca^{2+}) linkages on olivine (M_2SiO_4) 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_2O 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 7.2×10^{-1}, 4.7×10^4, and 1.5×10^9 s^{-1} [pseudo-first-order where (H_2O) is assumed to be constant], respectively, and for H_2O exchange at protonated Mg-O-Si and Ca-O-Si sites are 2.6×10^1 and 3.7×10^9 s^{-1} [pseudo-first-order where (H_2O) is assumed to be constant], respectively. Approach of an H_2O 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^{2+} to solution. For protonated Mg-O-Si sites, however, H_2O 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_2O exchange indicated formation of a hepta-coordinated Ca^{2+}, so neither H_2O 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 $Ni^{2+} < Mg^{2+} < Ca^{2+}$.

Keywords: Dissolution, silicate, reaction mechanism, density functional theory (DFT), quantum mechanical (QM), rate constant, H_2O exchange, hydrolysis, olivine