A first principles study of water adsorption and dissociation on olivine surfaces

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Reactivity of olivine minerals in mafic and ultramafic rocks have been utilized for geologic CO_2 sequestration, but an atomic-level understanding of the complex surface chemistry at the solid-liquid interface is needed to evaluate short and long time scale changes in these reservoirs.

As a first step towards understanding CO_2 surface chemistry at the aqueous olivine surfaces, we have examined the energetics of water and water dissociation pathways on olivine(010) surfaces using density functional theory (DFT) calculations. The DFT calculations incorporate dispersion via the D3 implementation of Grimme and co-workers [1]. After obtaining the adsorption energies of both molecular and dissociated water on the forsterite(010) surface, we also explored the effect of alkaline (Ca) and trace metals (Fe, Cr, Ni, and Co) on water adsorption by doping them on the surface. The climbing image nudged elastic band (NEB) method was employed to identify the transition state and activation barriers for water dissociation on the olivine surface. Our results indicate molecular water is more favored on both perfect and doped forsterite(010) surfaces, thus the dissocation is an endothermic process ($\Delta E_r > 0$), with alkaline metals showing less endothermicity. We will discuss ongoing calculations of the activation barriers on the perfect and doped olivine surfaces, along with fayalite and Ca-olivine surfaces. Based on the Brønsted-Evans-Polanyi (BEP) relationship, we predict Ca-doped surface is likely to dissociate water most efficiently. This result could be attributed to the charge of the different dopant metals [2] and the OH binding energy on the surface. We will also present the dynamics of water dissociation in the presence of a bilayer of water on the olivine surfaces. Our work will serve as a basis for future DFT studies of CO_2 chemistry at the aqueous olivine surfaces.

[1] Grimme, S. *et al* (2010) *J. Chem. Phys.*, **132**, 154104 [2] Kerisit, S. *et al* (2013) *Chem. Geol.*, **359**, 81-89