High Pressure ab initio Calculations of Pyrite-FeO_2H_x in the Earth's Lower Mantle

LESLIE INSIXIENGMAY[1] AND LARS STIXRUDE[1]

[1]Department of Earth, Planetary, and Space Sciences, University of California, Los Angeles, CA 90095

Water, in the form of hydrous minerals, is present in the subducting oceanic plate and plays a key role in the hydrogen cycle where dehydration from hydrous minerals takes place. As water descends into the Earth's mantle, the valence states of iron minerals present are affected by the subducted water. The hydrogen may alter the oxidation state and spin state of iron in minerals, resulting in important implications for hydrogen cycling and seismic signals in the Earth's mantle. Here, we use a model system, pyrite-FeO_2H_x, to better understand the effects of iron-hydrogen redox chemistry in the Earth's lower mantle. Recent studies propose the stability of pyrite-FeO_2H_x phase with variable amounts of hydrogen. However, hydrogen was not directly detected, leading us to focus our study on hydrogen content in this phase and its stability.

We explore the effects hydrogen content has on our pyrite-FeO_2H_x model system, ranging from hydrogen-free to hydrogen-bearing. This study applies density functional theory with a PBEsol generalized gradient approximation (GGA) using ab initio molecular dynamics and DFT+U (spin polarized) calculations through the Vienna ab initio Simulation Package (VASP). We compute material properties - including heat capacity, elasticity, self-diffusion coefficients, and the time-averaged crystalline structure – via analysis of the dynamical trajectories. At temperatures exceeding 2000K, we find the pyrite-FeO_2H_x to be in a superionic state, where hydrogen atoms are able to move freely throughout the crystal lattice. We discuss possible implications for phase stability, reaction rates, and electromagnetic sounding.