An ab-initio study on the thermodynamics of disulfide, sulfide, and bisulfide incorporation into apatite and the development of a more comprehensive temperature, pressure, pH, and composition-dependent model for ionic substitution in minerals

YOUNGJAE KIM[1,2,3,*,†], BRIAN KONECKE[1,4], ADAM SIMON[1,‡], ADRIAN FIEGE[1], AND UDO BECKER[1]

[1]Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.
[2]Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, Illinois 60439, U.S.A.
[3]Division of Earth and Environmental System Sciences, Major of Environmental Geosciences, Pukyong National University, Busan, 48513, Republic of Korea
[4]Fathom Geophysics, LLC, 12956 Claylick Road, Neward, Ohio 43056, U.S.A.

ABSTRACT

The mineral apatite, $Ca_{10}(PO_4)_6(F,OH,Cl)_2$, incorporates sulfur (S) during crystallization from S-bearing hydrothermal fluids and silicate melts. Our previous studies of natural and experimental apatite demonstrate that the oxidation state of S in apatite varies systematically as a function of oxygen fugacity (f_{O_2}). The S oxidation states –1 and –2 were quantitatively identified in apatite crystallized from reduced, S-bearing hydrothermal fluids and silicate melts by using sulfur K-edge X-ray absorption near-edge structure spectroscopy (S-XANES) where $S^{6+}/\Sigma S$ in apatite increases from ~0 at FMQ-1 to ~1 at FMQ+2, where FMQ refers to the fayalite-magnetite-quartz f_{O_2} buffer. In this study, we employ quantum-mechanical calculations to investigate the atomistic structure and energetics of S(-I) and S(-II) incorporated into apatite and elucidate incorporation mechanisms.

One S(-I) species (disulfide, S_2^{2-}) and two S(-II) species (bisulfide, HS^-, and sulfide, S^{2-}) are investigated as possible forms of reduced S species in apatite. In configuration models for the simulation, these reduced S species are positioned along the c-axis channel, originally occupied by the column anions F, Cl, and OH in the end-member apatites. In the lowest-energy configurations of S-incorporated apatite, disulfide prefers to be positioned halfway between the mirror planes at $z = 1/4$ and $3/4$. In contrast, the energy-optimized bisulfide is located slightly away from the mirror planes by ~0.04 fractional units in the c direction. The energetic stability of these reduced S species as a function of position along the c-axis can be explained by the geometric and electrostatic constraints of the Ca and O planes that constitute the c-axis channel.

The thermodynamics of incorporation of disulfide and bisulfide into apatite is evaluated by using solid-state reaction equations where the apatite host and a solid S-bearing source phase (pyrite and $Na_2S_{2(s)}$ for disulfide; troilite and $Na_2S_{(s)}$ for sulfide) are the reactants, and the S-incorporated apatite and an anion sink phase are the products. The Gibbs free energy (ΔG) is lower for incorporation with Na-bearing phases than with Fe-bearing phases, which is attributed to the higher energetic stability of the iron sulfide minerals as a source phase for S than the sodium sulfide phases. The thermodynamics of incorporation of reduced S is also evaluated by using reaction equations involving dissolved disulfide and sulfide species [$H_nS_{2(aq)}^{(2-n)}$ and $H_nS_{(aq)}^{(2-n)}$; n = 0, 1, and 2] as a source phase. The ΔG of S-incorporation increases for fluorapatite and chlorapatite, and decreases for hydroxylapatite, as these species are protonated (i.e., as n changes from 0 to 2). These thermodynamic results demonstrate that the presence of reduced S in apatite is primarily controlled by the chemistry of magmatic and hydrothermal systems where apatite forms (e.g., an abundance of Fe; solution pH). Ultimately, our methodology developed for evaluating the thermodynamics of S incorporation in apatite as a function of temperature, pH, and composition is highly applicable to predicting the trace and volatile element incorporation in minerals in a variety of geological systems. In addition to solid-solid and solid-liquid equilibria treated here at different temperatures and pH, the methodology can be easily extended to different pressure conditions by just performing the quantum-mechanical calculations at elevated pressures.

Keywords: Sulfur incorporation into apatite, oxybarometer, disulfide, bisulfide, sulfide, fluorapatite, chlorapatite, hydroxylapatite, density functional theory (DFT) calculation; Experimental Halogens in Honor of Jim Webster