

## An ab-initio study of the energetics and geometry of sulfide, sulfite, and sulfate incorporation into apatite: The thermodynamic basis for using this system as an oxybarometer

YOUNGJAE KIM<sup>1,\*</sup>, BRIAN KONECKE<sup>1</sup>, ADRIAN FIEGE<sup>1,2</sup>, ADAM SIMON<sup>1</sup>, AND UDO BECKER<sup>1</sup>

<sup>1</sup>Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48109-1005, U.S.A.

<sup>2</sup>Department of Earth and Planetary Sciences, American Museum of Natural History, New York, New York 10024-5192, U.S.A.

### ABSTRACT

Despite many studies reporting the presence of S-bearing apatite in igneous and hydrothermal systems, the oxidation states and incorporation mechanisms of S in the apatite structure remain poorly understood. In this study, we use ab initio calculations to investigate the energetics and geometry of incorporation of S with its oxidation states S<sup>6+</sup>, S<sup>4+</sup>, and S<sup>2-</sup> into the apatite end-members fluor-, chlor-, and hydroxylapatite, [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(F,Cl,OH)<sub>2</sub>]. The relative stability of different oxidation states of S in apatite is evaluated by using balanced reaction equations where the apatite host and a solid S-bearing source phase (e.g., gypsum for S<sup>6+</sup> and troilite for S<sup>2-</sup>) are the reactants, and the S-incorporated apatite and an anion sink phase are the products. Here, the reaction energy of the balanced equation indicates the stability of the modeled S-incorporated apatite relative to the host apatite, the source, and sink phases. For the incorporation of S into apatite, coupled substitutions are necessary to compensate for charge imbalance. One possible coupled substitution mechanism involves the replacement of La<sup>3+</sup> + PO<sub>4</sub><sup>3-</sup> ↔ Ca<sup>2+</sup> + SO<sub>4</sub><sup>2-</sup>. Our results show that the incorporation of SO<sub>4</sub><sup>2-</sup> into La- and Na-bearing apatite, Ca<sub>8</sub>NaLa(PO<sub>4</sub>)<sub>6</sub>(F,Cl,OH)<sub>2</sub>, is energetically favored over the incorporation into La- and Si-bearing apatite, Ca<sub>9</sub>La(PO<sub>4</sub>)<sub>5</sub>(SiO<sub>4</sub>)(F,Cl,OH)<sub>2</sub> (the difference in incorporation energy, Δ*E*<sub>rxn</sub>, is 10.7 kJ/mol). This thermodynamic gain is partially attributed to the electrostatic contribution of Na<sup>+</sup>, and the energetic contribution of La<sup>3+</sup> to the stability of SO<sub>4</sub><sup>2-</sup> incorporated into the apatite structure. Co-incorporation of SO<sub>4</sub><sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> is energetically favored when the lone pair electrons of SO<sub>3</sub><sup>2-</sup> face toward the anion column site, compared to facing away from it.

Full or partial incorporation of S<sup>2-</sup> is favored on the column anion site in the form of [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>S] and [Ca<sub>20</sub>(PO<sub>4</sub>)<sub>12</sub>SX<sub>2</sub>], where X = F, Cl, or OH. Upon full incorporation (i.e., replacing *all* column ions by sulfide ions), S<sup>2-</sup> is positioned in the anion column at *z* = 0.5 (halfway between the mirror planes at *z* = ¼ and *z* = ¾) in the energy-optimized structure. The calculated energies for partial incorporation of S<sup>2-</sup> demonstrate that in an energy-optimized structure, S<sup>2-</sup> is displaced from the mirror plane at *z* = ¼ or ¾, by 1.0 to 1.6 Å, depending on the surrounding species (F<sup>-</sup>, Cl<sup>-</sup>, or OH<sup>-</sup>); however, the probability for S<sup>2-</sup> to be incorporated into the apatite structure is highest for chlorapatite end-members.

Our results describe energetically feasible incorporation mechanisms for all three oxidation states of S (S<sup>6+</sup>, S<sup>4+</sup>, S<sup>2-</sup>) in apatite, along with structural distortion and concurring electronic structure changes. These observations are consistent with recently published experimental results (Konecke et al. 2017) that demonstrate S<sup>6+</sup>, S<sup>4+</sup>, and S<sup>2-</sup> incorporation into apatite, where the ratio of S<sup>6+</sup>/ΣS in apatite is controlled by oxygen fugacity (*f*<sub>O<sub>2</sub></sub>). The new computational results coupled with published experimental data provide the basis for using S in apatite as a geochemical proxy to trace variations in oxygen fugacity of magmatic and magmatic-hydrothermal systems.

**Keywords:** Apatite, S incorporation, S oxidation state, energetics, geometry, column anion, lanthanum, oxybarometry