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SPECIAL COLLECTION: APATITE: A COMMON MINERAL, UNCOMMONLY VERSATILE

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

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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^{6+}, S^{4+}, and S^{2-} into the apatite end-members fluor-, chlor-, and hydroxylapatite, $[Ca_{10}(PO_4)_6(F,Cl,OH)_2]$. 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^{6+} and troilite for S^{2-}) 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 $La^{3+} + PO_4^{3-} \leftrightarrow Ca^{2+} + SO_4^{2-}$. Our results show that the incorporation of SO_4^{2-} into La- and Na-bearing apatite, $Ca_8NaLa(PO_4)_6(F,Cl,OH)_2$, is energetically favored over the incorporation into La- and Si-bearing apatite, $Ca_9La(PO_4)_5(SiO_4)(F,Cl,OH)_2$ (the difference in incorporation energy, ΔE_{rxn}, is 10.7 kJ/mol). This thermodynamic gain is partially attributed to the electrostatic contribution of Na^+, and the energetic contribution of La^{3+} to the stability of SO_4^{2-} incorporated into the apatite structure. Co-incorporation of SO_4^{2-} and SO_3^{2-} is energetically favored when the lone pair electrons of SO_3^{2-} face toward the anion column site, compared to facing away from it.

Full or partial incorporation of S^{2-} is favored on the column anion site in the form of $[Ca_{10}(PO_4)_6S]$ and $[Ca_{20}(PO_4)_{12}SX_2)]$, where X = F, Cl, or OH. Upon full incorporation (i.e., replacing *all* column ions by sulfide ions), S^{2-} 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^{2-} demonstrate that in an energy-optimized structure, S^{2-} is displaced from the mirror plane at $z = ¼$ or ¾, by 1.0 to 1.6 Å, depending on the surrounding species (F^-, Cl^-, or OH^-); however, the probability for S^{2-} to be incorporated into the apatite structure is highest for chlorapatite end-members.

Our results describe energetically feasible incorporation mechanisms for all three oxidations states of S (S^{6+}, S^{4+}, S^{2-}) 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^{6+}, S^{4+}, and S^{2-} incorporation into apatite, where the ratio of $S^{6+}/\Sigma S$ in apatite is controlled by oxygen fugacity (f_{O_2}). 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