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\textsuperscript{2−}, S\textsuperscript{4+}, and S\textsuperscript{6+} into the apatite end-members fluor-, chlor-, and hydroxylapatite, [Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(F,Cl,OH)]. 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\textsuperscript{2−} and troilite for S\textsuperscript{4+}) 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\textsuperscript{3+} + PO\textsubscript{4}\textsuperscript{3−} ↔ Ca\textsuperscript{2+} + SO\textsubscript{4}\textsuperscript{2−}. Our results show that the incorporation of SO\textsubscript{4}\textsuperscript{2−} into La- and Na-bearing apatite, Ca\textsubscript{9}NaLa(PO\textsubscript{4})\textsubscript{6}(F,Cl,OH), is energetically favored over the incorporation into La- and Si-bearing apatite, Ca\textsubscript{9}La(PO\textsubscript{4})\textsubscript{6}(SiO\textsubscript{2})(F,Cl,OH)\textsubscript{2} (the difference in incorporation energy, ΔE\textsubscript{inc}, is 10.7 kJ/mol). This thermodynamic gain is partially attributed to the electrostatic contribution of Na\textsuperscript{+}, and the energetic contribution of La\textsuperscript{3+} to the stability of SO\textsubscript{4}\textsuperscript{2−} incorporated into the apatite structure. Co-incorporation of SO\textsubscript{4}\textsuperscript{2−} and SO\textsubscript{4}\textsuperscript{2−} is energetically favored when the lone pairs electrons of SO\textsubscript{4}\textsuperscript{2−} face toward the anion column site, compared to facing away from it.

Full or partial incorporation of S\textsuperscript{2−} is favored on the column anion site in the form of [Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}S] and [Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}SX\textsubscript{3}], where X = F, Cl, or OH. Upon full incorporation (i.e., replacing all column ions by sulfide ions), S\textsuperscript{2−} is positioned in the anion column at z = 0.5 (halfway between the mirror planes at z = ½ and z = ¿½) in the energy-optimized structure. The calculated energies for partial incorporation of S\textsuperscript{2−} demonstrate that in an energy-optimized structure, S\textsuperscript{2−} is displaced from the mirror plane at z = ½ or ¿½, by 1.0 to 1.6 Å, depending on the surrounding species (F, Cl, or OH); however, the probability for S\textsuperscript{2−} 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\textsuperscript{2−}, S\textsuperscript{4+}, S\textsuperscript{6+}) in apatite, along with structural distortion and concuring electronic structure changes. These observations are consistent with recently published experimental results (Konecke et al. 2017) that demonstrate S\textsuperscript{4+}, S\textsuperscript{6+}, and S\textsuperscript{2−} incorporation into apatite, where the ratio of S\textsuperscript{4+}/S\textsuperscript{2−} in apatite is controlled by oxygen fugacity (f\textsubscript{O2}). 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

INTRODUCTION

Apatite group minerals, with the general chemical formula [Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(F,Cl,OH)], are the most abundant phosphate minerals on Earth (Rakovan and Waychunas 2013; Harlov 2015). The diverse chemistry of apatite is related to its flexible structure, which can accommodate a large number of cations and anions (Hughes and Rakovan 2002). The Ca cation sites can be replaced by alkali, alkali earth and transition metals (e.g., Na, Ba, Sr, Mn, Pb), and rare earth elements (e.g., La, Ce), whereas the major oxyanions such as SiO\textsubscript{4}\textsuperscript{4−}, SO\textsubscript{4}\textsuperscript{2−}, CO\textsubscript{3}\textsuperscript{2−} can occupy the phosphate (PO\textsubscript{4}\textsuperscript{3−}) site (Hughes and Rakovan 2002).

Despite several studies demonstrating the evolution and variation of S recorded in apatite phases from igneous systems (Peng et al. 1997; Streck and Dilles 1998; Imai 2002; Parat et al. 2002; Parat and Holtz 2004, 2005), little is known about the structure and thermodynamic stability of S in apatite. The recent study by