1   **Revision #1 (MS# 6044)**

2   **An ab-initio study of the energetics and geometry of sulfide, sulfite and sulfate**

3   **incorporation into apatite: The thermodynamic basis for using this system as an**

4   **oxybarometer**

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11   **Abstract**

12   Despite many studies reporting the presence of S-bearing apatite in igneous and

13   hydrothermal systems, the oxidation states and incorporation mechanisms of S in the apatite

14   structure remain poorly understood. In this study, we use ab-initio calculations to investigate the

15   energetics and geometry of incorporation of S with its oxidation states S^{6+}, S^{4+}, and S^{2-} into the

16   apatite end-members fluor-, chlor-, and hydroxylapatite, $[Ca_{10}(PO_4)_6(F,Cl,OH)_2]$. The relative

17   stability of different oxidation states of S in apatite is evaluated by using balanced reaction

18   equations where the apatite host and a solid S-bearing source phase (e.g., gypsum for S^{6+} and

19   troilite for S^{2-}) are the reactants, and the S-incorporated apatite and an anion sink phase are the

20   products. Here, the reaction energy of the balanced equation indicates the stability of the

21   modeled S-incorporated apatite relative to the host apatite, the source, and sink phases. For the

22   incorporation of S into apatite, coupled substitutions are necessary to compensate for charge

23   imbalance. One possible coupled substitution mechanism involves the replacement of La^{3+} +

24   $PO_4^{3-} \leftrightarrow Ca^{2+} + SO_4^{2-}$. Our results show that the incorporation of SO_4^{2-} into La- and Na-bearing

25   apatite, $Ca_8NaLa(PO_4)_6(F,Cl,OH)_2$, is energetically favored over the incorporation into La- and

26   Si-bearing apatite, $Ca_9La(PO_4)_5(SiO_4)(F,Cl,OH)_2$ (the difference in incorporation energy, ΔE_{rxn},

27   is 10.7 kJ/mol). This thermodynamic gain is partially attributed to the electrostatic contribution

28   of Na^+, and the energetic contribution of La^{3+} to the stability of SO_4^{2-} incorporated into the

29   apatite structure. Co-incorporation of SO_4^{2-} and SO_3^{2-} is energetically favored when the lone pair

30   electrons of SO_3^{2-} face towards the anion column site, compared to facing away from it.

31   Full or partial incorporation of S^{2-} is favored on the column anion site in the form of

32   $[Ca_{10}(PO_4)_6S]$ and $[Ca_{20}(PO_4)_{12}SX_2)]$, where X = F, Cl, or OH. Upon full incorporation (i.e.,

33   replacing *all* column ions by sulfide ions), S^{2-} is positioned in the anion column at z = 0.5 (half

34   way between the mirror planes at z = 1/4 and z = 3/4) in the energy-optimized structure. The

35   calculated energies for partial incorporation of S^{2-} demonstrate that in an energy-optimized

36   structure, S^{2-} is displaced from the mirror plane at z = 1/4 or 3/4, by 1.0 to 1.6 Å, depending on

37   the surrounding species (F^-, Cl^- or OH^-); however, the probability for S^{2-} to be incorporated into

38   the apatite structure is highest for chlorapatite end-members.

39   Our results describe energetically feasible incorporation mechanisms for all three oxidations

40   states of S (S^{6+}, S^{4+}, S^{2-}) in apatite, along with structural distortion and concurring electronic

41   structure changes. These observations are consistent with recently published experimental results

42   (Konecke et al. 2017) that demonstrate S^{6+}, S^{4+} and S^{2-} incorporation into apatite, where the ratio

43   of $S^{6+}/\sum S$ in apatite is controlled by oxygen fugacity (fO_2). The new computational results

44   coupled with published experimental data provide the basis for using S in apatite as a

45   geochemical proxy to trace variations in oxygen fugacity of magmatic and magmatic-

46   hydrothermal systems.

47   **Keywords:** apatite, S incorporation, S oxidation state, energetics, geometry, column anion,

48   lanthanum, oxybarometry

49   INTRODUCTION

50   Apatite group minerals, with the general chemical formula [$Ca_{10}(PO_4)_6(F,Cl,OH)_2$], are the

51   most abundant phosphate minerals on Earth (Rakovan et al. 2013; Harlov 2015). The diverse

52   chemistry of apatite is related to its flexible structure, which can accommodate a large number of

53   cations and anions (Hughes and Rakovan 2002). The Ca cation sites can be replaced by alkali,

54   alkali earth and transition metals (e.g., Na, Ba, Sr, Mn, Pb) and rare earth elements (e.g., La, Ce),

55   whereas the major oxyanions such as SiO_4^{4-}, SO_4^{2-}, CO_3^{2-} can occupy the phosphate (PO_4^{3-}) site

56   (Hughes and Rakovan 2002).

57   Despite several studies demonstrating the evolution and variation of S recorded in apatite

58   phases from igneous systems (Peng et al. 1997; Streck and Dilles 1998; Imai 2002; Parat et al.

59   2002; Parat and Holtz 2004, 2005), little is known about the structure and thermodynamic

60   stability of S in apatite. The recent study by Konecke et al. (2017) is the first to show

61   qualitatively that variable abundances of S^{6+}, S^{4+}, and S^{2-} are incorporated into apatite as

62   crystallized from a mafic silicate melt under varying oxygen fugacity (fO_2) conditions. The new

63   experimental data on S redox chemistry in apatite highlight the need for theoretical

64   understanding of the structural incorporation of different S species in apatite.

65   In this study, the thermodynamics and geometry of S incorporation in the apatite structure

66   were investigated computationally. While common trace element impurities (e.g., Na, Si, REEs)

67   in natural apatite are taken into account (Hughes et al. 1991), we focus on evaluating some of the

68   most plausible scenarios that are consistent with experimental observations (e.g., $2P^{5+} \Leftrightarrow S^{6+} +$

69   S^{4+} and $2(F^-, Cl^-, OH^-) \Leftrightarrow S^{2-} +$ vacancy; Konecke et al. 2017). From a computational standpoint,

70   each type of reactant and product must be treated independently, while the same system

71   configuration and computational settings must strictly be applied for all species in a given

72   chemical equation (Walker and Becker, 2015). In our approach, all phases considered are solids,

73   and are quantum-mechanically modeled at ambient pressure (P) and temperature (T) conditions,

74   because calculations at elevated P and T are currently beyond the capability for the applied

75   approach. The relative stability of S with different oxidation states (S^{6+}, S^{4+}, and S^{2-}) in apatite is

76   evaluated using balanced reaction equations, where the host apatite and the source phase for S

77   (e.g., gypsum for SO_4^{2-} and troilite for S^{2-}) are the reactants, and the S incorporated apatite and

78   the sink phase that accommodates the replaced anions from apatite (e.g., monazite for PO_4^{3-}) are

79   the products. The host apatite, source, and sink phases are required for achieving a stoichiometric

80   and balanced reaction equation. Thus, the reaction energy of the balanced equation indicates the

81   stability of the S incorporated apatite, relative to coexisting solid phases. This computational

82   evaluation permits the determination of: [1] the energetic favorability of S incorporation into

83   apatite depending on substitutions required for charge balance, and [2] the electronic structure of

84   atoms and the structural distortion of the incorporation site upon S incorporation. Based on the

85   results of this study, chemical and crystallographic parameters that control the S incorporation

86   into apatite are identified, and provide the computational and thermodynamic framework

87   required to investigate the potential role of S in apatite as a proxy to trace redox in magmatic

88   systems.

89   **PREVIOUS WORK**

90   Historically, sulfate (S^{6+}) has been suggested as the only oxidation state of S in the apatite

91   structure (cf. Parat et al. 2011) based on the observation that S-rich (terrestrial) apatite,

92   containing up to 0.8 wt.% S, exists in oxidizing (anhydrite-bearing) environments, where sulfate

93   S^{6+} and sulfite S^{4+} are the dominant (or only) S oxidation states in the melt and fluid, respectively

94   (e.g., Rouse and Dunn 1982; Liu and Comodi 1993; Tepper and Kuehner 1999). Direct evidence

95   for the presence of S^{6+} in the apatite structure was reported by Paris et al. (2001) who used

96   synchrotron-radiation S K-edge micro X-ray absorption near-edge structure (μ−XANES)

97   spectroscopy to document the presence of sulfate in Durango apatite. Their results supported the

98   hypothesis that S is incorporated as S^{6+} into the apatite structure. There are, however,

99   experimental data from reduced systems, where sulfur is present mostly as sulfide (S^{2-}) in the

100   melt (Jugo et al. 2005), which suggests that apatite crystallizing from the melt may incorporate

101   S^{2-}. For instance, S concentrations in apatite from reduced lunar mare basalts (i.e., IW; iron-

102   wüstite fO_2 buffer; Sato et al. 1973) exceed 400 μg/g S (Greenwood et al. 2011; Boyce et al.

103   2014).

104   Recently, Konecke et al. (2017) provided qualitative evidence for the presence of S^{6+}, S^{4+},

105   and S^{2-} in apatite. Apatite crystals were crystallized from a hydrous, S-bearing mafic melt at

106   1,000°C, 300 MPa, and over a broad range of oxygen fugacities ((log(fO_2) = FMQ to FMQ+3;

107   FMQ = fayalite-magnetite-quartz solid buffer). Those authors used S μ−XANES to document the

108   presence of distinct sulfate S^{6+} (absorption edge energy of ~2482 eV), sulfite S^{4+} (~2478 eV) and

109   sulfide S^{2-} (~2470 eV) in the apatite structure (Figure 1). Specifically, apatite is dominated by S^{6+}

110   with a small contribution of S^{4+} under oxidizing conditions (FMQ+1.2 and +3); whereas S^{2-} is

111   the dominant S oxidation state at more reducing conditions (FMQ). Their results demonstrate

112   that once the S incorporation mechanism is determined, the S oxidation state in apatite may be

113   used as a geochemical tool to quantify oxygen, and perhaps sulfur fugacity at redox conditions

114   relevant to arc and MORB settings. However, the incorporation mechanisms and bonding

115   environments of each S oxidation state in apatite remain unknown, and are imperative to the

116   development of a quantitative S-in-apatite oxybarometer.

<div align="center">117   METHODS</div>

118   **Computational parameters**

119   The computational approach adopted in this study is based on density functional theory (DFT)

120   with planewaves representing functions for the overall wave function of upper valence and

121   conduction band electrons (basis functions), while inner valence and core electrons of an atom

122   and their interactions with the valence electrons are approximated using pseudopotentials. The

123   optimization was performed using the quantum-mechanical code CASTEP (Segall et al. 2002).

124   The Perdew-Wang generalized gradient scheme (GGA) was used in combination with ultrasoft

125   pseudopotentials. The GGA scheme was parameterized by the Perdew–Burke–Ernzerhof (PBE)

126   functional (Perdew et al. 1996). The energy cutoff for planewave expansion was 400.0 eV and

127   the Brillouin zone was sampled using a k-point separation of 0.05 $Å^{-1}$, according to the

128   Monkhorst-Pack scheme (Monkhorst and Pack 1976). Self-consistent field cycles were assumed

129   to converge with an energy difference of less than 2.0 x10^{-6} eV/atom. A spin-polarized approach

130   was implemented when the unit cell of a mineral included atoms with unpaired spins. For

131   example, ferrous iron, (Fe^{2+}) has four 3d unpaired spins in its high-spin state. The electronic

132   contribution of localized unpaired d states to materials properties may be incompletely described

133   using standard DFT approaches. For such cases, a Hubbard U correction was implemented to

134   account for the on-site Coulomb interaction (represented by the parameter, U) and the exchange

135   interaction (J). For this approach, the effective Hubbard U parameter, U_{eff} (= U-J) values, was

136   adopted from previous studies investigating the Fe 3d states in various silicates (U_{eff} = 2.9 and

137   4.8; Hsu et al. 2011; Stackhouse et al. 2010) and sulfides (U_{eff} = 2.0; Rohrbach et al. 2003).

Incorporation energy calculation

139   The reaction equation of S-incorporation consists of a pure (i.e., end-member) and impure

140   (i.e., trace elements-bearing) apatite in the form of host apatite (*apatite_host*) and S-incorporated

141   apatite (*apatite_S-incorporated*). Accordingly, appropriate solid sources for S (*source_i*) and sinks for

142   ions replaced in the mineral host (*sink_i*) were selected to maintain stoichiometry. A host apatite

143   phase and sources for S in different oxidation states are reactants, while S-incorporated apatite

144   and sinks for anions being liberated from the apatite host are products. The general equation for

145   this approach takes the form:

146   $$apatite_{host} + \sum_{i=1}^{n} a_i\, source_i \leftrightarrow apatite_{S-incorporated} + \sum_{i=1}^{m} b_i\, sink_i \qquad (1).$$

147   The incorporation reactions are balanced in order to involve one atom of S on both sides of

148   the equation, such that the calculated reaction energy (E_{rxn}) is defined as the energy required to

149   incorporate one mole of S in an apatite host phase (unless otherwise stated). In addition, this

150   setup allows for a consistent quantum-mechanical treatment; i.e., using the same computational

151   parameters throughout the equation, which is crucial to obtain reliable energetic data.

152   The role of a reaction medium, where an incorporation reaction occurs, can be important for

153   computationally simulating incorporation into the mineral phase in geologically relevant systems.

154   Examples for incorporation using solid sources and sinks can be found in Shuller et al. (2013,

155   2014). The atomistic assessment for hydrated ions incorporated into host minerals is rather

156   complicated and computationally difficult, as it involves a series of reaction equations that have

157   to be combined in order to constrain species of different characters (hydrated vs. vacuum,

158   charged vs. neutral, clusters vs. 3D periodic) in one net equation, while using a consistent

159   approach (cf. Walker and Becker 2015; Smith et al. 2016). Additionally, it is more challenging to

160   take into account the role of silicate melts or hydrothermal fluids under geologically relevant

161   pressures and temperatures for a quantum-mechanical computational assessment of the

162   incorporation process. Modeling magmatic-hydrothermal systems would require a quantum-

163   mechanical molecular-dynamics simulation using large unit cells at high P-T conditions that

164   approach or exceed the current limits of computational capability, and is otherwise beyond the

165   scope of this study. Therefore, all source and sink phases are periodic solids, which commonly

166   play a role in accommodating atoms that will be incorporated into and/or liberated from apatite.

167   In order to increase the geological significance of our evaluation, minerals or ionic compounds

168   that occur and are stable in magmatic or hydrothermal environments are selected as sources and

169   sinks for the reaction equations. Once energies of all phases involved in the incorporation

170   equations are computationally constrained, reaction energies for each incorporation equation can

171   be calculated using the general approach:

8

172 $$\Delta E_{rxn} = \sum E_{prod} - \sum E_{reac} \tag{2}$$

173   The resulting incorporation reaction energy indicates the stability of the S-incorporated

174 apatite relative to the corresponding host apatite, and the source and sink phases. In addition, the

175 relative stability of various incorporated apatite phases can be compared when common source

176 phases are used. The incorporation energies calculated using CASTEP are well described by

177 Shuller et al. (2013). Energies calculated using CASTEP include contributions from electronic

178 properties such as electronic relaxations and spin-spin interactions. The ΔE_{rxn} evaluated from the

179 CASTEP energies of the reactants and products are in good agreement with enthalpies, for the

180 reason that they are calculated at ambient pressure (VdP = 0). To evaluate ΔG_{rxn}, entropy

181 contributions (e.g., vibrational entropies of the solid phases used in our study) must be

182 considered. However, this requires significant computational efforts, and is outside the scope of

183 this study.

184

185   **The structure model of apatite**

186   The initial models for the apatite end-members are adopted from the natural apatite structure,

187 $[Ca_{10}(PO_4)_6(F, OH, Cl)_2]$ (P6$_3$/m; see Hughes et al. 1990; Hughes and Rakovan, 2015), and are

188 depicted in Figure 2 and Figure S.1 (Supplemental material A). The column anion site [00z] of

189 the apatite structure (P6$_3$/m) is mainly occupied by F$^-$, OH$^-$, and Cl$^-$. Natural apatite end-members

190 are subdivided into fluorapatite $[Ca_5(PO_4)_3F]$, chlorapatite $[Ca_5(PO_4)_3Cl]$, and hydroxylapatite

191 $[Ca_5(PO_4)_3(OH)]$ based on a single occupant of the anion column, but often occur as a solid

192 solution with binary or ternary anion columns (Hughes et al. 1990; Hughes and Rakovan 2002;

193   Hughes et al. 2016). The column anion site has the potential to accommodate other anions with

194   different radii and/or charge. A well-known example is the incorporation of carbonate (CO_3^{2-})

195   into hydroxylapatite, which occurs in both the phosphate and column anion sites (Fleet and Liu,

196   2007).

197   The apatite structure has two types of Ca sites as Ca1 and Ca2. The Ca1 type is coordinated

198   to nine O atoms, while the Ca2 site is coordinated to six O atoms and one column anion. In the

199    $P6_3/m$ space group, Ca2 atoms form triangles on the planes at z = 1/4 and 3/4. Each of the three

200   Ca atoms at the triangle corners is bonded to the central anion in the [00z] column (Hughes et al.

201   1990). Fluorine, the smallest of the column anions, is positioned on the mirror planes at z = 1/4

202   and 3/4 such that it is located at the center of the Ca triangle (Fig. 2a). The OH^- and Cl^- are too

203   large to be positioned in the center of the Ca2 triangle, and are thus displaced above or below the

204   planes. As a result of such displacement, OH^- and Cl^- have multiple possible positions along the

205   anion column in the apatite unit cell (see Hughes, 2015). Since all atoms in the apatite structure

206   are given full atomic occupancy in this study, the positions of Cl^- or OH^- below the planes at z =

207   1/4 and 3/4 were selected to complete the unit cell formula, $[Ca_{10}(PO_4)_6(F, Cl, OH)_2]$ (Fig. S.1).

208   Thus, the chlorapatite and hydroxylapatite structures reduce the symmetry to the $P6_3$ space group.

209   Similar approaches to simulate hexagonal apatite without the *m* plane have been successfully

210   tested in previous computational studies (e.g., Corno et al. 2006; Ulian et al. 2013). Using the

211   structural and computational parameters above, a good agreement in the unit cell parameter

212   values was found between calculated and natural end-member apatites reported by Hughes et al.

213   (1989; see also Table 1 and Figure S.1). The resulting structures are then used to geometrically

214   optimize the host and S-substituted apatite models (Fig. 3).

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215   Energy-dependent density of states (DOS) analysis was performed to obtain the electronic

216   structure of the apatite and S-bearing apatite configurations investigated in this study. Density of

217   states analysis can be further delineated into partial density of states (PDOS) plots for certain

218   angular momenta on atoms of interest (s, p, and d orbital characters in this study). The PDOS

219   spectra of apatite configurations are consistent with a previous report on the electronic structure

220   of Ca-phosphate crystals (Rulis et al. 2004). The electronic structure of non-S-bearing apatite

221   and S-bearing apatite configurations are described in detail in Supplemental Material A.

222

Sulfur replacement mechanisms in S-bearing apatite

224   An important step in the incorporation energy calculations is to identify replacement

225   mechanisms that may play a critical role in hosting S in natural apatite. All mechanisms tested in

226   this study are based on previous reports of natural and experimentally produced apatite.

Sulfate incorporation mechanisms

228   It has been suggested that the P site is the most likely location where substitution of SO_4^{2-}

229   occurs in the apatite structure (Streck and Dilles 1998; Pan and Fleet 2002; Parat et al. 2011),

230   where possible replacement mechanisms include:

231    $$P^{5+} + Ca^{2+} \leftrightarrow S^{6+} + Na^+ \qquad (3)$$

232    $$2P^{5+} \leftrightarrow S^{6+} + Si^{4+} \qquad (4)$$

233   In the current study, all calculations for SO_4^{2-} substitution are based on replacement

234   mechanisms (3) and (4). We used geologically relevant solid source and sink phases for the

11

235   calculations. For instance, anhydrite ($CaSO_4$) commonly coexists with S-rich apatite in oxidized

236   magmatic systems (Baker and Ruther 1996a; Streck and Dilles 1998) and, thus, is a geologically

237   relevant candidate as a source phase for SO_4^{2-}.

238   Moreover, in relatively oxidized magmatic systems (e.g., where the $S^{6+}/\Sigma S$ ratio of the melt

239   is > 0.5), Na^+ (replacing Ca^{2+}) and SiO_4^{4-} (replacing PO_4^{3-}) can be concomitant ions for S^{6+}

240   incorporation in apatite to maintain charge neutrality (Eq. 3 and 4). In addition, rare earth

241   elements (REE^{3+}) can substitute for Ca^{2+} in the apatite structure via the coupled substitutions

242    $REE^{3+} + Si^{4+} \leftrightarrow Ca^{2+} + P^{5+}$ and $REE^{3+} + Na^+ \leftrightarrow 2Ca^{2+}$ (Hughes et al. 1991; Pan and Fleet 2002).

243   Hughes et al. (1991) reported a total REE^{3+} concentration range of 2 to 16 wt% in REE-bearing

244   apatite samples and a good linear correlation between $[Na^+ + Si^{4+}]$ vs. $[\sum REE^{3+}]$ (~1:1 atomic

245   ratio), which can be well explained by the coupled substitutions reactions above. Streck and

246   Dilles (1998) reported variations in the S content in apatite, reaching up to 0.56 wt% S in apatite

247   from the Yerington batholith (Nevada), and a strong correlation between $[Si^{4+}+Na^+-\sum REE^{3+}]$ vs

248    $[S^{6+}]$ (~1:1 atomic ratio), which supports the coupled substitution of Si^{4+} and Na^+ with S^{6+} and/or

249   REE^{3+}. Based on these considerations, La-bearing apatite is selected as the host apatite phase,

250   which incorporates SO_4^{2-} in the structure. Two distinct scenarios involving La-bearing apatite,

251    $[Ca_8NaLa][(PO_4)_6]X_2$ and $[Ca_9La][(PO_4)_5(SiO_4)]X_2$, are evaluated individually, and the effects of

252   Na^+ and Si^{4+} on incorporating SO_4^{2-} into apatite are discussed in detail. Lanthanum-monazite

253   ($LaPO_4$), which commonly occurs as a P-bearing accessory mineral in igneous rocks (Foerster

254   1998), is selected as a mineral sink phase for PO_4^{3-} being replaced by SO_4^{2-} in order to account

255   the formation of La-bearing apatite. In models of *apatite_host* (S-free) and *apatite_S-incorporated*, Na^+

256   and La^{3+} are positioned on the Ca2 atomic sites at the mirror plane at z = 3/4 and one of the three

257   PO_4^{3-} sites nearest to the column anion is replaced by SiO_4^{4-} or SO_4^{2-} (Fig. 2b and Fig. S.1).

12

258

### Sulfate and sulfite incorporation mechanisms

260   A recent study identified the co-existence of S^{4+} and S^{6+} in natural and experimentally

261 produced apatite, and suggested a possible coupled substitution mechanism involving the

262 replacement of two phosphate atoms by SO_4^{2-} and SO_3^{2-} via the coupled substitution (Konecke et

263 al. 2017):

264     $2P^{5+} \leftrightarrow S^{6+} + S^{4+}$ (5)

265   The plausibility of the proposed co-incorporation of S^{4+} and S^{6+} into fluor-, chlor-, and

266 hydroxylapatite (eq. 5) is examined by balancing an incorporation reaction equation, in

267 combination with the nickel-nickel oxide (ΔNNO) oxygen fugacity buffer (e.g., to simulate

268 geologically relevant fO_2 conditions). A Na- and Si- apatite, $[Ca_7La_2Na][(PO_4)_5(SiO_4)](F, Cl,$

269 $OH)_2$, is selected as the host phase. Anhydrite and La-monazite are used as source and sink

270 phases, respectively. In models of *apatite_S-incorporated*, one of the three nearest phosphate sites at

271 the mirror plane at z = 1/4 and 3/4 to the anion column is replaced by SO_3^{2-} and SO_4^{2-},

272 respectively (see Fig. 2 and 3a).

Sulfide incorporation mechanisms

274   Henning et al. (2000) used single crystal X-ray diffraction to determine the structure of

275 synthetic S^{2-}-bearing apatite in the form $Ca_{10}(PO_4)_6S$, and reported that S occupies the anion

276 column via the following coupled substitution (Eq. 6):

277     $2(F, Cl, OH)^- \leftrightarrow S^{2-} + \text{vacancy}$ (6)

13
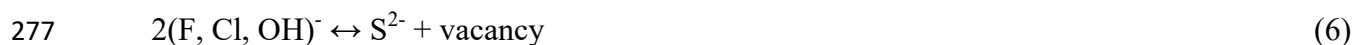
278   Hence, a testable scenario for the incorporation of S^{2-} into the anion column in apatite

279   involves FeS (troilite) and Na_2S as solid S^{2-} sources and is based on the affinity of Fe^{2+} and Na^+

280   for S^{2-} in geological processes (Fiege et al. 2015; Burns and Fyfe 1966). When F^- and Cl^- in

281   apatite are replaced by S^{2-} from these sources, metal fluorides and chlorides are produced as a

282   solid sink. To consider OH^- released from apatite, the metamorphic amphibole grunerite,

283    $[Fe_7Si_8O_{22}(OH)_2]$, is selected as a sink phase, while ferrosilite ($FeSiO_3$) and quartz (SiO_2) are

284   added as reactants to balance the composition of grunerite. Grunerite, as a key amphibole end-

285   member, possesses a broad stability field in the simple system of FeO-SiO_2-H_2O (Lattard and

286   Evans, 1992). Thermodynamic equilibria between grunerite and other Fe-silicates, such as

287   ferrosilite and fayalite, have been adopted as a tool to estimate temperature, pressure, and H_2O

288   activity in metamorphic, hydrothermal, and volcanic systems (e.g., Lattard and Evans 1992;

289   Elliott 2001). This makes it a suitable phase to investigate magmatic and magmatic-hydrothermal

290   scenarios.

291   When building initial models (i.e., ones subjected to geometry optimization), S^{2-} replaces two

292   F^-, Cl^-, or OH^- anions in fluor-, chlor- or hydroxylapatite (Eq. 6). Once placed in the column, S^{2-}

293   can be re-positioned to any unoccupied position of the column during the course of the geometry

294   optimization. The optimization algorithm calculates local minima in the energy landscape by

295   adjusting the lattice parameters, and the coordinates of each atom within the initial model.

296   Therefore, it is important to ensure an energetic or geometric variation in the optimization result

297   as the initial position of S^{2-} varies in the anion column. The position of F^-, Cl^- and OH^- in the

298   apatite anion column (i.e., (00z) calculated from the end-member apatite; see Table 1) is selected

299   as the position of S^{2-} in the initial models. Where necessary, initial S^{2-} is referred to as S(F, Cl,

300    $OH)_{ini}$, when a position near the anion column is chosen as the initial S^{2-} position replacing F^-, Cl^-,

14

301   or OH⁻ anions. For this type of replacement, full incorporation of S^{2-} in apatite is considered in

302   the form of $Ca_{10}(PO_4)_6S$. Moreover, we considered the partial incorporation of S^{2-} in the $1\times1\times2$

303   supercell of apatite in the form of $Ca_{20}(PO_4)_{12}S(F, OH$ or $Cl)_2$ (Fig. 3b). Notably, in the supercell,

304   a S^{2-} atom is located between two of column anions such that the optimized positions of the

305   column anions are the result of S^{2-} interacting with surrounding F^-, Cl^-, or OH⁻ anions. The

306   calculated reaction energy defines the energy required for the incorporation of one S^{2-} ion in the

307    $1\times1\times2$ supercell of apatite.

308

Computational scopes and errors

310   In a computational study like this, the sources of errors have more of a systematic character

311   and less of a random one as they occur in experimental studies. One source of variability is the

312   computational parameters, such as density functionals, pseudopotentials, as well a quantity and

313   types of basis functions. Testing all parameters for the examples used in this study would

314   increase the computational effort by at least an order of magnitude. Therefore, testing can be

315   done only with a limited number of examples and computational parameters. Importantly, we

316   concluded that the energy for stoichiometric reaction equations may be minimally susceptible to

317   the DFT functional chosen for calculation, as long as all computational parameters are consistent

318   within such equations. For example, two sets of the incorporation energy data for an

319   incorporation reaction equation were produced using the GGA scheme parameterized with the

320   PBE and the PerdewWang1991 (PW91) functional (the reaction equation in Table S.1 in

321   Supplemental Material A concerns all three different monovalent column anions). Although the

322   energy of respective mineral phase differs by up to a few tens of eV, the incorporation energy

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323   difference of calculation using the PBE and PW91 is only on the order of ~0.015 eV (or ~1.5

324   kJ/mol) and the relative stability among the apatites remain unchanged.

325   More important than such parameter testing is a good understanding of the limitations of the

326   model setup. This includes the structural model setup with a limited-sized unit cell, which

327   increases the relative concentration of the incorporated species, as well as the decision to use

328   selected solid source and sink phases. All of these decisions have been made to model

329   geologically relevant scenarios in reasonable computation times. Our approach is suitable to

330   learn about the thermodynamic stability with respect to references, and the atomic and electronic

331   structure of mineral phases. The thermodynamic energies of incorporation are relative quantities

332   that would change by choosing different sink/source phases or transitioning to dynamic

333   hydrothermal fluids, whereas the results for the electronic/atomic structure of incorporation

334   would remain unaffected.

335

RESULTS

Incorporation energy and geometry

Sulfate (SO_4^{2-})

339   The reaction equations and energies for S^{6+} incorporation into La-apatite phases are

340   presented in Table 2. In the equations, charge imbalance of La^{3+} in place of Ca^{2+} is compensated

341   by coupled substitution with Na^+ or Si^{4+} in the apatite structure. Incorporation energies

342   calculated from the Na-bearing apatite phases are lower than those of the Si-bearing phases for

16

343   all tested scenarios. In the Na-bearing system, the lowest incorporation energy is found in

344   fluorapatite, followed by chlorapatite and hydroxylapatite. Energy differences between those are

345   relatively small (3 to 6 kJ/mol). In the Si-bearing apatite, the incorporation of S^{6+} into

346   chlorapatite is energetically more favored than the incorporation into fluorapatite and

347   hydroxylapatite (by 10.4 kJ/mol).

348   The unit cell volume is changed as a function of cell parameters and, thus, can be indicative

349   of the net effect of replacing phosphate by SO_4^{2-} in the optimized structure. The cell volumes of

350   S-incorporated apatite phases are presented in Table 3. Exchange of $P^{5+} + Ca^{2+} \leftrightarrow S^{6+} + Na^+$ and

351   of $2P^{5+} \leftrightarrow S^{6+} + S^{4+}$ in the unit cell of fluor-, chlor-, and hydroxylapatite leads to a volume

352   expansion by 3 to 5 and 6 to 8 $Å^3$, respectively. The ionic radius of 4-coordinated S^{6+} (0.12 Å) is

353   smaller than that of P^{5+} (0.17 Å; Shannon, 1976). Thus, the volume expansion by the coupled

354   exchanges should be mainly due to the larger ionic size of Na^+ compared to Ca^{2+}, and Si^{4+}

355   compared to P^{5+}. Cations occupying the Ca2 site are 7-coordinated, and the size of 7-coordinated

356   Na^+ and Ca^{2+} are approximately 1.12 and 1.06 Å, respectively. The 4-coordinated Si^{4+} is 0.26 Å

357   and thus its occupancy in place of P^{5+} would lead to a volume expansion of the unit cell.

358   Although, accounting for less than 1.4 % of the unit cell volume, such a variation in the unit cell

359   volume shows a monotonic increase with increasing column anion size ($Cl^- > OH^- > F^-$) in the

360   S^{6+} incorporated Si-bearing apatite series.

361   In the optimized S^{6+} incorporated Na- and Si-bearing apatite phases, bond lengths and angles

362   measured from incorporated SO_4^{2-} molecules are similar to reported values for the SO_4^{2-}

363   molecule (109.5° and 1.49 Å) with a maximum deviation of 2.7° and 0.02 Å. The nearest PO_4^{3-}

364   and SO_4^{2-} to the column site have two O atoms displaced above and below the planes at z = 1/4

17

365   and 3/4 while the other two O atoms are placed on the planes (Fig. 4a). The former two O atoms

366   face toward S on the (0 0 z) column anion such that their positions may be more susceptible to

367   the property of the column ion than the latter two. The angle formed between the S center and

368   the column-oriented O atoms (O-S-O) are presented in Fig. 4a and Table 3. In the S^{6+}

369   incorporated Na-bearing apatite series, the O-S-O angle tends to increase with increasing column

370   anion size from 107.9° to 108.4° whereas the O-P-O angle in fluorapatite changes from 107.2°

371   (X = F) to 107.7° in chlorapatite (Table 3).

372

373   *Sulfate (SO_4^{2-}) and sulfite (SO_3^{2-})*

374   The reaction equations and energies for co-incorporation of sulfite (S^{4+}) with sulfate (S^{6+})

375   into La-bearing fluor-, chlor-, and hydroxylapatite are presented in Table 2. In the reaction, La-

376   monazite ($LaPO_4$) is used as a sink phase to accommodate phosphate released from the host

377   apatite. Solid nickel ($Ni_{(s)}$) is introduced to play a role as an oxygen buffer to take up one O atom

378   of the sulfate SO_4^{2-} molecule forming a sulfite SO_3^{2-} molecule (reduction of S^{6+} to S^{4+}). The

379   molecular geometry of SO_3^{2-} is a trigonal pyramid with a lone pair of electrons at one corner. As

380   mentioned above, two of the four PO_4^{3-} (or SO_4^{2-}) O atoms are displaced from the planes at z =

381   1/4 and face toward the (0 0 z) anion column. The other two are placed on the plane and face

382   away from the column (Fig. 4a). In building a model for SO_3^{2-} replacing PO_4^{3-}, one of either the

383   former two or the latter two O atoms is replaced by a lone pair of electrons (Fig. 4b and c). In

384   Figure 4 and Table 2, the two cases are labeled A-type and B-type SO_3^{2-}, respectively.

385   The incorporation energy is the lowest in chlorapatite compared to fluorapatite and

386   hydroxylapatite, and the energy difference between the former and the latter two are 19 kJ/(1 mol

18

387   SO_3^{2-} + 1 mol SO_4^{2-}) and 22 kJ/(1 mol SO_3^{2-} + 1 mol SO_4^{2-}), respectively (Table 2). The

388   orientation of the SO_3^{2-} loan pair influences the stability of the incorporated apatite. Lower

389   incorporation energy is found for A-type SO_3^{2-}-incorporated apatite when compared to B-type

390   SO_3^{2-}-incorporated apatite (the energy difference is 14 to 16 kJ/(1 mol SO_3^{2-} + 1 mol SO_4^{2-}) for

391   each apatite end-member). Thus, the co-incorporation mechanism of sulfate and A-type sulfite is

392   energetically more likely than the mechanism involving B-type sulfite.

393   In the optimized S-incorporated apatite phases, bond lengths and angles measured from the

394   incorporated SO_3^{2-} molecules are in good agreement with previous reported values (104.3° and

395   1.53 Å) (Andersen and Lindqvist, 1984). The cell volumes and distances between S^{4+} and F^-, Cl^-,

396   or OH^- in optimized S-incorporated apatite phases are presented in Table 4. Larger cell volumes

397   are found for B-type SO_3^{2-}-incorporated apatite when compared to A-type SO_3^{2-}-incorporated

398   apatite. B-type SO_3^{2-}-incorporated apatite has 0.05 to 0.2 Å longer (F, Cl, OH)–S^{4+} and (F, Cl,

399   OH)–S^{6+} distances than A-type SO_3^{2-} apatite. The cell volume results coincide with the (F, Cl,

400   OH)–S distance variation in the sense that the longer atomic distance generally contributes to the

401   larger cell volume of the mineral. The calculated z fractional coordinate of the S center of SO_4^{2-}

402   is barely displaced from the plane at Z = 3/4 (< 0.03 Å). The S atom of A-type SO_3^{2-} is displaced

403   ~0.2 Å from the plane at Z = 1/4 whereas the B-type SO_3^{2-} deviates by less than 0.05 Å from the

404   same plane.

405   *Sulfide (S^{2-})*

406   The equations and calculated energies of reactions for S^{2-} incorporation into fluor-, chlor-,

407   and hydroxylapatite in the Fe-S and Na-S, and Fe-Si-S systems are presented in Table 5. Lattice

408   parameters of the initial and optimized S^{2-} incorporated apatite structures are summarized in

19

409   Table 6. The calculated reaction energies for S^{2-} incorporation are highly dependent on selected

410   source and sink phases. Energies calculated by using Fe-bearing phases (Fe-S system) are higher

411   than incorporation energies calculated using Na-bearing phases (Na-S system). This effect arises

412   from the higher stability of troilite (FeS) used as a source phase relative to Fe-bearing sink phase

413   solids than the stability of Na_2S relative to Na sink phases. However, in a given system, where

414   source phases and/or sink phases are fixed, the stability of S-incorporated apatite phases can be

415   evaluated relative to host apatite phases. In case of hydroxylapatite, because Si-bearing minerals

416   are used as source phases in addition to FeS, the stability of apatite phases is not comparable

417   between the Fe-S and Fe-Si-S systems. Full incorporation of S^{2-} into the Cl site (denoted by

418    $S(Cl)_{ini}$ in Table 5) of chlorapatite is more stable than into the F site ($S(F)_{ini}$) of fluorapatite. The

419   calculated incorporation energy difference between fluorapatite and chlorapatite is 256 and 265

420   kJ/mol in the Fe-S and Na-S systems, respectively. Full incorporation of S^{2-} into the

421   hydroxylapatite structure achieves appreciable stability relative to Fe-silicates (-71.9 kJ/mol;

422   Table 5).

423   The optimized structures of fully S^{2-} incorporated apatite are compared with a previous study

424   of synthetic sulfoapatite, $[Ca_{10}(PO_4)_6S]$ (Henning et al. 2000; Table 6). Calculated cell

425   parameters are in good agreement with the measured parameters. In the optimized structure of

426   S^{2-} full incorporation, the position of S^{2-} is at z = 0.5018 and 0.5004 in the hydroxylapatite and

427   chlorapatite structures, respectively and at z = 0.75 in the fluorapatite structure where F^- is

428   replaced by S^{2-} in the initial model. When located at (0, 0, 0.70) in the initial model of

429   fluorapatite, however, S^{2-} is relaxed to the position at z = 0.5 during geometry optimization,

430   resulting in the incorporation energy lower than one having S^{2-} at z = 0.75 (the energy difference

431   of 129 kJ/mol) (Table 5 and 6). This indicates that S^{2-} in the F^- position (z =1/4 or 3/4, at the

20

432   center of the Ca triangle) is metastable for S^{2-} larger than F^-, and (0, 0, 0.5) is the most likely

433   position of column anion S^{2-} in sulfoapatite, $[Ca_{10}(PO_4)_6S]$. This result is in good agreement with

434   experimental data for synthetic sulfoapatite ($z = 0.5$) (Henning et al. 2000).

435   Lower reaction energies are found in cases of partial incorporation into chlorapatite when

436   compared to those of fluorapatite (Table 5). The incorporation energy also depends on where S^{2-}

437   is incorporated in the anion column of the initial model structure (denoted by (F, Cl, OH)$_{ini}$ in

438   Table 6). Upon the partial incorporation into fluorapatite, S^{2-} on a F^- position (S(F)$_{ini}$) is less

439   stable than S^{2-} on Cl^- and OH^- positions (S(Cl)$_{ini}$ and S(OH)$_{ini}$) (energy difference of 55 to 56

440   kJ/mol). When partially incorporated into chlorapatite, the dependence of the S stability on the

441   column position is relatively lower and leads to energy differences between S(F, Cl, OH)$_{ini}$ less

442   than 6 kJ/mol. From these results, one can infer that the probability of S^{2-} being incorporated into

443   apatite is enhanced when S^{2-} is partitioned into the Cl-bearing apatite structure or when Cl^-

444   coexists with S^{2-} in the anion column site. Upon partial substitution of S^{2-} in hydroxylapatite, the

445   stability of incorporated S^{2-} is higher at the Cl or OH site relative to the F site.

446   Column anion positions in the optimized structures of partially S^{2-} substituted apatite are

447   depicted in Figure 5. The anion column S is located at $z = 0.57$ in the optimized structure of

448   fluorapatite when S^{2-} is initially positioned at the Cl^- or OH^- site (denoted by (F, Cl, OH)$_{ini}$ in

449   Table 6). The minimum energy configurations are found when the position of S^{2-} is (0, 0, 0.61)

450   in the hydroxylapatite structure. The anion column S^{2-} is positioned at $z = 0.51$ in S^{2-}

451   incorporated chlorapatite, regardless of its initial position. Interaction with surrounding column

452   anions is an important factor that determines the position of S^{2-}. In the anion column

453   environment tested here where S is located between two anions–i.e. F^-, Cl^-, or OH^-, at or near $z =$

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454   1/4 and 5/4 (with respect to the initial $1 \times 1 \times 1$ unit cell) in the $1 \times 1 \times 2$ supercell (Fig. 5) –the

455   lowest-energy configuration shows that S^{2-} in the anion column is located at z = 0.50 to 0.61.

456   The presence of S^{2-} in the anion column results in displacing the remaining F^-, Cl^-, or OH^- above

457   or below the planes at z = 1/4.

458

DISCUSSION

Parameters that control the sulfur oxyanions (SO_4^{3-} and SO_3^{2-}) incorporation into apatite

461   Generally, higher reaction energies result from stable reactants or unstable products.

462   Therefore, the lower S^{6+} incorporation energies observed for the La-Na-bearing apatite when

463   compared to La-Si-bearing apatite (Table 2) indicate that (i) the La-Si-bearing host apatite is

464   more stable than La-Na-bearing host apatite or (ii) that S^{6+} incorporation into apatite becomes

465   energetically more stable when SO_4^{2-} is coordinated with Na^+ and PO_4^{3-} than with Ca^{2+} and

466   SiO_4^{4-}. The incorporation energies of La^{3+} and Na^+ versus La^{3+} and Si^{4+} into apatite were

467   calculated in order to consider the stability of the impure apatite hosting S oxidation states

468   relative to the pure end-member fluor-, chlor-, and hydroxylapatite (Table 7). Incorporation

469   energies of La^{3+} and Na^+ into apatite are higher than those of La^{3+} and Si^{4+} into apatite for

470   fluorapatite and hydroxylapatite. Hence, scenario (i) may be favored for fluorapatite and

471   hydroxylapatite. Scenario (ii) can be evaluated using linear combinations of equations for S^{6+}

472   incorporation into La^{3+}-bearing apatite (Table 2) and for La^{3+} incorporation into end-member

473   apatite (Table 7). The incorporation energies of S^{6+} and Na^+-bearing apatite are lower than those

474   of S^{6+} and Si^{4+}-bearing apatite for all apatite end-members, which supports scenario (ii). In

22

475   addition, comparison between equations for S^{6+} incorporation into host apatite phases (Table 2

476   and 7) suggests that incorporation of SO_4^{2-} into La-bearing apatite may be energetically more

477   favorable than the incorporation into the end-member fluor-, chlor-, and hydroxylapatite.

478   Since replacements of Ca^{2+} and PO_4^{3-} by other ions (Na^+, La^{3+}, SiO_4^{4-} and SO_4^{2-}) are made at

479   the nearest position to the column anions (F, Cl, OH) in all models tested, it is expected that

480   energy differences among fluorapatite, chlorapatite, and hydroxylapatite used as reactants and

481   products arise mainly from chemical or structural environments on the column anion sites (Fig.

482   2). In this regard, the first and second possibilities above ((i) and (ii)) can be understood in terms

483   of interatomic interactions. In host and S-incorporated apatite, the Ca2 triangle that surrounds the

484   column anion has one or two Ca^{2+} ions replaced by Na^+ or La^{3+} (Fig. 2b). Cations positioned at

485   the triangle corners are electrostatically repelled from each other and attracted to the column

486   anion and surrounding phosphate and other oxyanions. The Coulomb energy between the

487   interacting ions is defined in a classical manner such that the energy is proportional to the

488   product of the charges of the two ions, q_i and q_j, and increases inversely with the distance

489   between the two, r_{ij}. When multiple atoms are present in a system, the Coulomb energy is

490   defined as Equation 7.

491   $$E_{coulomb} = \frac{e^2}{4\pi\varepsilon_0} \sum_{i>j} \frac{q_i q_j}{r_{ij}} \qquad (7)$$

492   Here, the Coulomb force of the cations in a triangle involves two contributions: (i) repulsion

493   between the cations and (ii) attraction of the triangle cations with the surrounding anions. A

494   higher repulsive force is exerted on the triangle structure when La^{3+} is located at a corner of the

495   triangle than when Na^+ or Ca^{2+} is there. In this case, the effect of La^{3+} ion can be counteracted by

496   coexistence with SiO_4^{4-} that makes the triangle less unstable. That is, the attractive coulombic

23

497   force between cations and SiO_4^{4-} with a 4- charge is stronger than the force exerted by PO_4^{3-} with

498   a 3- charge. This indicates that La-bearing apatites can be stabilized by coexisting with silicate

499   ions (the first possibility above). On the other hand, the presence of Na^+ or SiO_4^{4-} near SO_4^{2-} can

500   make a large contribution to the stability of S^{6+}-incorporated apatites. Na^+ is electrically less

501   attractive to SO_4^{2-} than Ca^{2+} while SiO_4^{4-} is more repulsive to SO_4^{2-} than PO_4^{3-}. This means that

502   electrical interaction of SO_4^{2-} with Na^+ or SiO_4^{4-} alone does not increase the stability of

503   incorporated SO_4^{2-}. However, Na^+ on the Ca2 site and SiO_4^{4-} on a neighboring phosphate site

504   both can contribute to energy lowering of the anion column triangle. Na^+ occupying the Ca2 site

505   has a lower repulsive force than Ca^{2+}, which lowers the instability of the triangular arrangement

506   by cation-cation repulsion. The presence of a neighboring silicate anion will counteract the

507   repulsive force between the triangle Ca^{2+} ions. However the effect of SiO_4^{4-} on Ca^{2+} ions will be

508   less than the case of La^{3+} included in the host apatite. The net effect of these contributions might

509   enable some of the S-incorporated apatites to be more stable in the coexistence with Na^+ than

510   with Si^{4+} (the second possibility).

511   The effect of the anion column on S^{6+} incorporation into La-bearing apatite is more

512   pronounced in the Si-bearing apatite system when compared to the Na-bearing apatite system.

513   That is, the Si-bearing system shows greater differences in the incorporation energies among the

514   apatite end members than the Na-bearing system (Table 2). In the former system, the lowest

515   incorporation energy is found for chlorapatite, followed by fluorapatite and hydroxylapatite. The

516   repulsive force between SO_4^{2-} and column anion F^-, OH^- or Cl^- is one possible contribution to the

517   stability of S^{6+}-incorporated apatite. In the optimized S-incorporated apatite, the center-to-center

518   distance is 3.55 Å between F^- and S^{6+}, 3.92 Å between Cl^- and S^{6+} and 3.61 Å between OH^- and

24

519   S^{6+} (Table 3). Therefore, chlorapatite is expected to experience the smallest repulsive force

520   between the column anion (Cl⁻) and SO_4^{2-}.

521   The lower energy of co-incorporation of S^{4+} with S^{6+} into the La-bearing apatite is found for

522   chlorapatite when compared to flour- and hydroxylapatite (Table 2). This may again be attributed

523   to the longest distance and thus the lowest repulsive force between the sulfur oxyanions and

524   column anion Cl⁻ compared to F⁻ and OH⁻ (Table 4). The stability of sulfite-substituted apatite

525   can be affected by the geometry mismatch with the phosphate site (trigonal pyramid vs

526   tetrahedron). Differences in incorporation energy and geometry between apatites with A- and B-

527   type SO_3^{2-} indicate that the oxygen site replaced by the lone pair electron of SO_3^{2-} can cause local

528   defects in the apatite structure and govern the stability of sulfite that substitutes the phosphate

529   site (Table 2 and Figure 3).

530   In summary, the relative stability of incorporated SO_4^{2-} and/or SO_3^{2-} into apatite can depend

531   on accompanying trace elements and the column anion. The replacement energies in Table 2

532   suggest that when La^{3+} and PO_4^{3-} are replaced by Ca^{2+} and SO_4^{2-}, it is more energetically

533   favorable to do this in a system that compensates for the La^{3+} charge by replacing Ca^{2+} by Na^+

534   rather than PO_4^{3-} by SiO_4^{4-}. The relative stability for the sulfur oxyanion substituted into

535   chlorapatite is greater than ones for fluorapatite and hydroxylapatite. The orientation of the

536   sulfite molecule can matter upon substitution with the phosphate site in apatite unlike sulfate

537   with the identical molecular geometry with phosphate.

538   **Effect of site preference of trace elements on sulfur substitution into apatite**

539   Site preference of atoms is important in understanding the crystal chemical behavior of trace

540   elements that substitute for the Ca sites in apatite (Fleet and Pan 1995). Na^+ has been found to

541   occupy both Ca1 and Ca2 sites, but has a strong preference for the Ca1 site (Hughes et al. 1991;

542   Fleet and Pan 1995; Rakovan and Hughes 2000). REE including La^{3+} generally tend to occupy

543   the Ca2 site (Hughes et al. 1991). For consistency, we selected the Ca2 site that is closer to the

544   column anion than the Ca1 site, for the position of both Na^+ and La^{3+}, although this site is rather

545   uncommon for Na^+ in natural apatite. One important question is whether the site preference of

546   neighboring trace elements may influence the energetics and geometry of sulfur incorporation

547   into apatite. As an example, incorporation energy of sulfate into the La-Na bearing apatite is

548   calculated considering the site preference of Na^+ between the Ca1 and Ca2 site (Table 8). Na^+ is

549   swapped between the Ca1 and Ca2 site (denoted by S' and S'' in Fig. S.1a and b) in the model

550   configuration of S^{6+} incorporated fluor- and chlorapatite. The incorporation energy of S^{6+} into

551   La-bearing apatite decreases by 2.1 and 9.0 kJ/mol for fluor- and chlorapatite, respectively, as

552   Na^+ is positioned at the Ca1 site than at the Ca2 site (compare with the equivalent reaction

553   equation and energy in Table 2). The energies required to exchange Na^+ between the Ca2 and

554   Ca1 site of apatite in the form of $[Ca_9Na][(PO_4)_5(SO_4)]X_2$ (X = F and Cl) are negative, indicating

555   increase in the stability of SO_4^{2-} incorporated apatite with Na^+ positioned at the Ca1 site (Table

556   8). These results support that the site preference of elements in the apatite structure is an

557   important factor in predicting the stability of sulfur incorporated apatite. Future research could be

558   aimed at systematic investigation for the role of site preference of trace elements on sulfur

559   incorporation into apatite.

560

Sulfide (S^{2-}) site stability in the apatite structure

561

562 The incorporation energy of S^{2-} into apatite is closely correlated with the optimized structure

563 of S-bearing apatite. Full or partial substitution of S^{2-} into fluor-, chlor-, or hydroxylapatite

564 results in lower incorporation energies when S^{2-} is positioned in the Cl^- and OH^- site relative to

565 the F^- site (Table 5 and 6). The occupancy of S^{2-} at (0, 0, 0.75) results in an increase in the Ca-Ca

566 distance in the Ca2 triangle at z = 3/4 by ~10 %. Such structural alteration by S on the F site can

567 significantly contribute to higher incorporation energy when compared to S^{2-} incorporation on

568 the Cl^- and OH^- site. It is inferred that the substitution of S^{2-} on the F^- site in the apatite structure

569 is energetically and geometrically less likely. In the lowest-energy configurations for the partial

570 substitution, the predicted position of the S^{2-} ion in fluor-, chlor- and hydroxylapatite is 1 to

571 1.6 Å displaced from the mirror plane at z = 1/4 or 3/4 (Fig. 5 and Table 6), which is close to the

572 Cl^- site in the natural apatite structure (0.182 displacement in the z value from the mirror planes;

573 Table 1). These results suggest that the Cl^- site can be one of the energetically stable sites for S^{2-}

574 incorporation in the apatite structure.

575 The relative stability of a substituent ion in an atomic site of a mineral structure can be

576 explained on the basis of the Goldschmidt's substitution rules, which states that the "native" ions

577 in a given site are more likely to be substituted by foreign ions with a similar radius, charge, and

578 ionic nature (e.g., chemical hardness and electronegativity; Klein et al. 2002). The reported ionic

579 radii of F^-, Cl^-, and S^{2-} are 1.33, 1.81, and 1.84 Å, respectively (Shannon, 1976). The ionic radius

580 of S^{2-} is very close to that of Cl^- (difference by 1.6 %) whereas there is an appreciable difference

581 in ionic radius between S^{2-} and F^- anions by 27.7 %. This confirms that incorporation of S^{2-} on

582 the F^- site is rather unlikely. In addition, S^{2-} is similar in its chemical nature to Cl^-. The chemical

27

583   hardness of S^{2-} is classified as a soft base, which gives rise to its affinity with various soft

584   transition metals such as Fe^{2+}, Cu^+, and Hg^{2+} in geological processes, e.g., ore-formation

585   (Pearson 1968). Chlorine is chemically soft and less electronegative than fluorine. Such chemical

586   similarities between S^{2-} and Cl^- may contribute to affinity of the two anions in apatite.

587

Future work

589   As H_2S in a silicate melt is deprotonated, S^{2-} may be partitioned into mineral phases as either

590   S^{2-} or HS^-. The possibility of HS^- incorporation into apatite was not addressed in this study

591   because the results of Henning et al. (2000) already indicate that S^{2-} may be the favored S species,

592   but future work should examine whether HS^- can also be an important component in the anion

593   column site as it may behave like OH^-. Moreover, examination by quantum-mechanical

594   molecular dynamics (MD) may enable evaluation of the energy and structure of periodic solids

595   (e.g., minerals) under high pressure or temperature (Segall et al. 2002). Recent studies have

596   successfully demonstrated applications of ab-initio MD approaches for evaluating hydrothermal

597   reactions involving molecular or aqueous species (e.g., Sherman 2007; Mei et al. 2013). To our

598   knowledge, however, the published literature is currently lacking studies applying MD tools to

599   incorporation into minerals under magmatic-hydrothermal conditions. In this regard, treatment of

600   high pressure and temperature dynamics (with or without H_2O) on S-bearing apatite should be

601   the subject of future studies.

602   We highlight that the interpretation of S behavior in this study is based on the traditional

603   paradigm that SO_4^{2-} and S^{2-} are the only relevant S species in silicate melts (Baker and

604   Rutherford, 1996b); however, this assumption has been challenged by the discovery of the S

605   radical ions (e.g., S_2^-, S_3^-) in hydrothermal fluids and silicate melts (Winther et al. 1998;

606   Jacquemet et al. 2014; Pokrovski and Dubessy 2015) and by the possible presence of (un-

607   quenchable) S^{4+} in silicate melts (Métrich et al. 2009). Therefore, it is important to consider the

608   role of various S species and oxidation states in geological fluids and melts when S-bearing

609   phases (e.g., apatite) that are subject to high temperatures and pressures are investigated in future

610   studies.

611

IMPLICATIONS

613   This study addresses the structural incorporation of multiple oxidation states of S into apatite

614   and the response of the apatite structure to these substituents. The crystallographic characteristics

615   and energetic stability of the S-incorporated apatite structure vary depending on the S oxidation

616   state and can be significantly influenced by [1] the neighboring column anion (F^-, Cl^-, or OH^-), [2]

617   the concomitant substitutions for Ca^{2+} and P^{5+} (e.g., La^{3+}, Na^+, Si^{4+}) and their site preferences

618   (particularly between the Ca1 and Ca2 site), and [3] the molecular geometry and orientation of S

619   oxyanions in the structure.

620   Sulfide (S^{2-}) occupancy in the anion column site (S^{2-} + vacancy) in the apatite structure is a

621   likely mechanism in reduced geological systems (e.g., around fayalite-magnetite-quartz (FMQ)

622   buffer). Of the model configurations tested, the scenarios with S^{2-} accommodated in the

623   chlorapatite structure and with S^{2-} positioned closely to Cl^- site in the anion column are most

624   energetically plausible. In most natural systems, however, F^-, Cl^-, and OH^- are the three major

625   column anions in apatite, while S is a trace element, independent of its oxidation state (< 1 wt%

626   S; Parat et al. 2011; Konecke et al. 2017). Thus, the presence of S^{2-} in natural apatite is probably

29

627   not limited to chloroapatite or Cl-rich apatite. The thermodynamic advantage of S^{2-} in the Cl site

628   may play a role in determining the S content in apatite that forms under Cl- and S-rich reduced

629   environments. This is consistent with the positive correlation between Cl and S contents found

630   from lunar apatite (Boyce et al. 2014) and the XANES-determined presence of S^{2-} in apatite

631   crystallized from a mafic melt under reducing redox conditions (~FMQ, Konecke et al. 2017).

632   The energetics data about S^{6+} incorporation into the La-bearing apatite support that the

633   replacement mechanism of $P^{5+} + Ca^{2+} \leftrightarrow S^{6+} + Na^{+}$ is energetically more favored over the

634   mechanism of $2P^{5+} \leftrightarrow S^{6+} + Si^{4+}$. However, it seems important to consider all replacement

635   mechanisms in natural systems where sulfate is only a minor substituent for phosphate in apatite

636   as documented for apatite from the Yerington batholith (Streck and Dilles 1998). The results for

637   oxidized sulfur species (S^{4+}, S^{6+}) presented in this study indicate that there are more energetic or

638   geometric constraints (e.g., the orientation of the S lone pair electrons) on SO_3^{2-} incorporation

639   into the apatite structure than on SO_4^{2-} incorporation. The data from this study and Konecke et al.

640   (2017) support the hypothesis that the substitution of SO_3^{2-} into apatite is relatively minor, but

641   appreciable if coexisting with SO_4^{2-} in apatite formed under oxidizing conditions.

642   The abundance and relative proportions of S^{2-}, S^{4+} and S^{6} in geologic systems is a function of

643   oxygen fugacity (fO_2), and recorded directly in the S chemistry of apatite (Konecke et al. 2017).

644   The modeling of different S species in the apatite structure in this study, combined with the

645   experimental results reported by Konecke et al (2017), implies that the oxidation state of S in

646   apatite has the potential to serve as a geochemical proxy to probe the fO_2 of magmatic and

647   hydrothermal systems.

648

649 **ACKNOWLEDGEMENTS**

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809   **FIGURE CAPTIONS**

810   **Figure 1.** S XANES analysis of apatite crystallized from a mafic melt at 1,000 ºC, 300 MPa and

811   different fO_2 conditions (modified from Figure 2 in Konecke et al. (2017)).

812   **Figure 2.** (**a**) The column anion site and the nearest Ca (Ca2) and P atoms in the hexagonal

813   apatite structure viewed parallel to the c-axis. (**b**) The coordination environment of X (= F, OH,

814   Cl) on the plane of z = 3/4 in the host or S^{6+}-incorporated apatite where A1 = P or Si, A2 = P or

815   S, C1 = Ca or Na and C2 = Ca or La. Atoms Ca, C1 and C2 form the triangle whose corners are

816   Ca2 sites. In both (**a**) and (**b**), oxygen atoms are omitted.

817   **Figure 3.** Examples of S-incorporated apatite models. (**a**) The unit cell of SO_4^{2-}- and SO_3^{2-}-

818   incorporated fluorapatite, $Ca_9Na(PO_4)_3(SiO_4)(SO_4)(SO_3)F_2$ and (**b**) the $1\times1\times2$ supercell of S^{2-}-

819   incorporated apatite, $Ca_{20}(PO_4)_{12}SF_2$.

820   **Figure 4.** Atomistic-level view of (**a**) SO_4^{2-} near the F column in S^{6+}-incorporated Na-bearing

821   apatite and (**b**) A-type and (**c**) B-type SO_3^{2-} near the F column in S^{6+} and S^{4+} co-incorporated

822   apatite. Orbital contours for SO_3^{2-} are shown to indicate the lone pair (l.p.) electrons and S-O

823   bonding (see text for more details).

824   **Figure 5.** The optimized positions of column anions in hexagonal end-member and partially S^{2-}-

825   incorporated apatite in the $1\times1\times2$ supercell. (**a**) fluorapatite (**b**) chlorapatite and (**c**)

826   hydroxylapatite systems are depicted respectively. Initial S^{2-} is referred to as S (F, Cl, OH)$_{ini}$ to

827   denote a position near the anion column chosen as the initial S^{2-} position replacing F⁻, Cl⁻ and

828   OH⁻. The fractional coordinate of z (with respect to the unit cell) in the optimized structure is

829   presented for S at or near z = 3/4. Note that the column anion site at z = 7/4 (coordinate with

830   respect to the original $1\times1\times1$ unit cell, not shown) is vacant in the supercell whose zero charge is

831   compensated with a charge of 2- from S.

832

833

834 **TABLES**

835

836 **Table 1.** Lattice parameters for natural and calculated (CASTEP) apatite

	a (Å)	c (Å)	z value[b] of (F, Cl, OH)
Fluorapatite			
Calculated	9.469	6.894	0.2500
Natural[a]	9.397	6.878	0.2500
Deviation (%)	0.76	0.22	
Chlorapatite			
Calculated	9.525	6.895	0.0621
Natural[a]	9.598	6.776	0.0677
Deviation (%)	0.76	1.76	
Hydroxylapatite			
Calculated	9.763	6.757	0.2128
Natural[a]	9.417	6.875	0.1979
Deviation (%)	3.68	1.71	

837

838 *Notes:* [a] Hughes and Rakovan (2002) [b] The z value of anion column position (0, 0, z).

839

840 **Table 2.** Reaction equations and energies of incorporation of S^{6+} and co-incorporation of S^{4+}

841 with S^{6+} into apatite.

Incorporation reaction	ΔE_{rxn} (kJ/mol)		
S^{6+}-incorporation into La-bearing apatite	X = F	Cl	OH
Na-bearing: $[Ca_8NaLa][(PO_4)_6]X_2 + CaSO_4 \leftrightarrow$ $[Ca_9Na][(PO_4)_5(SO_4)]X_2 + LaPO_4$	-1.74	1.16	4.34
Si-bearing: $[Ca_9La][(PO_4)_5(SiO_4)]X_2 + CaSO_4 \leftrightarrow$ $[Ca_{10}][(PO_4)_4(SiO_4)(SO_4)]X_2 + LaPO_4$	15.44	5.02	15.44
S^{4+}, S^{6+}-incorporation into La-bearing apatite	X = F	Cl	OH
$[Ca_7La_2Na][(PO_4)_5(SiO_4)](F, Cl, OH)_2 + 2CaSO_4 + Ni$ $\leftrightarrow$ $[Ca_9Na][(PO_4)_3(SiO_4)(SO_4)(SO_3)](F, Cl, OH)_2 +$ $2LaPO_4 + NiO$			
A-type S^{4+}	117.71	95.52	117.71
B-type S^{4+}	132.19	111.92	131.22

842

843

844   **Table 3.** Summary of geometric parameters for SO_4^{2-} incorporated apatite phases.

Optimized structure	Cell volume (Å^3)	X-S distance [a] (Å)	O-S-O angle [a] (degree)
Fluorapatite			
S, Na-bearing	538.9	3.68	107.9
S, Si-bearing	541.1	3.55	107.6
End-member	535.3	3.64	107.2
Chorapatite			
S, Na-bearing	563.7	4.02	108.3
S, Si-bearing	568.4	3.92	108.2
End-member	560.6	3.97	107.7
Hydroxylapatite			
S, Na-bearing	545.9	3.73	108.2
S, Si-bearing	547.6	3.61	108.4
End-member	541.8	3.67	107.6

845

846   *Notes:* [a] For the apatite end-members, (F^-, Cl^-, or OH^-)-S distance and O-S-O angle is measured

847   for P in place of S.

848

849   **Table 4.** Summary of geometric parameters for SO_4^{2-} and SO_3^{2-} incorporated apatite.

Optimized structure	Cell volume (Å^3)	X-S^{4+} distance (Å)	X-S^{6+} distance (Å)	z[a] of S^{4+}	z[a] of S^{6+}
Fluorapatite					
Incorporation of					
A-type SO_3^{2-}	542.3	3.63	3.61	0.2230	0.7507
B-type SO_3^{2-}	543.9	3.68	3.68	0.2500	0.7500
Chlorapatite					
A-type SO_3^{2-}	570.4	3.75	3.85	0.2204	0.7502
B-type SO_3^{2-}	574.5	3.97	3.94	0.2462	0.7503
Hydroxylapatite					
A-type SO_3^{2-}	548.5	3.67	3.64	0.2186	0.7461
B-type SO_3^{2-}	551.7	3.73	3.74	0.2432	0.7533

850   *Notes:* [a] The z value of fractional coordination (x, y, z)

851

852   **Table 5.** Reaction equations and energies of S^{2-} full and partial incorporation into apatite.

	ΔE_{rxn} (kJ/mol)		
	Column geometry of S^{2-}		
Fe-S system	$S(F)_{ini}$	$S(Cl)_{ini}$	$S(OH)_{ini}$
Full incorporation			
$Ca_{10}(PO_4)_6F_2 + FeS \leftrightarrow Ca_{10}(PO_4)_6(S) + FeF_2$	362.02 (232.83)[a]	–	–
$Ca_{10}(PO_4)_6Cl_2 + FeS \leftrightarrow Ca_{10}(PO_4)_6(S) + FeCl_2$	–	105.11	–
Partial incorporation			
$Ca_{20}(PO_4)_{12}F_4 + FeS \leftrightarrow Ca_{20}(PO_4)_{12}(S)F_2 + FeF_2$	399.53	343.37	344.21
$Ca_{20}(PO_4)_{12}Cl_4 + FeS \leftrightarrow Ca_{20}(PO_4)_{12}(S)Cl_2 + FeCl_2$	101.77	97.10	102.83
Na-S system			
Full incorporation			
$Ca_{10}(PO_4)_6F_2 + Na_2S \leftrightarrow Ca_{10}(PO_4)_6(S) + 2NaF_2$	203.76 (74.59)[a]	–	–
$Ca_{10}(PO_4)_6Cl_2 + Na_2S \leftrightarrow Ca_{10}(PO_4)_6(S) + 2NaCl$	–	-61.32	–
Partial incorporation			
$Ca_{20}(PO_4)_{12}F_4 + Na_2S \leftrightarrow Ca_{20}(PO_4)_{12}(S)F_2 + 2NaF_2$	241.27	185.11	185.95
$Ca_{20}(PO_4)_{12}Cl_4 + Na_2S \leftrightarrow Ca_{20}(PO_4)_{12}(S)Cl_2 + 2NaCl$	-64.66	-69.33	-63.60
Fe-Si-S system			
Full incorporation			
$Ca_{10}(PO_4)_6(OH)_2 + FeS + 6FeSiO_3 + 2SiO_2 \leftrightarrow$ $Ca_{10}(PO_4)_6(S) + Fe_7Si_8O_{22}(OH)_2$			-71.86
Partial incorporation			
$Ca_{20}(PO_4)_{12}(OH)_4 + FeS + 6FeSiO_3 + 2SiO_2 \leftrightarrow$ $Ca_{20}(PO_4)_{12}(S)(OH)_2 + Fe_7Si_8O_{22}(OH)_2$	58.35	40.97	46.84

853

854   *Notes:* [a] The calculated incorporation energy of S^{2-} into fluorapatite when initially positioned at
855   (0, 0, 0.7).

856

857

858

859   **Table 6.** The cell and lattice parameters of initial and optimized configurations of S^{2-} fully and

860   partially incorporated apatite.

| Optimized structure | z^{b} of (F, Cl, OH)$_{ini}$ | Full incorporation | | | Partial incorporation |
		a (Å)	b (Å)	z^{c} of S^{2-}	z^{c} of S^{2-}
S-apatite (experiment)[a]		9.462	6.834	0.5	
S in the fluorapatite structure	0.25 and 0.75	9.825	6.739	0.7500 (0.5016)[d]	0.57
Deviation (%)		3.84	1.39		
S in the chlorapatite structure	0.062 and 0.562	9.566	6.843	0.5018	0.51
Deviation (%)		1.10	0.13		
S in the hydroxyapatite structure	0.213 and 0.713	9.542	6.859	0.5004	0.61
Deviation (%)		0.85	0.36		

861

862   *Notes:* [a] *Henning et al. (2000)*

863   [b] The z value of column anion position (0, 0, z) used in the initial S^{2-} incorporation

864   models. In the models, (F, Cl, OH) at or near the mirror plane at z = 3/4 is replaced by S^{2-}.

865   [c] The z value of S^{2-} position (0, 0, z) in the lowest-energy configurations. See Figure 5 for

866   details.

867   [d] The optimized position of S^{2-} in fluorapatite when initially positioned at (0, 0, 0.7).

868

42

869 **Table 7.** Reaction equations and energies of La^{3+}- and S^{6+}-incorporation into end-member apatite.

	ΔE_{rxn} (kJ/mol)		
La^{3+}-incorporation into end-member apatite	X = F	Cl	OH
La^{3+} and Na^+: $Ca_{10}(PO_4)_6X_2 + 1/3Na_3PO_4 + LaPO_4 \leftrightarrow$ $[Ca_8NaLa][(PO_4)_6]X_2 + 2/3Ca_3(PO_4)_2$	91.28	68.12	77.29
La^{3+} and Si^{4+}: $Ca_{10}(PO_4)_6X_2 + Ca_2SiO_4 + LaPO_4 \leftrightarrow$ $[Ca_9La][(PO_4)_5(SiO_4)]X_2 + Ca_3(PO_4)_2$	75.45	69.76	70.72
S^{6+}-incorporation into end-member apatite	X = F	Cl	OH
S^{6+} and Na^+: $Ca_{10}(PO_4)_6X_2 + 1/3Na_3PO_4 + CaSO_4 \leftrightarrow$ $[Ca_9Na][(PO_4)_5(SO_4)]X_2 + 2/3Ca_3(PO_4)_2$	89.54	69.28	81.63
S^{6+} and Si^{4+}: $Ca_{10}(PO_4)_6X_2 + Ca_2SiO_4 + CaSO_4 \leftrightarrow$ $[Ca_{10}][(PO_4)_4(SiO_4)(SO_4)]X_2 + Ca_3(PO_4)_2$	90.89	74.78	86.16

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888   **Table 8.** Reaction equations and energies of incorporation of S^{6+} into La- and Na-bearing apatite

889   (Na^+ positioned at the Ca1 site and La^{3+} at the Ca2 site) and of Na^+ exchange between the Ca2

890   and Ca1 site of S^{6+} incorporated apatite.

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Reaction	ΔE_{rxn} (kJ/mol)	
S^{6+}-incorporation into La-bearing apatite with Na^+ at the Ca1 site	X = F	Cl
Na-bearing: $[Ca_8NaLa][(PO_4)_6]X_2 + CaSO_4 \leftrightarrow$ $[Ca_9Na][(PO_4)_5(SO_4)]X_2 + LaPO_4$	-3.85	-7.85
Exchange of Na^+ in the S^{6+}-bearing apatite structure	X = F	Cl
$[Ca_9Na][(PO_4)_5(SO_4)]X_2$ (Na^+ at the Ca2 site) $\leftrightarrow [Ca_9Na][(PO_4)_5(SO_4)]X_2$ (Na^+ at the Ca1 site)	-22.46	-7.76

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Figure 1. S XANES analysis of apatite crystallized from a mafic melt at 1,000 ºC, 300 MPa and different fO$_2$ conditions (modified from Figure 2 in Konecke et al. (2017)).

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Figure 2. (a) The column anion site and the nearest Ca (Ca2) and P atoms in the hexagonal apatite structure viewed parallel to the c-axis. (b) The coordination environment of X (= F, OH, Cl) on the plane of z = 3/4 in the host or S^{6+}-incorporated apatite where A1 = P or Si, A2 = P or S, C1 = Ca or Na and C2 = Ca or La. Atoms Ca, C1 and C2 form the triangle whose corners are Ca2 sites. In both (a) and (b), oxygen atoms are omitted.

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Figure 3. Examples of S-incorporated apatite models. (**a**) The unit cell of SO_4^{2-}- and SO_3^{2-}-incorporated fluorapatite, $Ca_9Na(PO_4)_3(SiO_4)(SO_4)(SO_3)F_2$ and (**b**) the $1\times1\times2$ supercell of S^{2-}-incorporated apatite, $Ca_{20}(PO_4)_{12}SF_2$.
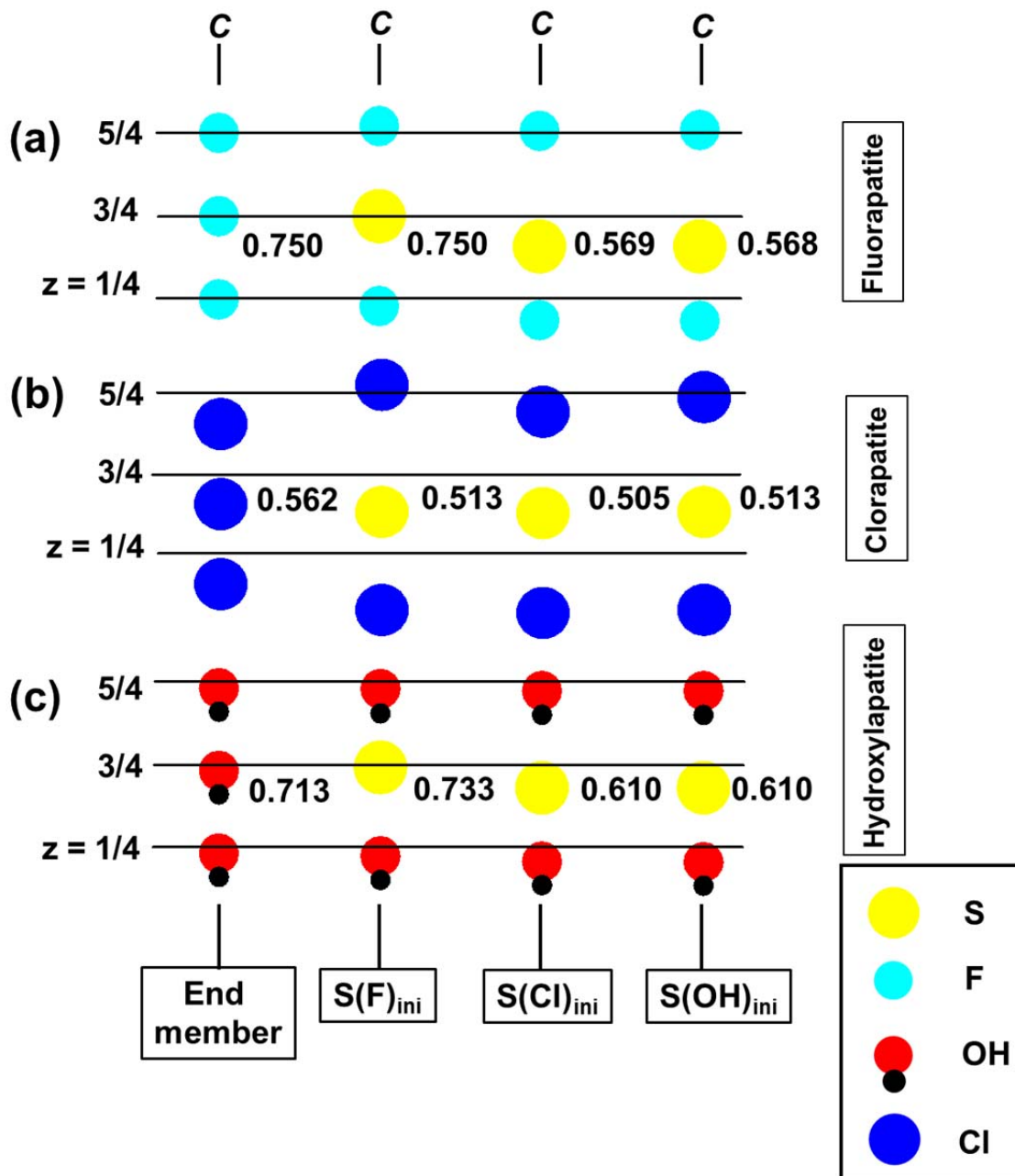
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Figure 4. Atomistic-level view of (**a**) SO_4^{2-} near the F column in S^{6+}-incorporated Na-bearing apatite and (**b**) A-type and (**c**) B-type SO_3^{2-} near the F column in S^{6+} and S^{4+} co-incorporated apatite. Orbital contours for SO_3^{2-} are shown to indicate the lone pair (l.p.) electrons and S-O bonding (see text for more details).

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Figure 5. The optimized positions of column anions in hexagonal end-member and partially S^{2-}-incorporated apatite in the $1\times1\times2$ supercell. (**a**) fluorapatite (**b**) chlorapatite and (**c**) hydroxylapatite systems are depicted respectively. Initial S^{2-} is referred to as S (F, Cl, OH)$_{ini}$ to denote a position near the anion column chosen as the initial S^{2-} position replacing F^-, Cl^- and OH^-. The fractional coordinate of z (with respect to the unit cell) in the optimized structure is presented for S at or near z = 3/4. Note that the column anion site at z = 7/4 (coordinate with

925   respect to the original 1×1×1 unit cell, not shown) is vacant in the supercell whose zero charge is

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