



**Figure S1.** The fractions of dissolved disulfide species,  $\text{H}_2\text{S}_2$ ,  $\text{HS}_2^-$ , and  $\text{S}_2^{2-}$  ( $n_1$ ,  $n_2$ , and  $n_3$ , respectively, where  $n_1 + n_2 + n_3 = 1$ ), sulfide species,  $\text{H}_2\text{S}$ ,  $\text{HS}^-$ , and  $\text{S}^{2-}$  ( $m_1$ ,  $m_2$ , and  $m_3$ , respectively, where  $m_1 + m_2 + m_3 = 1$ ), and F species,  $\text{HF}$  and  $\text{F}^-$  ( $k_1$  and  $k_2$ , respectively, where  $k_1 + k_2 = 1$ ) are calculated as a function of pH assuming thermodynamic equilibrium at 25 °C.

**Table S1.** Reaction equations and Gibbs free energies of relevant solid-state and solid-aqueous solution reactions. The computed thermodynamic data of this study are combined with these experimental thermodynamic data (Dean, 1990) to evaluate  $\Delta G_{\text{rxn}}$  of incorporation reactions involving various kinds of source and sink phases. See Method section for details.

(a) Reactions involving disulfide		(d) Reactions involving sulfide	
solid state reactions with FeS <sub>2(s)</sub> (pyrite) as product	$\Delta G$ (kJ/mol)	solid state reactions with FeS <sub>(s)</sub> (troilite) as product	$\Delta G$ (kJ/mol)
$\text{Na}_2\text{S}_{2(s)} + \text{FeF}_{2(s)} \leftrightarrow 2 \text{NaF}_{(s)} + \text{FeS}_{2(s)}$	-214.2	$\text{Na}_2\text{S}_{(s)} + \text{FeF}_{2(s)} \leftrightarrow 2 \text{NaF}_{(s)} + \text{FeS}_{(s)}$	-166.6
$\text{Na}_2\text{S}_{2(s)} + \text{FeCl}_{2(s)} \leftrightarrow 2 \text{NaCl}_{(s)} + \text{FeS}_{2(s)}$	-254.2	$\text{Na}_2\text{S}_{(s)} + \text{FeCl}_{2(s)} \leftrightarrow 2 \text{NaCl}_{(s)} + \text{FeS}_{(s)}$	-206.6
$\text{Na}_2\text{S}_{2(s)} + \text{FeOH}_{2(s)} \leftrightarrow 2 \text{NaOH}_{(s)} + \text{FeS}_{2(s)}$	-60.8	$\text{Na}_2\text{S}_{(s)} + \text{FeOH}_{2(s)} \leftrightarrow 2 \text{NaOH}_{(s)} + \text{FeS}_{(s)}$	134.3
solid - aqueous solution reactions with H <sub>2</sub> S <sub>2(aq)</sub> as a product		solid - aqueous solution reactions with H <sub>2</sub> S <sub>(aq)</sub> as product	
$\text{Na}_2\text{S}_{2(s)} + 2 \text{HF}_{(aq)} \leftrightarrow 2 \text{NaF}_{(s)} + \text{H}_2\text{S}_{2(aq)}$	-109.1	$\text{Na}_2\text{S}_{(s)} + 2 \text{HF}_{(aq)} \leftrightarrow 2 \text{NaF}_{(s)} + \text{H}_2\text{S}_{(aq)}$	-162.1
$\text{Na}_2\text{S}_{2(s)} + 2 \text{H}^+_{(aq)} + 2 \text{F}^-_{(aq)} \leftrightarrow 2 \text{NaF}_{(s)} + \text{H}_2\text{S}_{2(aq)}$	-144.5	$\text{Na}_2\text{S}_{(s)} + 2 \text{H}^+_{(aq)} + 2 \text{F}^-_{(aq)} \leftrightarrow 2 \text{NaF}_{(s)} + \text{H}_2\text{S}_{(aq)}$	-197.5
$\text{Na}_2\text{S}_{2(s)} + 2 \text{H}^+_{(aq)} + 2 \text{Cl}^-_{(aq)} \leftrightarrow 2 \text{NaCl}_{(s)} + \text{H}_2\text{S}_{2(aq)}$	-120.9	$\text{Na}_2\text{S}_{(s)} + 2 \text{H}^+_{(aq)} + 2 \text{Cl}^-_{(aq)} \leftrightarrow 2 \text{NaCl}_{(s)} + \text{H}_2\text{S}_{(aq)}$	-173.9
$\text{Na}_2\text{S}_{2(s)} + 2 \text{H}_2\text{O}_{(l)} \leftrightarrow 2 \text{NaOH}_{(s)} + \text{H}_2\text{S}_{2(aq)}$	119.6	$\text{Na}_2\text{S}_{(s)} + \text{H}_2\text{O}_{(l)} \leftrightarrow 2 \text{Na}_2\text{O}_{(s)} + \text{H}_2\text{S}_{(aq)}$	202.2
solid - aqueous solution reactions with HS <sub>2</sub> <sup>-</sup> <sub>(aq)</sub> as product		solid - aqueous solution reactions with HS <sup>-</sup> <sub>(aq)</sub> as product	
$\text{Na}_2\text{S}_{2(s)} + \text{HF}_{(aq)} + \text{F}^-_{(aq)} \leftrightarrow 2 \text{NaF}_{(s)} + \text{HS}_{2(aq)}^-$	-98.2	$\text{Na}_2\text{S}_{(s)} + \text{HF}_{(aq)} + \text{F}^-_{(aq)} \leftrightarrow 2 \text{NaF}_{(s)} + \text{HS}^-_{(aq)}$	-140.4
$\text{Na}_2\text{S}_{2(s)} + \text{H}^+_{(aq)} + 2 \text{F}^-_{(aq)} \leftrightarrow 2 \text{NaF}_{(s)} + \text{HS}_{2(aq)}^-$	-115.9	$\text{Na}_2\text{S}_{(s)} + \text{H}^+_{(aq)} + 2 \text{F}^-_{(aq)} \leftrightarrow 2 \text{NaF}_{(s)} + \text{HS}^-_{(aq)}$	-158.1
$\text{Na}_2\text{S}_{2(s)} + \text{H}^+_{(aq)} + 2 \text{Cl}^-_{(aq)} \leftrightarrow 2 \text{NaCl}_{(s)} + \text{HS}_{2(aq)}^-$	-92.3	$\text{Na}_2\text{S}_{(s)} + \text{H}^+_{(aq)} + 2 \text{Cl}^-_{(aq)} \leftrightarrow 2 \text{NaCl}_{(s)} + \text{HS}^-_{(aq)}$	-134.5
$\text{Na}_2\text{S}_{2(s)} + \text{H}_2\text{O}_{(l)} + \text{OH}^-_{(aq)} \leftrightarrow 2 \text{NaOH}_{(s)} + \text{HS}_{2(aq)}^-$	58.5	$\text{Na}_2\text{S}_{(s)} + \text{OH}^-_{(aq)} \leftrightarrow \text{Na}_2\text{O}_{(s)} + \text{HS}^-_{(aq)}$	152.0
(b) Gibbs free energy of formation of apatite <sup>a</sup>	$\Delta G$ (kJ/mol)	(e) Acidity of dissolved chemical species <sup>c</sup>	pKa
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	-12878(83) <sup>b</sup>	$\text{H}_2\text{S}_{2(aq)}$	5.0
$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$	-12468(50)	$\text{HS}_{2(aq)}^-$	9.7
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	-12593(64)	$\text{H}_2\text{S}_{(aq)}$	6.9
(c) Dissolution of source and sink phases	$\Delta G$ (kJ/mol)	$\text{HS}^-_{(aq)}$	12.0
$\text{NaF}_{(s)} = \text{Na}^+_{(aq)} + \text{F}^-_{(aq)}$	2.8	$\text{HF}_{(aq)}$	3.1
$\text{NaCl}_{(s)} = \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)}$	-9.0	$\text{HCl}_{(aq)}$	-6.0
$\text{Na}(\text{OH})_{(s)} = \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)}$	-39.6	$\text{H}_2\text{O}_{(l)}$	15.7
$\text{Na}_2\text{O}_{(s)} + \text{H}^+_{(aq)} = 2 \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)}$	-304.5		
$\text{Na}_2\text{S}_{2(s)} = 2 \text{Na}^+_{(aq)} + \text{S}_{2(aq)}^{2-}$	-65.6		
$\text{Na}_2\text{S}_{(s)} + \text{H}^+_{(aq)} = 2 \text{Na}^+_{(aq)} + \text{HS}^-_{(aq)}$	-151.9		

<sup>a</sup> Drouet (2015)

<sup>b</sup> values in ( ) are uncertainties of the last two digits

<sup>c</sup> Jordan (1979); Kumagai and Abiko (2017)

**Table S2.** Cell and lattice parameters for natural and calculated apatite

	$a$ (Å)	$c$ (Å)	z value <sup>a</sup> of (F,OH, Cl) <sup>-</sup>
<u>fluorapatite</u>			
calculated	9.47	6.89	0.25
experimental <sup>b</sup>	9.40	6.88	0.25
deviation (%)	0.76	0.22	
<u>chlorapatite</u>			
calculated	9.53	6.90	0.06
experimental	9.60	6.78	0.07
deviation (%)	0.76	1.76	
<u>hydroxylapatite</u>			
calculated	9.76	6.76	0.21
experimental	9.42	6.88	0.20
deviation (%)	3.68	1.71	

<sup>a</sup> the z value of anion column position (0, 0, z).

<sup>b</sup> Hughes and Rakovan (2002)

**Table S3.** The cell parameters of optimized configurations of disulfide-, bisulfide-, and sulfide-incorporated apatite and the z values of S species in apatite.

	disulfide ( $S_2^{2-}$ )				bisulfide ( $HS^-$ )				sulfide ( $S^{2-}$ )			
	complete incorporation			partial incorporation	complete incorporation			partial incorporation	complete incorporation			partial incorporation
	<i>a</i> (Å)	<i>c</i> (Å)	z of $S_2^{2-}$	z of $S_2^{2-}$	<i>a</i> (Å)	<i>c</i> (Å)	z of $HS^-$	z of $HS^-$	<i>a</i> (Å)	<i>c</i> (Å)	z of $HS^-$	z of $HS^-$
S in fluorapatite structure	9.99	6.76	0.51	0.49	9.90	6.81	0.75	0.76	9.83	6.74	0.50	0.57
deviation (%) <sup>a</sup>	5.5	-2.0			4.6	-1.2			3.8	-2.2		
S in chlorapatite structure	9.89	6.82	0.50	0.49	9.95	6.78	0.72	0.70	9.57	6.84	0.50	0.51
deviation (%)	3.8	-1.0			4.5	-1.7			0.4	-0.8		
S in hydroxylapatite structure	9.97	6.75	0.51	0.50	9.89	6.81	0.71	0.71	9.54	6.86	0.50	0.61
deviation (%)	2.1	-0.1			1.3	0.8			-2.3	1.5		

<sup>a</sup> structural deviation of S-incorporated apatite with respect to respective host apatite (fluor-, chlor-, and hydroxylapatite).

**Table S4.** The z value, interatomic distance, and channel radius (see Fig. 8) of the Ca2 and O3 planes across the c-axis channel.

	type of atom	z value	interatomic distance (Å)	channel radius (Å)
fluorapatite	O3	0.93	5.1	1.7
	Ca2	0.75	4.0	1.3
	O3	0.57	5.1	1.7
	O3	0.43	5.1	1.7
	Ca2	0.25	4.0	1.3
	O3	0.07	5.1	1.7
hydroxylapatite	O3	0.93	5.0	1.6
	Ca2	0.75	4.2	1.4
	O3	0.57	5.2	1.7
	O3	0.43	5.0	1.6
	Ca2	0.25	4.2	1.4
	O3	0.07	5.2	1.7
chlorapatite	O3	0.93	5.3	1.8
	Ca2	0.76	4.4	1.5
	O3	0.56	5.5	1.9
	O3	0.43	5.3	1.8
	Ca2	0.26	4.4	1.5
	O3	0.06	5.5	1.9

## References cited

- Dean, J.A. (1990) Lange's handbook of chemistry. Material and manufacturing process, 5(4), 687-688.
- Drouet, C. (2015) A comprehensive guide to experimental and predicted thermodynamic properties of phosphate apatite minerals in view of applicative purposes. The Journal of Chemical Thermodynamics, 81, 143-159.
- Hughes, J.M., and Rakovan, J. (2002) The crystal structure of apatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$ . Reviews in mineralogy and geochemistry, 48(1), 1-12.
- Jordan, J. (1979) Instrumental analysis of sulfur compounds in coal process streams. Quarterly technical progress report, January-March 1979. Pennsylvania State Univ., University Park (USA). Dept. of Chemistry.
- Kumagai, Y., and Abiko, Y. (2017) Environmental electrophiles: protein adducts, modulation of redox signaling, and interaction with persulfides/polysulfides. Chemical research in toxicology, 30(1), 203-219.