

APPENDIX

TABLE S1. The contents of Fe, As, SO₄, and divalent metal cations (Me(II)s) in the Natural-scorodite.

Element	Fe	As	SO ₄	Cu	Zn	Pb	Cd
Unit	wt%	wt%	wt%	g/kg	g/kg	g/kg	g/kg
Contents	22.6	30.5	2.87	12.6	0.3	0.3	0.6

TABLE S2. The percentage of various SO₄ complexing species in terms of the total SO₄²⁻ concentration in 0.1 M As(V), 0.15 Fe³⁺, 0.22 M SO₄²⁻ with various Na⁺ concentrations calculated using Visual MINTEQ v 3.1 by KTH (J.P. Gustafsson, Sweden; <https://vminteq.lwr.kth.se/>).

Species	pH 1.2				pH 1.8			
	0 M Na ⁺	1 Na ⁺	2 Na ⁺	4 Na ⁺	0 M Na ⁺	1 Na ⁺	2 Na ⁺	4 Na ⁺
SO ₄ ²⁻	9.76	6.77	3.69	0.92	17.13	10.04	5.02	1.103
HSO ₄ ⁻	24.26	17.79	12.7	6.65	10.87	6.54	4.265	1.981
FeSO ₄ ⁺	56.08	56.39	59.25	63.41	54.70	55.96	58.60	62.741
Fe(SO ₄) ₂ ⁻	9.90	7.43	6.10	4.38	17.31	10.74	8.02	5.118
NaSO ₄ ⁻	0	11.62	18.26	24.66	0	16.72	24.10	29.057
Ionic strength	0.24	0.73	1.19	2.13	0.22	0.70	1.16	2.12

TABLE S3. Results of cell refinement for scorodite and SO₄-scorodite formed at different initial Na concentrations. Refinement range from 10° to 60° 2θ.

Samples	a (Å)	b (Å)	c (Å)	Cell volume	R value
Scorodite	8.95012	10.32739	10.04005	928.02 Å ³	8.19 %
1 M Na ⁺	8.93889	10.31014	10.03465	924.80 Å ³	3.19 %
2 M Na ⁺	8.91063	10.29478	10.02334	919.47 Å ³	3.13 %
4 M Na ⁺	8.92361	10.30501	10.03249	922.57 Å ³	3.78 %
Scorodite (a)	8.9530	10.3250	10.0380	927.91 Å ³	

(a): Kitahama et al. 1975.

TABLE S4. The log(solubility products) (log K_{sp}) of römerite, coquimbite, jarosite, Fe₂(SO₄)₃, and scorodite.

Minerals	Equilibrium formula	log K_{sp}
Römerite	$\text{Fe}_3(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O} = 2\text{Fe}^{3+} + 4\text{SO}_4^{2-} + \text{Fe}^{2+} + 14\text{H}_2\text{O}$	-11.628
Coquimbite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O} = 2\text{Fe}^{3+} + 3\text{SO}_4^{2-} + 9\text{H}_2\text{O}$	-8.976
Jarosite (Na)	$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+ = 3\text{Fe}^{3+} + \text{Na}^+ + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O}$	6.738
Fe ₂ (SO ₄) ₃	$\text{Fe}_2(\text{SO}_4)_3 = 2\text{Fe}^{3+} + 3\text{SO}_4^{2-}$	0.038
Scorodite	$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O} + 2\text{H}^+ = \text{H}_2\text{AsO}_4^- + \text{Fe}^{3+} + \text{H}_2\text{O}$	-7.368

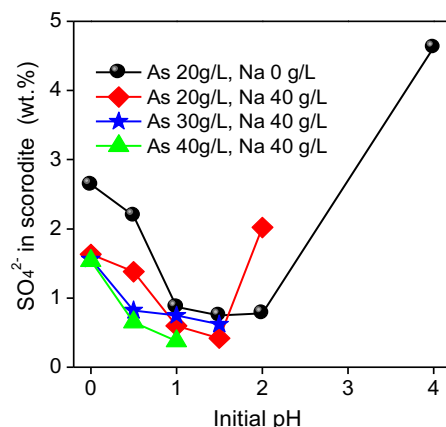


FIGURE S1. Contents of SO_4^{2-} in scorodite as a function of initial pH values at various As and Na^+ concentrations. These were calculated in terms of S content and obtained from Fujita et al. (2009a).

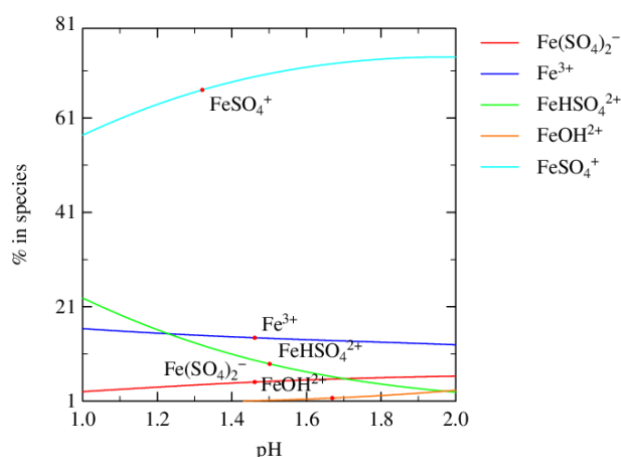


FIGURE S2. The percentage of Fe(III)-SO_4^{2-} species in terms of total Fe as a function of pH calculated using PhreePlot (Kinniburgh and Cooper 2011). The concentrations of Fe(III) and SO_4^{2-} were set as 150 and 225 mM respectively, corresponding to our experimental conditions.

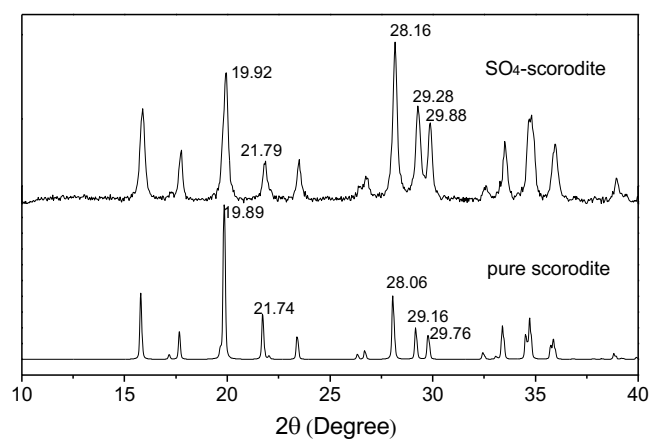


FIGURE S3. Comparison of the diffraction peak position in SO₄-scorodite with pure scorodite in the 2θ range from 10° to 40°.

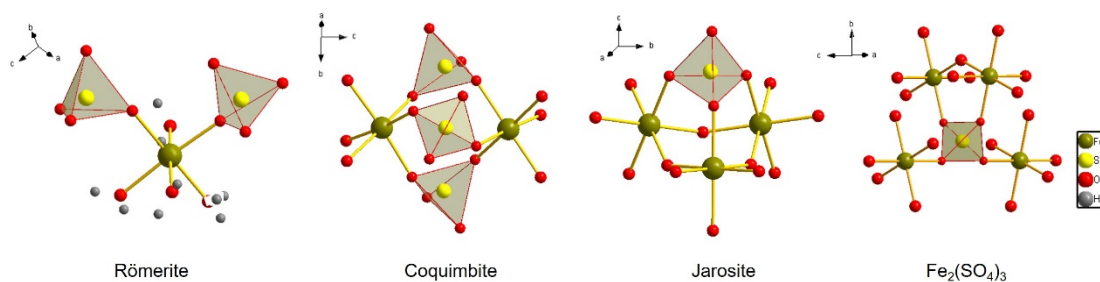


FIGURE S4. SO₄²⁻ local coordination environments in römerite (Fe²⁺Fe³⁺₂(SO₄)₄·14H₂O) (Mereiter 2018), coquimbite (KFe³⁺₃(SO₄)₂(OH)₆) (Fang and Robinson, 1970), jarosite (KFe³⁺₃(SO₄)₂(OH)₆) (Kato and Miura, 1975), and Fe₂(SO₄)₃ (Ventruti et al. 2005).

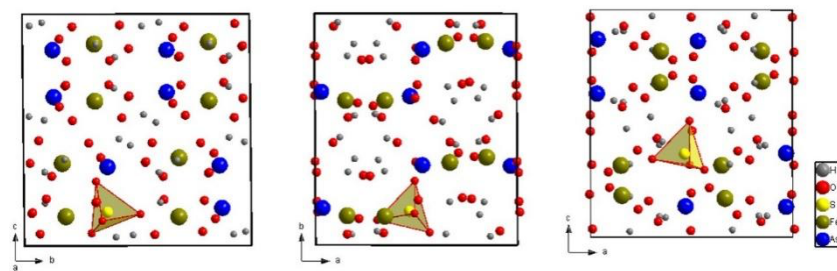


FIGURE S5. DFT optimized unit cell of SO_4^{2-} doped scorodite.

References

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