

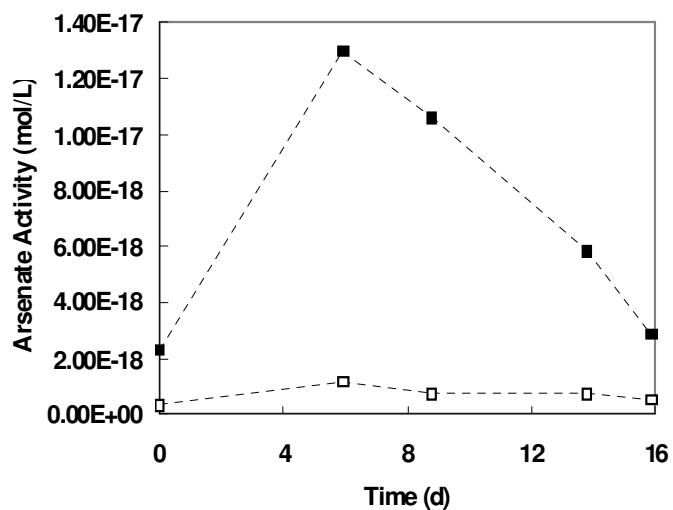


Fig. S1a. Arsenate activity calculated using the hydrolysis constant from Table S3 and Supplementary Equations.

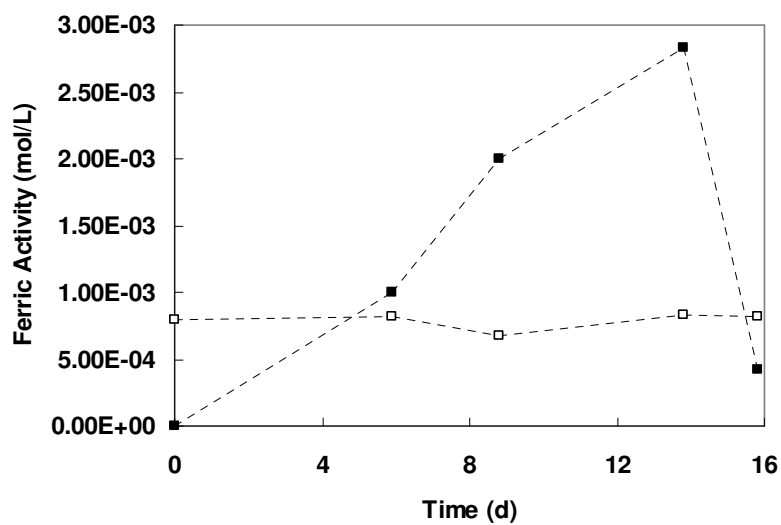


Fig. S1b. Ferric iron activity calculated using the hydrolysis constant from Table S3 and Supplementary Equations.

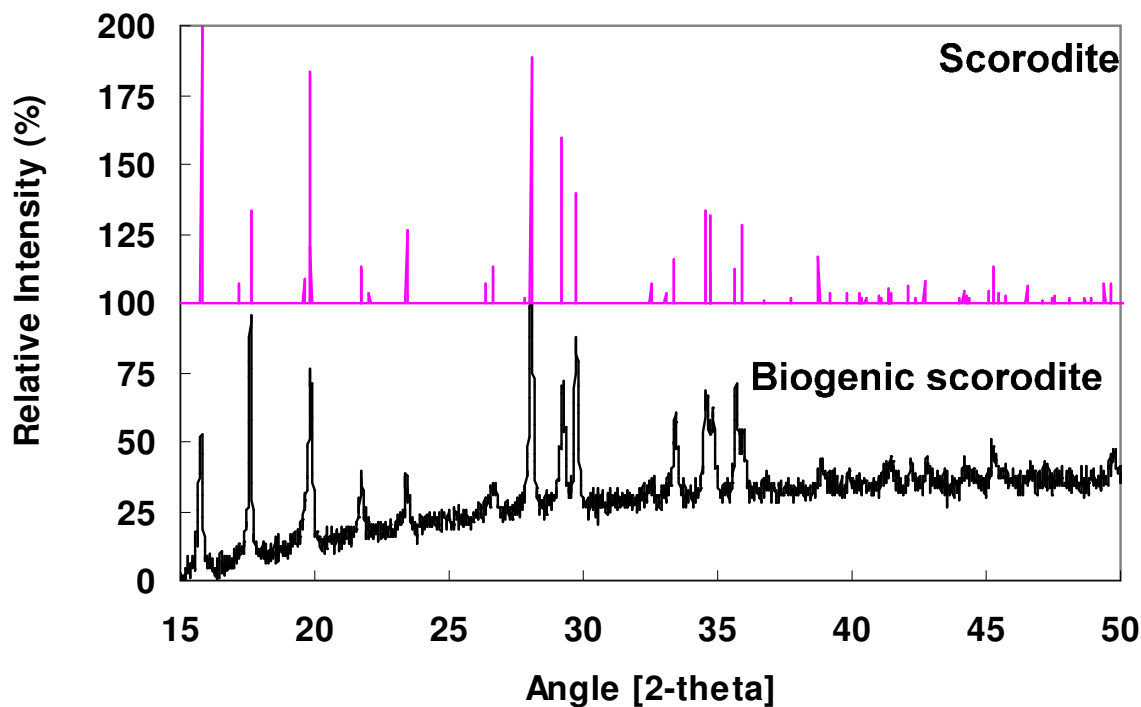


Fig. S2. X-Ray Diffraction of biogenic scorodite obtained at 80°C and 1 g L⁻¹ As⁵⁺ compared with the XRD pattern for natural scorodite [1, 2]. The solids in our experiments were identified as high crystalline scorodite and no other precipitates were identified in the samples.

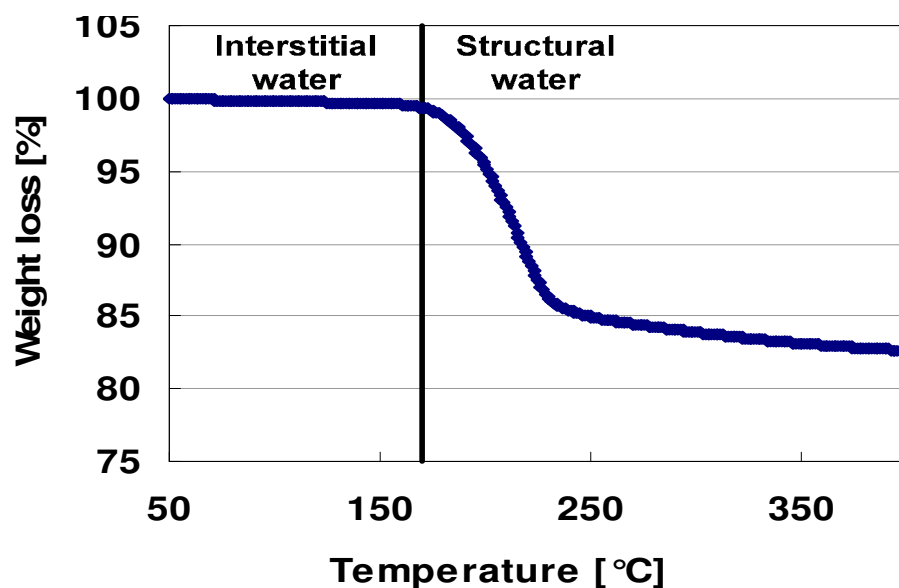


Fig. S3. Evolution of Thermo Gravimetric Analyzer (TGA) weight loss of biogenic scorodite obtained at 80°C and 1 g L⁻¹ As⁵⁺. Up to 240°C, the TGA curve of biogenic scorodite is in agreement with the

TGA curve reported for hydrothermal scorodite [2-5], with a sudden trend downward between 170 to 240°C which corresponds to 15.08% loss of structural water.

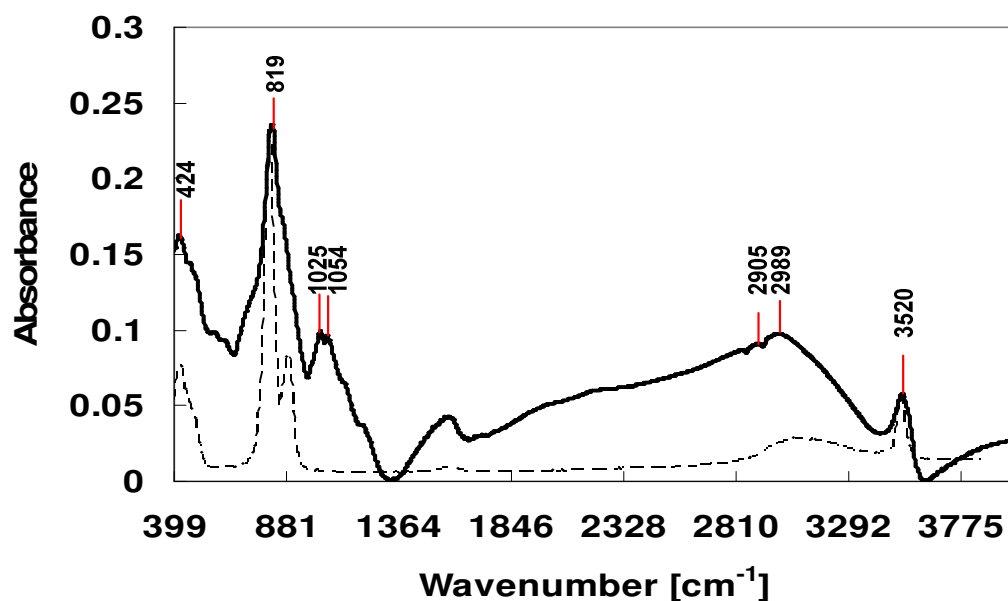


Fig. S4. FT-IR of biogenic scorodite obtained at 80°C and 1 g L⁻¹ As⁵⁺ (KBr-mode, pellet of KBr with ~1 (wt%) of scorodite) compared with the FT-IR pattern for natural scorodite [6-9] in order to identify arsenate vibrations (424-819) and O-H linkages (3520) of biogenic scorodite.

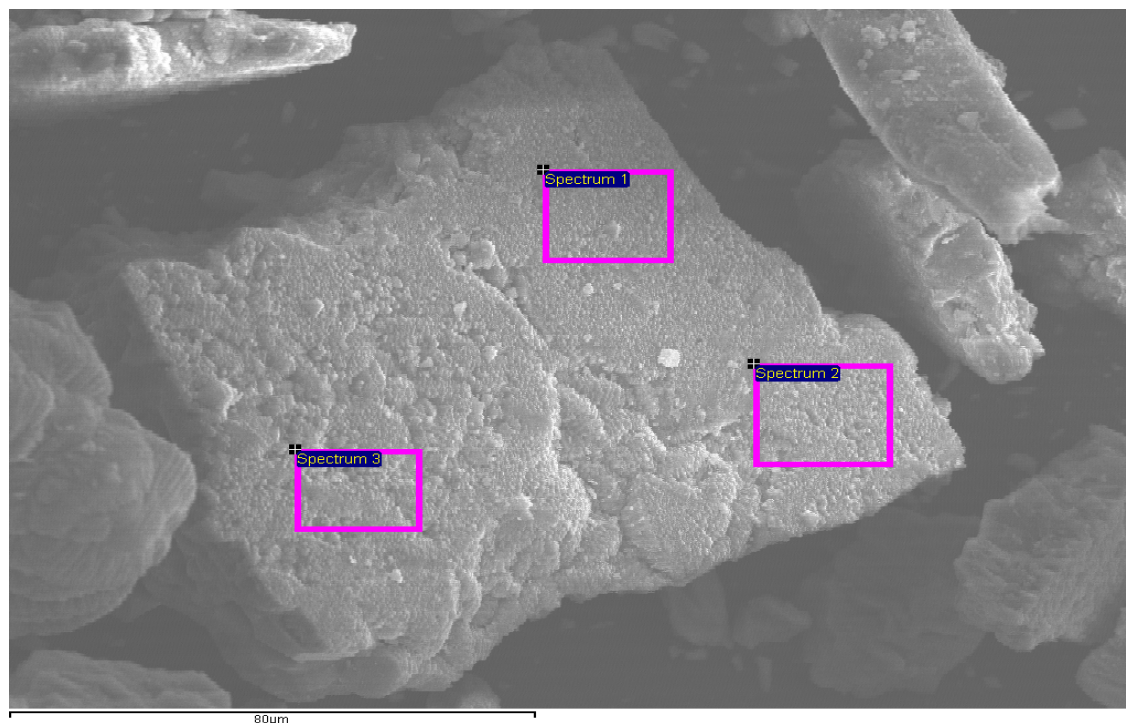


Fig. S5a. SEM-EDX evaluation points for Habit II of biogenic scorodite obtained at 80°C and 1 g L⁻¹ As⁵⁺.

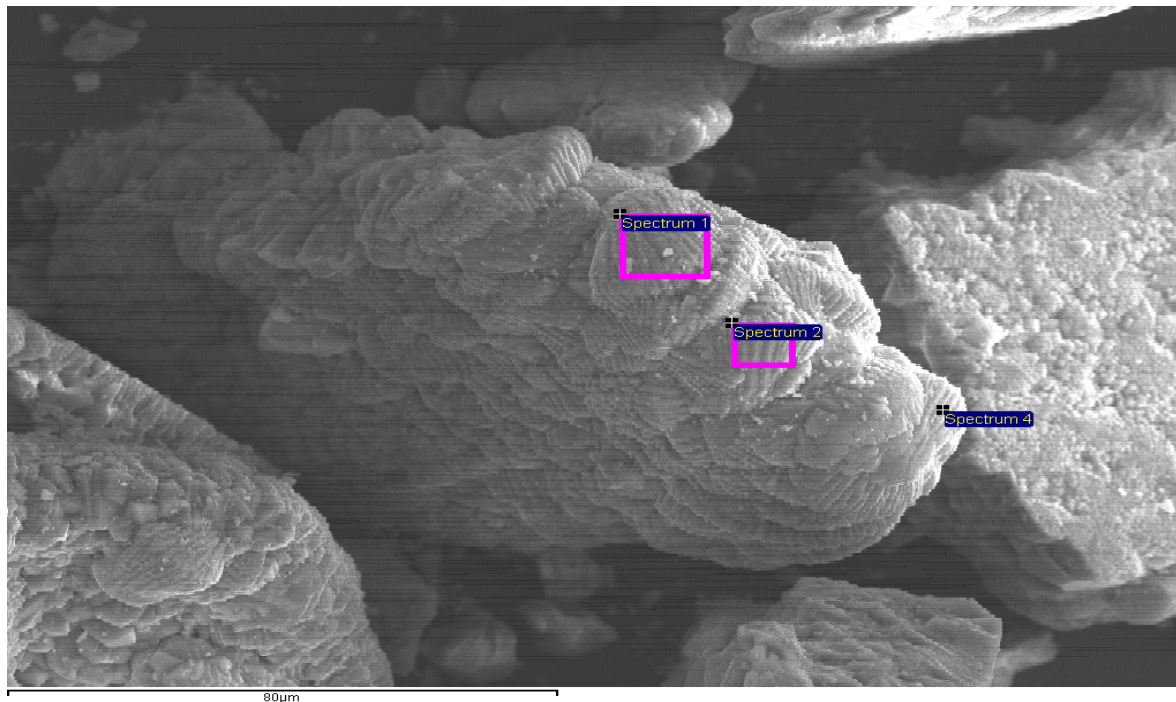


Fig. S5b. SEM-EDX evaluation points for Habit II of biogenic scorodite obtained at 80°C and 1 g L⁻¹ As⁵⁺.

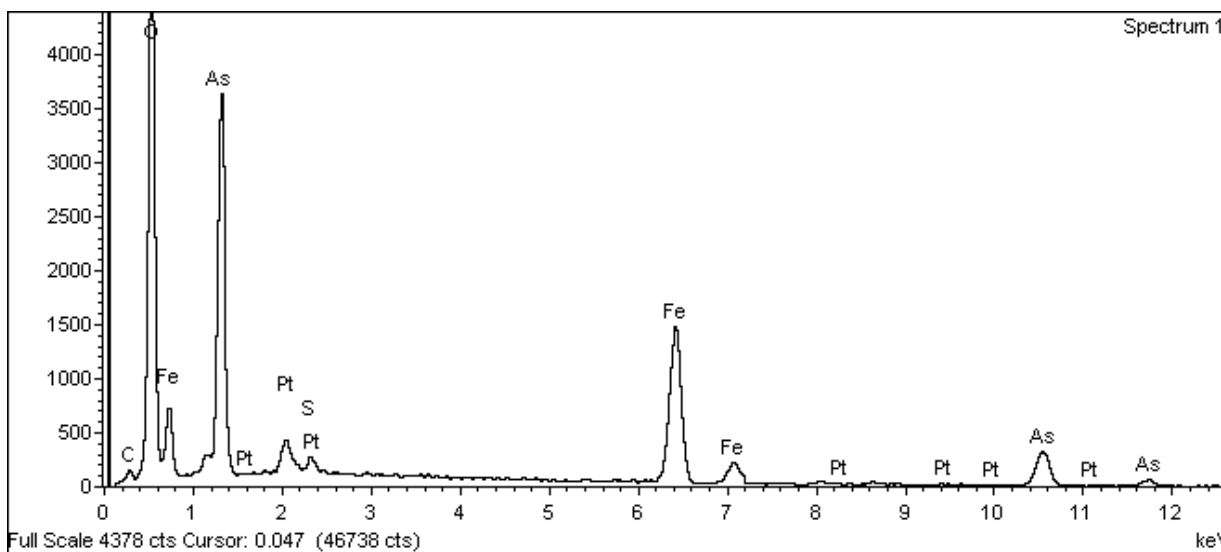


Fig. S5c. Typical SEM-EDX spectrum of biogenic scorodite obtained at 80°C and 1 g L⁻¹ As⁵⁺.

Table S1. Growth medium 88 for *Acidianus suldifivorans* DSM 18786.

Ingredients	Amount
(NH ₄) ₂ SO ₄	1.30 g
KH ₂ PO ₄	0.28 g
MgSO ₄ x 7 H ₂ O	0.25 g
CaCl ₂ x 2 H ₂ O	0.07 g
FeCl ₃ x 6 H ₂ O	0.02 g
MnCl ₂ x 4 H ₂ O	1.80 mg
Na ₂ B ₄ O ₇ x 10 H ₂ O	4.50 mg
ZnSO ₄ x 7 H ₂ O	0.22 mg
CuCl ₂ x 2 H ₂ O	0.05 mg
Na ₂ MoO ₄ x 2 H ₂ O	0.03 mg
VOSO ₄ x 2 H ₂ O	0.03 mg
CoSO ₄	0.01 mg
Yeast extract (Difco)	1.0 g
Demineralized water	1000 ml

The medium 88 was recommended by DSM to growth *Acidianus suldifivorans*. Also the medium 150 was recommended by DMS (verbal communication). The ingredients were dissolved (except yeast extract or other substrates) and the pH was adjust at room temperature to 2 using 10 N H₂SO₄ and autoclave. For DSM 18786 was only used 0.1 g L⁻¹ yeast extract and supplement medium with 10 g L⁻¹ sulfitic ore (e.g., chalcopyrite). Sterilize ore by heating at 150 °C over night. Adjust pH of the medium to 0.8.

Table S2. Hydrolysis constants of arsenate and ferric iron. The constants at 80°C determined by Eq.S2-2 were used for the IAP calculation.

Temperature of hydrolysis constants	pK (25 °C)	pK (80°)	pK (80°)	pK (80°)
Calculation method used	Literature [10, 11]	Eq.S2-1 [12]	Eq.S2-2 [12]	HCS [13]
Arsenate				
$\text{H}_3\text{AsO}_4 = \text{H}_2\text{AsO}_4^- + \text{H}^+$	2.24	2.54	2.27	2.53
$\text{H}_2\text{AsO}_4^- = \text{HAsO}_4^{2-} + \text{H}^+$	6.86	7.00	6.95	6.81
$\text{HAsO}_4^{2-} = \text{AsO}_4^{3-} + \text{H}^+$	11.49	-	11.51	11.28
Ferric Iron				
$\text{Fe}^{3+} + \text{H}_2\text{O} = \text{Fe}(\text{OH})^{2+} + \text{H}^+$	2.19	-	2.18	-
$\text{Fe}(\text{OH})^{2+} + \text{H}_2\text{O} = \text{Fe}(\text{OH})_2^+ + \text{H}^+$	3.48	-	3.47	-
$\text{Fe}(\text{OH})_2^+ + \text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + \text{H}^+$	6.33	-	6.31	-
$\text{Fe}(\text{OH})_3 + \text{H}_2\text{O} = \text{Fe}(\text{OH})_4^- + \text{H}^+$	9.6	-	9.57	-

The effect of the temperature in the hydrolysis constant of arsenate and ferric iron was corrected by the tabulated constant used in Equation S2-1 [12]. It was not possible to find all the tabulated data. Therefore the hydrolysis constants were corrected by van't Hoff Equation S2-2 and matched to the previous data obtained by Equation S2-1. Van't Hoff Equation S2-2 assumes that the heat capacity of the reactions is zero. This means that the van't Hoff Equation was integrated assuming the enthalpy of the reaction as constant [12] (Equation S2-2). However this is only valid for temperatures up to 50°C [12].

$$\log K_T = a + bT + \frac{c}{T} + d \log_{10} T + \frac{e}{T^2} \quad \text{Equation S2-1}$$

$$-\log K_2 = -\log K_1 + \frac{\Delta H_r^\circ}{4.576} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{Equation S2-2}$$

The calculation of hydrolysis constants at 80°C can be achieved by using HSC Chemistry[®] software [13]. HSC makes a Criss-Croble extrapolation for the heat capacity of aqueous species at elevated temperatures (>25 °C to 300°). Criss-Croble extrapolation is only used if the temperature coefficients of the heat capacity function are not given in the HSC database.

Table S3. Solubility product of scorodite reported in literature for 20-25°C.

Solubility product of scorodite log IAP	System ferric arsenate in:	pH	Literature Reference
-20.66	HNO ₃	2.05	Chukhlantsev <i>et al</i> (1956) from [14]
-19.86	H ₂ SO ₄	1.9	Chukhlantsev <i>et al</i> (1956) from [14]
-21.08	H ₂ SO ₄	1.82	Tozawa <i>et al</i> (1978) from [14]
-23.08	HNO ₃	3	Makhmetov <i>et al</i> (1981) from [14]
-21.32	HCl, NaOH	5.53	Dove and Rimstidt (1985) [15]
-22.69	-	0.5	Robins (1987) [16]
-24.6	H ₂ SO ₄	0.97	Krause and Ettel (1987) from [14]
-24.41	H ₂ SO ₄	1.76	Krause and Ettel (1988) [16]
-26.05	H ₂ SO ₄		Krause and Ettel (1989) [17]
-24.78	-	1.3	Robins (1990) from [18]
-24.97	-	1.48	Nishimura and Robins (1996) from [18]
-23.44	water		Zhu and Merkel (2001) [19]
-22	-		Jia <i>et al</i> (2006) [20]
-25.83	-	2.18	Langmuir <i>et al</i> (2006) [18]

Table S4. Literature summary of scorodite precipitation research.

Ref.	As (g·L ⁻¹)	Fe/As molar ratio	T° C	Seeds	Oxidant used	%As removal	Scor. Precip.
Biologically induced scorodite crystallization							
This study	1 (V)	1/1 Fe (II)	80	No	O ₂ in air (Biological oxidation)	80	Yes
Hydrothermal scorodite crystallization							
[21]	13 (V)	2/1 Fe(III)	200	No	O ₂ overpressure	95	Yes
[3]	25 (V)	3/1 Fe (III)	160	No	O ₂ overpressure	-	Yes
Atmospheric scorodite crystallization							
[22]	2 (V)	1/1 Fe(III)	95	No	-	-	No (a)
[22]	2 (V)	1/1 (III)	95	2 g L ⁻¹ scorodite	-	86	Yes (b)
[23]	10 (V)	1/1 (III)	95	20 g L ⁻¹ scorodite	-	95	Yes (c)
[24]	10 (V)	1/1 (III)	90	80 g L ⁻¹ gypsum	-	90	Yes (c)
[25]	1As(III)	1/1 Fe(II)	95	20-80 g L ⁻¹ scorodite	H ₂ O ₂	85-88	Yes
[26]	50 (V)	1.5/1 (II)	95	No	O ₂	98	Yes
[27]	20 As(III)	1/1 Fe(II)	85	20 g L ⁻¹ scorodite	H ₂ O ₂	50	Yes (c)
[28]	50 (V)	1.5/1 (II)	70	No	O ₂	98	Yes

(a) Procedure: faster wise-step pH that produce a yellow beige powder; (b) procedure: slow wise-step pH with pH control; (c) procedure: low wise-step pH without pH control.

Supplementary Equations 1, 2, and 3.

Equations used for the calculation of the Ion Activity Product (IAP) of Scorodite[10, 14, 17]. Equations 2 and 3 are indicated for the calculation of the activity of arsenate and ferric iron.

$$IAP_{SCORODITE} = (a_{Fe^{3+}})(a_{AsO_4^{3-}}) \quad (\text{eq 1})$$

$$a\text{AsO}_4^{3-} = \frac{\text{Arsenate}_{\text{total}}}{1 + \frac{a_{\text{H}^+}}{K_3} + \frac{(a_{\text{H}^+})^2}{K_2 K_3} + \frac{(a_{\text{H}^+})^3}{K_1 K_2 K_3}} \quad (\text{eq 2})$$

$$a\text{Fe}^{3+} = \frac{\text{Ferric}_{\text{total}}}{1 + \frac{K_1}{a_{\text{H}^+}} + \frac{K_1 K_2}{(a_{\text{H}^+})^2} + \frac{K_1 K_2 K_3}{(a_{\text{H}^+})^3} + \frac{K_1 K_2 K_3 K_4}{(a_{\text{H}^+})^4}} \quad (\text{eq 3})$$

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