Supplementary information

Sulfidation of copper oxide nanoparticles and properties of resulting copper sulfide

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Table S1. Sulfide to CuO Molar Ratios and Volumes of 100 mM Na_2S. Each vessel contained 100 mg/L CuO NPs.

Name	S/Cu	100 mM Na_2S (mL)
CuS 1	0.22	1.09
CuS 2	0.43	2.17
CuS 3	0.62	3.10
CuS 4	0.86	4.57
CuS 5	0.94	4.97
CuS 6	2.16	11.41

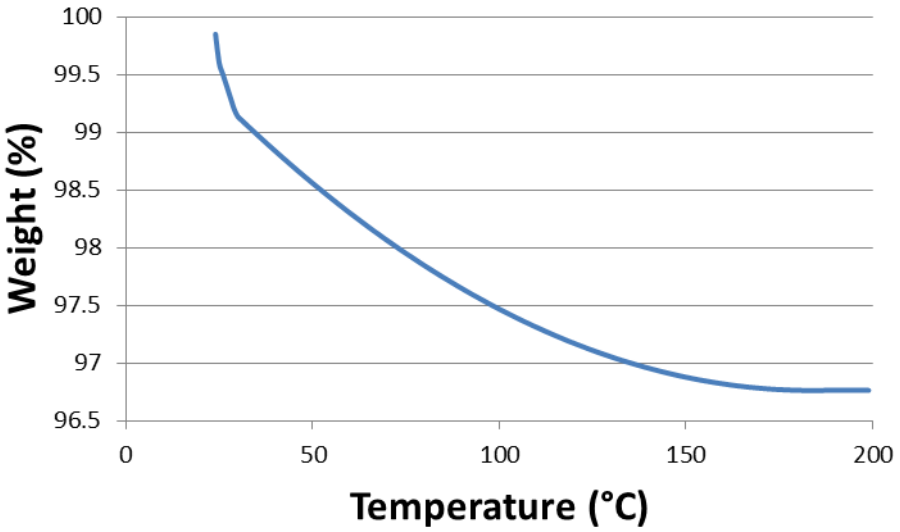

Figure S1. Weight (%) loss upon heating in air using TGA.

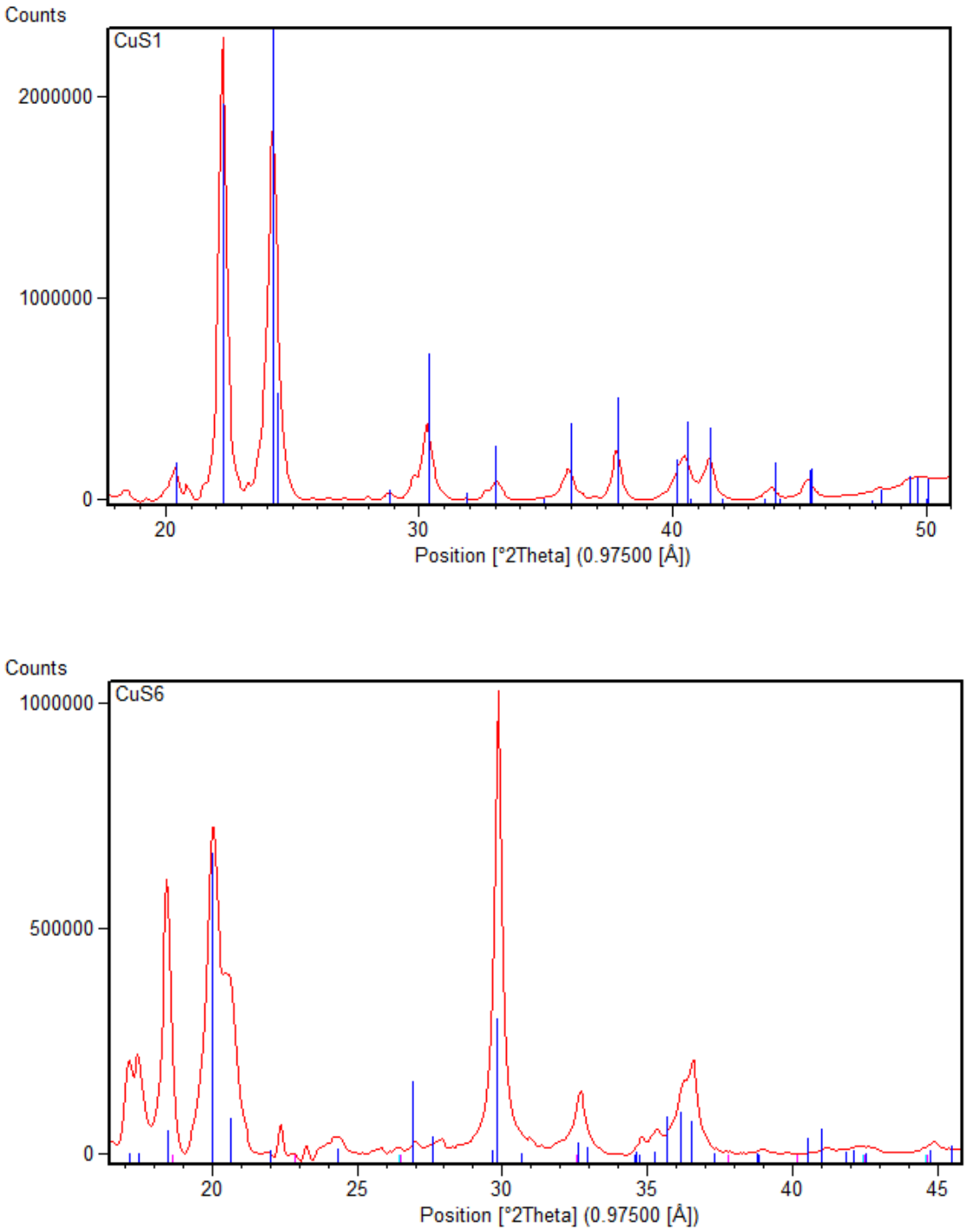

Figure S2. CuS 1 (S/Cu 0.22, top) and CuS 6 (S/Cu 2.16, bottom) XRD peak matching using X'pert High Scores. Red peaks were measured and blue spikes indicate matches for tenorite (top) and for covellite (bottom) taken from the mineralogy database.

Table S2. Linear Combination fitting using CuO, Cu_2S and CuS as model compounds (*k* from 2 to 9).

	CuO (%)	Cu_2S (%)	CuS (%)	Sum	R
S/Cu 0.22	80	6	2	88	0.17
S/Cu 0.43	44	7	4	55	0.2
S/Cu 0.62	33	22	6	58	0.27
S/Cu 0.86	11	55	12	78	0.24
S/Cu 0.94	12	57	17	86	0.16
S/Cu 2.16	12	54	21	87	0.15

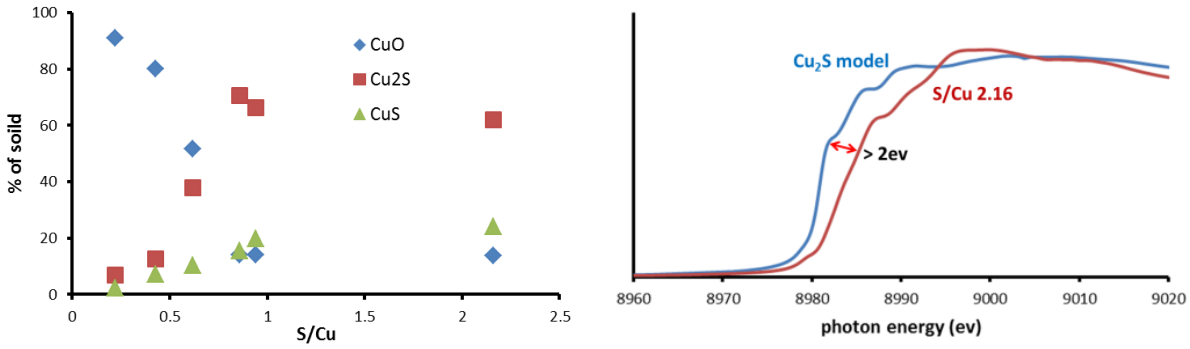

Figure S3. Percentage (left) of CuO and CuS as a function of the S/Cu ratio. The normalized Cu K edge XANES region of the XAS spectra (right) for Cu_2S and S/Cu 2.16.

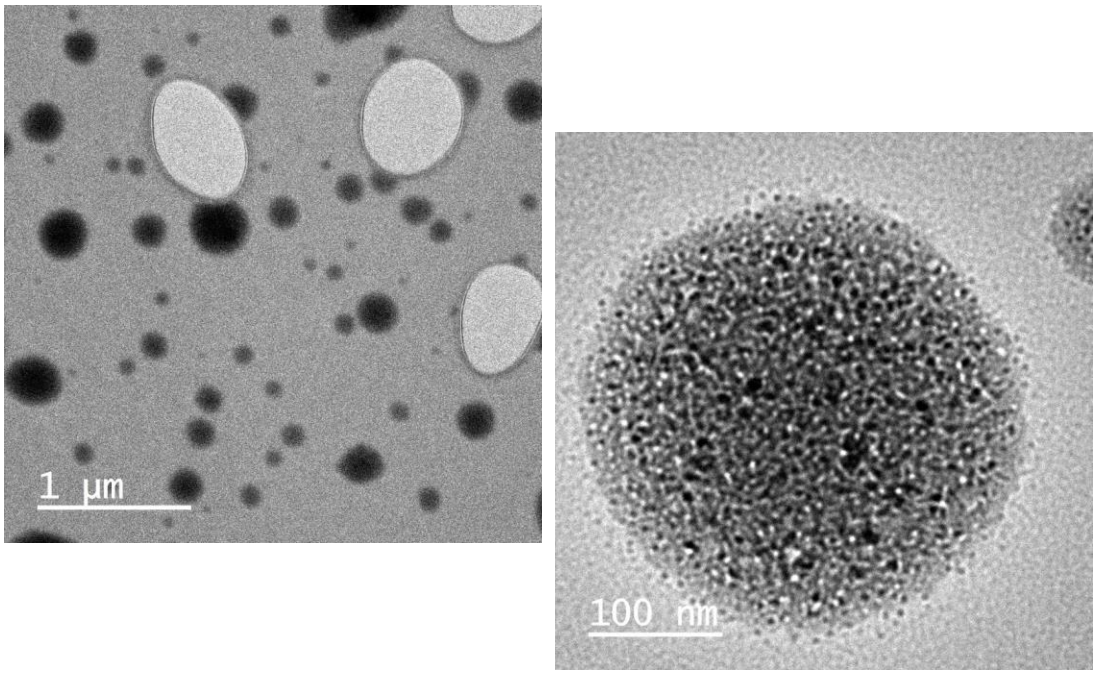

Figure S4. TEM images of relatively amorphous particles in the fully sulfidized Cu_xS_y (Cu/S ratio of 2.16). There is a range of NP aggregate sizes and the particles are highly beam sensitive. Dark spots tended to form with time in the beam.

Calculation of solubility of the amorphous $Cu_{1.18}S$ phase.

Poorly crystalline copper sulfide is a potential source of observed copper solubility that significantly exceeded thermodynamic predictions for crystalline solids. Using the solubility equilibria developed by Shea and Helz[1] copper solubility was predicted based on the following reaction:

$$H^+ + \frac{x-1}{x} S_{(s)} + \frac{1}{x} Cu_x S \leftrightarrow Cu^{2+}_{(aq)} + HS^-_{(aq)} \qquad \text{(R1)}$$

Data for x= 1.18 are provided by Shea and Helz and are used in this calculation (i.e., pK_{sp} = 18.9). Assuming the activity of the sulfide solid to be unity, the solubility relationship from (R1) can be described by:

[1] Shea, Damian, and George R. Helz. "Solubility product constants of covellite and a poorly crystalline copper sulfide precipitate at 298 K." *Geochimica et Cosmochimica Acta* 53.2 (1989): 229-236.

$$K_{sp} = \frac{\{Cu^{2+}_{(aq)}\}\{HS^{-}_{(aq)}\}}{\{H^{+}\}\{S_{(s)}\}^{(x-1)/x}} \quad \text{(E1)}$$

Solving this equation for the ion product of copper and bisulfide at experimental pH and assuming that the activities of copper and bisulfide are equal in solution, the free copper (and bisulfide) activity can be expressed as a function of elemental sulfur activity, which Shea and Helz note may not necessarily be unity.

$$\{Cu^{2+}_{(aq)}\} = \sqrt{K_{sp}\{H^{+}\}\{S_{(s)}\}^{(x-1)/x}} = \{HS^{-}_{(aq)}\} \quad \text{(E2)}$$

With thermodynamic data taken from Benjamin[2], the total copper solubility (Cu_T) can be calculated after accounting for complexation with hydroxide and bisulfide.

$$Cu_T = [Cu^{2+}_{(aq)}] + [CuOH^{+}] + [Cu(OH)^{0}_{2}] + [Cu(OH)^{-}_{3}] + [Cu(OH)^{2-}_{4}] + [Cu(HS)^{-}_{3}] \quad \text{(E3a)}$$

$$Cu_T = \{Cu^{2+}_{(aq)}\} \cdot \left(\frac{1}{\gamma_2} + \frac{\beta_1^{OH}\{OH^{-}\}}{\gamma_1} + \frac{\beta_2^{OH}\{OH^{-}\}^2}{\gamma_0} + \frac{\beta_3^{OH}\{OH^{-}\}^3}{\gamma_1} + \frac{\beta_4^{OH}\{OH^{-}\}^4}{\gamma_2} + \frac{\beta_3^{HS}\{HS^{-}\}^3}{\gamma_1}\right) \quad \text{(E3b)}$$

[2] Benjamin, Mark M. *Water chemistry*. New York: McGraw-Hill, 2002.

Substituting (E2) into (E3b), the total dissolved copper can be expressed as a function of elemental sulfur activity. Evaluating this expression between $-8 \leq \log\{S_{(s)}\} \leq 0$ shows that the maximum copper solubility for poorly crystalline $Cu_{1.18}S$ is 8.49×10^{-14} M. Figure 1 illustrates the log-log linear relationship between soluble copper and elemental sulfur activity described by this model.

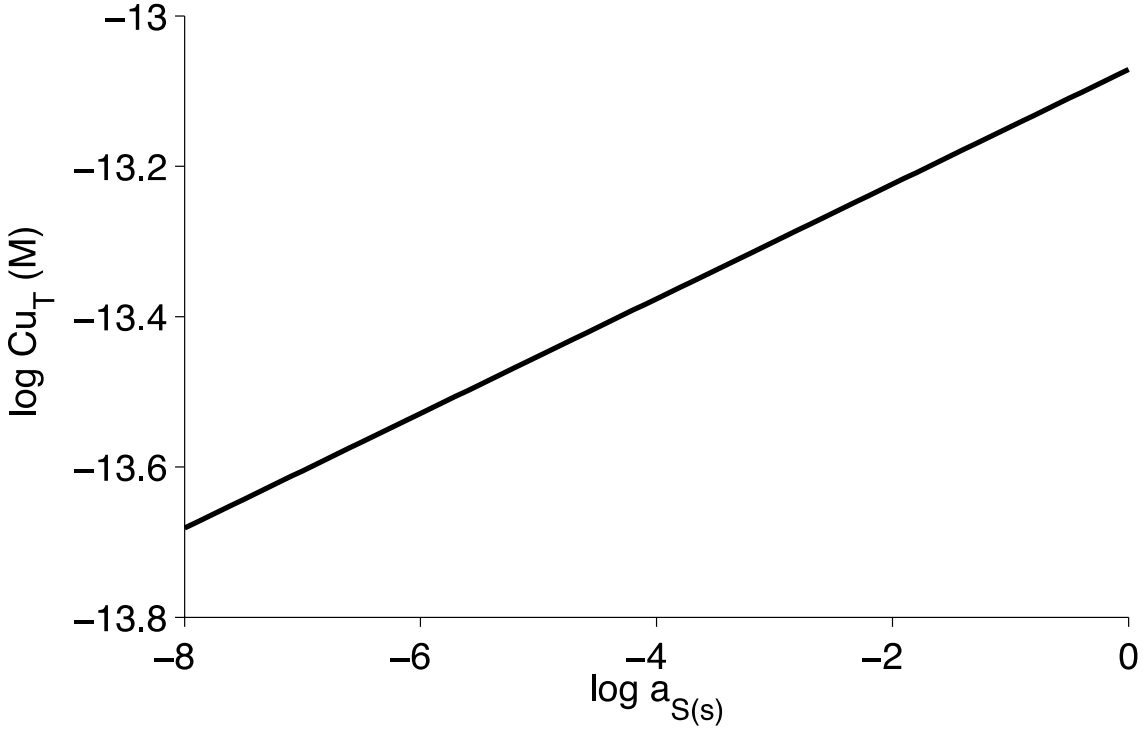

Figure S5. Calculated total soluble copper in equilibrium with poorly crystalline $Cu_{1.18}S$ using the solubility product of Shea and Helz[1] and aqueous stability constants from Benjamin[2]. Model developed for T = 25 ˚C and I = 0.01 M.