Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Table S1. ICP-MS data for Cu, Zn, and Pb for the depth profiles of site 1.

Depth (cm)	Concentration (ppm)		
	Cu	Pb	Zn
1	9220	447	3280
2	8510	518	2770
3	7480	495	2440
4	5470	358	2390
5	3500	262	2721
6	2808	190	2295
7	1743	119	1942
8	1449	97	1600
9	911	75	1576
10	265	38	964
12.5	106	27	682

Table S2. Compiled data regarding the relative molar ratios and corresponding volumes between mooihoekite/ferrihydrite/magnetite/maghemite. Sample calculations given below table.

Transformation Reaction	Molar Ratio	Molar Volumes (cm^3/mol)	Volume (cm^3)
$10Cu_9Fe_9S_{16} \rightarrow 9Fe_{10}O_{14}(OH)_2$	1 : 0.9	363 → 167	363 → 150
$3Fe_{10}O_{14}(OH)_2 \rightarrow 10Fe_3O_4$	1 : 3.3	167 → 45	150 → 149
$2Fe_3O_4 \rightarrow 3Fe_2O_3$	1 : 1.5	45 → 44	149 → 66

Sample calculation for molar ratio.

Assume 1 mol of mooihoekite (Mhk) dissolves to form ferrihydrite (Fhyd).

$$x \text{ mol Fhyd} = 9 \text{ mol Fhyd} \times \frac{1 \text{ mol Mhk}}{10 \text{ mol Mhk}} \quad \text{[as per stoichiometry]}$$

$$x \text{ mol Fhyd} = 0.9 \text{ mol Fhyd} \quad \text{[per 1 mol Mhk]}$$

Sample calculation for volumes produced after the transformation of Mhk to Fhyd.

$$x \text{ Volume Fhyd} = 0.9 \text{ mol Fhyd} \times 167 \text{ cm}^3/\text{mol} \quad \text{[as per molar ratio]}$$

$$x \text{ Volume Fhyd} = 150 \text{ cm}^3 \text{ Fhyd}$$

Fig S1. Site 1 vegetation and 0-15 cm soil profile. GPS Coordinates (latitude/longitude) 48.544719/-81.067873.

Fig S2. Site 2 (control) 0-15 cm soil profile. GPS Coordinates (48.599656/-81.009367)

Fig S3. Site 2 (control) 0-15 cm soil profile. GPS Coordinates 48.55593/-81.055307)

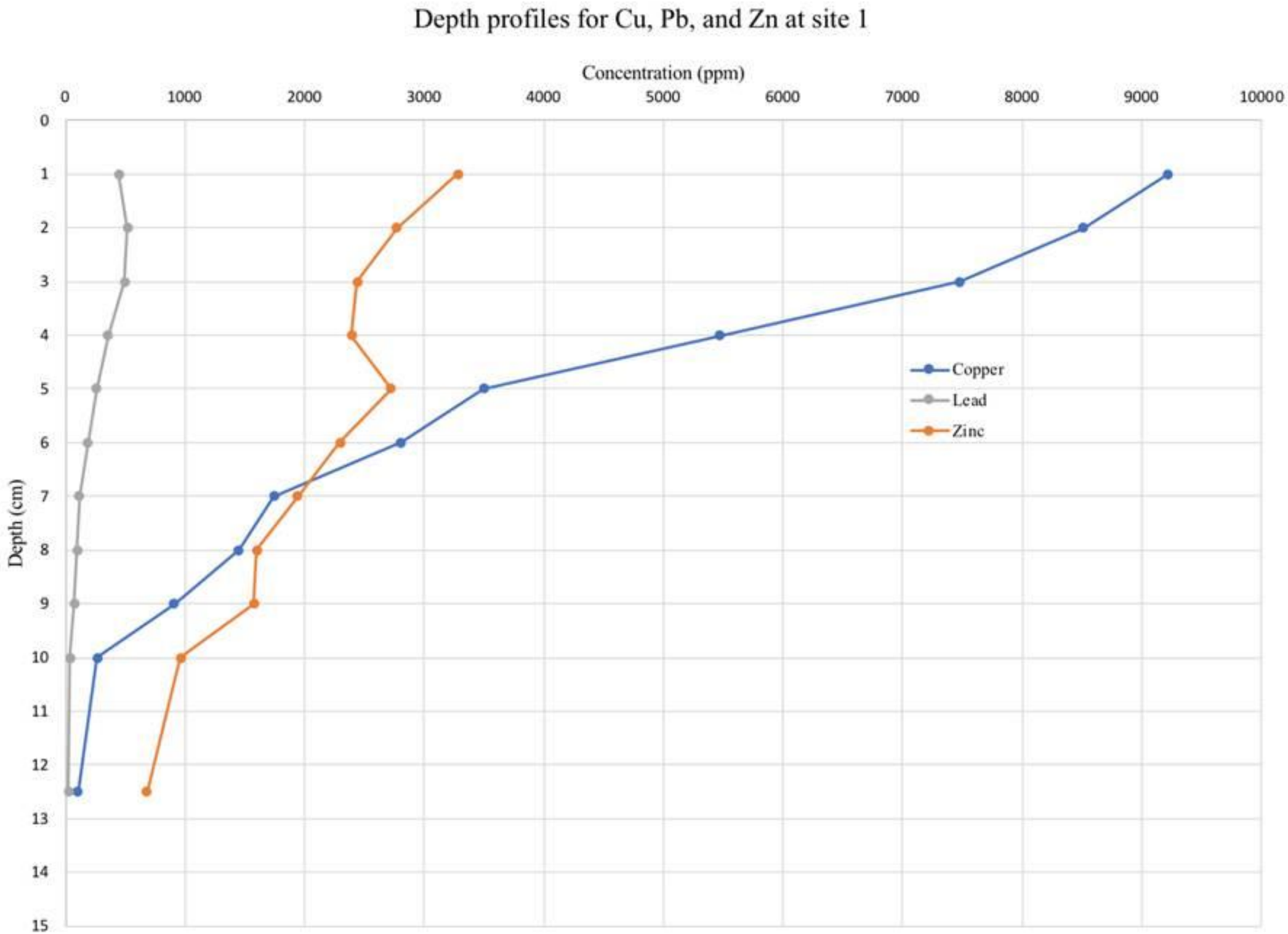


Fig S4. Depth profile of Cu (blue), Pb (gray), and Zn (orange) at site 1. The first 10 cm were digested and analyzed in 1 cm increments, then the 10-15 cm layerwas analyzed as one fraction. Soil was digested using an aqua regia digest and ICP-MS measurements were done at the Geo Labs.

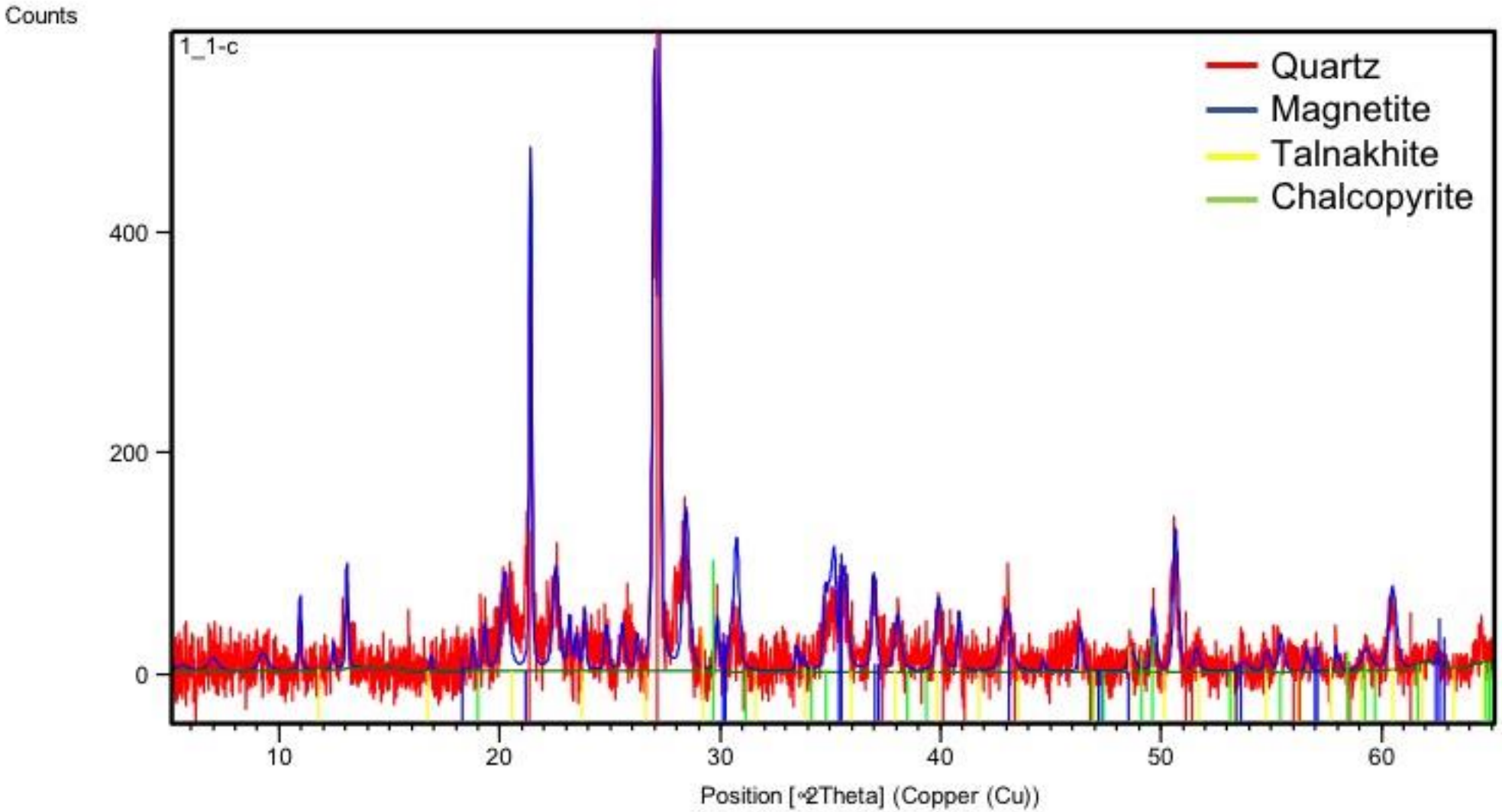


Fig S5. X-ray diffraction pattern of the coarse fraction from the 0-5 cm fraction of site 1, indicated by the blue outline. Coloured lines underneath the spectrum indicate the identified minerals.

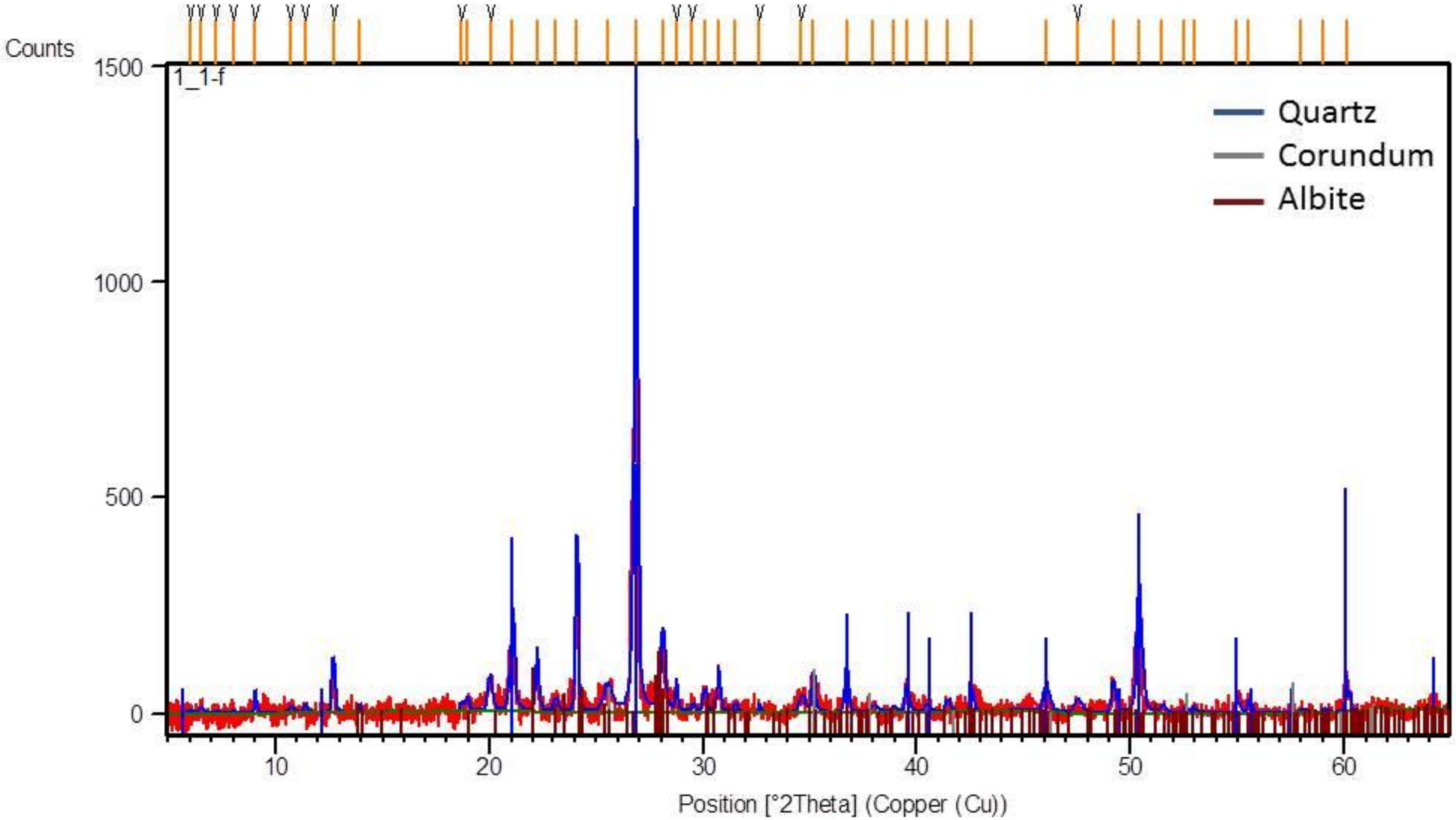


Fig S6. X-ray diffraction patterns from the fine fraction shown by the blue outline. Coloured lines underneath the spectrum indicate the related minerals

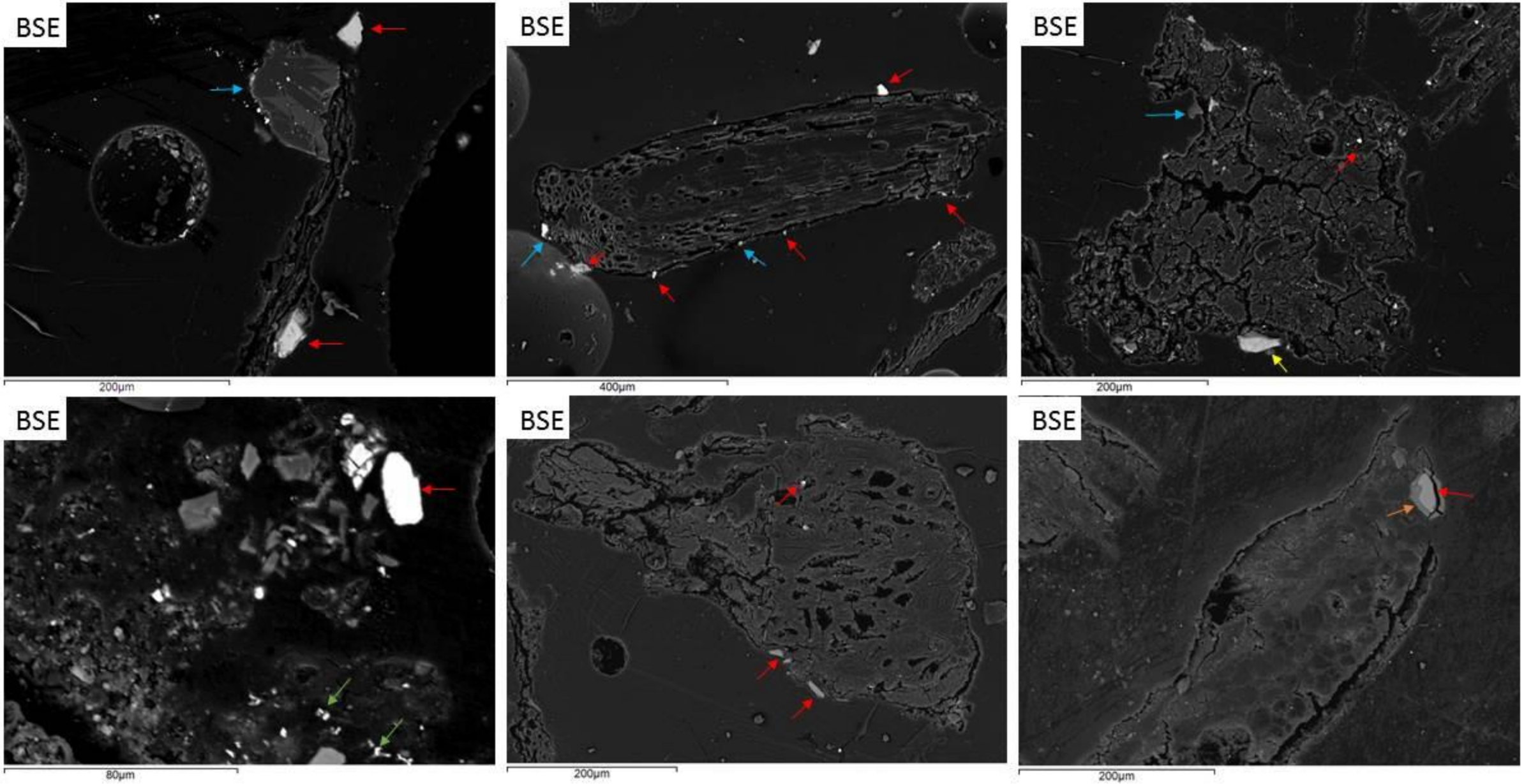


Fig S7. SEM backscattered electron images from the 0-5 cm, coarse fraction from site 1 indicating the predominance of Cu-Fe-sulfide grains (red arrows), minor amounts of silicon-based grains (blue arrows), and rare occurrences of various non-sulfide copper species (green arrows) or iron sulfides (yellow arrow). Orange arrow shown in last pane indicates an iron oxide layer.

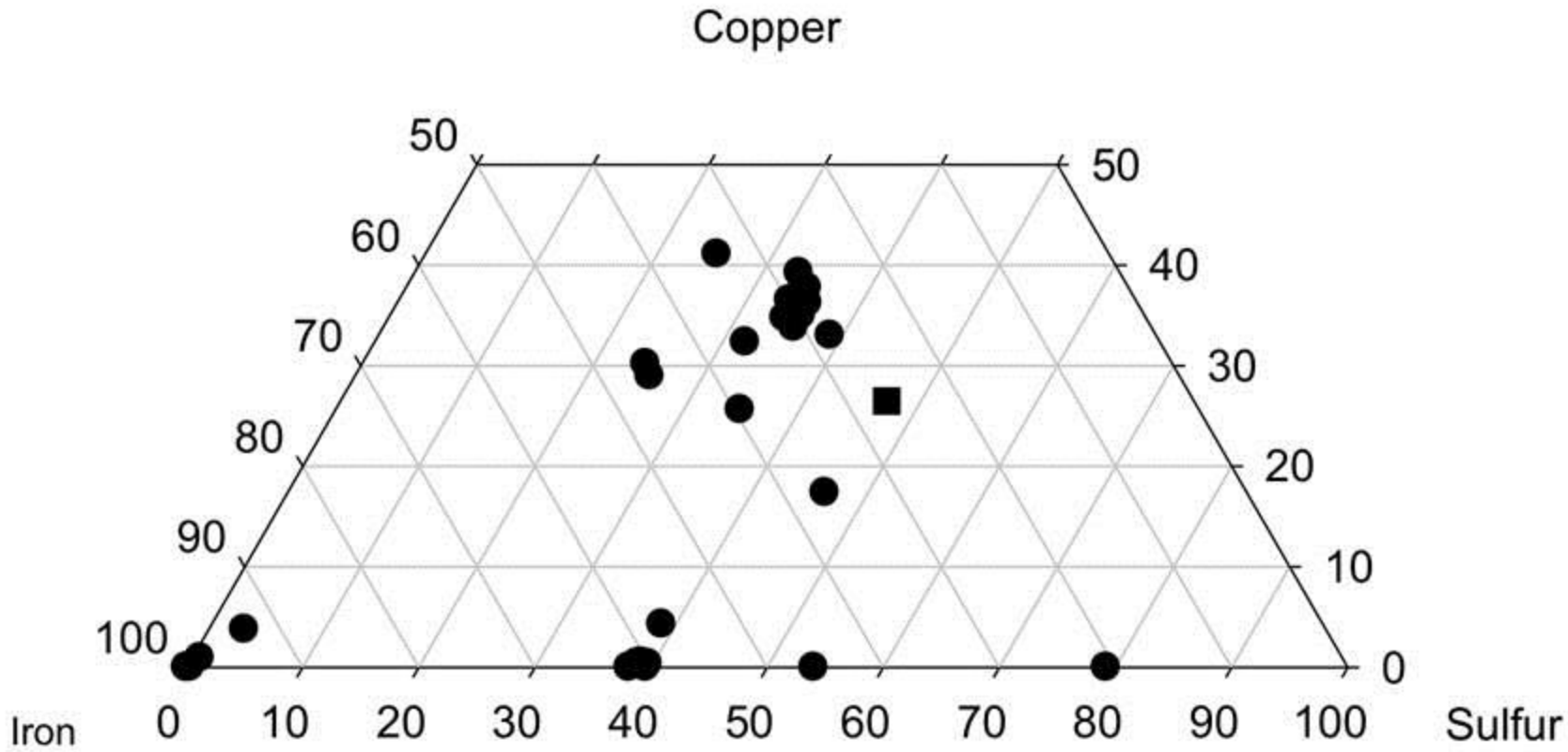


Fig S8. Ternary plot compiled using data from electron microprobe analysis of 63 mineral grains attached to organic residues in the coarse fraction of site 1. Circular dots in the middle represent a Cu/Fe/S fraction of 35:65:50, those on the Fe/S axis are likely iron sulfide minerals, and those that appear to be 100 % Fe are likely iron oxide species. The square dot indicates the ratio of Cu/Fe/S of mooihoekite. SEM backscattering electron images of the FIB extraction process.

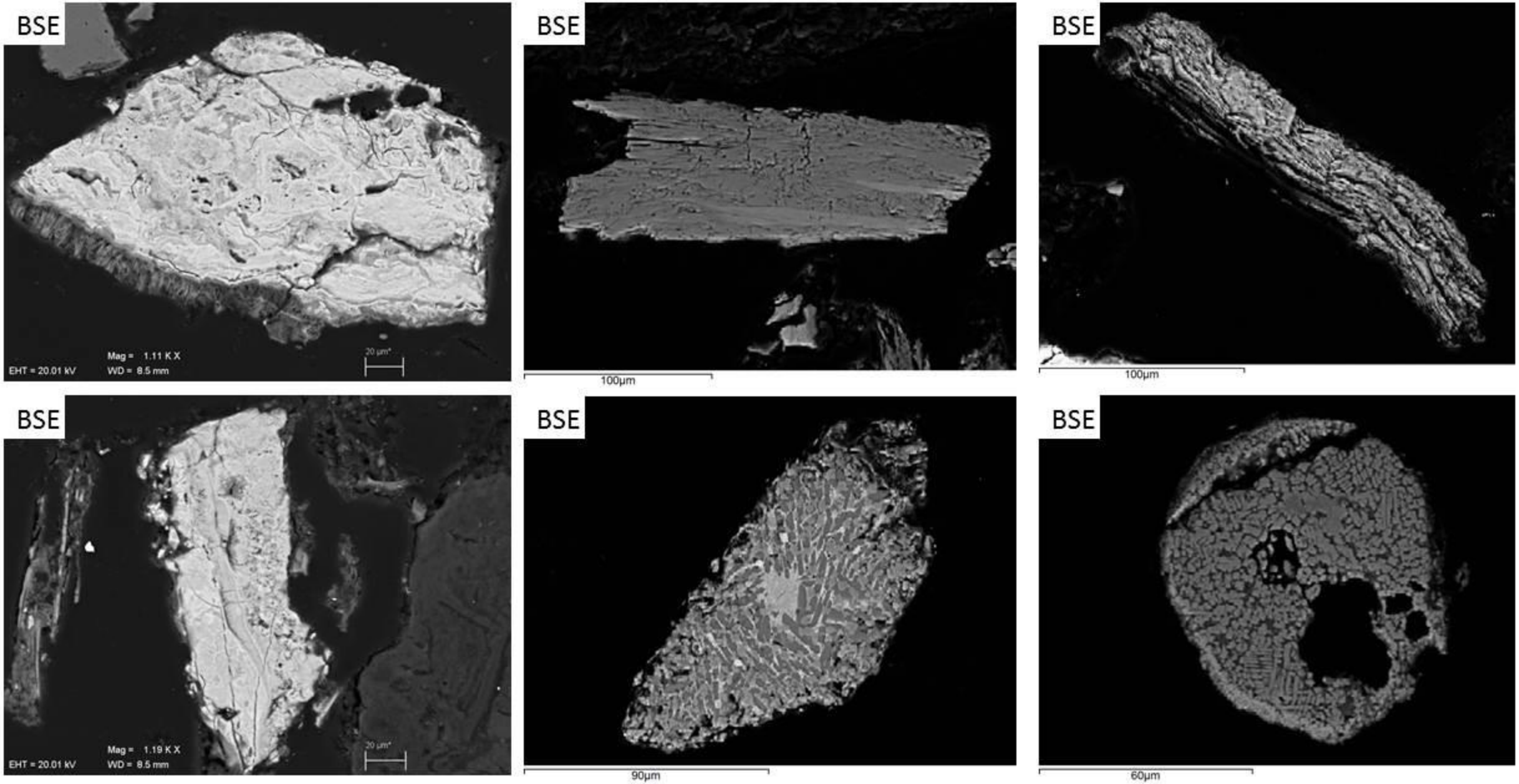


Fig S9. SEM backscattered electron images from the 0-5 cm, fine fraction (< 180 µm) from site 1 indicating silicified organic material, wind-blown slag particles, and smelter-derived PM.

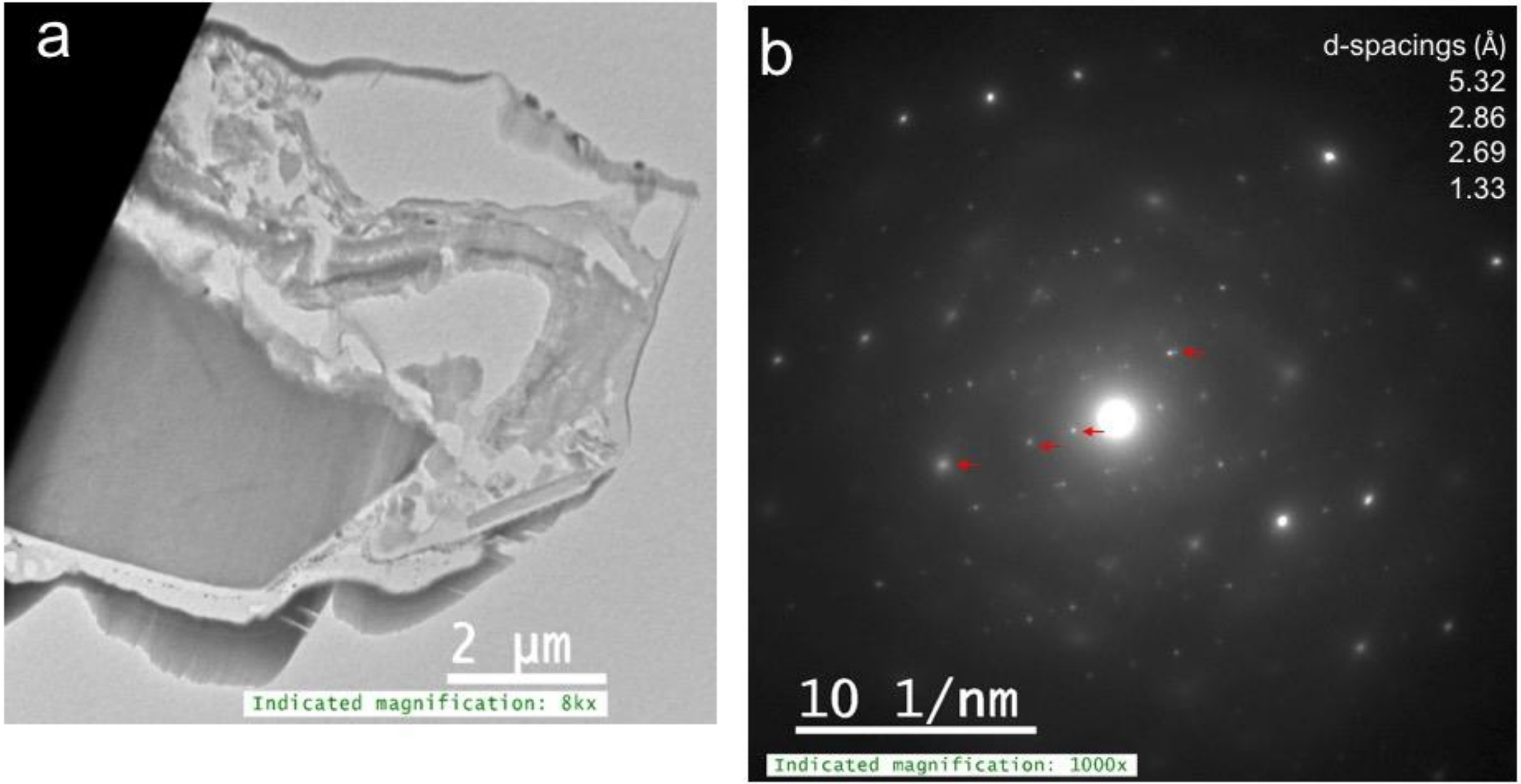


Fig S10. (a) TEM image and (b) Selected area electron diffraction (SAED) pattern of the main sulfide grain, mooihoekite.

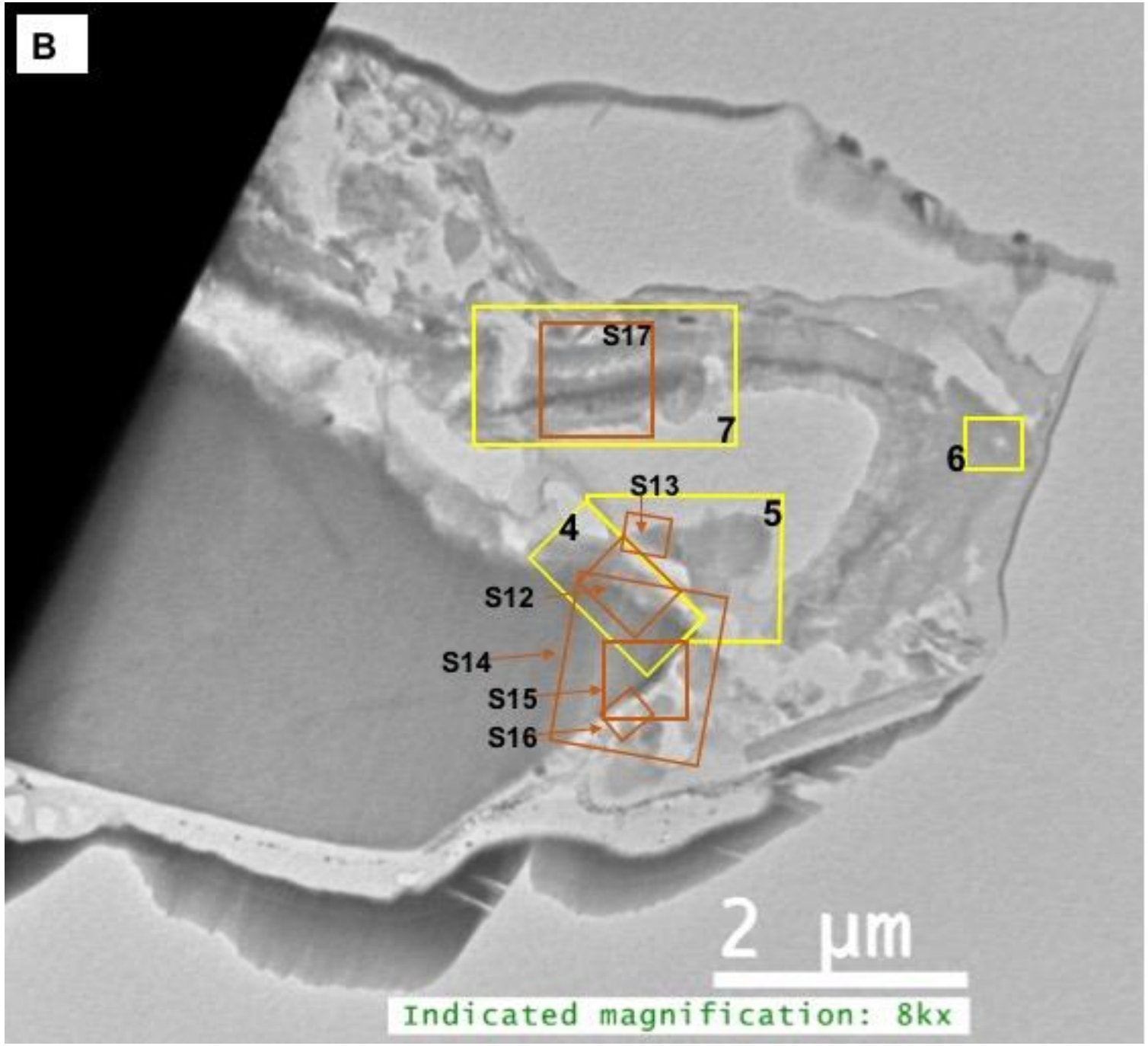
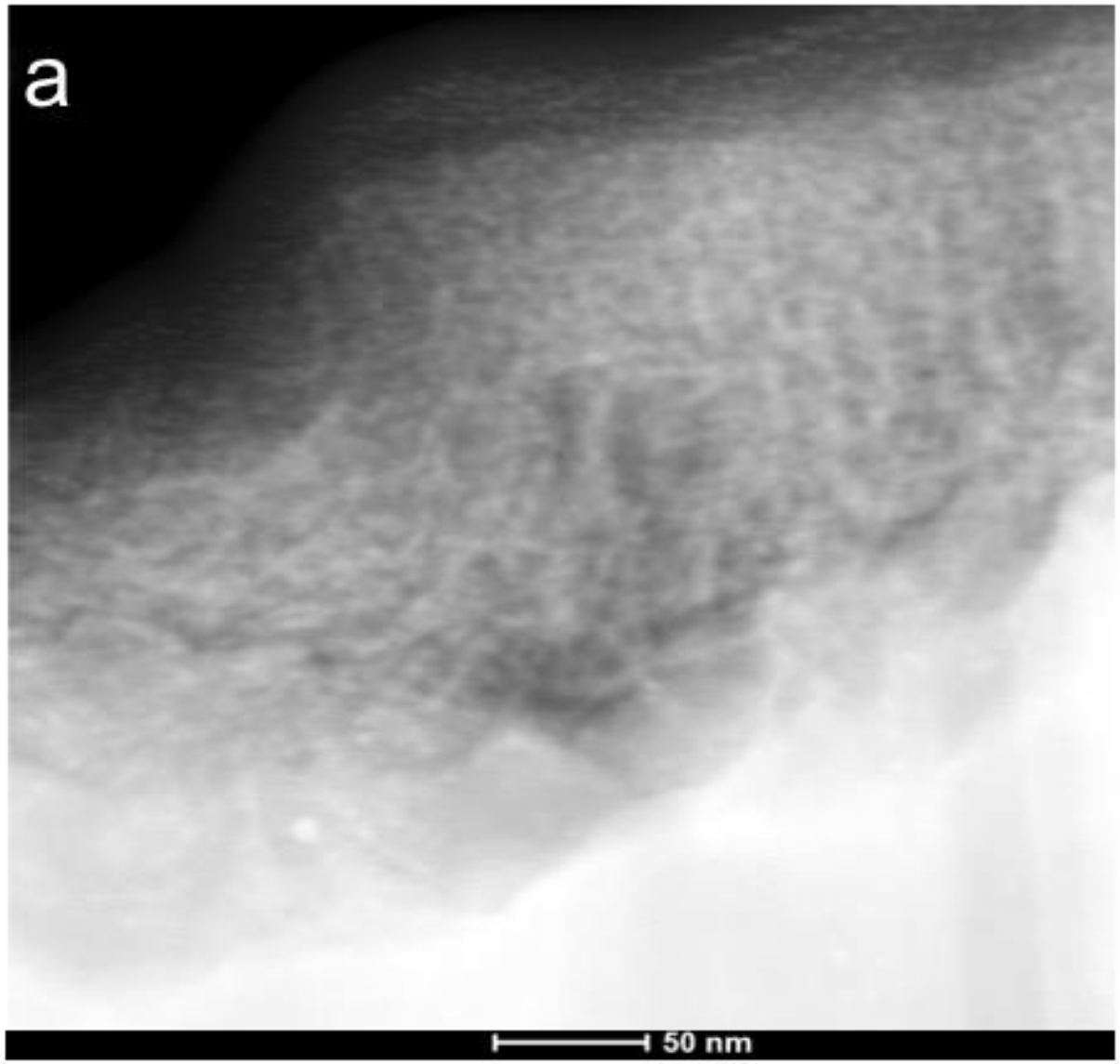


Fig S11. Map of figures (yellow) and SI figures (orange) for FIB section 1.



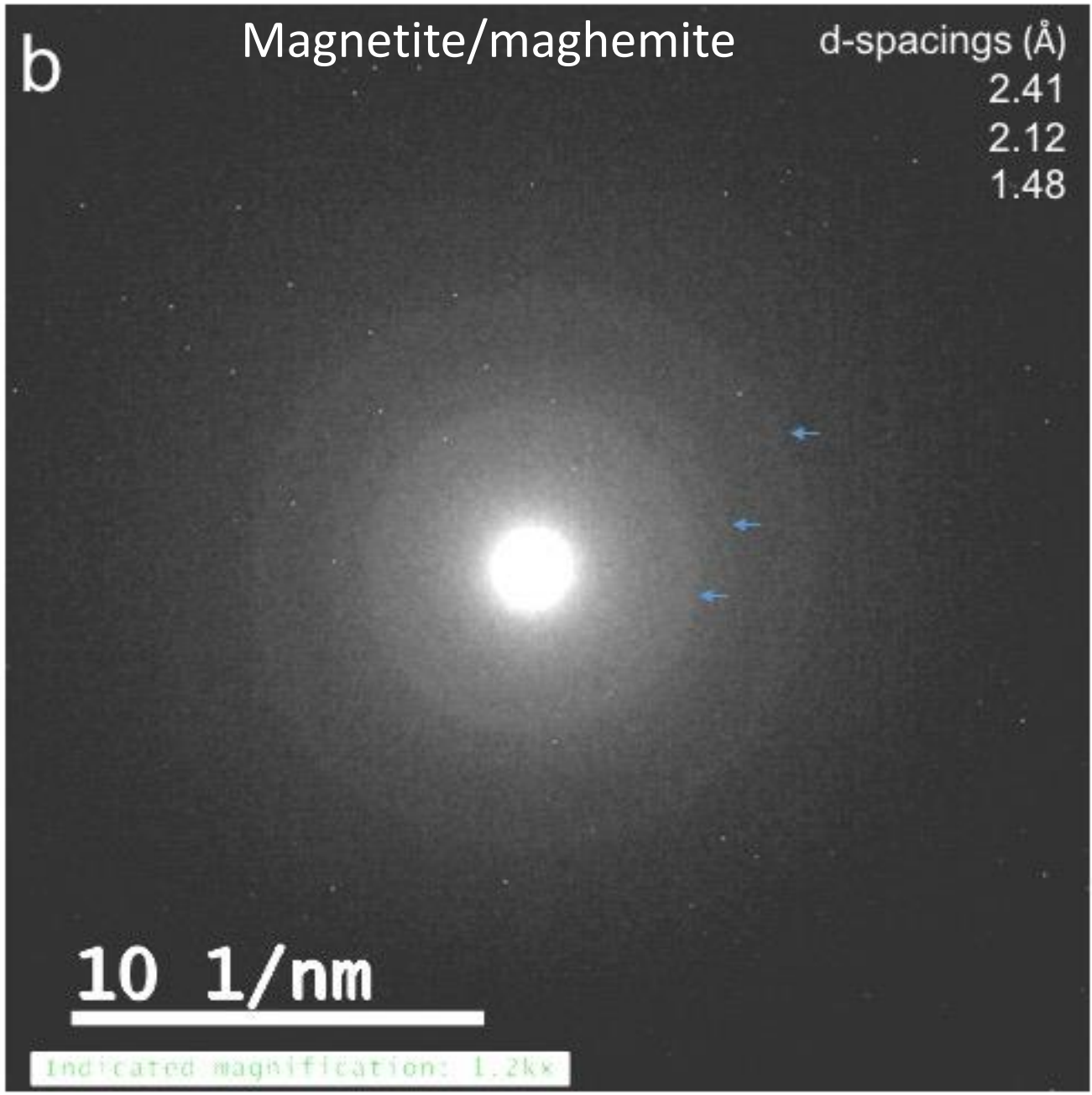
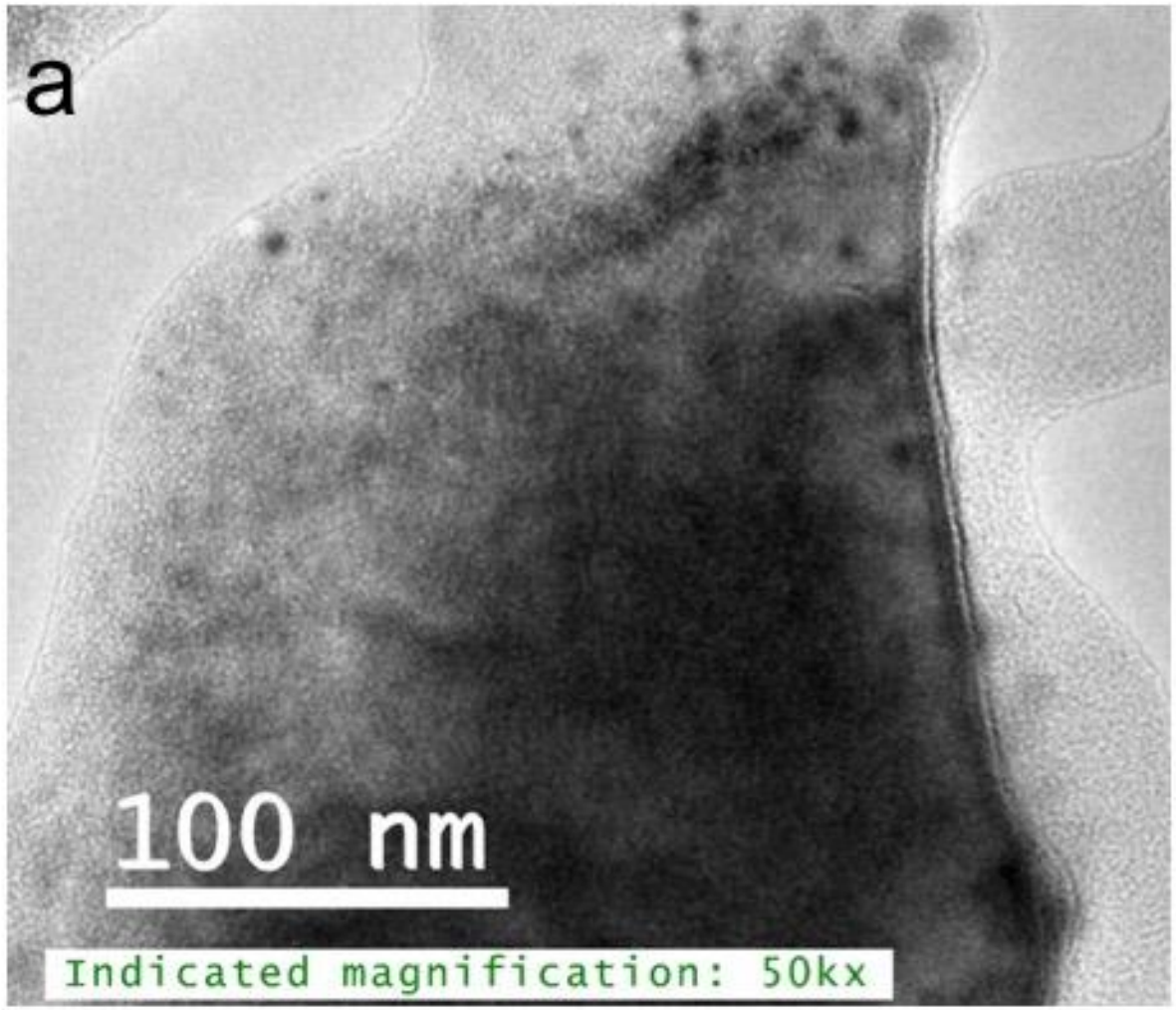


Fig S12. (a) TEM image and Selected area electron diffraction (SAED) pattern of the Fe-oxide alteration layer.



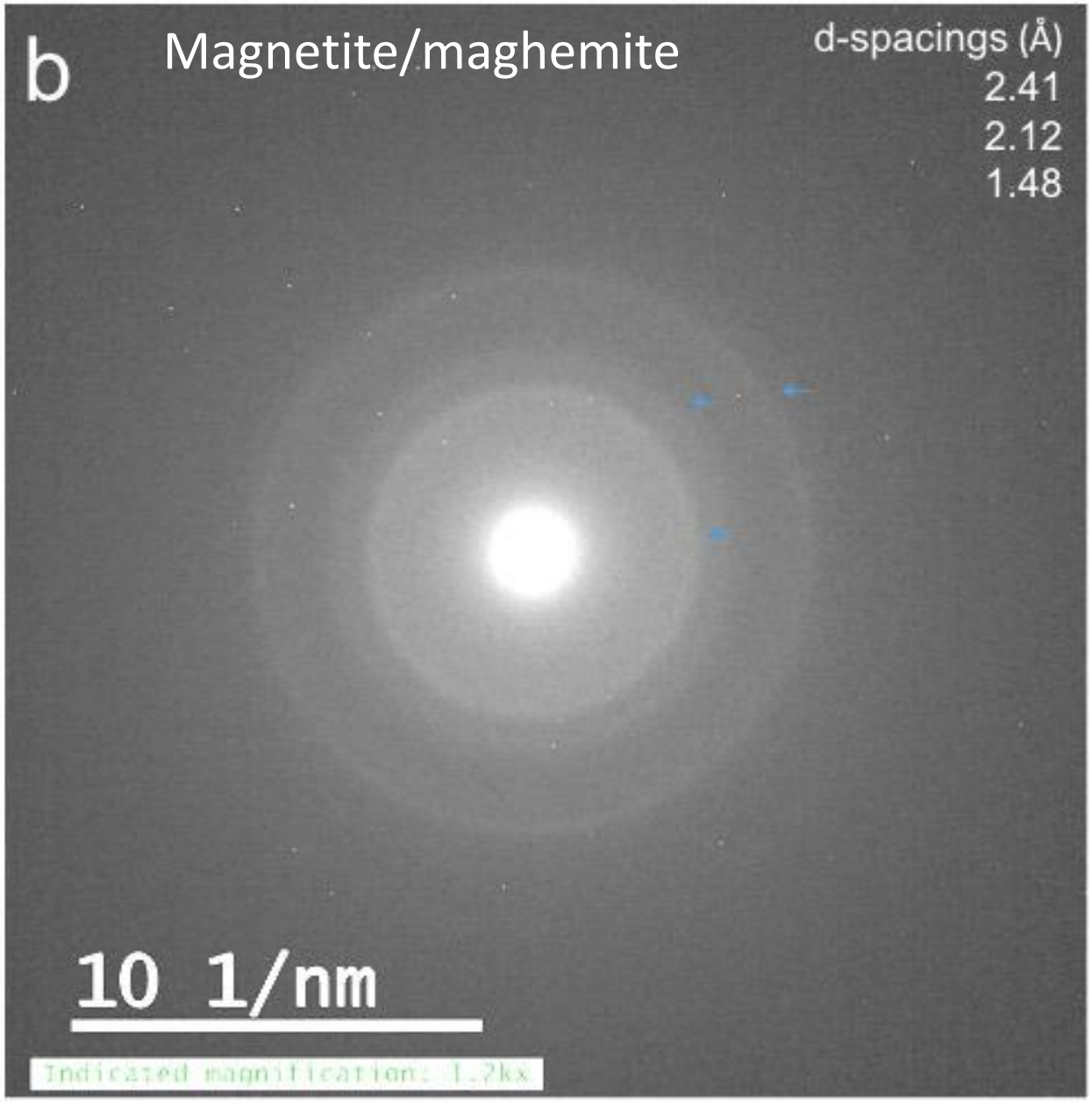
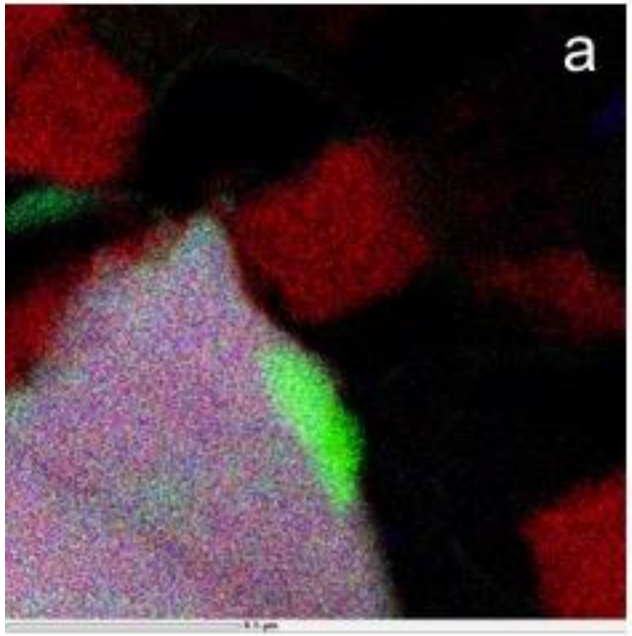
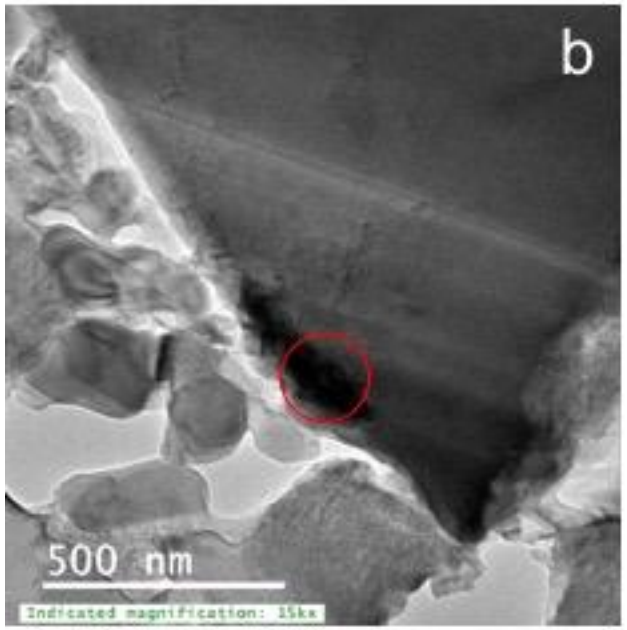
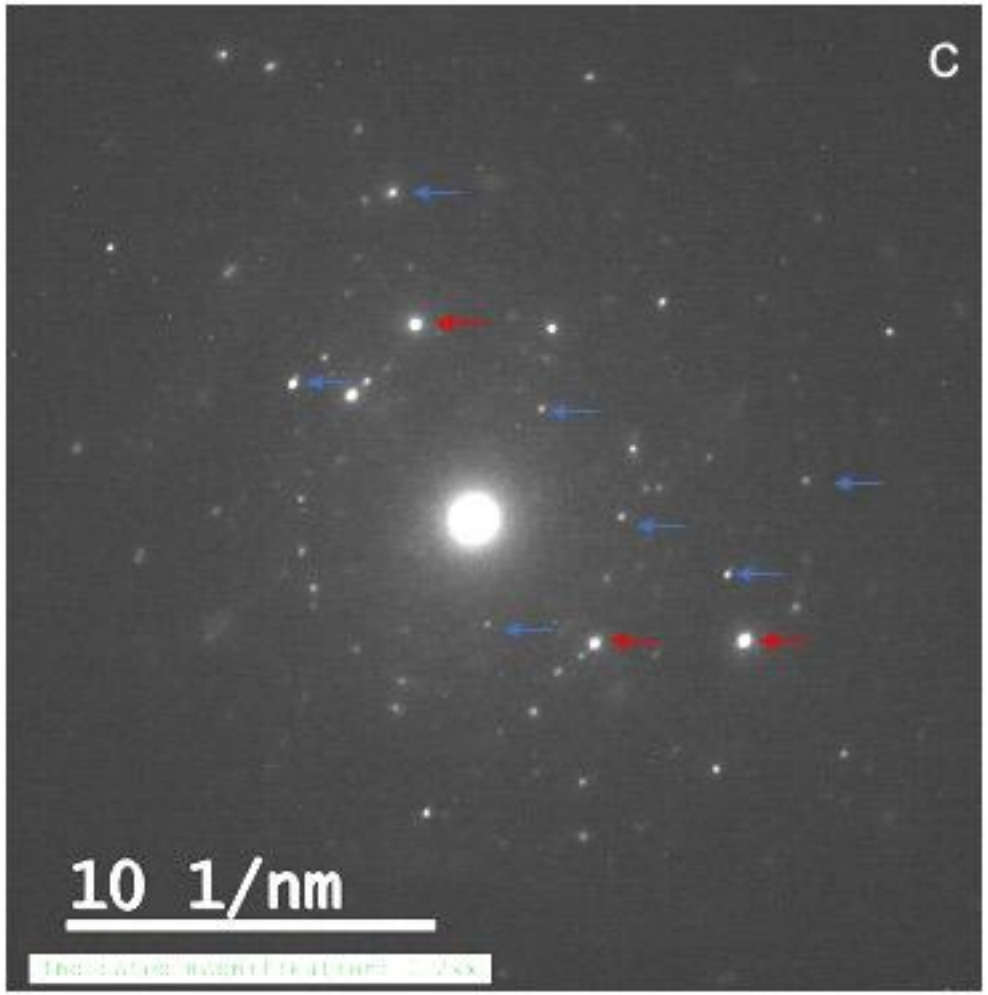


Fig S13. (a) TEM image and (b) SAED pattern of a Fe-oxide fragment at the interface between sulfide and organic matter.



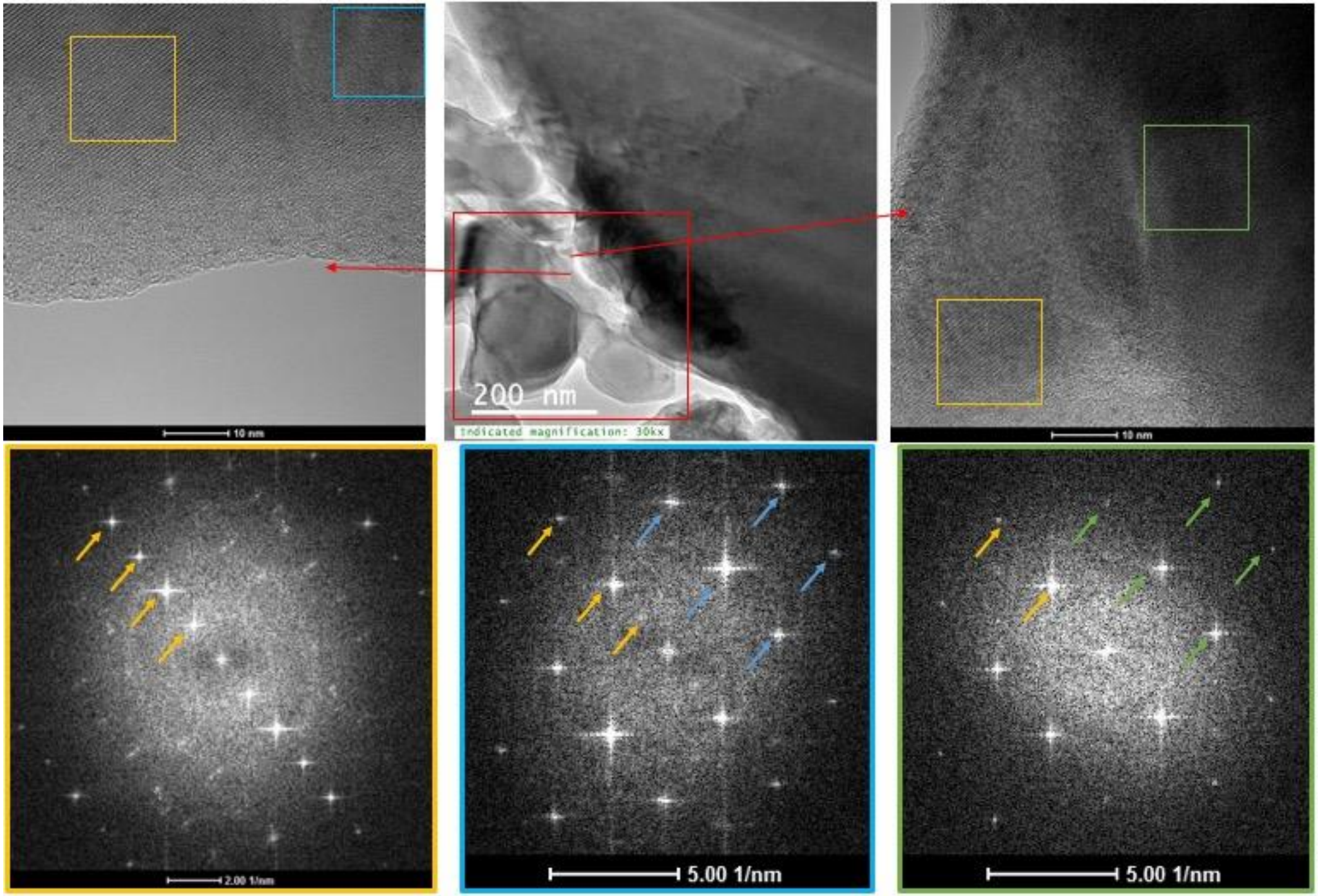




Unidentified d-spacings (Å)
3.35
2.85
2.51
1.63
1.42
1.10
1.06

Metallic Cu d-spacings (Å)
2.11
1.83
1.27

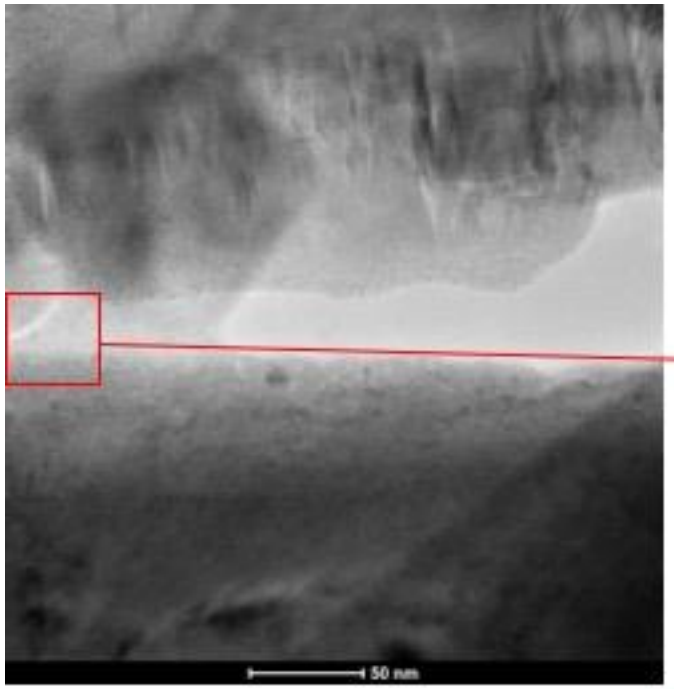
Fig S14. (a) EDS mapping with Cu (green), Fe (red), and S (blue), revealing the Cu-rich rim. Rotated 180 °; (b) STEM image with corresponding (c) SAED pattern (red circle) of the Cu-rich area on the edge of the main sulfide where red arrows indicate d-spacings for metallic copper and blue arrows are various other spacings. EDS quantification indicated a ratio of 56/17/27 for Cu/Fe/S.

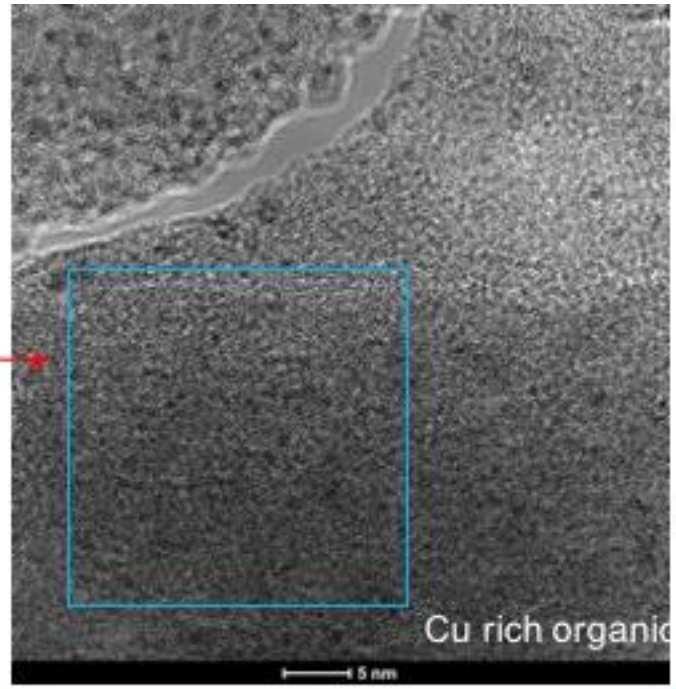


Boehmite
d-spacings (Å)
5.96
3.01
2.00
1.50

Diaspore
d-spacings (Å)
2.52
2.27
1.71
1.32
1.27

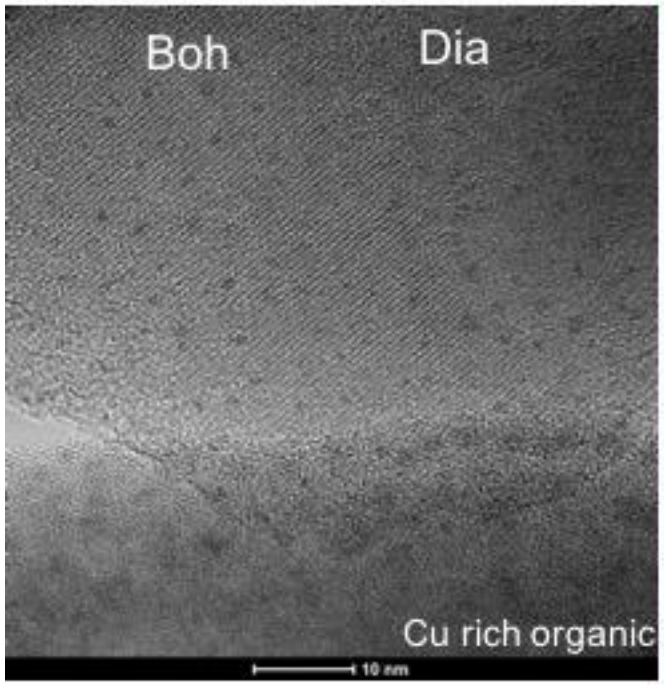
Fig S15. TEM images and FFT pattern for boehmite (γ-AlO(OH), yellow arrows) and diaspore (α-AlO(OH), blue & green arrows).





Metallic Cu
d-spacings (Å)
2.04
1.80
1.29

Unidentified
d-spacings (Å)
3.08
2.38
1.54
1.40



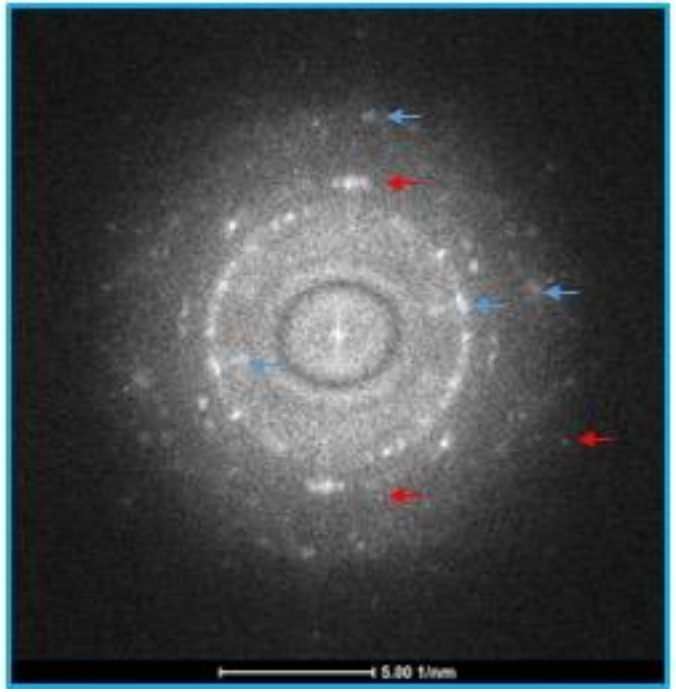
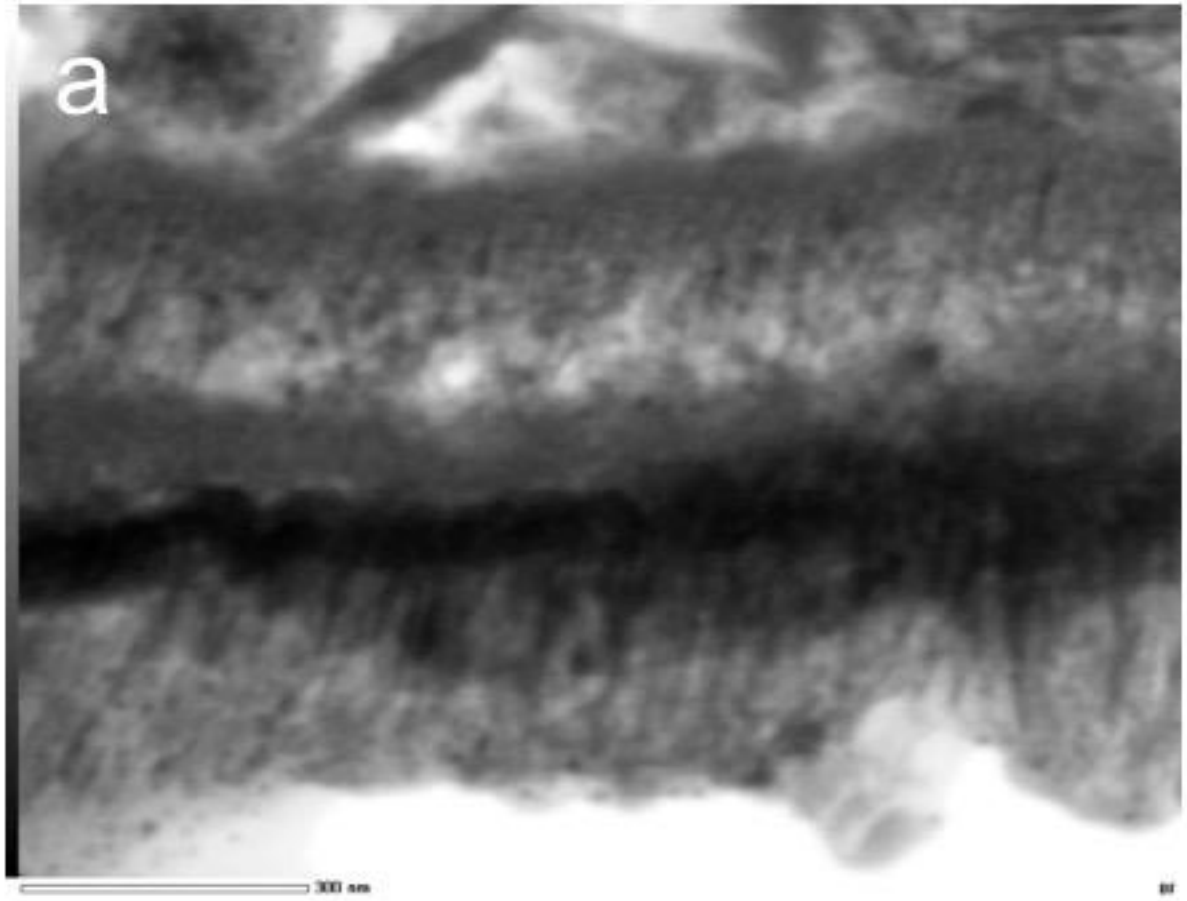


Fig S16. Scanning-TEM images and fast Fourier transformation pattern of lattice fringes of nanoparticles within organic material and boehmite (Boh) and diaspore (Dia). Red arrows in FFT indicate metallic Cu, blue arrows indicate unknown d spacings.



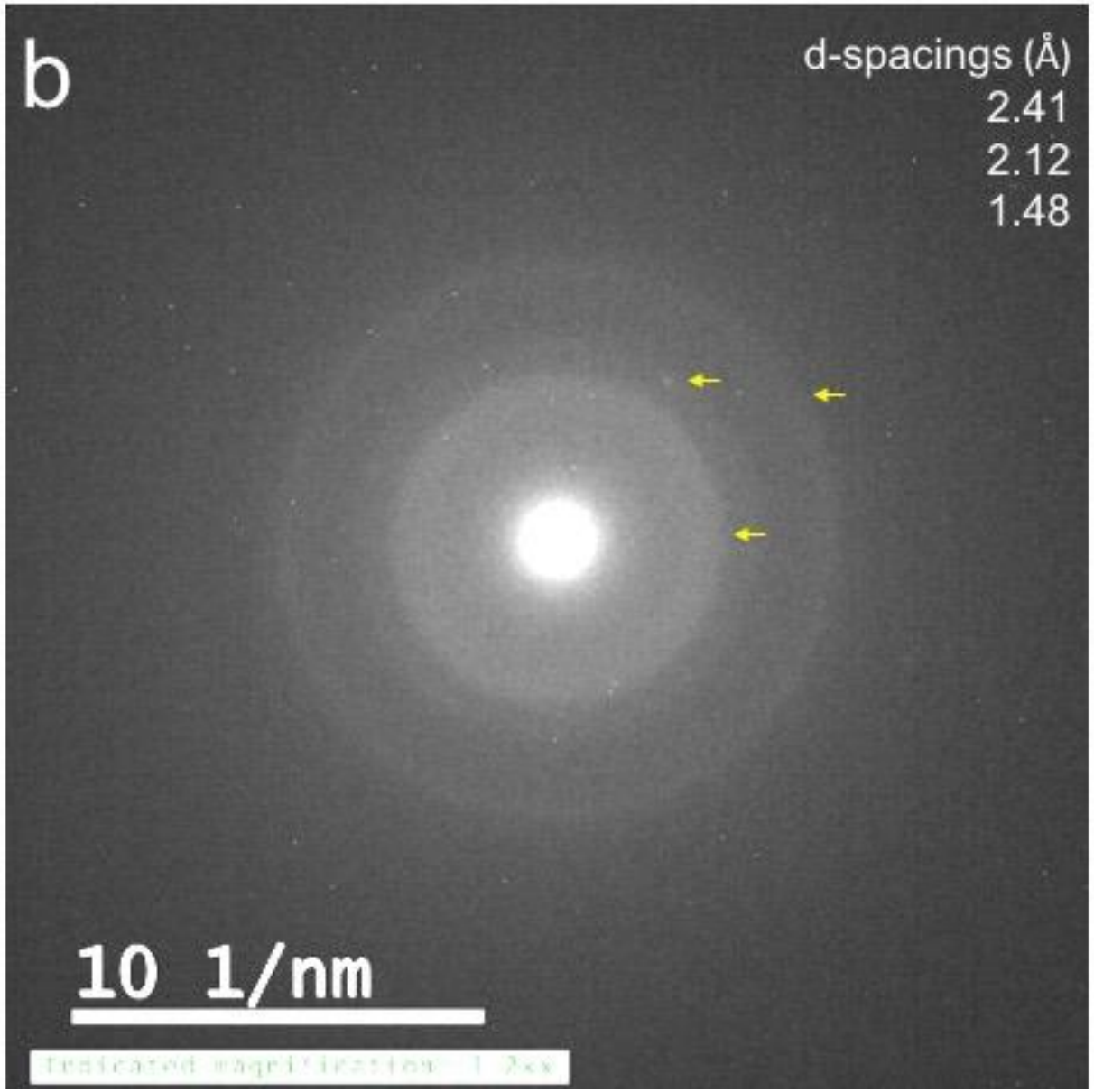


Fig S17. (a) TEM image and (b) Selected area electron diffraction pattern of the iron oxide core surrounded by organic material.

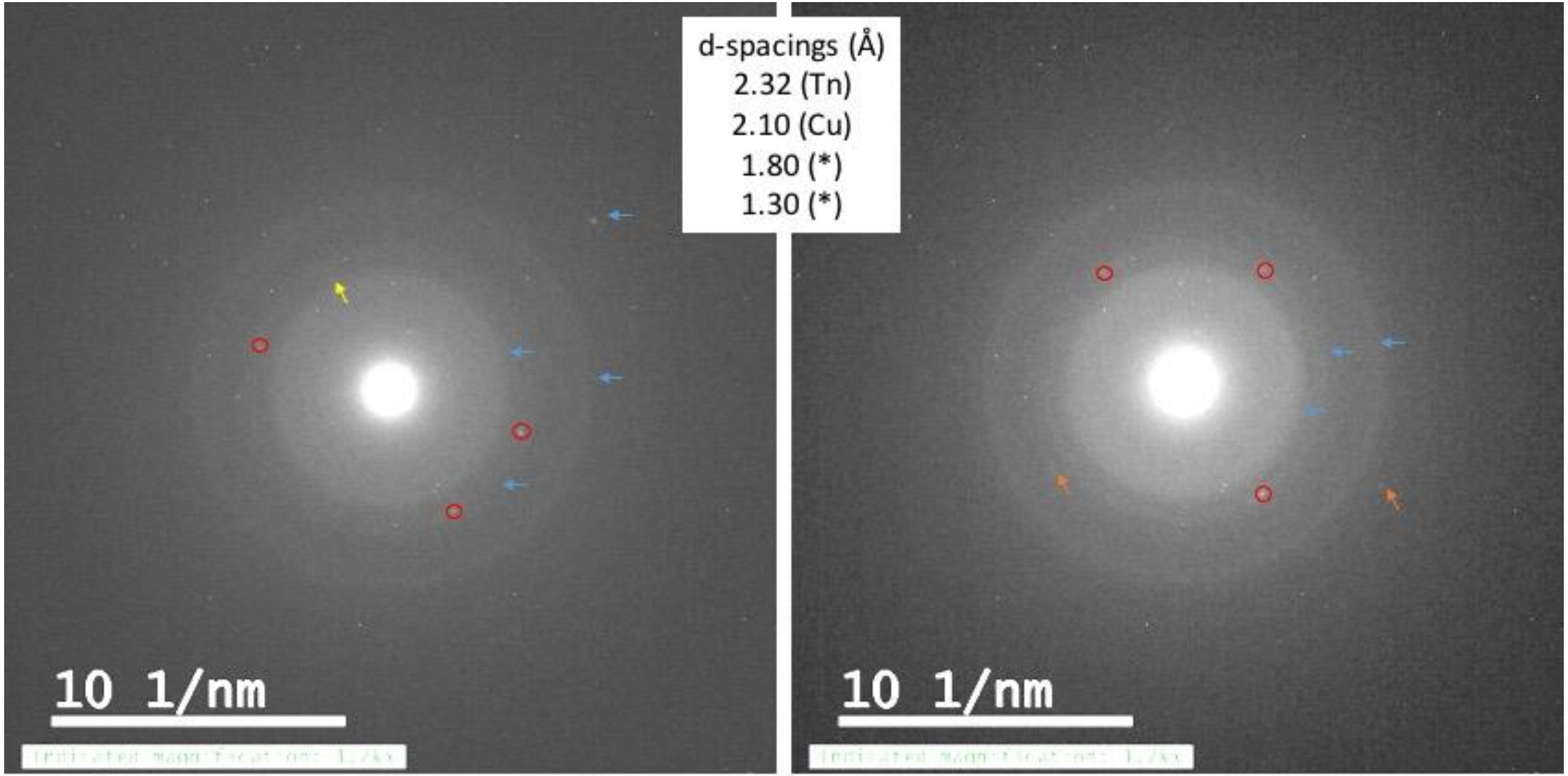
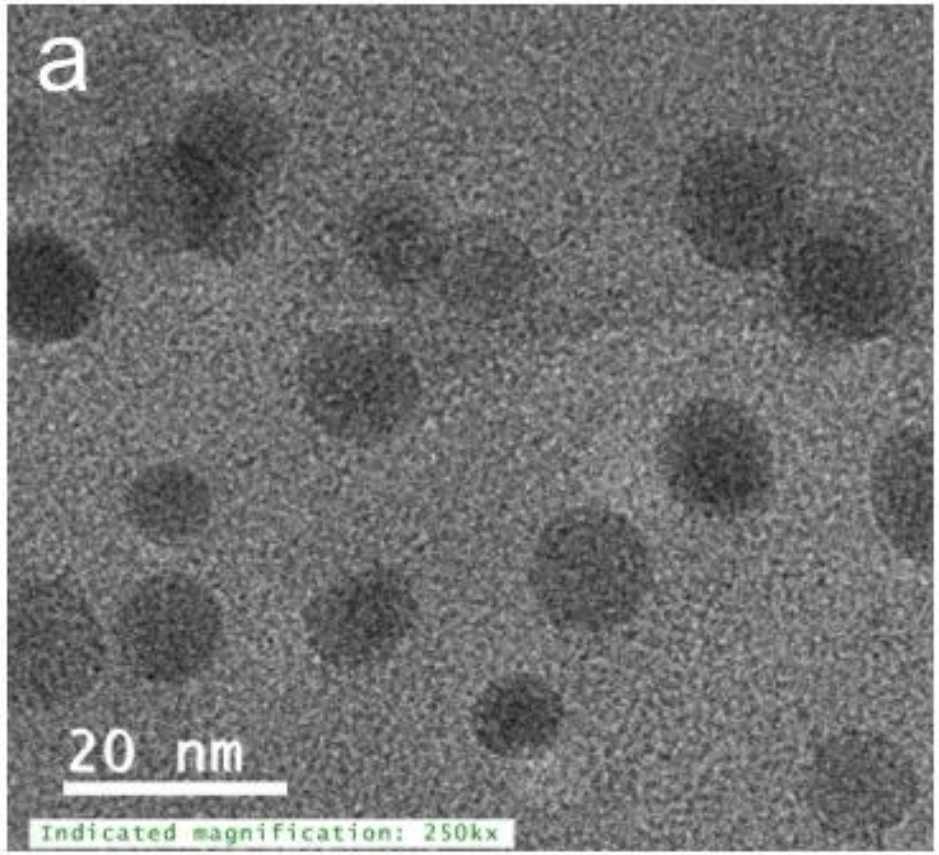


Fig S18. SAED patterns of Cu-based nanoparticles within and surrounding the iron oxide core. Red circles indicate metallic Cu, yellow arrows indicate tenorite (Tn), orange arrows can be either metallic Cu or tenorite (*), and blue arrows indicate magnetite/maghemite.



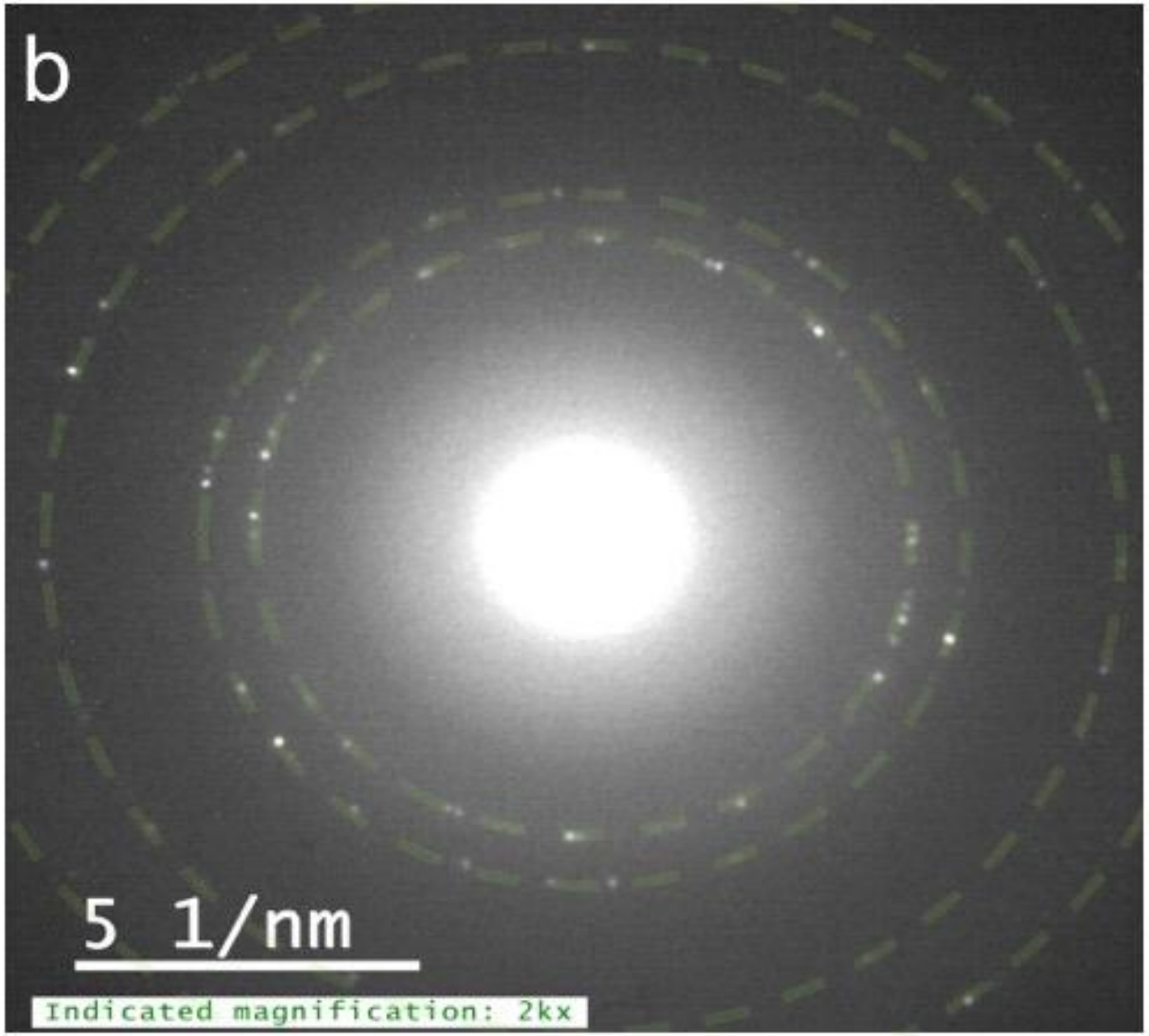


Fig S19. (a) TEM image and (b) SAED pattern of Cu-based nanoparticles in the second FIB. The 3 green circles indicate the (111), (200), and (220) planes of metallic copper, while the fourth indicates the (311) plane which is sometimes listed in diffraction data.

d-spacings (Å) : 2.08, 1.80, 1.27, 1.07

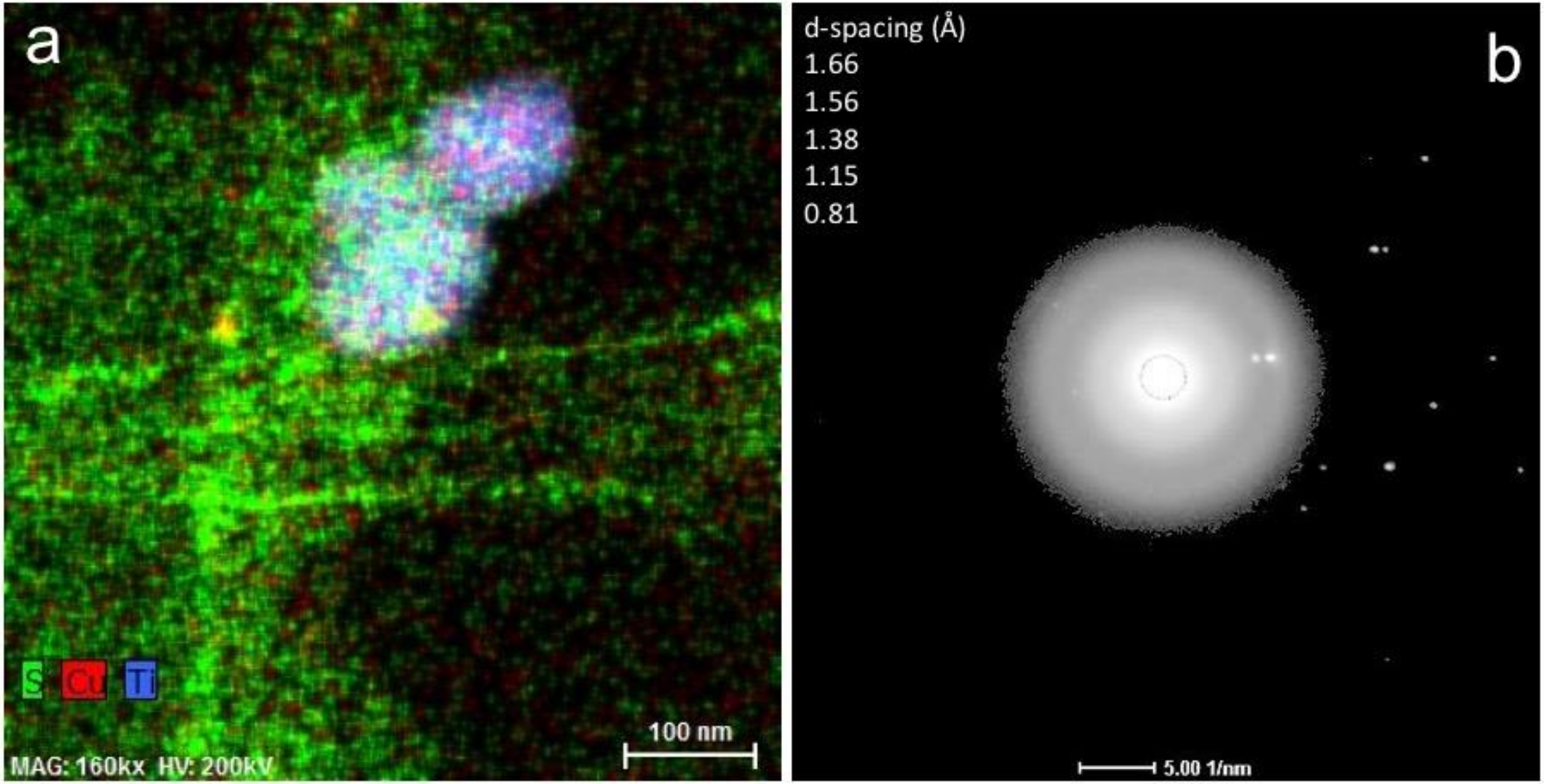
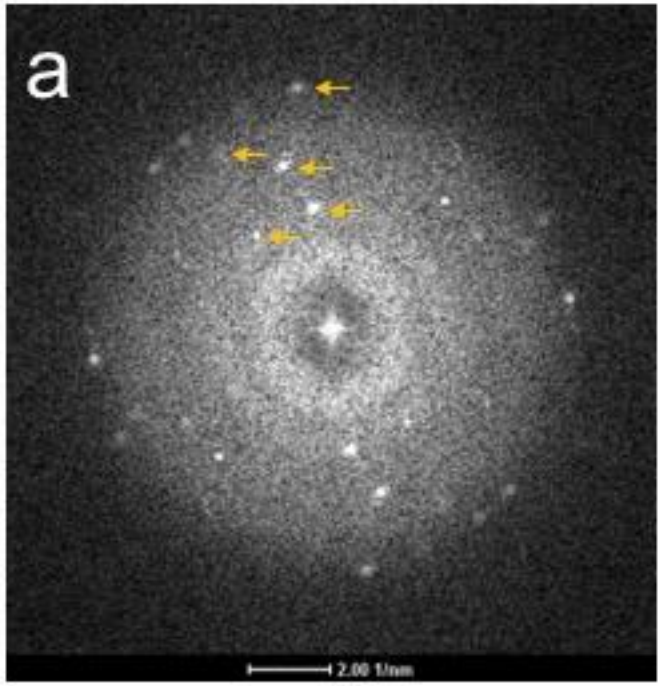
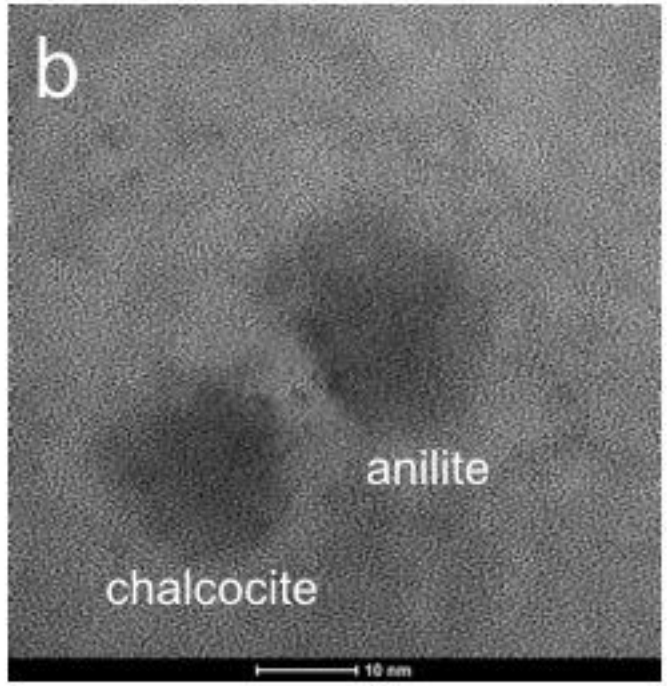


Fig S20. (A) Scanning-TEM-EDS chemical distribution map showing the presence of Cu-S (yellow) and Cu-O bearing NPs (violet) on the TiOx colloid (blue) and (b) the SAED pattern of the unidentified titanium oxide crystals.





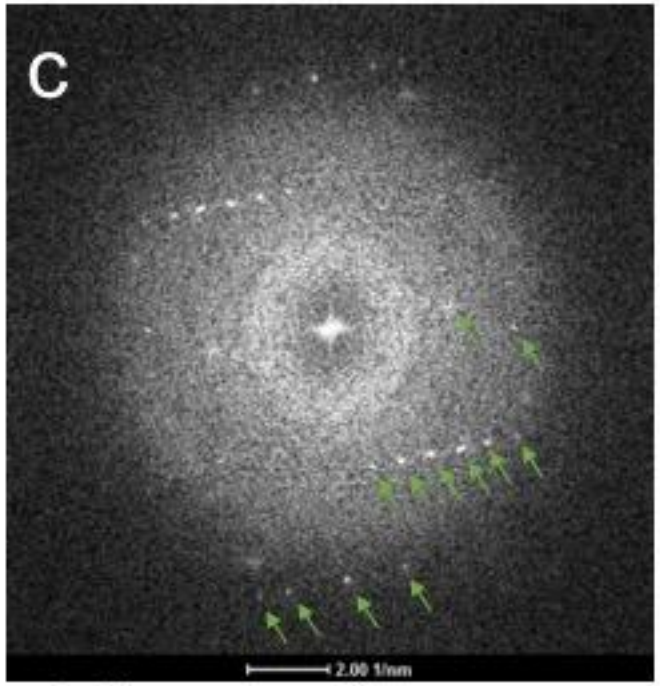
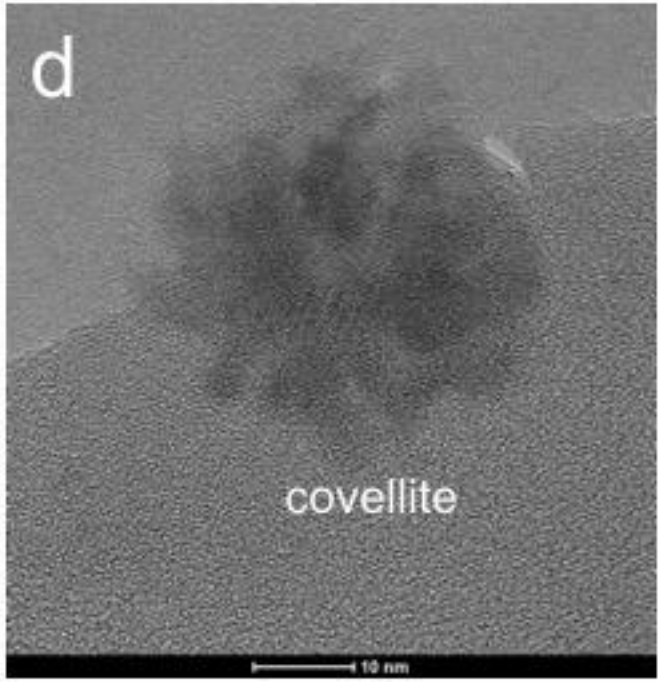
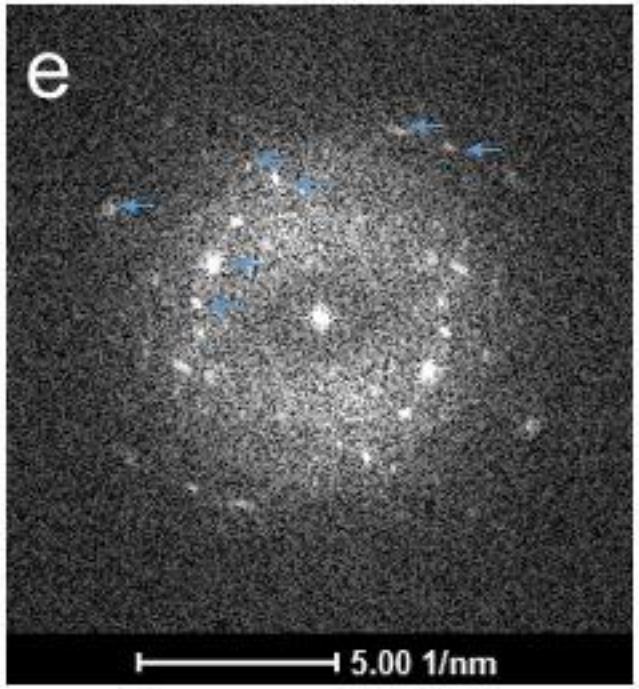


Fig S21. TEM and SAED pattern of (a)-(b) chalcocite (orange), (b)-(c) anilite (green), and (d)-(e) covellite (blue).





Anilite d-spacings (Å)		Covellite d-spacings (Å)
3.35	2.11	3.28
2.83	1.90	3.12
2.74	1.64	2.70
2.54	1.63	2.36
2.30	1.54	1.94
2.21	1.48	1.85
		1.67

Chalcocite d-spacings (Å)	
3.40	2.39
3.34	1.69