

Figure S1. HAADF STEM images for the overviews of studied foils. Foil#1 and #2 were cut from the irregular, coarser sphalerite (Sp) inclusions in pyrrhotite; note the later phlogopite+chlorite (Phl/Chl) crosscut the Sp inclusion. Foil#3 and #4 were cut from the smaller Sp blebs. Foil#5 was cut from the coarser lobate Sp; note the chalcopryrite (Cp) nanoparticles trails in the Sp and the boundary between Sp and pyrrhotite contains Si, O, Cu and Ag-Bi sulfosalts.

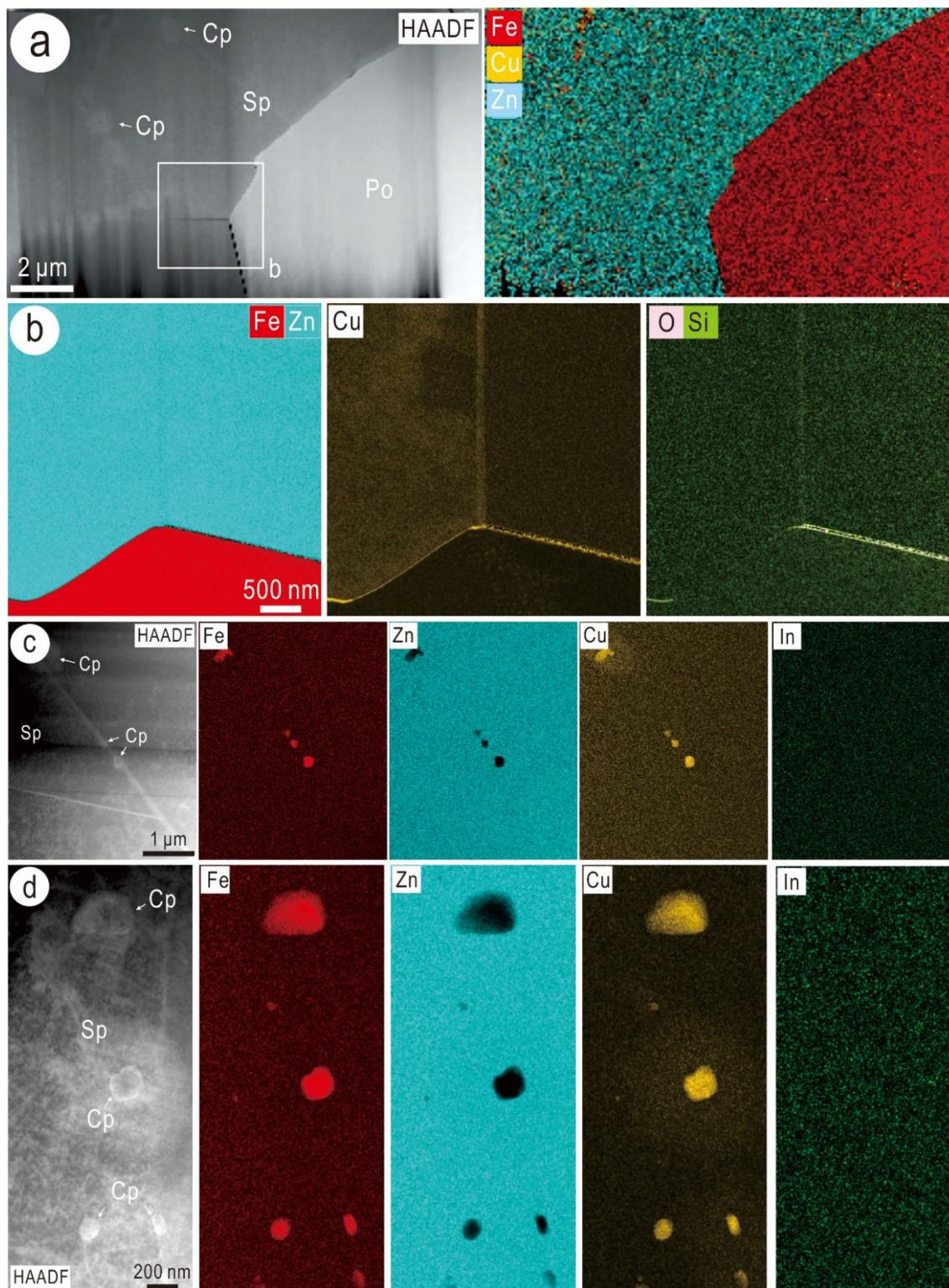


Figure S2. HAADF STEM images and STEM EDS maps for selected elements in detailed areas in Foil #5. In (a-b), note the boundary between sphalerite (Sp) and pyrrhotite (Po) containing Cu, O and Si. In (c-d), note the chalcopyrite (Cp) nanoparticles trails in the Sp.

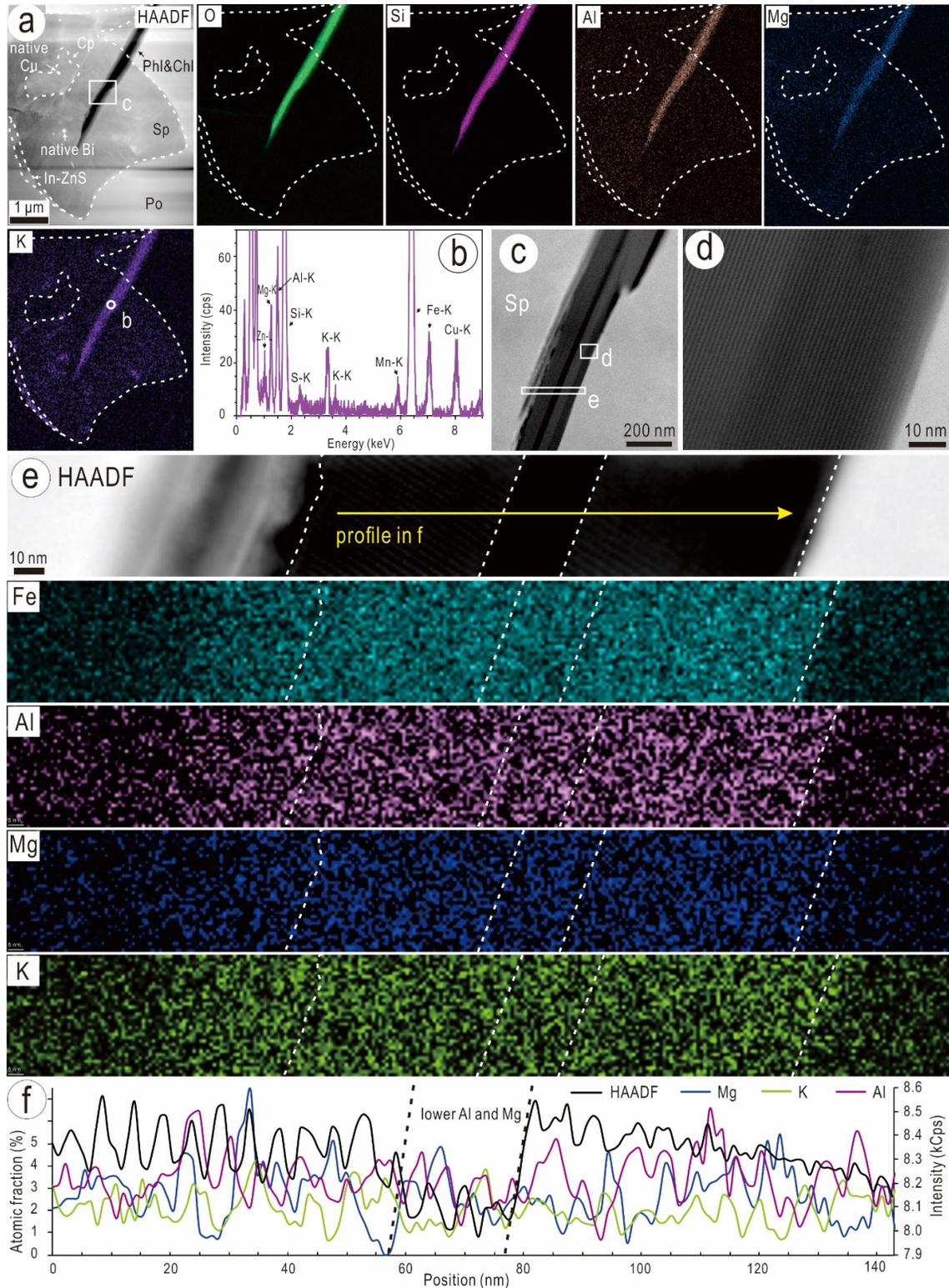


Figure S3. (a) HAADF STEM image (left) and STEM EDS maps for selected elements in detailed areas in Foil #2. (b) EDS spectra for mineral species (phlogopite+chlorite, Phl/Chl) identified in (a). (c-d) HAADF STEM images showing the details of textures of Phl/Chl. (e) HAADF STEM image (top) and STEM EDS maps for selected elements in detailed areas in (c). (f) EDS spectrum showing the variation of selected compositions in (f).

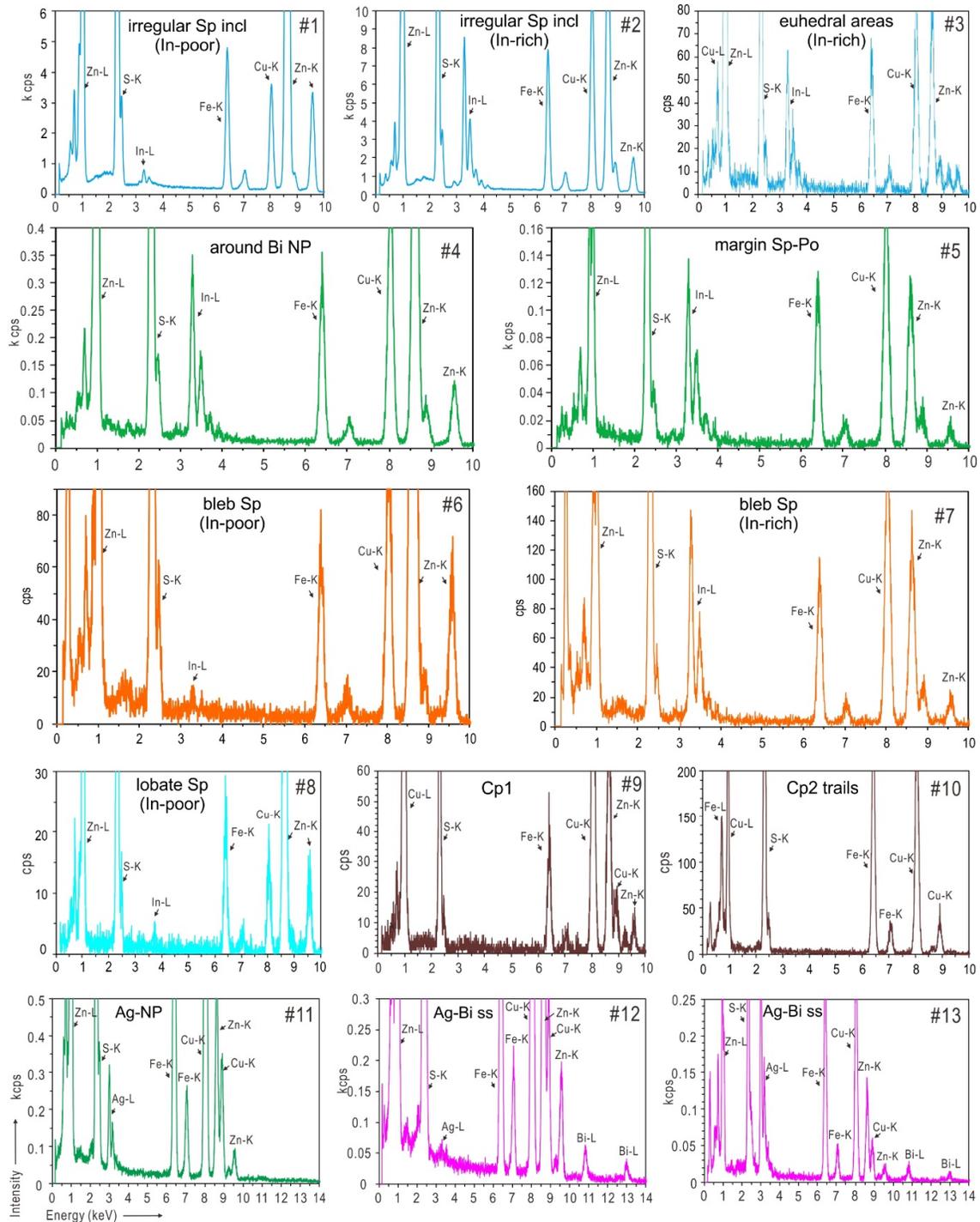


Figure S4. (a) Representative EDS spectra for mineral species identified in the examined foils. Cp-chalcopyrite; Po-pyrrhotite; Sp-sphalerite. Ag-NP and Bi-NP are nanoparticles of native silver and native bismuth; ‘Ag-Bi ss’ is an unidentified Ag-Bi-sulfosalt phase. Spot analysis # numbers are collected from areas marked on the maps in Figures 3-5. Spectra #12 and 13 are from the Ag-Bi-enriched margin between lobate sphalerite and pyrrhotite as shown in Figure S1 for Foil #5.

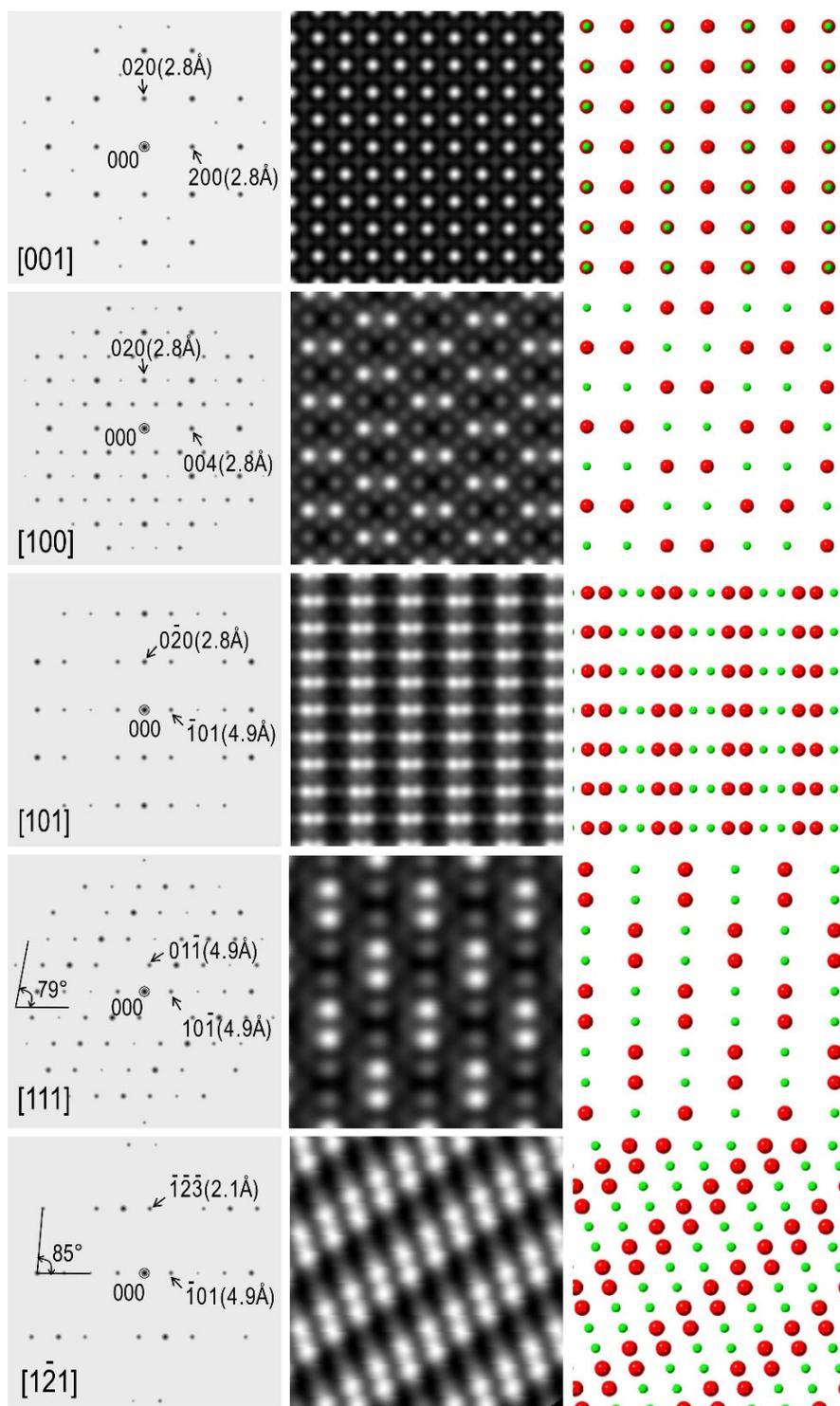


Figure S5. From left to right, selected area of electron diffraction (SAED) simulations, STEM simulations, and crystal structural models for roquesite viewed on [001], [100], [101], [111] and $[1\bar{2}1]$ zone axes.

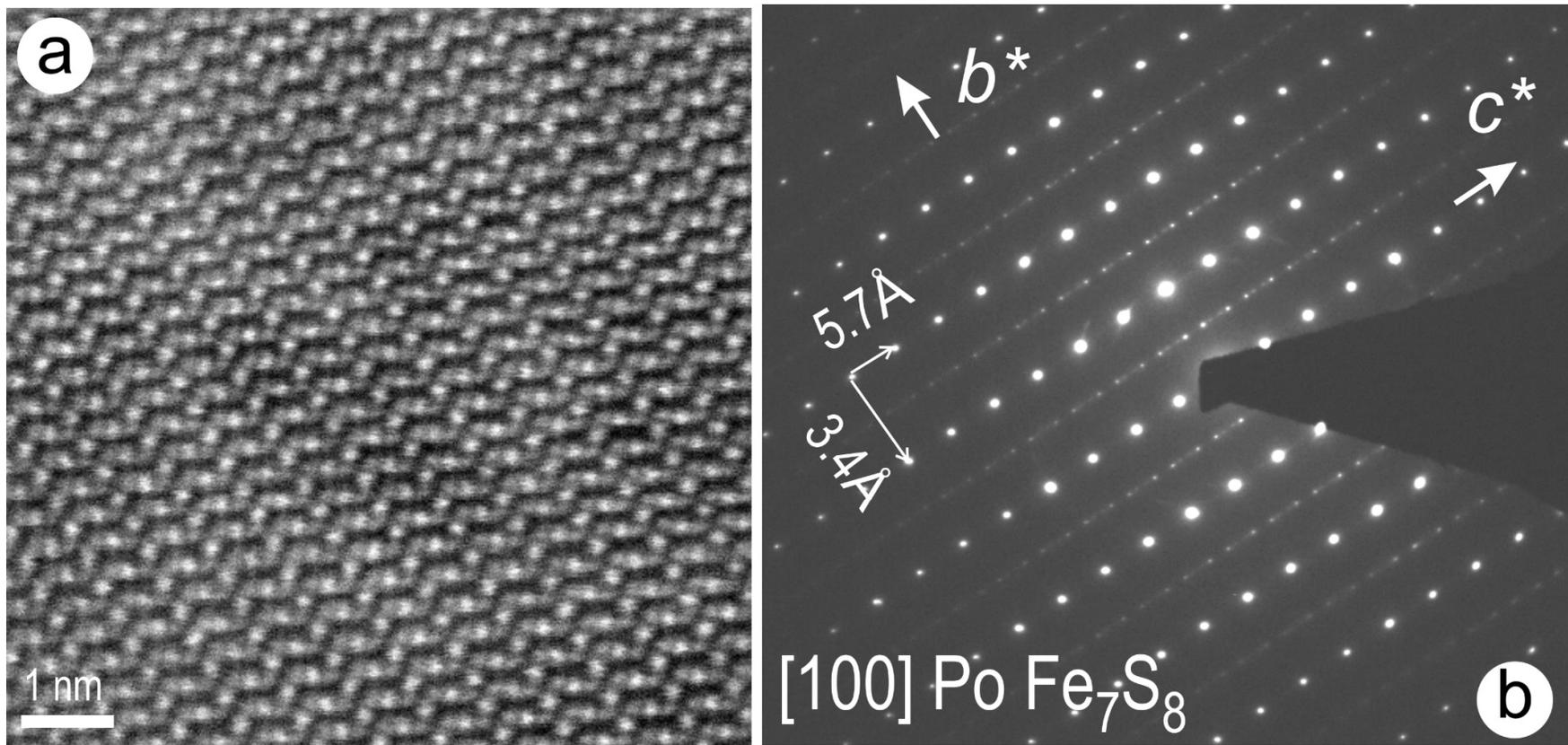


Figure S6. High-resolution HAADF STEM image (a) and selected area of electron diffraction (SAED) in (b) for pyrrhotite host to sphalerite inclusions. The SAED displays satellite reflections (arrowed) along rows parallel to c^* corresponding to ordering of metal vacancies in pyrrhotite.