

Supplemental Information

Oxidation state and additional chemical characteristics of solid precipitates were determined using X-ray absorption spectroscopy (XAS). X-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory on beamline 4-3 using a Si(220) double-focusing monochromator through the K-edge of cobalt—from 7500 to 8700 eV. Incident and transmitted intensities were measured with N₂-filled ionization chambers; fluorescence intensity was measured using a 13-element Ge detector. Internal energy calibration for each sample was accomplished using a cobalt foil positioned between the second and third in-line ionization chambers with the first inflection point set to 7709 eV.

Samples were prepared by mounting a sealed glass ampoule in the beam path such that the x-ray beam passed directly through it. The ampoule contained unfiltered samples in their natural condition. This system allowed the sample solutions with precipitates to be analyzed in an anaerobic environment, preventing oxidation during analysis. Standards including CoS, CoS₂, Co₂O₃, and KCo(III)EDTA (the reactant) were analyzed for comparison to the reaction products. Both CoS and CoS₂ were synthesized as standards for solid-phase analysis. The monosulfide was prepared by reacting CoCl₂ (0.1 M) with an equimolar concentration of Na₂S·6H₂O under an N₂ atmosphere. Cobalt disulfide was synthesized by reacting sodium sulfide (0.1 mol) at 200 °C in a muffle furnace with elemental sulfur (0.1 mol) to form NaS₂ and then adding cobalt (II) chloride, 6-hydrate to the mixture (0.1 mol).

Analyses of the X-ray absorption near-edge (XANES) spectra were performed using the first-derivative of each spectrum to maximize the differences in edge position. These spectra were then fit with a linear combination of standard spectra. The large difference between the absorption edge positions of CoS, and Co(III) allow these chemical species to easily be separated—Co(II) bound to sulfur absorbed near 7716 eV while Co(III) bound to O absorbed near 7722 eV.

Black precipitates formed in CoEDTA samples reacted with sulfide and those reacted with sulfate and *D. vulgaris*. The spectra of the reaction products were identical and thus only that for Co(III)EDTA⁻ reduced by sulfide is shown. On the basis of spectral finger prints in the XANES region, Co is present as a sulfide complex in the solids; the absorption edge is at approximately 7716 eV, consistent with the CoS spectrum. Optimal fits were obtained using only the CoS model spectrum. Slight differences in the post-edge region (near 7730 eV) indicate that the precipitates may have slightly different structures. Nevertheless, all of the samples studied indicate the formation of a phase similar to CoS.

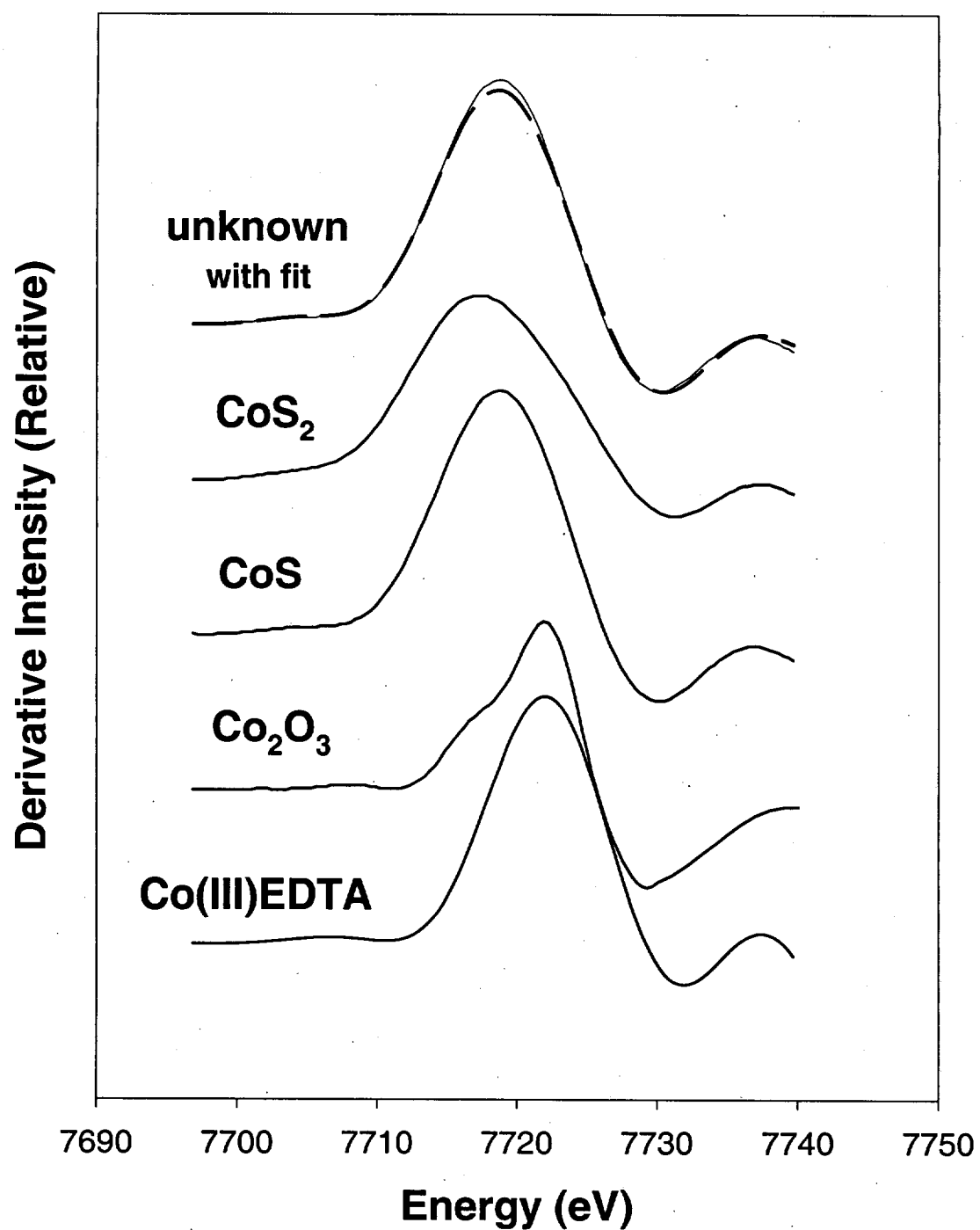


Figure S1. Cobalt K-edge XANES spectra of model compounds and Co(III)EDTA reduced by dissolved sulfide ("unknown"). The "unknown" spectra (solid line) is compared to an optimal fit composed exclusively of the CoS model spectrum (dashed line)