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Supporting information for article:

Beam-induced redox transformation of arsenic during As K-edge XAS measurements: availability of reducing or oxidizing agents and As speciation

Young-Soo Han, Hoon Young Jeong, Sung Pil Hyun, Kim F. Hayes and Chul-Min Chon

S1. Mineralogy of FeS and its oxidation products

SM Figure 1 shows XRD patterns of FeS samples before and after the air exposure. The synthesized FeS was identified as poorly crystalline mackinawite based on its XRD pattern. The thoroughly aerated FeS was found to consist of several Fe(III) (oxyhydr)oxides (e.g., magnetite, hematite, and goethite) and elemental sulfur. Of all these, goethite, hematite, and elemental sulfur were the major oxidation products of FeS. SM Figure 2 shows the XRD patterns of the partially aerated FeS over the 24 h aeration period. In SM Figure 2, the reflection peaks of mackinawite was retained till 4 h aeration at pH 5 and 6 h aeration at pH 9. Also, elemental sulfur and ferrihydrite was detected as the FeS oxidation products in the 7 h aerated FeS at pH 5 and the 12 h aerated FeS at pH 9. The formation of ferrihydrite in the partially aerated FeS was confirmed by the characteristic broad peaks at $2\theta = 34°$ and 61°, which corresponded to 2-line poorly crystalline ferrihydrite (Zhu et al., 2015). As indicated in SM Figure 1B, this poorly crystalline phase was eventually transformed to a mixture of goethite and hematite. Due to the poor crystallinity (thus larger surface area), ferrihydrite present in the partially aerated FeS was expected to facilitate electron transfer during the photo-oxidation. Nonetheless, the thoroughly aerated FeS was used to assess the vulnerability of As reference compounds to the photo-oxidation under O_2-free conditions.

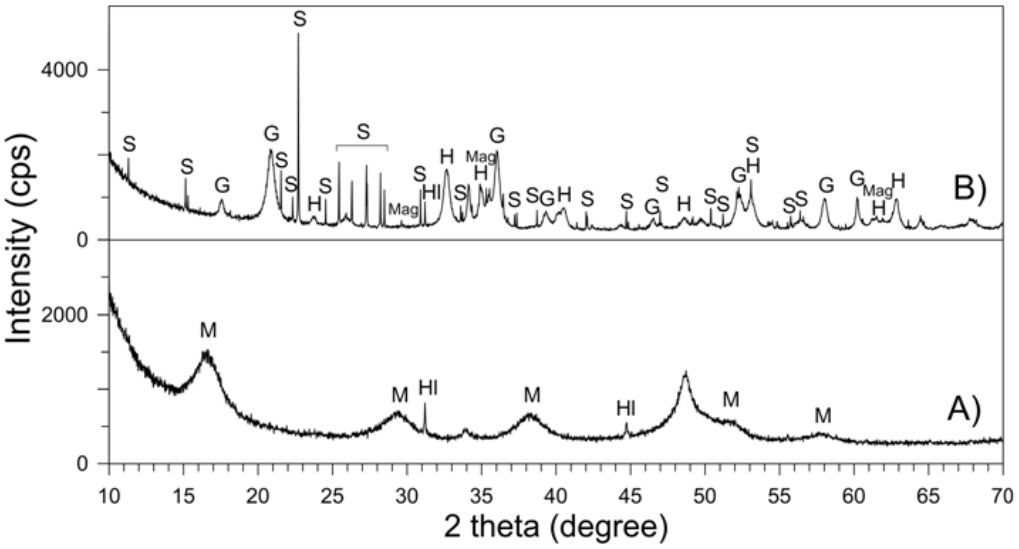

Figure S1 Synchrotron X-ray diffraction patterns of synthesized FeS (**A**) and thoroughly aerated FeS (**B**). Symbols M, P, S, G, H, Mag, and HI correspond to mackinawite, pyrrhotite, elemental sulfur, goethite, hematite, magnetite, and halite, respectively.

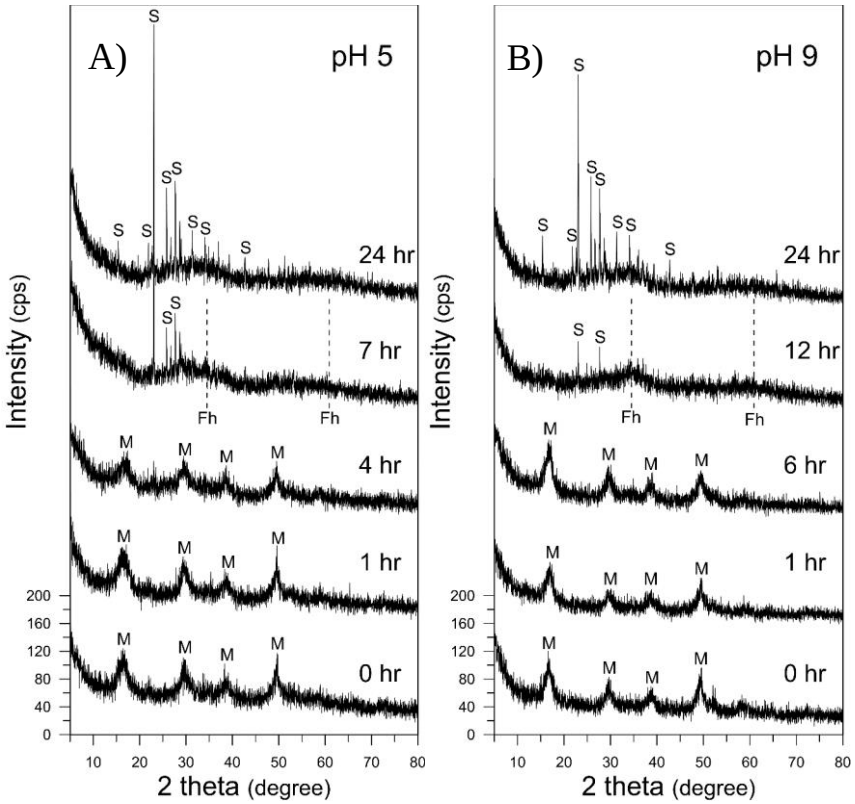

Figure S2 Laboratory-based X-ray diffraction patterns of partially aerated FeS at pH 5 (**A**) and pH 9 (**B**). Symbols M, S, and Fh correspond to mackinawite, elemental sulfur, and ferrihydrite, respectively. The sample aerated for 0 h is unoxidized FeS.

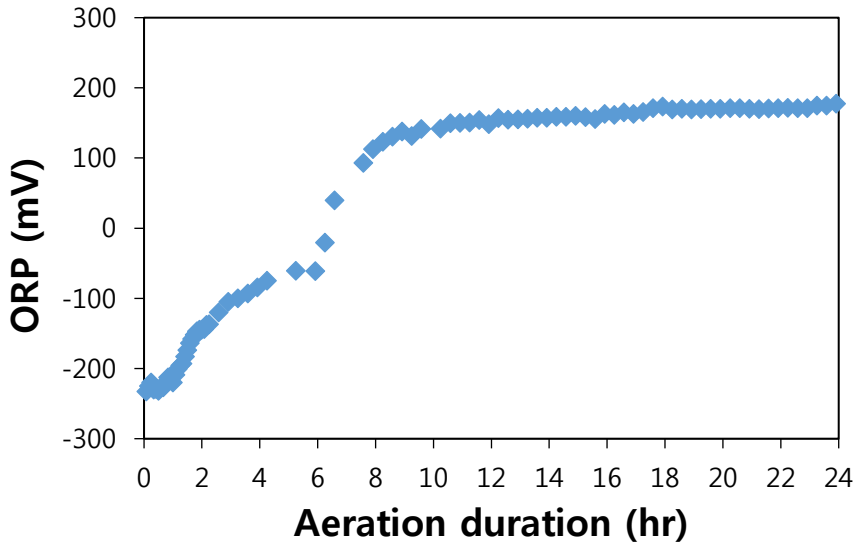

Figure S3 Oxidation reduction potential (ORP) changes in 1g/L FeS (pH not controlled) over 24 hours of air-exposure.

Table S1 Linear combination fitting (LCF) results of samples presented in Figures 2, 3 and 5.

Samples	As(0)	Arsenic sulfide	Aqueous As(III)	Aqueous As(V)	Component Sum	R factor
1. 0hr_scan1 in Figure 2	0.00 +/- 0.032	0.99 +/- 0.178	0.00 +/- 0.047	0.01 +/- 0.015	1	0.0195
2. 1hr_scan1 in Figure 2	0.00 +/- 0.009	0.99 +/- 0.196	0.00 +/- 0.052	0.01 +/- 0.018	1	0.0201
3. 4hr_scan1 in Figure 2	0.00 +/- 0.007	0.38 +/- 0.041	0.46 +/- 0.009	0.16 +/- 0.003	1	0.0006
4. 4hr_scan2 in Figure 2	0.00 +/- 0.008	0.39 +/- 0.046	0.34 +/- 0.011	0.25 +/- 0.004	1	0.0009
5. 4hr_scan3 in Figure 2	0.00 +/- 0.008	0.42 +/- 0.052	0.26 +/- 0.013	0.27 +/- 0.004	1	0.0011
6. 7hr_scan1 in Figure 2	0.00 +/- 0.011	0.137 +/- 0.046	0.532 +/- 0.014	0.33 +/- 0.005	1	0.0021
7. 7hr_scan2 in Figure 2	0.00 +/- 0.0119	0.137 +/- 0.0467	0.532 +/- 0.0141	0.33 +/- 0.0054	1	0.0026
8. 7hr_scan3 in Figure 2	0.00 +/- 0.0	0.10 +/- 0.051	0.50 +/- 0.015	0.40 +/- 0.006	1	0.0026
9. 24h_scan1 in Figure 2	0.04 +/- 0.012	0.22 +/- 0.071	0.30 +/- 0.019	0.44 +/- 0.006	1	0.0023
10. 24h_scan2 in Figure 2	0.05 +/- 0.013	0.19 +/- 0.073	0.29 +/- 0.019	0.46 +/- 0.006	1	0.0023
11. 0hr_scan1 in Figure 3	0.00 +/- 0.013	0.88 +/- 0.016	0.12 +/- 0.039	0.00 +/- 0.006	1	0.0067
12. 6hr_scan1 in Figure 3	0.00 +/- 0.014	0.22 +/- 0.017	0.79 +/- 0.015	0.00 +/- 0.006	1	0.0068
13. 12hr_scan1 in Figure 3	0.00 +/- 0.014	0.02 - 0.081	0.92 +/- 0.021	0.06 +/- 0.007	1	0.0013
14. 24hr_scan1 in Figure 3	0.00 +/- 0.0	0.03 +/- 0.006	0.55 +/- 0.007	0.39 +/- 0.003	1	0.0022
15. 24hr_scan2 in Figure 3	0.00 +/- 0.011	0.03 +/- 0.067	0.52 +/- 0.006	0.45 +/- 0.006	1	0.0026
16. 24hr_scan3 in Figure 3	0.00 +/- 0.0	0.03 +/- 0.007	0.50 +/- 0.008	0.47 +/- 0.003	1	0.0026
17. pH 5 As(III)_scan1 in Figure 5	0.00 +/- 0.019	0.96 +/- 0.118	0.04 +/- 0.022	0.00 +/- 0.008	1	0.0032
18. pH 7 As(III)_scan1 in Figure 5	0.00 +/- 0.039	0.86 +/- 0.211	0.14 +/- 0.044	0.00 +/- 0.015	1	0.0113
19. pH 9 As(III)_scan1 in Figure 5	0.00 +/- 0.028	0.81 +/- 0.158	0.19 +/- 0.032	0.00 +/- 0.011	1	0.0062
20. pH 5 As(V)_scan1 in Figure 5	0.00 +/-0.027	0.46 +/-0.038	0.10 +/-0.030	0.44 +/-0.055	1	0.0132
21. pH 7 As(V)_scan1 in Figure 5	0.00 +/-0.022	0.18 +/-0.031	0.10 +/-0.025	0.72 +/-0.046	1	0.0223
22. pH 9 As(V)_scan1 in Figure 5	0.00 +/-0.050	0.29 +/-0.044	0.00 +/-0.025	0.71 +/-0.014	1	0.0248
23. pH 9 As(V)_scan2 in Figure 5	0.00 +/-0.037	0.385 +/-0.052	0.134 +/-0.041	0.48 +/-0.083	1	0.0454
24. pH 9 As(V)_scan3 in Figure 5	0.00 +/-0.047	0.49 +/-0.066	0.15 +/-0.052	0.36 +/-0.102	1	0.0455
25. pH 9 As(V)_scan4 in Figure 5	0.00 +/-0.047	0.56 +/-0.066	0.21 +/-0.052	0.24 +/-0.102	1	0.0815