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Long-term arsenic sequestration in biogenic pyrite from contaminated groundwater: Insights from field and laboratory studies

Supplementary Materials

Table S1. Groundwater pH versus collection date of samples.

Well	05/15/2018 (Pre-Injection)	06/28/2018 (Week 1)	07/06/2018 (Week 2)	07/12/2018 (Week 3)	07/19/2018 (Month 1)	08/23/2018 (Month 2)	09/20/2018 (Month 3)	12/14/2018 (Month 6)	03/18/2019 (Month 9)
I-1	6.8	4.43	5.8	6.17	6.4	6.03	6	6.3	6.18
I-2	6.47	4.85	5.75	6.05	6.16	6.12	6.1	6.21	6.16
I-3	6.54	4.81	5.51	5.64	6.02	5.50	6.03	5.9	5.68
I-4	6.08	4.46	5.02	5.29	5.18	5.24	5.27	5.14	5.31
I-5	5.61	4.23	5.38	5.23	4.75	5.71	5.56	5.57	5.64
I-6	6.83	5.06	5.5	5.62	5.69	6.02	6.18	6.65	6.38
I-7	6.93	5.77	6.58	6.69	6.68	6.49	6.43	6.76	6.26
I-8	5.13	4.63	4.25	4.35	4.66	4.34	4.85	5.16	5.33
I-9	5.74	5.44	5.41	5.57	5.67	5.37	5.64	5.57	5.64
I-10	6.63	6.25	6.16	6.12	6.12	6.17	6.35	6.34	6.05
I-11	5.95	4.77	5.18	4.88	4.52	5.58	5.61	6.14	5.73
LH-2	5.47	5.19	5.09	5.11	5.16	4.75	4.95	5.15	5.18
LH-4	6.2	5.82	5.84	5.79	5.83	5.77	5.95	5.83	5.9
LH-5	6.96	6.57	6.62	6.57	6.68	5.95	6.05	6.01	5.96
LH-7	5.96	5.64	5.62	5.52	5.63	5.62	5.7	5.93	5.91
LH-10	6.65	6.36	5.67	5.65	5.8	5.90	6.37	6.2	6.02
M-1	6.14	4.65	4.78	4.68	5	5.08	5.15	5.39	5.54
M-3	5.62	5.2	5.32	5.14	5.3	5.37	5.58	5.51	5.47
RA-9	6.77	6.23	6.23	6.14	6.14	5.70	5.87	5.84	5.83
RA-10	6.93	5.9	5.41	6.77	6.24	6.66	6.38	6.71	6.53
RA-11	7.33	6.97	6.83	6.76	6.93	6.41	6.45	6.27	6.21
RA-12	6.45	6.16	6.18	6.16	6.19	5.72	5.59	5.58	5.5
RA-13	5.25	5.52	5.42	4.8	5.35	5.84	6	5.88	5.71
RA-14	6.31	6.22	6.07	6.01	6.1	6.41	6.38	6.5	6.15

Table S2. Groundwater oxidation-reduction potential (ORP) (mV) versus collection date of samples.

Well	05/15/2018 (Pre-Injection)	06/28/2018 (Week 1)	07/06/2018 (Week 2)	07/12/2018 (Week 3)	07/19/2018 (Month 1)	08/23/2018 (Month 2)	09/20/2018 (Month 3)	12/14/2018 (Month 6)	03/18/2019 (Month 9)
I-1	-5	-7	-99	-138	-131	-219	36	81	-66
I-2	33	66	-184	-161	-142	-30	44	-27	2
I-3	37	-2	-141	-133	-189	-244	-25	-85	-37
I-4	30	21	-78	-94	25	-57	-15	-30	11
I-5	48	25	-94	-90	-42	-114	42	-25	-1
I-6	44	-53	-129	-118	-87	-139	9	-70	-14
I-7	79	-83	-180	-165	-132	-141	43	-163	-10
I-8	28	-4	85	184	128	-33	24	-30	11
I-9	9	39	-1	52	51	-2	2	-9	6
I-10	62	56	27	43	39	17	4	46	24
I-11	55	25	-52	-10	25	-84	41	-56	12
LH-2	-7	12	5	38	52	-111	25	-63	-7
LH-4	48	22	-9	12	15	-13	-11	-10	9
LH-5	38	-38	-18	-11	-42	-261	-56	-74	-75
LH-7	61	21	16	2	13	-12	-22	-34	20
LH-10	20	-66	14	-135	-158	-262	-32	-153	-92
M-1	4	-31	8	-99	-89	-237	67	-93	56
M-3	55	-1	-40	-36	7	-111	-26	-86	-36
RA-9	45	-9	-39	-93	-72	-248	-17	-77	-34
RA-10	73	-26	-14	-6	-84	-131	-20	-118	-47
RA-11	74	57	19	46	-17	35	79	26	3
RA-12	24	46	-9	84	99	-58	56	-57	4
RA-13	19	-2	19	75	80	-43	-3	-24	-23
RA-14	38	19	76	90	-61	47	9	99	87

Table S3. Dissolved oxygen (DO) (mg/L) versus collection date of samples.

Well	05/15/2018 (Pre-Injection)	06/28/2018 (Week 1)	07/06/2018 (Week 2)	07/12/2018 (Week 3)	07/19/2018 (Month 1)	08/23/2018 (Month 2)	09/20/2018 (Month 3)	12/14/2018 (Month 6)	03/18/2019 (Month 9)
I-1	1.21	0.04	0.08	0.08	0.1	0.10	0.14	2.45	0.05
I-2	2.61	0.06	0.06	0.13	0.12	0.57	0.14	0.12	0.17
I-3	0.93	0.08	0.13	0.1	0.08	0.08	0.16	0.08	0.09
I-4	0.54	0.03	0.16	0.17	0.12	4.01	0.15	0.1	0.05
I-5	0.07	0.04	0.07	0.08	0.13	0.05	0.14	0.08	0.08
I-6	0.05	0.17	0.06	0.12	0.07	0.05	0.11	0.08	0.07
I-7	0.09	0.06	0.07	0.07	0.07	0.08	0.15	0.1	0.07
I-8	0.5	0.83	0.68	0.83	0.26	0.07	0.14	0.09	0
I-9	0.01	0.1	0.08	0.08	0.38	0.07	0.14	0.1	0.06
I-10	0.15	0.93	0.61	0.61	0.22	0.80	0.62	0.19	0.37
I-11	0.08	0.1	0.13	0.07	0.14	0.05	0.13	0.05	0.06
LH-2	0.08	0.08	0.12	0.1	0.12	0.10	0.16	0.08	0.08
LH-4	0.15	0.08	0.13	0.1	0.09	0.08	0.15	0.07	0.08
LH-5	0.13	0.28	0.3	0.2	0.19	0.09	0.12	0.1	0.08
LH-7	0.08	0.1	0.27	0.17	0.18	0.13	0.14	0.05	0.1
LH-10	0.05	0.06	0.09	0.08	0.11	0.07	0.1	0.07	0.08
M-1	0.06	0.06	0.13	0.1	0.15	0.09	0.17	0.09	0.08
M-3	0.03	0.07	0.08	0.14	0.09	0.08	0.13	0.06	0.1
RA-9	1.89	0.06	0.12	0.12	0.15	0.10	0.12	0.08	0.06
RA-10	0.19	0.06	0.18	0.11	0.07	0.06	0.15	0.09	0.06
RA-11	0.09	0.57	0.37	1.04	0.57	0.11	1.57	0.11	0.05
RA-12	1.7	2.83	0.12	2.52	1.79	0.17	0.15	0.07	0.05
RA-13	1.12	0.27	0.11	0.12	0.18	0.07	0.13	0.14	0.05
RA-14	0.08	2.76	2.09	1.99	0.18	0.20	0.45	1.63	6.11

Table S4. Dissolved arsenic (mg/L) versus collection date of filtered groundwater samples.

Well	05/15/2018 (Pre-Injection)	06/28/2018 (Week 1)	07/06/2018 (Week 2)	07/12/2018 (Week 3)	07/19/2018 (Month 1)	08/23/2018 (Month 2)	09/20/2018 (Month 3)	12/14/2018 (Month 6)	03/18/2019 (Month 9)
I-1	0.412	0.183	0.0484	0.123	0.176	0.113	0.18	0.0966	0.233
I-2	0.649	0.803	0.174	0.17	0.191	0.518	0.728	1.02	0.934
I-3	1.81	0.0978	0.107	0.102	0.444	0.0474	0.173	0.233	0.513
I-4	0.4	0.15	0.0126	0.0283	0.0543	0.0303	0.0369	0.0405	0.0825
I-5	0.111	0.03	0.068	0.0387	0.0606	0.159	0.094	0.13	0.171
I-6	0.0732	0.0106	0.00171	0.00369	0.00753	0.0403	0.048	0.495	0.0704
I-7	0.0932	0.368	0.113	0.173	0.2	0.103	0.0977	0.102	0.124
I-8	0.0168	0.0123	0.00633	0.00876	0.0154	0.00806	0.00698	0.00808	0.0204
I-9	0.00361	0.00413	0.00661	0.00726	0.00428	0.0184	0.0221	0.0393	0.0418
I-10	0.00352	0.00357	0.0029	0.00358	0.00301	0.00386	0.00311	0.00379	0.00756
I-11	0.147	0.0277	0.015	0.0236	0.0105	0.0175	0.0167	0.0219	0.0835
LH-2	0.57	0.506	0.473	0.569	0.627	0.032	0.0279	0.0351	0.0122
LH-4	0.00116	0.00221	0.00206	0.00193	0.00116	0.00137	0.0046	0.00046	0.00102
LH-5	0.318	1.49	1.06	0.787	0.823	0.781	0.86	0.339	0.439
LH-7	0.00388	0.00363	0.00512	0.0036	0.0058	0.00259	0.00108	0.00298	0.00421
LH-10	0.0132	0.0198	0.0124	0.00566	0.00384	0.00521	0.00415	0.00307	0.00303
M-1	0.0835	0.018	0.0139	0.0188	0.023	0.0177	0.0176	0.0157	0.0128
M-3	0.141	0.151	0.193	0.197	0.285	0.0643	0.0487	0.17	0.0581
RA-9	0.768	0.448	0.618	0.444	0.722	0.254	0.4	0.0785	0.101
RA-10	0.210	4.08	8.65	2.15	7.12	4.84	1.71	0.872	0.538
RA-11	0.00733	0.013	0.0291	0.0281	0.0244	0.0134	0.0129	0.0164	0.0158
RA-12	0.0985	0.0671	0.101	0.055	0.0689	0.2412	0.232	0.155	0.305
RA-13	0.00144	0.0031	0.0046	0.00499	0.00357	0.00491	0.00842	0.0346	0.0256
RA-14	0.00188	0.00181	0.00198	0.00219	0.00265	0.00172	0.00204	0.00135	0.00239

Table S5. Iron (Fe) (mg/L) versus collection date of groundwater samples.

Well	05/15/2018 (Pre-Injection)	06/28/2018 (Week 1)	07/06/2018 (Week 2)	07/12/2018 (Week 3)	07/19/2018 (Month 1)	08/23/2018 (Month 2)	09/20/2018 (Month 3)	12/14/2018 (Month 6)	03/18/2019 (Month 9)
I-1	1.25	78.4	15.1	5.85	2.71	3.21	1.6	0.563	1.41
I-2	1.12	44.9	15.7	5.61	3.4	3.55	2.35	5.97	6.43
I-3	0.681	41.5	18.3	8.33	4.64	27.6	4.99	4.74	12.3
I-4	2.07	108	25.6	15.6	13.5	8.02	9.61	12.9	18.4
I-5	1.08	173	20.7	24.7	49.9	10.9	9.01	4.33	4.59
I-6	1.53	75.7	30.3	11.2	12.5	7.19	3.31	3.47	3.48
I-7	0.221	17.6	1.96	1.25	1.28	1.13	1.25	1.95	0.891
I-8	1	2.7	1.76	1.76	1.36	7.55	7.51	21.3	26.6
I-9	0.789	0.612	0.943	0.858	0.666	2.2	2.4	5.9	10.4
I-10	0.892	0.675	0.942	0.595	0.764	1.09	0.681	1.34	3.04
I-11	3.78	34.2	14.3	17.6	39.7	6.75	6.58	3.78	3.35
LH-2	0.822	1.31	1.06	0.935	0.958	16.7	8.26	2	3.48
LH-4	0.494	0.842	0.504	0.552	0.73	0.854	1.13	0.495	0.914
LH-5	0.363	0.402	0.349	0.317	0.327	2.24	9.316	4.63	27.3
LH-7	1.95	2.02	1.81	1.74	1.83	1.75	1.17	1.34	0.871
LH-10	2.15	2.28	2.21	3.3	5.53	5.68	2.07	1.67	1.06
M-1	2.02	96.9	58.4	36.5	32.1	29.1	12.4	3.79	2.63
M-3	1.81	1.04	1.35	0.614	1.81	0.763	0.671	1.83	2.07
RA-9	0.308	0.611	0.755	0.863	1.14	6.83	3.21	7.33	8.5
RA-10	0.13	23.7	73.2	1.77	24.2	24.4	13.5	3.57	5.87
RA-11	0.348	0.105	0.298	0.114	0.408	0.479	0.352	1.55	3.31
RA-12	0.778	0.33	0.256	0.0905	0.17	0.903	9.15	13.1	14.9
RA-13	0.337	0.38	0.344	0.31	0.345	0.793	0.877	4.3	4.69
RA-14	0.663	0.499	0.229	0.706	0.425	0.119	0.232	0.3	0.534

Table S6. Sulfate (SO_4) (mg/L) versus collection date of groundwater samples.

Well	05/15/2018 (Pre-Injection)	06/28/2018 (Week 1)	07/06/2018 (Week 2)	07/12/2018 (Week 3)	07/19/2018 (Month 1)	08/23/2018 (Month 2)	09/20/2018 (Month 3)	12/14/2018 (Month 6)	03/18/2019 (Month 9)
I-1	17.9	98.7	11.6	12.8	16.2	111	78.5	33.9	13.4
I-2	21.4	85.8	126	125	114	110	61.4	8.94	1.4
I-3	21.5	127	83.5	78.8	86.7	86.8	21.4	1.4	7.83
I-4	19.7	153	14	30.6	13.2	144	23.8	1.4	8.28
I-5	16.5	275	66	40.7	50.9	45.5	29	23	12.3
I-6	17.4	134	33.9	14.2	9.97	63.3	24.5	35.9	23.4
I-7	21.9	30.4	18.6	21.6	17.5	6.7	17.1	9.2	5.32
I-8	32.7	40.7	44.5	33.2	43.3	43.5	12.7	1.4	5.83
I-9	8.62	13.2	12.9	16.8	18.4	17.5	1.4	1.4	2.79
I-10	20	10.9	8.32	6.35	8.62	6.43	5.25	7.9	4.54
I-11	30.4	61.9	34.2	38.1	67.3	27.4	31.9	30.2	18.3
LH-2	29.6	29.6	32.9	34.4	30.2	56.9	3.54	1.4	1.4
LH-4	5.01	4.93	4.01	4.49	3.93	3.55	3.8	1.4	4.08
LH-5	7.61	16.3	16.1	15.2	13.9	21.3	187	60.5	8.47
LH-7	20.4	24.3	30.7	33.1	33.6	51.8	27.3	1.4	1.4
LH-10	17.4	25.9	31.4	33.1	40.1	38.1	11.6	15.1	11.1
M-1	23.8	209	105	42.1	30.8	22.4	1.51	10.1	13.9
M-3	14.5	19.3	19.6	19	21.4	11	24.3	1.4	8.95
RA-9	12.6	33.7	32.1	39.8	39.5	55.9	24.8	10.4	19.1
RA-10	18.6	109	140	26.2	15.1	7	21.1	5.91	10.8
RA-11	20.8	18.1	21.1	21.1	24.3	5.81	4.06	4.27	1.4
RA-12	13.4	30.2	27.4	29.1	147	55.1	78	1.4	5.12
RA-13	14.4	51.1	52.2	13	47.9	21.2	9.48	1.4	1.4
RA-14	6.38	11.5	4.34	3.6	6.5	9.73	16.4	7.01	2.02

Table S7. Saturation indices of pyrite, arsenian pyrite, orpiment, and realgar were calculated along the I-1 to RA-9 flow transect using the following formulas.

$Saturation\ Index = \log[reaction\ quotient\ (Q)/equilibrium\ constant\ (K)]$	(1)
$logQ_{pyrite} = \log(Fe) + 2\log(SO_4) - 16pH - 236.6Eh$	(2)
$logK_{pyrite} = -83.6063\ (at\ 25°C)$	(3)
$logQ_{arsenianpyrite} = \log(Fe) + 1.995\log(SO_4) - 16pH - 236.6Eh + 0.01\log(As)$	(4)
$logK_{arsenianpyrite} = -101.2263\ (at\ 25°C)$	(5)
$logQ_{orpiment} = 3\log(SO_4) - 32pH - 405.6Eh + 2\log(As)$	(6)
$logK_{orpiment} = -180.4364\ (at\ 25°C)$	(7)
$logQ_{realgar} = \log(SO_4) - 12pH - 152.1Eh + \log(As)$	(8)
$logK_{realgar} = -69.889\ (at\ 25°C)$	(9)

Figure S1. The sand bag installed prior to injection (left panel) and black precipitates observed on the sand bag 5 months after the injection (right panel). XRD and XRF analysis confirmed the black precipitate contained arsenian pyrite. .

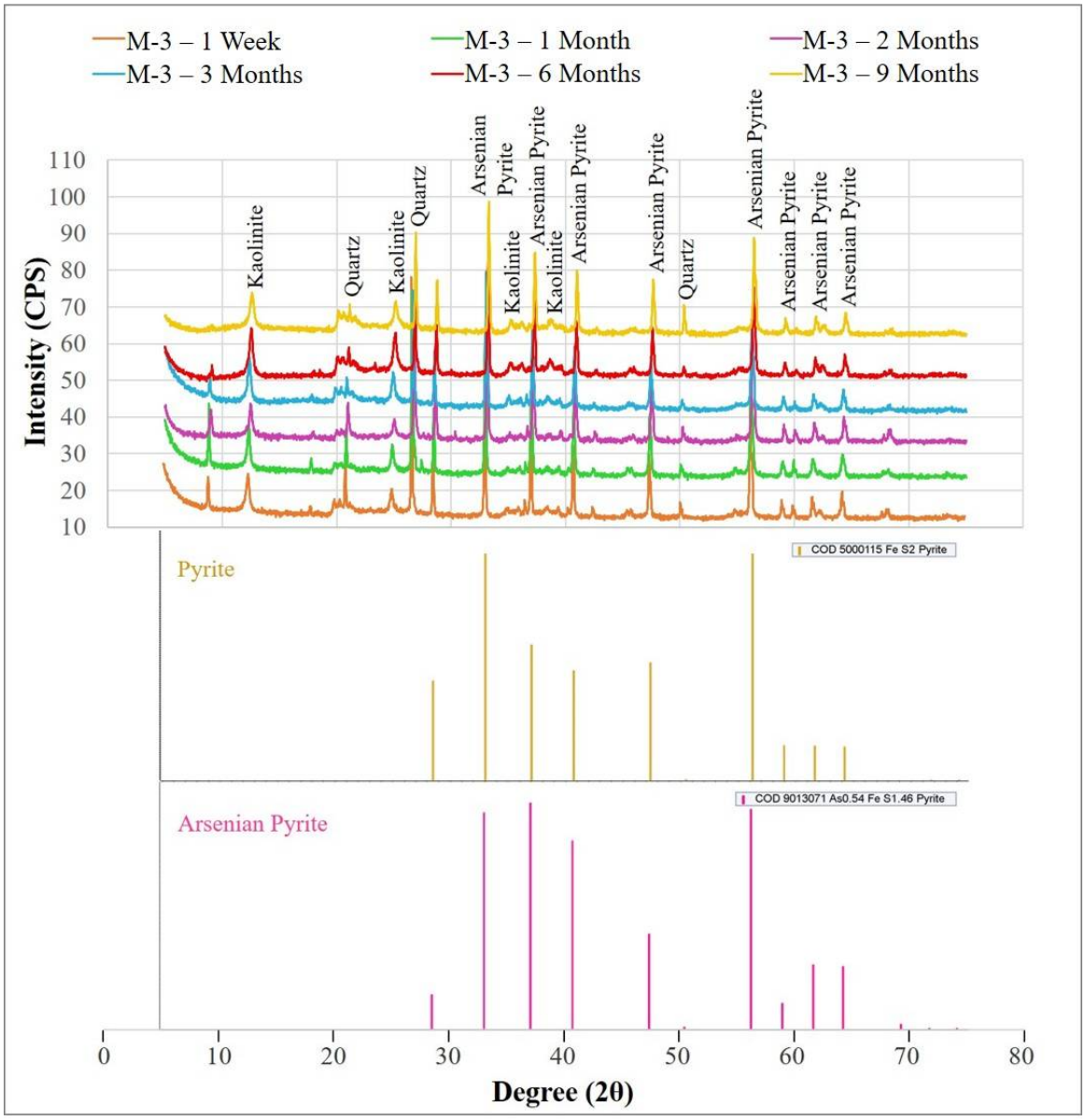

Figure S2. Peak positions of arsenian pyrite and pyrite, as confirmed from the COD database spectra, in the precipitated biominerals from monitoring well M-3. Distinct arsenian pyrite peaks are seen at the 2θ values of 28.5°, 33.0°, 37.0°, 40.7°, 47.3°, and 56.2°.

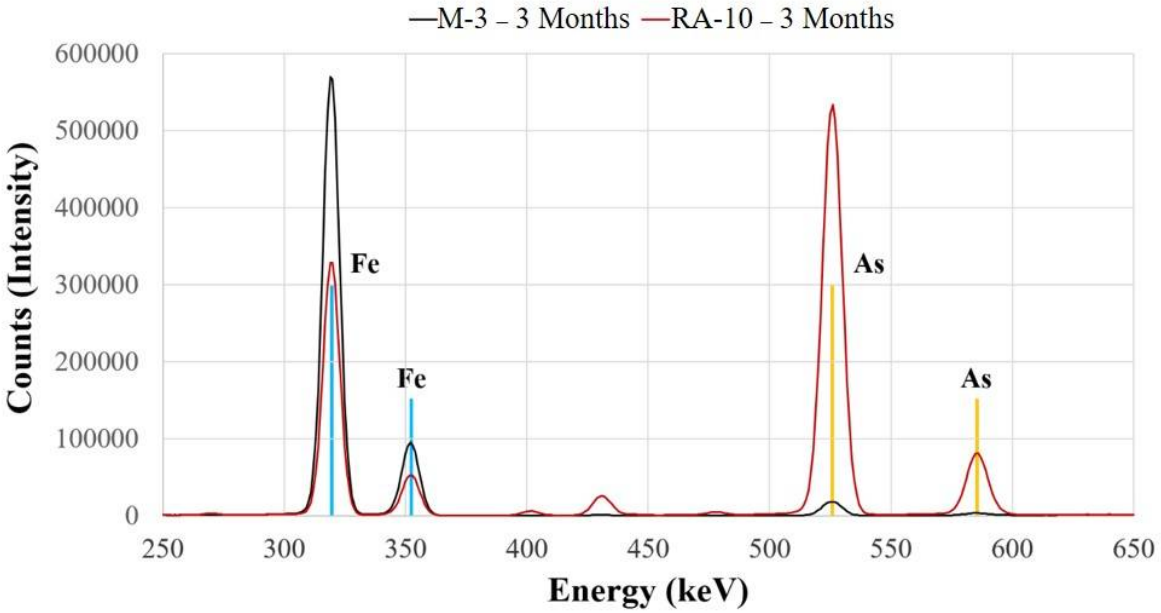

Figure S3. XRF spectra of biominerals from monitoring wells M-3 and RA-10 three months after the injection. The spectra from M-3 are representative of the Fe-rich spectral pattern with low-intensity arsenic peaks from 60% of the samples. The spectra from RA-10 represent the As- and Fe-rich spectral pattern from approximately 40% of the samples. The relative counts of arsenic increased throughout the following months, with a majority of the samples (52%) exhibiting medium-large As peaks after nine months. As a general note, sulfur cannot be detected with the XRF red filter, which was used to detect heavy elements above calcium like arsenic.

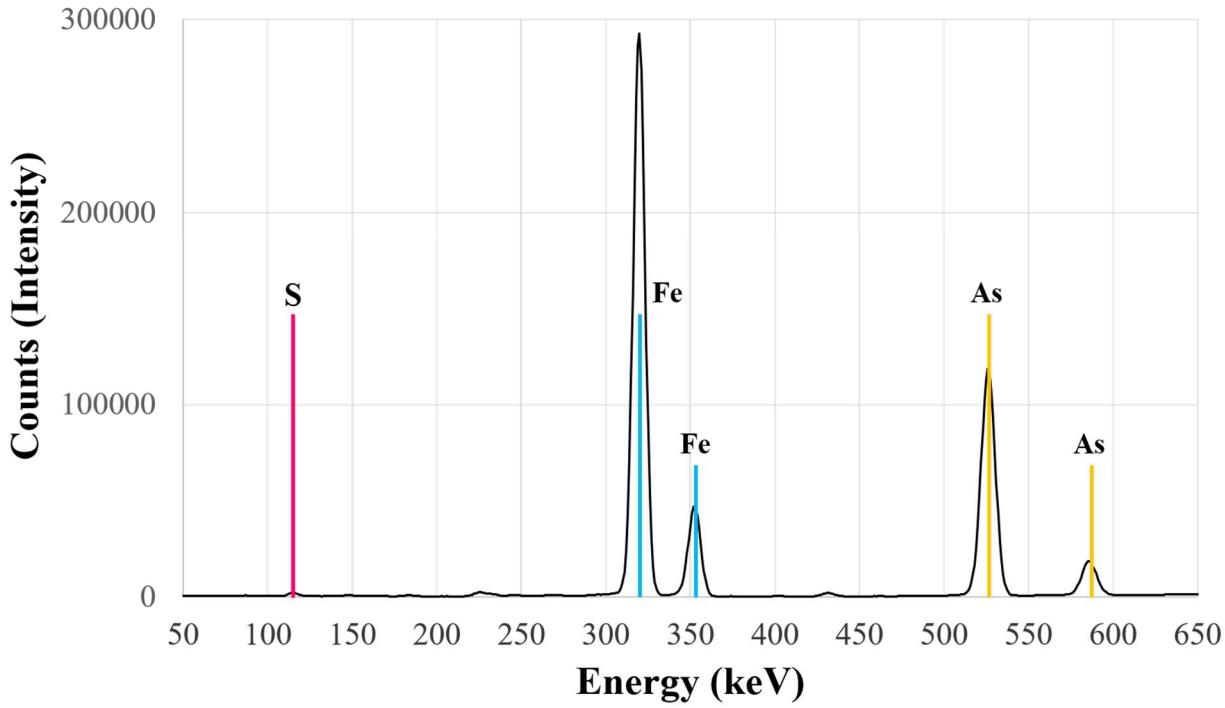

Figure S4. XRF spectra of biominerals from monitoring well RA-9 after one month of biostimulation, with the sulfur, iron, and arsenic peaks displayed. The XRF red filter, necessary for measuring arsenic, is designed mainly to detect heavy elements above calcium, explaining the low levels of sulfur in the XRF analysis of arsenian pyrite. .

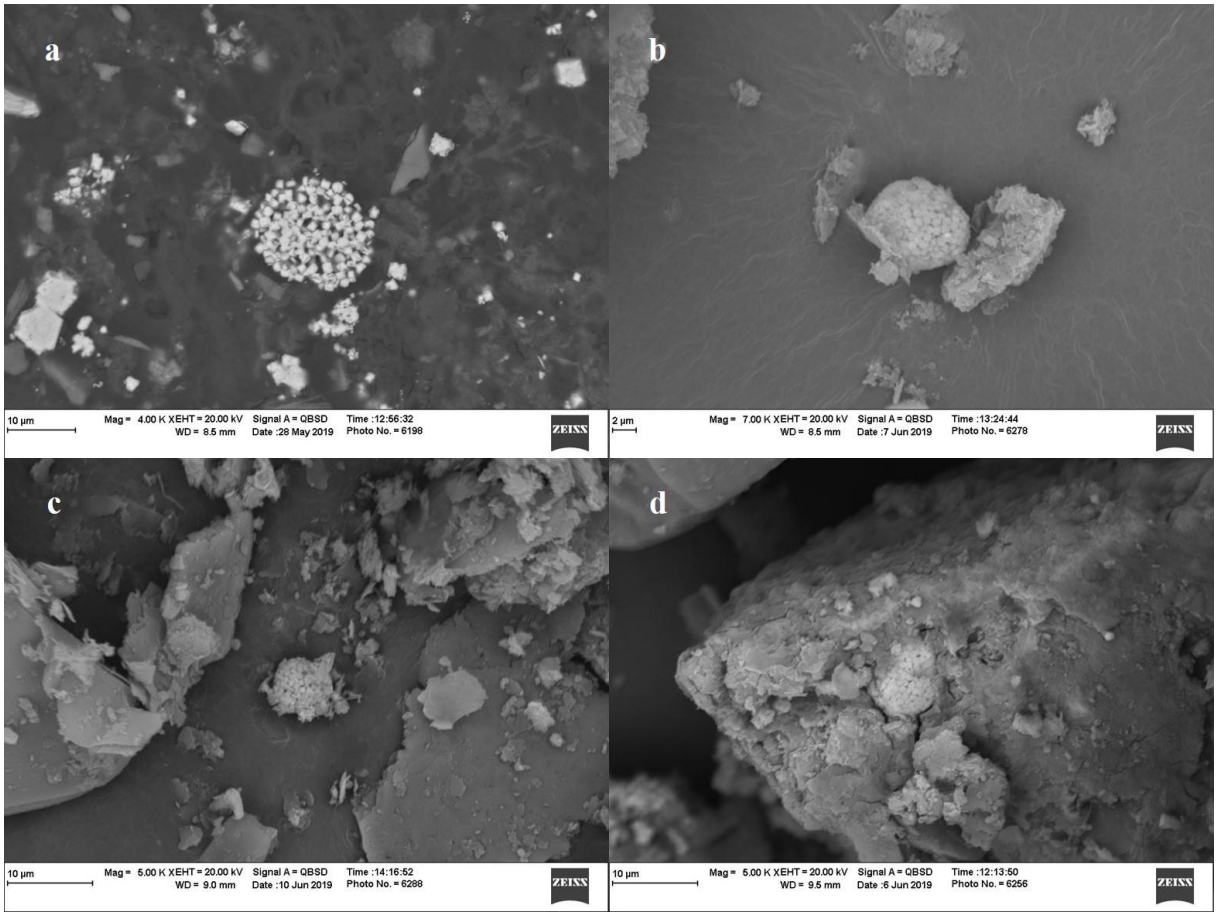

Figure S5. SEM backscatter images of arsenian pyrite from I-2 over the experiment duration. (**a**) A 15-µm arsenian pyrite framboid at 4,000x magnification two weeks post-injection. The framboid appears unconsolidated, with the nanocrystalline pyrite loosely held together. (**b**) An 8-µm arsenian pyrite framboid at 7,000x magnification three months post-injection. The framboid appears consolidated. (**c**) An 8-µm arsenian pyrite framboid at 5,000x magnification six months post-injection. (**d**) A 6-µm arsenian pyrite framboid at 5,000x magnification nine months post-injection.

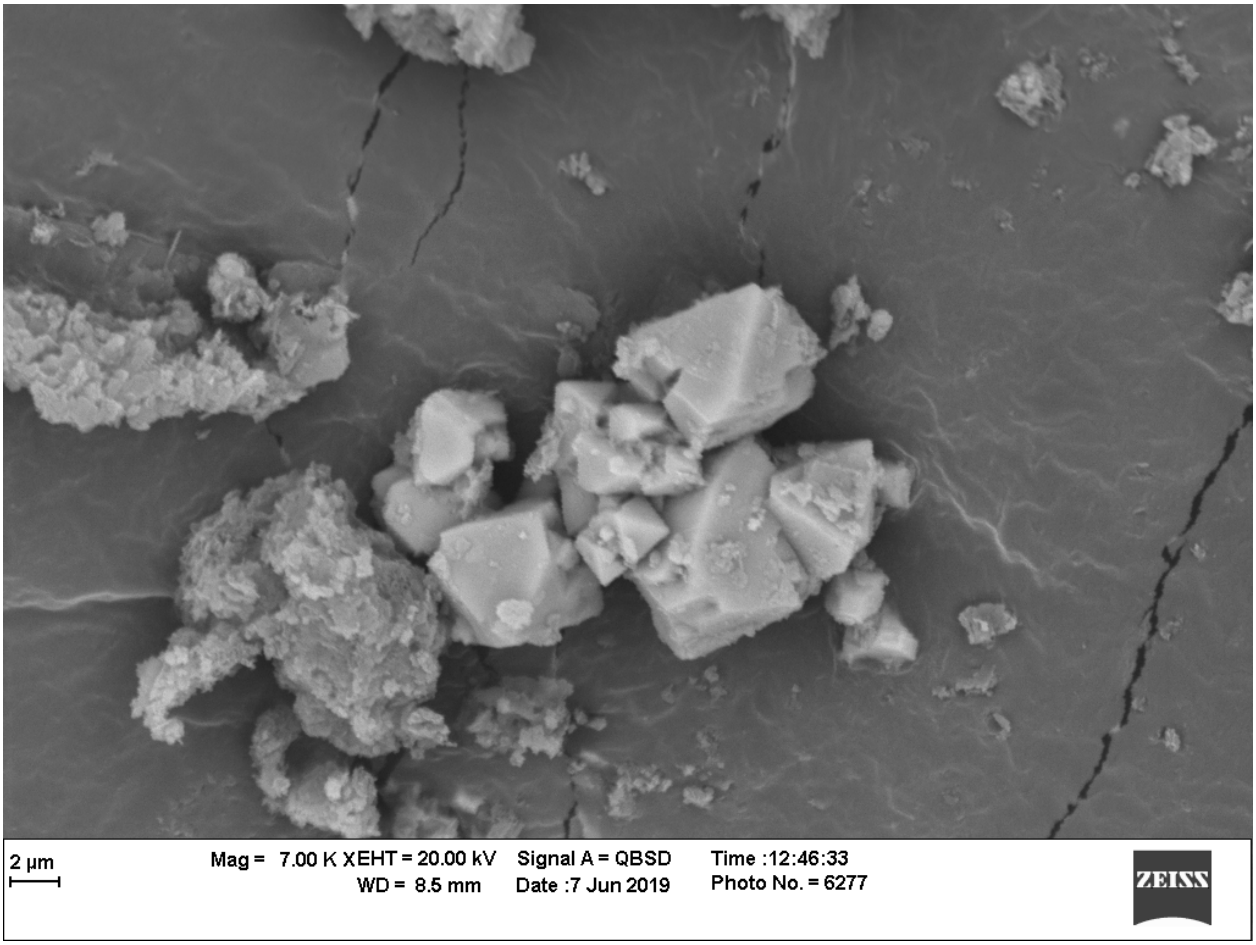

Figure S6. SEM backscatter image of 8-µm euhedral pyrite crystals at 7,000x magnification from injection well I-2 three months post-injection. SEM chemical analysis confirmed the mineral as pyrite and not arsenian pyrite.

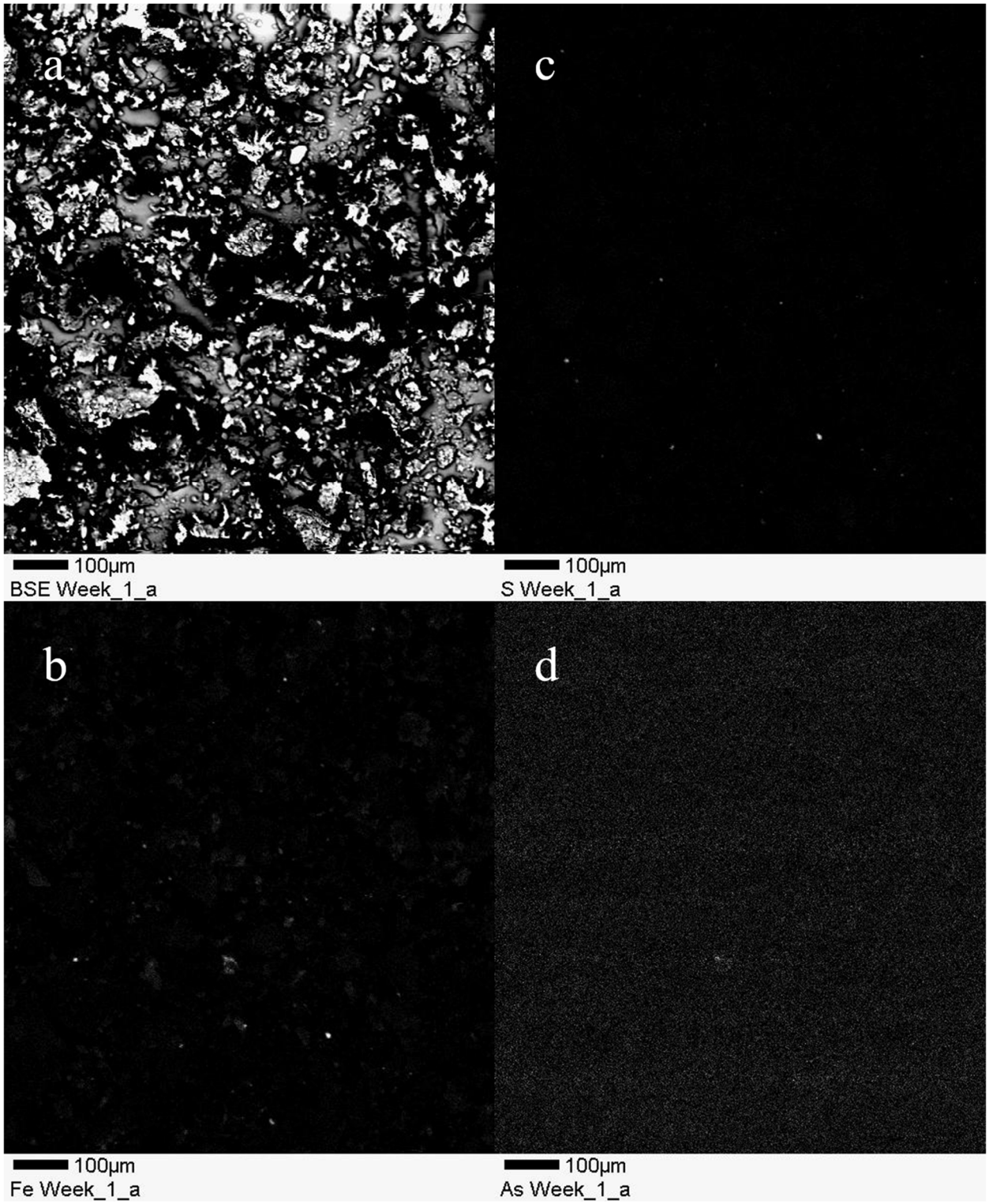

Figure S7. EMP backscatter images of solids and precipitated biominerals from injection well I-2 one week post-injection. (**a**) Backscatter image of the gold-covered stub (1,000 µm x 900 µm area). (**b**) Backscatter mapping of iron in the grains. (**c**) S mapping in the grains. (**d**) As mapping in the grains. 15 grains in the thin sections of each sample were analyzed for the EMP mineralogical analysis (considering that some samples during the first week of the experiment had little arsenian pyrite formation), and 25 thin sections across the experiment duration were analyzed in the SEM imaging analysis. Overall, low concentrations of iron, sulfur, and arsenic are present.

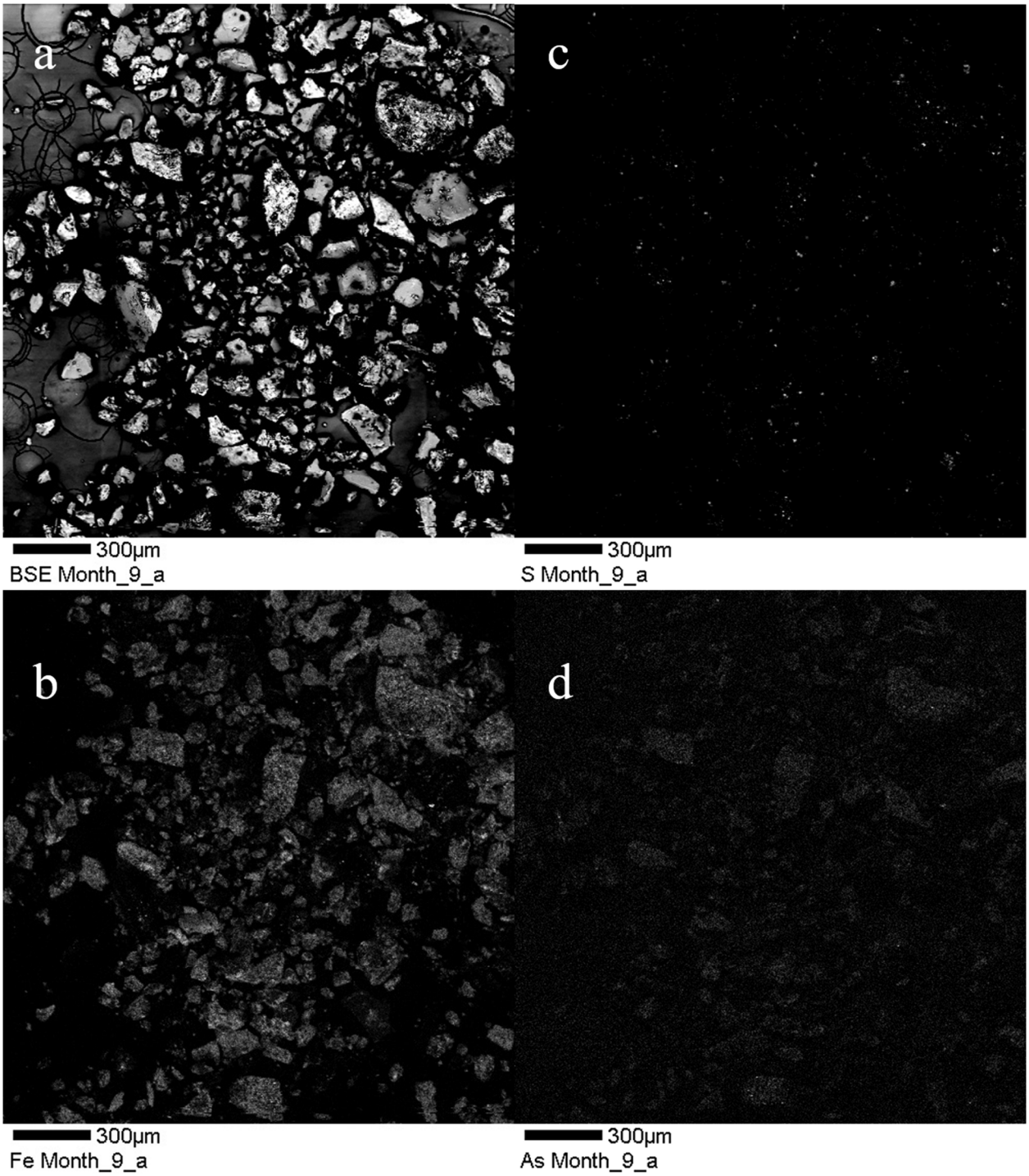

Figure S8. EMP backscatter images of solids and precipitated biominerals from injection well I-2 nine months post-injection. (**a**) Backscatter image of the gold-covered stub (2,400 µm x 1,950 µm area). (**b**) Backscatter iron mapping in the grains. (**c**) S mapping in the grains. (**d**) As mapping in the grains. Overall, these grains and biominerals have higher concentrations of iron, sulfur, and arsenic compared to one week post-biostimulation. This increase in iron, sulfur, and arsenic indicates that over the course of bioremediation, pyrite increasingly precipitated and sequestered arsenic. These images also indicate the heterogeneity of arsenian pyrite, with arsenic present in the biominerals in certain spots and not evenly distributed throughout the grains.