

I

Supporting information to Chapter 4 Dissolved phosphate decreases the stability of amorphous ferric arsenate and nano-crystalline yukonite.

SUPPLEMENTARY MATERIAL

Dissolved phosphate decreases the stability of amorphous ferric arsenate and nano-crystalline yukonite

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21 pages, 11 figures, 11 tables

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1 Sample characterization

Table S1. Overview of the samples used for the batch experiment.

Sample	3 hours	8 hours	24 hours	3 days	9 days	30 days	90 days	1 year
AFA	L	L	L	L	L	L + S	L + S	L + S
Yuk	L	L	L	L	L	L + S	L + S	L + S
MW	L	L	L	L	L	L	L	L + S
Soil	L	L	L	L	L	L	L	L + S

L = liquid solution, S = solid phase

Table S2. Values of Eh, electrical conductivity (E.C.), and bicarbonate in the solutions of the experiment after one year. All RSD values were below 10 % for Eh with the exception of 0.5 MW (RSD = 23.5 %) and for bicarbonate below 3 % with the exception of the 0 Soil (RSD = 20 %).

	Eh mV	E.C. μS/cm	E.C. 1 st	E.C. 2 nd	HCO ₃ ⁻ mg/l
0 AFA	738	648	140		
0.5 AFA	732	651	148		
50 AFA	590	3580	312	16	
0 Yuk	386	292	53		112
0.5 Yuk	378	300	42		117
50 Yuk	485	3620	185	39	188
0 MW	761	430	87		
0.5 MW	647	375	42		
50 MW	572	3450	220	22	
0 Soil	450	39	6		8
0.5 Soil	469	83	8		12
50 Soil	494	3550	228	37	103

Note. Additional two columns listed for E.C. represent values measured during the washing steps of the sample with deionized water (1st = first washing procedure, 2nd = second washing procedure).

Table S3. Reference materials digested in mineral acids expressed in mg/kg (average \pm SD, n = 3) and measured by ICP-OES.

Element	NIST 2710a Montana I Soil Measured		Certified	
As	1540	\pm 9	1540	\pm 100
Ba	626	\pm 83	792	\pm 36
Ca	7450	\pm 347	9640	\pm 450
Cd	12.1	\pm 0.7	12.3	\pm 0.3
Cr	20.6	\pm 0.8	23	\pm 6
Cu	3110	\pm 56	3420	\pm 50
Fe	36900	\pm 1850	43200	\pm 800
K	16600	\pm 891	21700	\pm 1300
Mn	1980	\pm 32	2140	\pm 60
Na	7800	\pm 683	8940	\pm 190
Ni	5.77	\pm 0.38	8	\pm 1
P	960	\pm 36	1050	\pm 40
Pb	5150	\pm 50	5520	\pm 30
Sb	43.9	\pm 1.7	52.5	\pm 1.6
Ti	3080	\pm 20	3110	\pm 70
V	80.0	\pm 0.9	82	\pm 9
Zn	4080	\pm 20	4180	\pm 150

Table S4. Total digestions in mineral acids expressed in mg/kg. All RSD were below 15 % (n = 2); n.d. = not determined.

Sample	As	Ba	Ca	Cd	Cr	Cu	Fe	K	Mn	Na	Ni	P	Pb	S	Sb	Ti	V	Zn
AFA	241000	n.d.	n.d.	n.d.	n.d.	n.d.	243000	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	18700	n.d.	n.d.	n.d.	n.d.
Yuk	261000	n.d.	111000	n.d.	n.d.	n.d.	177000	n.d.	n.d.	2510	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MW	44900	259	474	2.23	88.0	235	37600	20000	122	1380	10.7	1020	1080	n.d.	10.7	4760	106	120
Soil	13600	261	4220	2.20	19.1	41	27800	24100	1180	1750	5.2	988	90	n.d.	21.4	2270	148	194

Table S5. Sequential extraction of composite materials expressed in mg/kg \pm SD (% of the total elemental concentration of the relevant sample).

Sample	Sulfate extraction				Oxalate extraction			
	As	Ca	Fe	P	As	Fe	P	Oxalate Fe/As
MW	67.6 \pm 0.6 (0.2)	106 \pm 1 (22)	175 \pm 2 (0)	< 0.25	26500 \pm 200 (59)	30800 \pm 200 (82)	469 \pm 11 (46)	1.56
0 MW	165 \pm 8 (0.5)	21.5 \pm 1 (2.5)	90.5 \pm 3.7 (0.2)	< 0.25	25900 \pm 100 (73)	32700 \pm 100 (68)	436 \pm 6 (41)	1.69
0.5 MW	138 \pm 2 (0.3)	38.4 \pm 5.2 (5.2)	293 \pm 210 (0.6)	0.85 \pm 0.60 (0.05)	25100 \pm 100 (63)	31600 \pm 400 (69)	1050 \pm 10 (66)	1.69
50 MW*	50.4 (0.1)	42.5 (4.3)	13.1 (0.0)	197 (3)	17600 (45)	29141 (61)	5860 (91)	2.22
Soil	47.4 \pm 2.8 (0.3)	1260 \pm 60 (30)	0.68 \pm 0.05 (0.00)	16.3 \pm 0.6 (1.7)	12800 \pm 600 (94)	15300 \pm 900 (55)	627 \pm 42 (63)	1.61
0 Soil	27.9 \pm 1.9 (0.2)	1050 \pm 20 (20)	0.17 \pm 0.00 (0.00)	9.1 \pm 1.2 (0.9)	11800 \pm 100 (94)	15400 \pm 100 (46)	555 \pm 1 (57)	1.76
0.5 Soil*	26.1 (0.2)	1060 (20)	0.12 (0.00)	22.6 (1.9)	11400 (90)	15400 (45)	782 (65)	1.81
50 Soil	9.29 \pm 0.16 (0.08)	484 \pm 6 (9.4)	0.36 \pm 0.11 (0.00)	210 \pm 2 (6.6)	11300 \pm 100 (97)	17100 \pm 250 (48)	2530 \pm 10 (80)	2.03

Note. The Ca extracted by oxalate extraction was always below the limit of detection (< 0.01 mg/l). The number stated before the samples represent the concentration of phosphate used for one year leaching experiment: 0 = 0 M, 0.5 = 0.5 mM, 50 = 50 mM.

**sample misses SD due to an error in a sampling

Table S6. Total digestion of solid phases exposed to different concentrations of phosphate (0 = 0 mM, 0.5 = 0.5 mM, 50 = 50 mM). All analyses were performed in duplicates, with the exception of synthetic phases sampled after one and three months.

Sample	Time months	As mg/kg	Ca mg/kg	Fe mg/kg	P mg/kg	S mg/kg
MW	0	44900 ± 500	474 ± 49	37600 ± 1200	1020 ± 12	n.d.
0 MW	12	35700 ± 1100	860 ± 100	48100 ± 100	1060 ± 50	n.d.
0.5 MW	12	39800 ± 100	740 ± 10	46100 ± 200	1600 ± 30	n.d.
50 MW*	12	39600	1000	47800	6470	n.d.
Soil	0	13600 ± 200	4220 ± 290	27800 ± 2200	988 ± 34	n.d.
0 Soil	12	12500 ± 700	5270 ± 180	33400 ± 700	971 ± 46	n.d.
0.5 Soil*	12	12640	5280	34000	1200	n.d.
50 Soil	12	11700 ± 100	5140 ± 140	35500 ± 200	3180 ± 50	n.d.
AFA	0	241000 ± 1000	n.d.	243000 ± 1000	< 200	18700 ± 100
0 AFA	1	253000	n.d.	260000	< 200	7150
0 AFA	3	248000	n.d.	255000	< 200	5410
0 AFA	12	243000 ± 1000	n.d.	251000 ± 2000	< 200	6160 ± 110
0.5 AFA	1	241000	n.d.	250000	7450	4410
0.5 AFA	3	240000	n.d.	248000	7930	3160
0.5 AFA	12	241000 ± 5000	n.d.	250000 ± 5000	7720 ± 160	4330 ± 30
50 AFA	1	167000	n.d.	243000	58400	598
50 AFA	3	145000	n.d.	250000	74600	326
50 AFA	12	128000 ± 500	n.d.	248000 ± 1000	82800 ± 300	246 ± 31
Yuk	0	261000 ± 2000	111000 ± 2000	177000 ± 3000	< 200	n.d.
0 Yuk	1	245000	103000	190000	< 200	n.d.
0 Yuk	3	246000	99900	197000	< 200	n.d.
0 Yuk	12	218000 ± 20000	87500 ± 8400	177000 ± 17000	< 200	n.d.
0.5 Yuk	1	236000	101000	187000	7410	n.d.
0.5 Yuk	3	234000	97200	192000	7800	n.d.
0.5 Yuk	12	197000 ± 25000	80800 ± 10000	162000 ± 20000	6490 ± 610	n.d.
50 Yuk	1	120000	93100	178000	81200	n.d.
50 Yuk	3	121000	98100	1910000	88000	n.d.
50 Yuk	12	105000 ± 6000	89900 ± 5400	173000 ± 11000	86200 ± 5800	n.d.

Note. * Standard Deviation is missing due to the absence of a replicate caused by an error in one of the samplings.

Table S7. Values of pH in the solutions during different sampling times of the experiment. All RSD values were below 6 %.

	As release*	pH 3 h	8 h	1 d	3 d	9 d	30 d	90 d	365 d
0 AFA		3.04	2.94	2.88	2.85	2.70	2.77	2.76	2.85
0.5 AFA	20	3.12	2.95	2.87	2.86	2.86	2.80	2.78	2.91
50 AFA	140	3.91	3.81	3.74	3.71	3.74	3.71	3.73	3.86
0 Yuk		8.61	8.58	8.88	8.90	8.93	8.89	8.88	8.81
0.5 Yuk	2	7.38	7.67	8.06	8.25	8.35	8.26	8.27	8.48
50 Yuk	12	5.58	5.64	5.70	5.72	5.73	5.67	5.70	5.86
0 MW		3.92	3.83	3.77	3.76	3.79	3.42	3.28	3.15
0.5 MW	4	3.95	3.89	3.82	3.83	3.80	3.70	3.60	3.37
50 MW	20	4.01	3.95	3.95	3.96	4.02	4.03	4.11	4.33
0 Soil		6.29	5.96	6.00	6.06	5.98	5.86	5.77	5.85
0.5 Soil	2	5.84	5.80	5.87	5.94	5.92	5.86	5.69	5.72
50 Soil	5	4.74	4.80	4.87	4.95	5.02	5.06	5.21	5.53

Note. *Arsenic release factor represents the increase in As release in low- and high-phosphate samples compared to the DI water sample.



Figure S1. Color change in the synthetic phases after exposure to different phosphate solutions for a year (0 = 0 mM, 0.5 = 0.5 mM, 50 = 50 mM).

Table S8. Calculated saturation indices for the synthetic samples after 1 year (and 3 hours for yukonite) using the PHREEQC software.

Time		0 AFA	0.5 AFA	50 AFA		0 Yuk	0.5 Yuk	50 Yuk
3 h	AFA	-1.35	-1.31	-1.39	Yukonite	-7.17	-8.09	-15.91
3 h	Ferrihydrite	-0.47	-1.62	-1.79	Arseniosiderite	4.71	5.67	3.41
3 h	Goethite	2.25	1.09	0.92	CaHPO ₄	-4.16	-0.94	0.13
3 h	Scorodite	1.48	1.52	1.44	Brushite	-4.46	-1.24	-0.16
3 h	Strengite	-0.48	1.28	2.57	Hydroxyapatite	0.19	5.65	2.41
8 h	AFA	-1.02	-1.22	-1.25	Yukonite	-7.96	-9.45	-15.67
8 h	Ferrihydrite	-0.49	-1.80	-1.95	Arseniosiderite	4.39	4.72	3.60
8 h	Goethite	2.22	0.92	0.77	CaHPO ₄	-4.00	-0.87	0.21
8 h	Scorodite	1.81	1.61	1.58	Brushite	-4.29	-1.17	-0.08
8 h	Strengite	-0.46	0.93	2.51	Hydroxyapatite	0.95	7.24	2.98
1 d	AFA	-0.99	-0.91	-0.89	Yukonite	-9.23	-8.71	-15.24
1 d	Ferrihydrite	-0.56	-1.41	-1.80	Arseniosiderite	3.55	4.74	3.82
1 d	Goethite	2.15	1.30	0.91	CaHPO ₄	-3.80	-0.90	0.23
1 d	Scorodite	1.84	1.92	1.97	Brushite	-4.10	-1.19	-0.06
1 d	Strengite	-0.49	0.54	2.70	Hydroxyapatite	2.91	8.89	3.24
3 d	AFA	-0.92	-0.80	-0.79	Yukonite	-8.98	-8.45	-15.16
3 d	Ferrihydrite	-0.59	-1.16	-1.90	Arseniosiderite	3.62	4.70	3.88
3 d	Goethite	2.13	1.55	0.81	CaHPO ₄	-3.72	-1.02	0.18
3 d	Scorodite	1.91	2.03	2.04	Brushite	-4.01	-1.31	-0.12
3 d	Strengite	-0.51	0.00	2.62	Hydroxyapatite	3.86	9.43	3.02
9 d	AFA	-1.01	-0.66	-0.39	Yukonite	-6.91	-8.31	-15.06
9 d	Ferrihydrite	-0.92	-1.03	-1.63	Arseniosiderite	4.71	4.68	3.95
9 d	Goethite	1.79	1.69	1.09	CaHPO ₄	-3.67	-1.20	0.17
9 d	Scorodite	1.82	2.17	2.44	Brushite	-3.96	-1.49	-0.13
9 d	Strengite	-0.75	0.00	2.87	Hydroxyapatite	4.34	9.40	3.02
30 d	AFA	-0.76	-0.57	-0.24	Yukonite	-8.40	-7.98	-15.36
30 d	Ferrihydrite	-0.75	-1.09	-1.73	Arseniosiderite	4.03	5.00	3.87
30 d	Goethite	1.96	1.62	0.99	CaHPO ₄	-3.40	-1.35	0.11
30 d	Scorodite	2.07	2.26	2.59	Brushite	-3.70	-1.64	-0.19
30 d	Strengite	-0.42	-0.10	2.79	Hydroxyapatite	5.25	8.88	2.57
90 d	AFA	-0.68	-0.56	-0.12	Yukonite	-8.21	-7.85	-15.19
90 d	Ferrihydrite	-0.73	-1.13	-1.72	Arseniosiderite	4.17	5.07	3.95
90 d	Goethite	1.98	1.59	0.99	CaHPO ₄	-3.13	-1.49	0.09
90 d	Scorodite	2.15	2.27	2.71	Brushite	-3.42	-1.79	-0.20
90 d	Strengite	-0.62	-0.93	2.75	Hydroxyapatite	6.20	8.62	2.59
365 d	AFA	-0.51	-0.31	0.17	Yukonite	-7.90	-7.72	-12.65
365 d	Ferrihydrite	-0.48	-0.77	-1.41	Arseniosiderite	4.44	4.93	5.19
365 d	Goethite	2.23	1.94	1.30	CaHPO ₄	-2.87	-1.47	0.21
365 d	Scorodite	2.32	2.52	3.00	Brushite	-3.16	-1.77	-0.08
365 d	Strengite	-0.44	0.03	2.95	Hydroxyapatite	6.92	9.69	3.50

2 X-ray diffraction analysis

The mineralogical compositions of the synthetic phases and complex material samples were assessed by X-ray diffraction analysis (XRD) using a PANalytical X'Pert Pro diffractometer (PANalytical, the Netherlands) equipped with a diffracted-beam monochromator and X'Celerator multichannel detector, using Cu K α radiation (40 keV, 30 mA). Samples were scanned from 5° to 80° 2 θ , in steps of 0.01°Th per 350 s. The diffraction data were analyzed using X'Pert HighScore Plus software, version 1.0d.

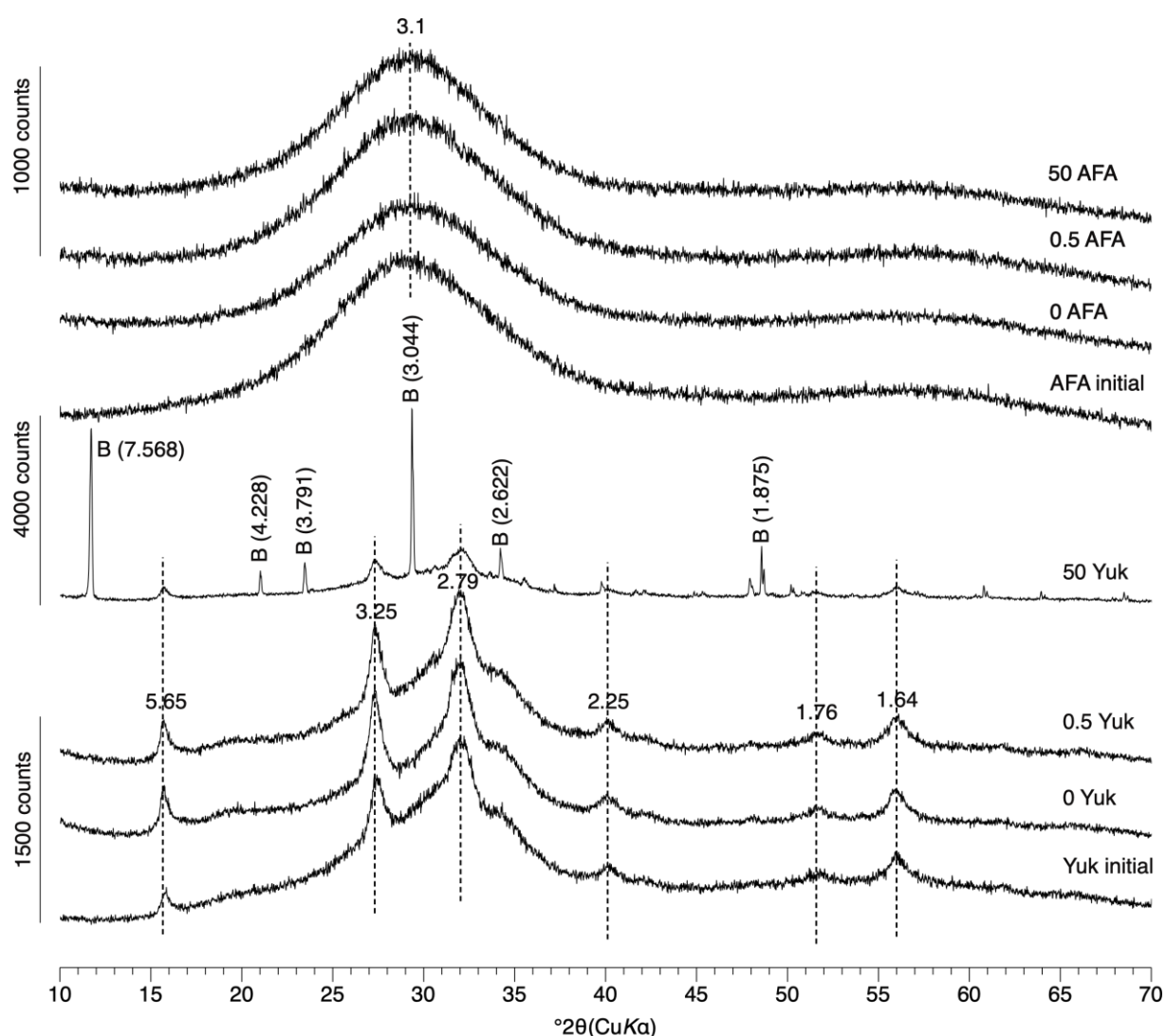


Figure S2. X-ray diffractograms of synthetic phases after a year in different phosphate solutions compared to the initial synthesized phase. The 50 Yuk sample shows a newly precipitated Ca phosphate: brushite (B).

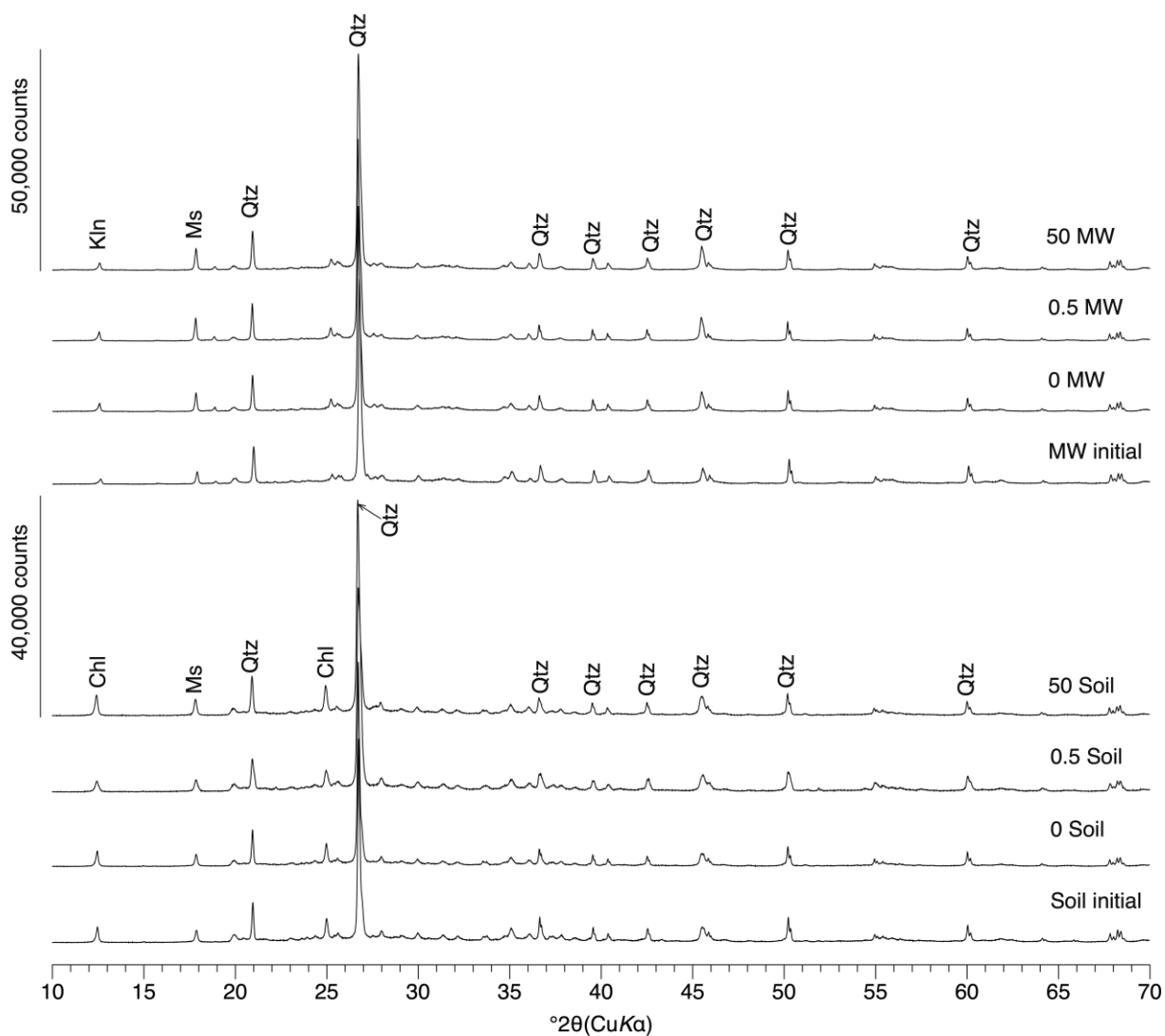


Figure S3. X-ray diffractograms of composite samples after a year in different phosphate solutions compared to the initial synthesized phase. Abbreviations: Chl: chlorite; Kln: kaolinite; Ms: muscovite; Qtz: quartz

3 Raman spectroscopy & FTIR

Raman spectra of synthetic phases were collected with a Renishaw InVia Reflex spectrometer with Leica optical microscope and Bruker Senterra equipped with an Olympus BX-Serie with FlexFocus optical microscope and ANDOR DU420-OE CCD camera with a thermoelectric cooling system. Data were collected across the range of 80–1500 cm^{-1} with a 785 nm laser. The laser was focused using 50 \times objective. Spectra were acquired under 10 mW and 25 mW with an acquisition time of 30 s with 10 repetitions and 10s with 30 scans for AFA and yukonite, respectively.

FTIR spectra at room temperature were recorded on a Thermo Fisher Scientific Nicolet iS50 FTIR spectrometer (4 cm^{-1} resolution, Happ-Genzel apodization) in the 400–4000 cm^{-1} (KBr beamsplitter) and 100–1800 cm^{-1} (Solid substrateTM beamsplitter) regions using ATR (diamond crystal) techniques. Standard ATR correction (software Thermo Nicolet Omnic 9.2) was applied to the recorded spectra. Additionally, the DRIFTS (samples mixed with KBr) techniques were also collected on the Thermo Fisher Scientific Nicolet iS50 FTIR spectrometer (4 cm^{-1} resolution, Happ-Genzel apodization) in the 400–4000 cm^{-1} (KBr beamsplitter).

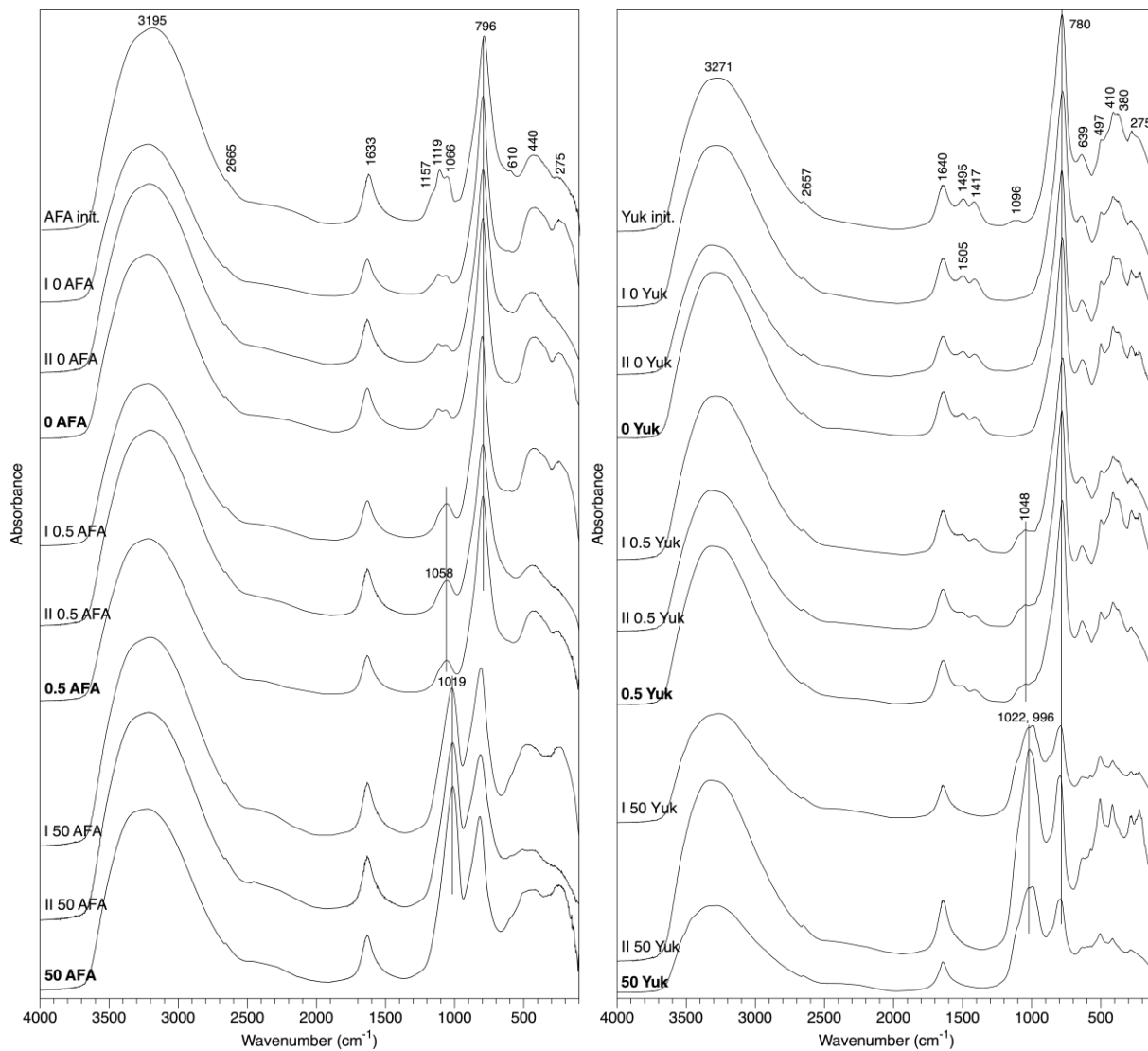


Figure S4. FTIR (ATR) spectra of AFA and yukonite (compiled MID and FAR regions) displayed an increasing concentration of phosphate in the solution from the top. Samples collected after a month and three months are marked with I and II, respectively. Samples collected after one year are marked in **bold**.

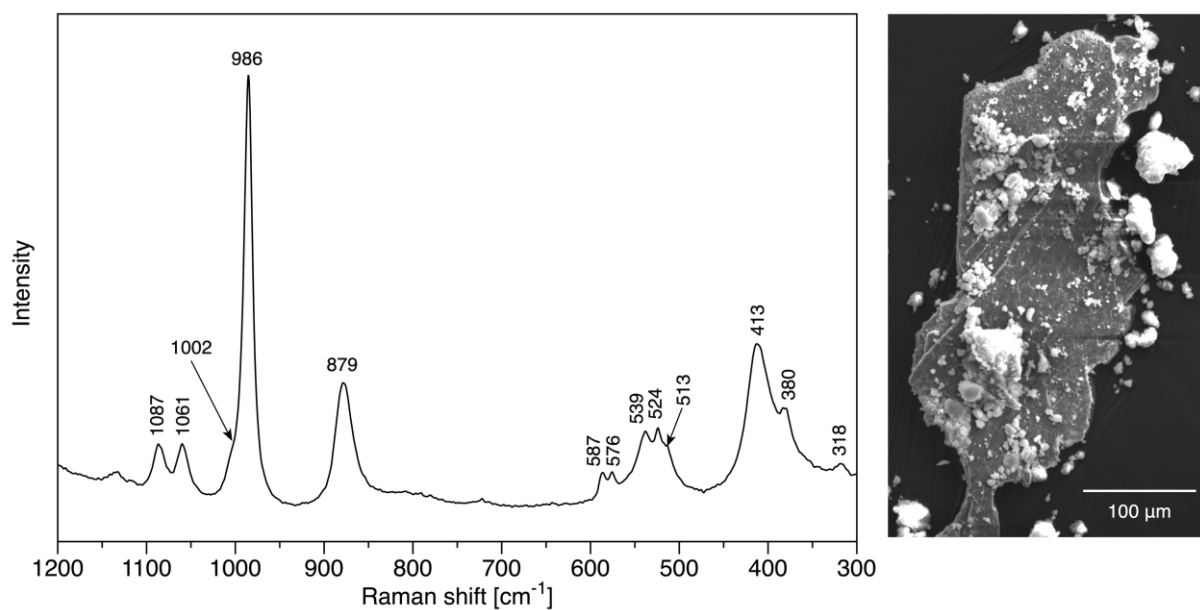


Figure S5. Raman spectra and SEM image of the newly precipitated Ca phosphate: brushite in the high phosphate yukonite.

Table S9. FTIR (ATR) wavenumbers (cm⁻¹) of synthetic phases, samples collected after 1 and 3 months are marked I and II, respectively.

AFA init.	0 AFA	0.5 AFA	50 AFA	I 0 AFA	I 0.5 AFA	I 50 AFA	II 0 AFA	II 0.5 AFA	II 50 AFA	Stretching vibration
275 mb	247 mb 417 mb	260 mb 417 mb	245 mb	240 mb 417 mb	245 mb 430 mb	260 mb		280 mb	275 mb	External modes v ₂ PO ₄ , v ₂ AsO ₄
440 mb			450 mb	00		475 mb	440 mb	440 mb	440 mb	v ₂ PO ₄ , v ₂ SO ₄
610 sh	614 sh			619 sh						v ₄ SO ₄
796 s	796 s	794 s 1058 mb	817 s 1012 s	796 sb	800 sb 1061 mb	807 sb 1019 sb	792 sb	795 sb 1058 sb	815 sb 1015 sb	v ₃ AsO ₄ , v ₁ AsO ₄ v ₃ PO ₄
1065 m	1066 w			1065 w			1066 w			v ₃ SO ₄
1119 m	1119 w			1116 w	1104 sh		1119 w			v ₃ SO ₄
1157 sh	1154 sh			1155 sb			1151 sh			v ₃ SO ₄ , v AsO ₄
1633 mb	1633 mb	1633 mb	1633 mb	1633 mb	1631 mb	1632 mb	1634 mb	1632 mb	1632 mb	δ H ₂ O
2468 wb	2450 wb	2430 wb	2476 wb	2470 wb	2465 wb	2485 wb	2480 wb	2439 wb	2455 wb	v O-H...O
2665 sh	2663 sh	2663 sh	2661 sh	2663 sh	2660 sh	2660 sh	2664 sh	2663 sh	2660 sh	v O-H...O
3195 sb	3226 sb	3212 sb	3225 sb	3219 sb	3216 sb	3201 sb	3207 sb	3195 sb	3208 sb	v O-H...O
Yukonit init.	0 Yuk	0.5 Yuk	50 Yuk	I 0 Yuk	I 0.5 Yuk	I 50 Yuk	II 0 Yuk	II 0.5 Yuk	II 50 Yuk	Stretching vibration
275 mb	277 m	277 m	288 mb	280 mb	280 mb	280 mb	270 mb	275 mb	280 mb	External modes
380 mb	374 mb	374 sh		374 sh	374 sh		371 mb	383 mb		v ₂ AsO ₄
410 m	411 m	413 m	417 m	410 mb	412 mb	417 mb	410 m	412 m	417 m	v ₂ AsO ₄
497 mb	498 m	500 m	505 m 578 m 600 m	500 m	498 mb	504 mb 575 m	498 m	499 m	505 m 574 sh	v ₄ AsO ₄ v ₄ AsO ₄ v ₄ AsO ₄
639 mb	634 mb	634 m	633 m	639 mb	639 mb	634 mb	637 mb	635 mb	629 mb	v ₄ AsO ₄
780 sb	779 sb 854 sh	780 sb 854 sh	792 s 859 sh 996 s 1048 sh 1022 s 1099 sh	777 sb 865 sh	777 sb 851 sh	791 sb 864 sh	784 sb 856 sh	781 sb 951 sh 1000 sh 1045 wb 1086 sh	794 sb 960 sh 1000 sh 1016 sb 1090 sh	v ₃ AsO ₄ , v ₁ AsO ₄ v ₃ AsO ₄ v ₁ PO ₄ v ₃ PO ₄ v ₃ PO ₄
1096 vwb*					1087 sh	1100 sh				v ₃ CO ₃
1417 wb	1417 wb	1417 wb		1417 wb	1417 wb		1416 wb	1417 wb		v ₃ CO ₃
1495 wb	1505 wb	1505 wb		1505 wb	1505 wb		1505 wb	1519 wb		v ₃ CO ₃
1640 mb	1634 mb	1644 mb	1644 mb	1644 mb	1641 mb	1644 mb	1644 mb	1644 mb	1643 mb	δ H ₂ O

2657 sh	2390 vwb	2430 wb	2656 sh	2658 sh	2656 sh	2657 sh	2657 sh	2657 sh	2654 sh	2656 sh	2656 sh	v O-H....O
3271 sb	3288 sb	3316 sb	3273 sb	3291 sb	3289 sb	3270 sb	3316 sb	3327 sb	3322 sb			v O-H....O
												v O-H....O

Note. The CO₃ vibration bands are related to the synthesis under oxic conditions and the SO₄ bands to reagents used for the synthesis of the arsenate phases.
 *band assigned to the ν₃ SO₄

4 Dissolved concentrations of As, P, Ca & Fe

The following figures present dissolved concentrations of As, P, Fe, Ca and pH in solutions leached with different phosphate concentrations (0 = 0 mM, 0.5 = 0.5 mM, 50 = 50 mM) over 1 year. The time scale is logarithmic and contains sampling after 3 hours, 8 hours, and 1, 3, 9, 30, 90, and 365 days.

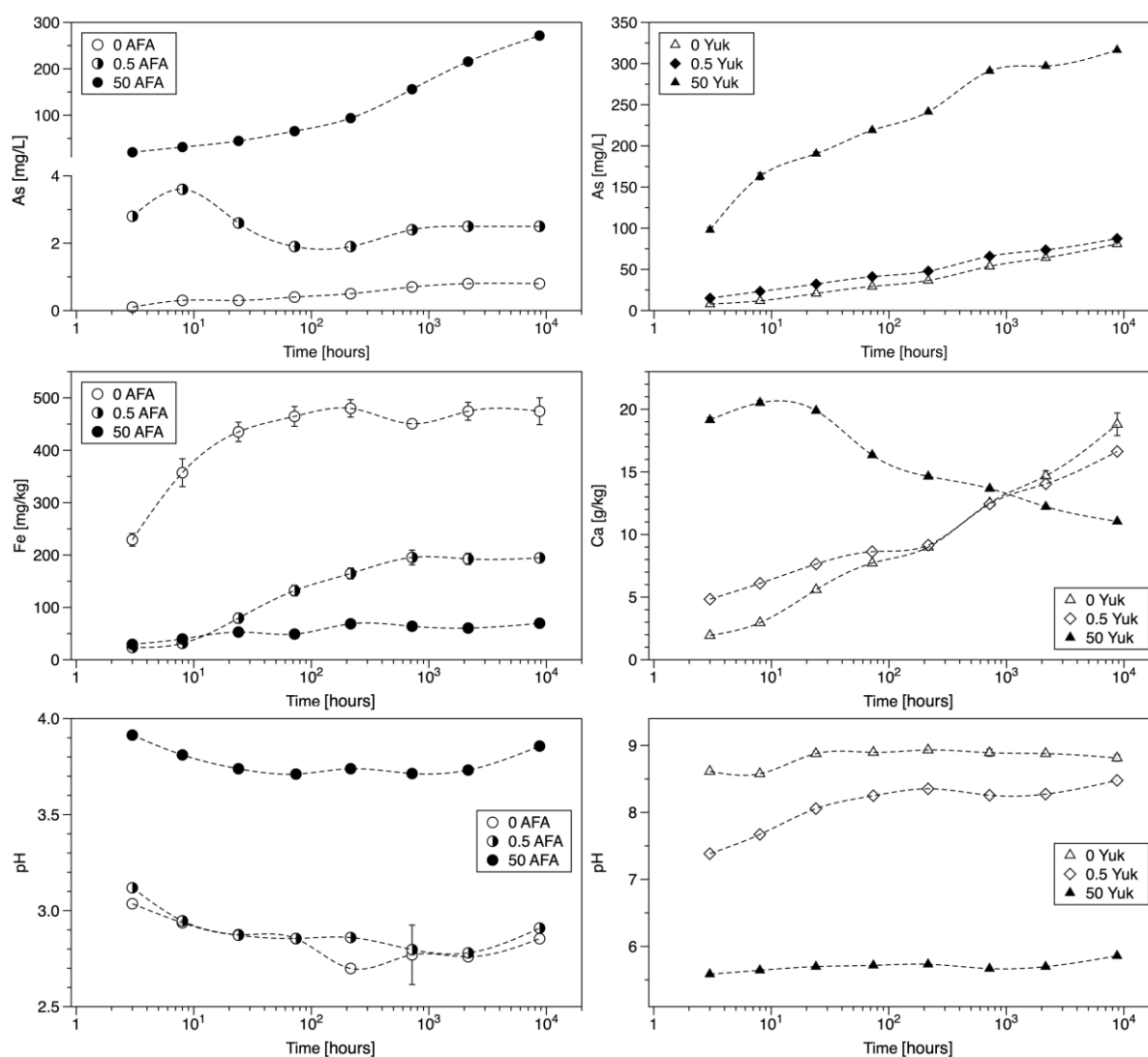


Figure S6. Trends of dissolved concentrations of As, P, Fe, Ca, and pH levels for synthetic AFA and yukonite samples. If not present, the error bars are within the size of the symbol except for 0.5 and 50 Yuk of 3 months where they are missing due to an error in the sampling.

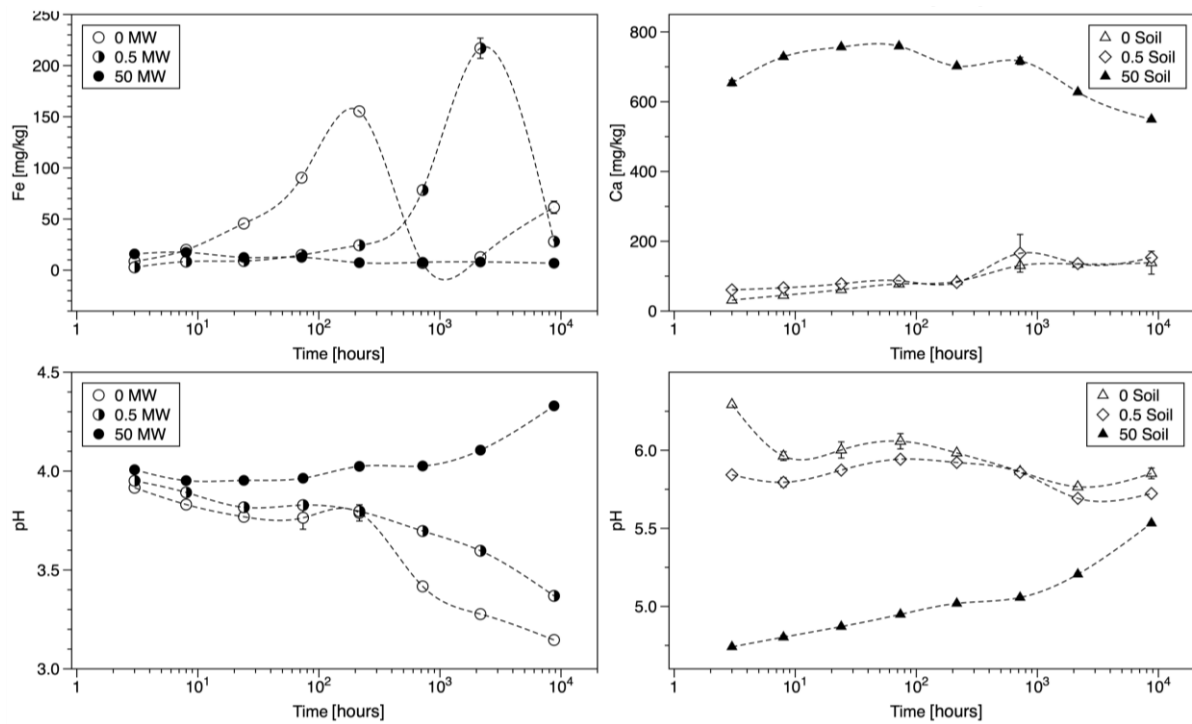


Figure S7. Trends of dissolved concentrations of As, P, Ca, Fe, and pH levels for mine waste containing Fe arsenates and soil containing Ca-Fe arsenates. If not present, the error bars are within the size of the symbol.

5 Statistics

Table S10. Spearman's rank order correlation test on different phosphate solutions (0, 0.5 and 50 mM). The correlation coefficients $r > 0.7$ are shown in bold, $n = 8$ ($n = 7$ for 50 MW), and the significance levels $p < 0.05$ and < 0.01 are marked * and **, respectively.

0 mM phosphate			0.5 mM phosphate			50 mM phosphate					
	AFA pH	AFA Fe	AFA P		AFA pH	AFA Fe	AFA P		AFA pH	AFA Fe	AFA P
AFA As	-0.8*	0.79*	–	AFA As	0.5	-0.60	0.55	AFA As	-0.29	0.88*	-1.00**
AFA Fe	–	–	–	AFA Fe	–	–	-0.91**	AFA Fe	–	–	-0.88**
	Yuk Ca	Yuk pH	Yuk P		Yuk Ca	Yuk pH	Yuk P		Yuk Ca	Yuk pH	Yuk P
Yuk As	1.00**	0.4	–	Yuk As	1.00**	0.93**	-1.00**	Yuk As	-0.79*	0.5	-0.91**
Yuk Ca	–	–	–	Yuk Ca	–	–	-1.00**	Yuk Ca	–	–	0.86**
	MW Ca	MW Fe	MW P		MW Ca	MW Fe	MW P		MW Ca	MW Fe	MW P
MW As	0.98**	0.14	–	MW As	0.60	1.00**	-1.00**	MW As	0.79*	-0.86**	-0.97**
MW Ca	–	0.12	–	MW Ca	–	0.60	-0.60	MW Ca	–	-0.57	-0.82*
MW Fe	–	–	–	MW Fe	–	–	-1.00**	MW Fe	–	–	0.79*
	Soil Ca	Soil Fe	Soil P		Soil Ca	Soil Fe	Soil P		Soil Ca	Soil Fe	Soil P
Soil As	0.98**	–	0.95**	Soil As	0.91**	–	-1.00**	Soil As	-0.53	–	-0.98**
Soil Ca	–	–	0.98**	Soil Ca	–	–	-0.91**	Soil Ca	–	–	0.50

6 EPMA & SEM

The polished sections prepared from the complex materials were examined using a field emission gun electron probe microanalyzer (FEG-EPMA; JEOL JXA-8530F, Japan) equipped with five wave dispersive detectors (WDS) used to obtain spot chemical analyses (accelerating voltage: 15 kV, beam current: 10–20 nA) and composition maps (accelerating voltage: 15 kV, beam current: 40–50 nA).

The scanning electron microscope (SEM; TESCAN Vega, Czech Republic) equipped with energy dispersive detector (EDS; X-Max 50, Oxford Instruments, UK) was used for the analysis of As-phases (accelerating voltage: 15 kV, beam current: 1 nA).

Table S11. Standards of the EPMA measurements.

Oxide	X-ray line	Spectrometer	Standard	Formula	DL [wt. %]
Al ₂ O ₃	K α	TAP	Alumina	Al ₂ O ₃	0.015
P ₂ O ₅	K α	TAP	Apatite	Ca ₅ (PO ₄) ₃ (F,Cl,OH)	0.036
As ₂ O ₅	L α	TAP	Gallium arsenide	GaAs	0.040
K ₂ O	K α	PETJ	Sanidine	KAlSi ₃ O ₈	0.013
CaO	K α	PETJ	Apatite	Ca ₅ (PO ₄) ₃ (F,Cl,OH)	0.034
SO ₃	K α	PETJ	Sphalerite	ZnS	0.031
Sb ₂ O ₅	L α	PETJ	Stibnite	Sb ₂ S ₃	0.033
BaO	L α	PETJ	Barite	BaSO ₄	0.040
Fe ₂ O ₃	K α	LIFL	Magnetite	Fe ₃ O ₄	0.029
MnO	K α	LIFL	Rhodonite	MnSiO ₃	0.023
Na ₂ O	K α	TAP	Albite	NaAlSi ₃ O ₈	0.020
SiO ₂	K α	TAP	Quartz	SiO ₂	0.034
MgO	K α	TAP	Magnesium oxide	MgO	0.021

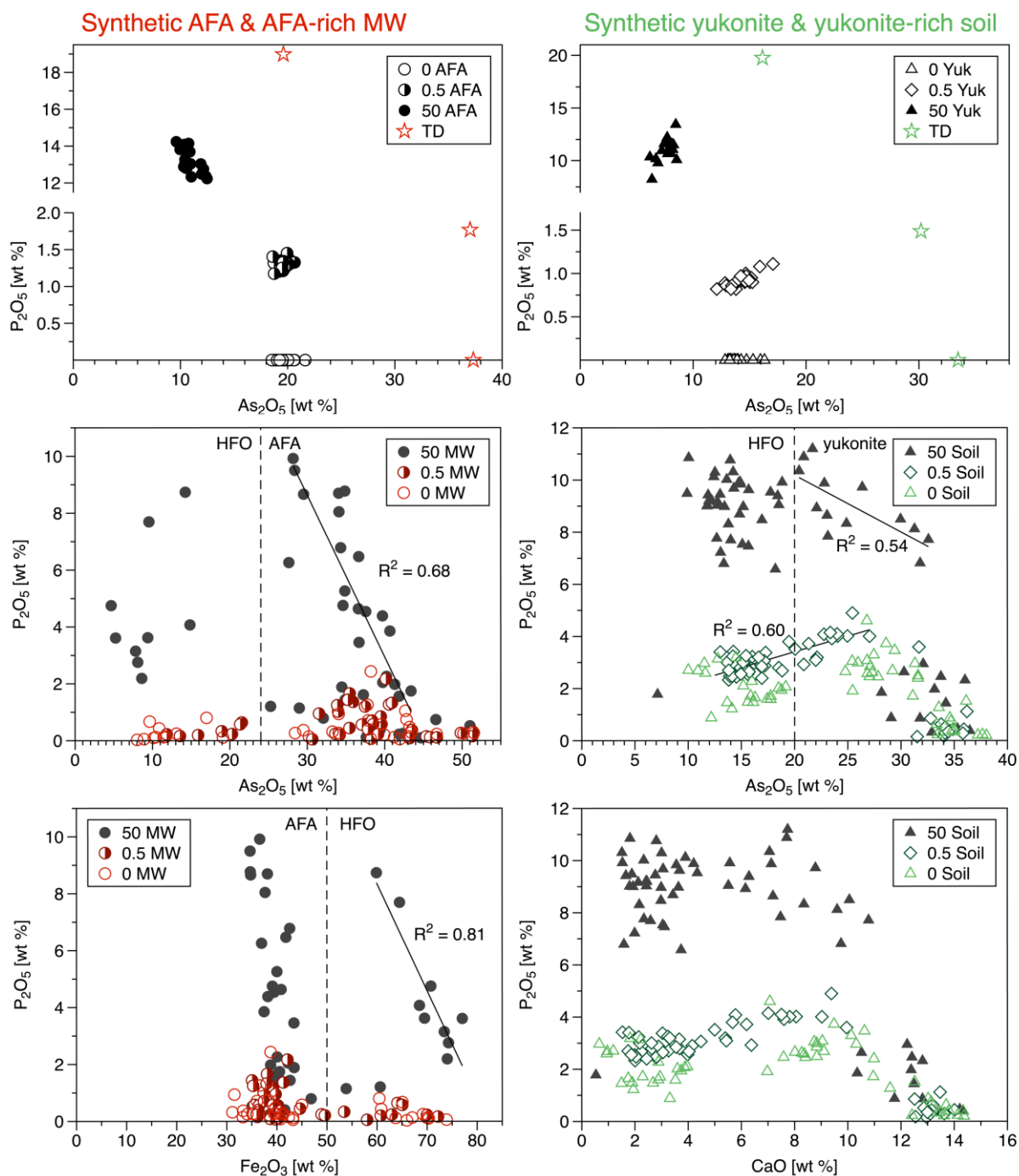


Figure S8. SEM and EPMA analysis data for synthetic AFA, yukonite and composite samples containing them naturally. SEM data for AFA and yukonite are qualitative and the stars represent calculated values based on a total digestion of solid phases at the end of the experiment. The lines separating HFOs and As phases were adopted from data published by Drahota et al. (2018). HFO = Fe (oxyhydr)oxides, TD = total digestions

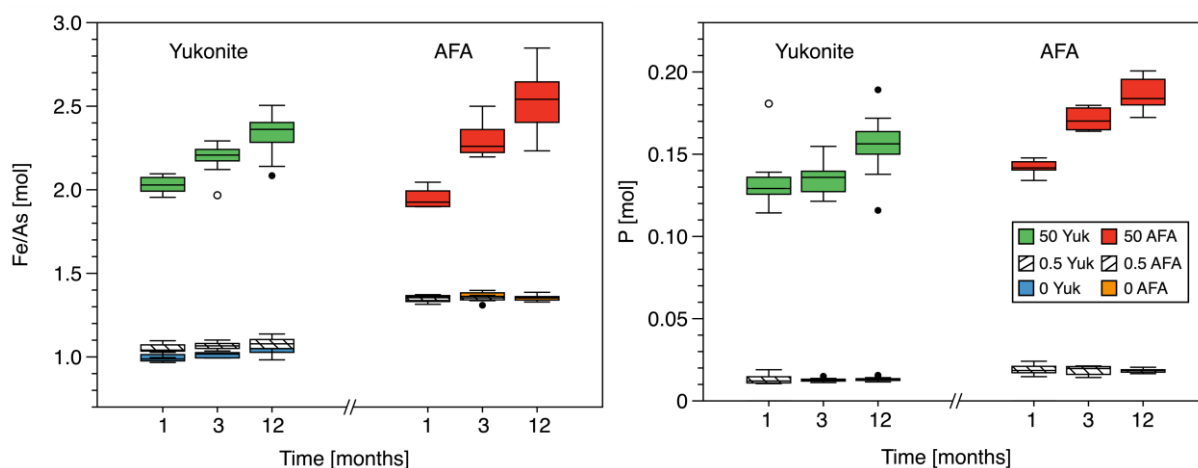


Figure S9. SEM analysis of synthetic AFA and yukonite collected after 1, 3, and 12 months of the experiment. The box border of Tuckey's box plot represents the 25th and 75th quartiles and the bar inside the median.

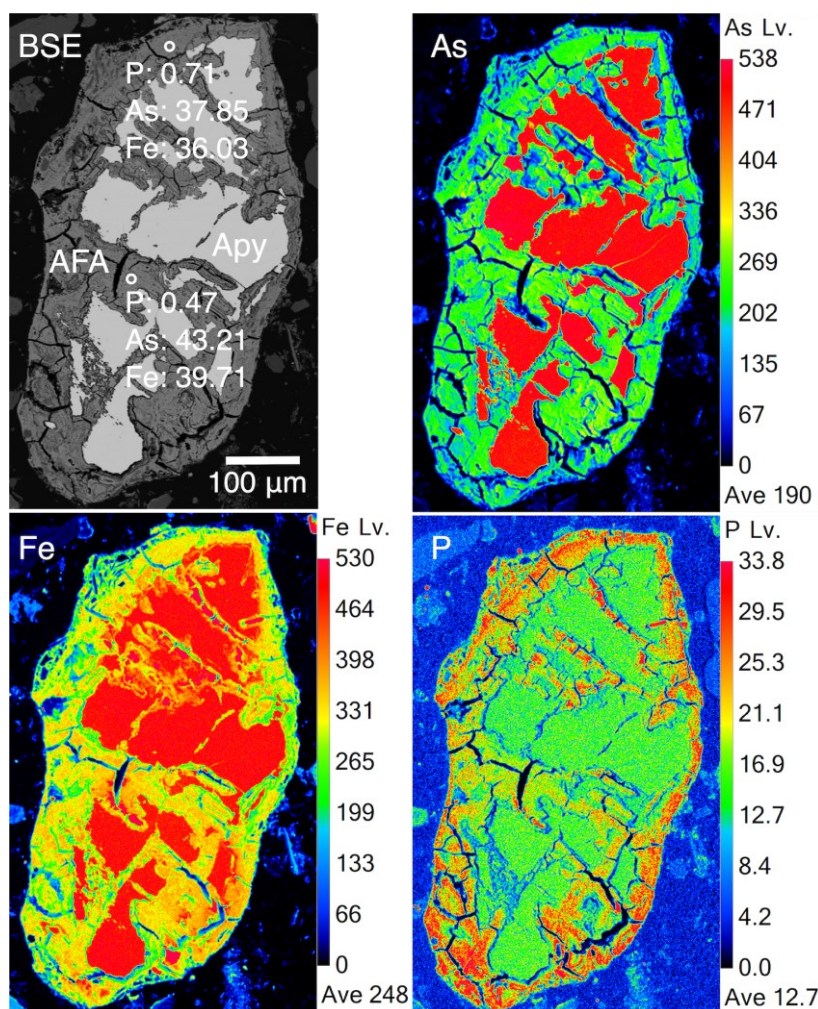


Figure S10. Composition map of arsenopyrite grain with AFA from MW sample in DI water. Elemental concentrations are given in wt. % of oxides (As: As_2O_5 , P: P_2O_5 , Fe: Fe_2O_3). BSE: back-scattered electrons, Apy: arsenopyrite.

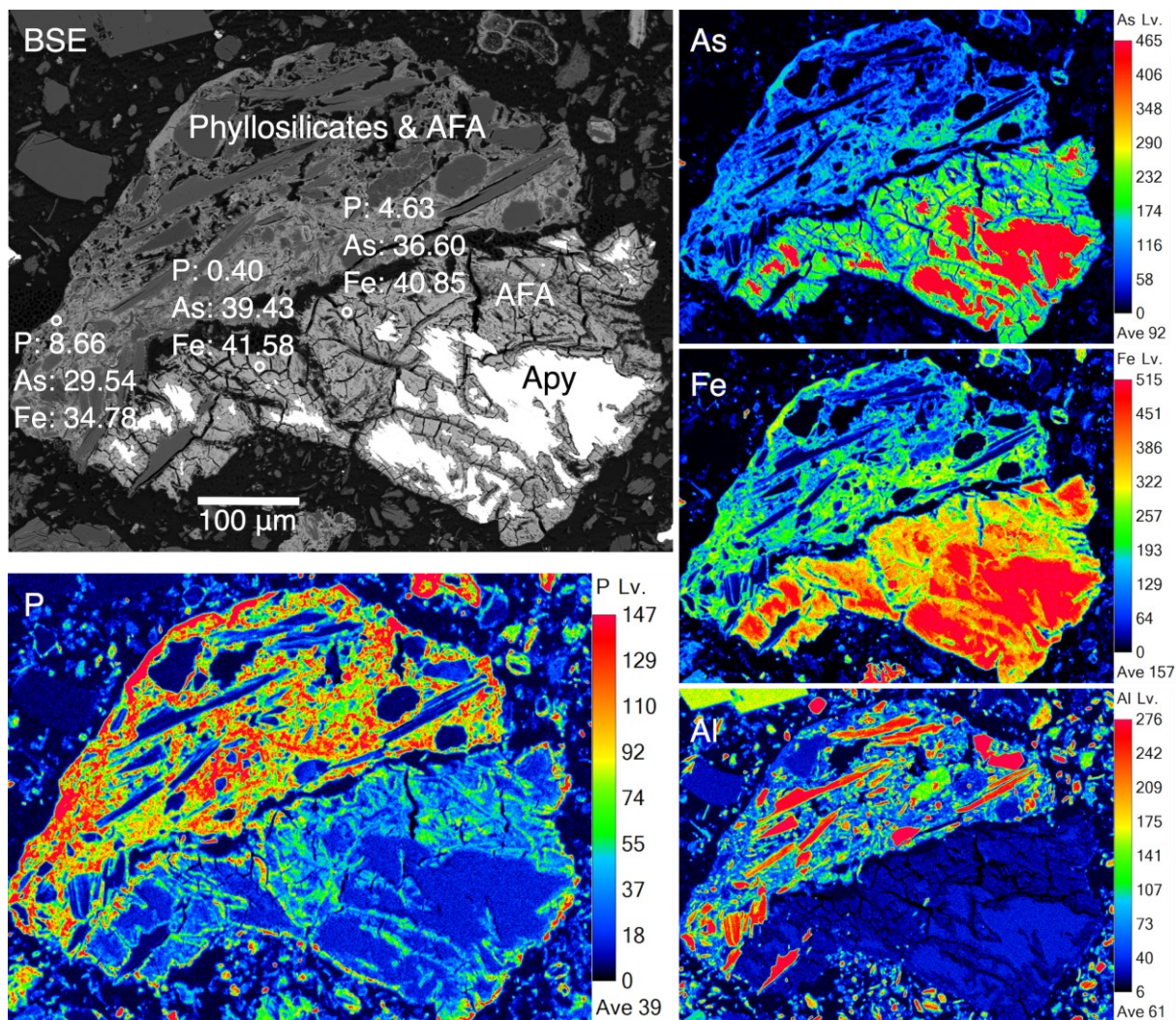


Figure S11. Compositional map of AFA/phyllsilicate grain from MW sample in highest phosphate solution after one year. Elemental concentrations of As, P, and Fe are given in wt. % of oxides (As_2O_5 , P_2O_5 , Fe_2O_3). BSE: back-scattered electrons, Apy: arsenopyrite.