

Appendix B4

Phosphate stabilisation experiment 3

Coating stage pH and conductivity

Cumulative coating solution (ml)	Column A		Column B		Column C		Column E		Column F		Column G	
	pH	cond	pH	cond	pH	cond	pH	cond	pH	cond	pH	cond
200	5.37	62125	5.35	56760	5.34	53310	5.74	33300	5.57	33600	5.35	29490
400	5.35	70800	5.31	54870	5.21	56550	5.35	36870	5.15	34080	4.98	21870
600	5.38	67520	5.36	55380	5.27	60650	5.23	37620	4.80	36000	4.56	27090
800	5.43	74840	5.40	55890	5.27	68640	5.03	31530	4.52	35520	4.16	32010
1000	5.40	79080	5.38	57870	5.27	42840	4.81	37380	4.17	38460	3.92	27450
1200	5.42	68440	5.38	75400	5.27	67560	4.81	53160	4.24	44010	4.03	26280
1400	5.38	70880	5.38	67360	5.30	58600	4.79	43440	4.03	39930	4.02	25380
1600	5.37	61960	5.39	73880	5.29	68400	4.90	71000	4.32	42540	4.20	24540
1800	5.37	98100	5.38	69120	5.30	55080	4.91	58880	4.37	44960	4.14	27900
2000	5.39	97500	5.38	67080	5.26	54630	4.92	45960	4.43	41430	4.28	27750
2200	5.36	92050	5.36	52120	5.29	63840	4.92	46440	4.44	34110	4.22	21810
2400	5.38	71650	5.35	66080	5.28	58240	4.98	42510	4.50	39360	4.36	25080
2600	5.37	79160	5.33	73920	5.28	58000	4.98	40650	4.51	33090	4.30	19980
2800	5.61	88750	5.58	67800	5.52	65200	5.35	45360	4.88	32280	4.67	23160
3000	5.62	87050	5.59	67080	5.54	61640	5.40	43710	4.91	38790	4.66	23100
3200	5.56	74000	5.52	72480	5.41	59680	5.39	50490	4.86	39360	4.56	22830
3400	5.57	85300	5.54	74040	5.47	49160	5.40	55710	4.90	33240	4.55	21400
3600	5.64	71550	5.66	70280	5.61	57920	5.61	41490	5.08	33630	4.74	24870
3800	5.70	69850	5.67	78240	5.62	56200	5.61	49080	5.18	35100	4.78	19380
4000	5.71	80600	5.67	68680	5.60	57600	5.49	41160	5.19	31800	4.80	17910
4200	5.66	82150	5.65	75680	5.60	57120	5.66	49950	5.29	38430	4.87	21740
4400	6.00	82950	5.98	66240	5.91	52640	6.06	51090	5.63	33750	5.14	17280
4600	5.89	94600	5.98	58040	5.92	53640	6.15	43380	5.71	38000	5.21	20910
4800	5.93	84000	5.96	59520	5.90	56800	6.16	44190	5.74	19260	5.27	17130
5000	5.90	88700	5.96	68120	5.88	54280	6.24	52680	5.81	34590	5.35	18000

cond – conductivity reported in $\mu\text{S}/\text{cm}$ at 25 °C.

Dissolution stage pH and conductivity

Cumulative coating solution (ml)	Column A		Column B		Column C		Column E		Column F		Column G	
	pH	cond	pH	cond	pH	cond	pH	cond	pH	cond	pH	cond
200	7.04	2626	7.14	1986	7.27	780	6.89	1422	6.16	1799	5.22	1579
400	7.31	1941	7.29	1679	6.96	442	6.86	1091	6.30	1443	5.22	1264
600	7.16	1808	7.11	1443	6.80	341	6.84	825	6.44	1053	5.38	979
800	7.17	1416	7.11	1088	6.76	242	6.91	667	6.56	857	5.66	694
1000	7.01	1261	6.91	1021	6.66	239	6.88	570	6.60	720	5.52	609
1200	7.07	993	6.95	802	6.64	186	6.93	497	6.66	627	5.60	551
1400	6.99	893	6.93	701	6.61	174	6.92	426	6.69	530	5.81	485
1600	7.04	754	6.99	563	6.61	141	6.99	380	6.74	487	5.83	442
1800	6.93	712	6.87	562	6.53	143	6.96	354	6.72	441	5.86	410
2000	6.97	645	6.95	455	6.49	122	6.97	325	6.78	410	6.02	384
2200	6.96	539	6.89	433	6.45	119	6.97	288	6.82	359	5.89	357
2400	6.95	517	6.93	381	6.54	103	6.99	287	6.82	362	6.01	360
2600	6.82	534	6.79	407	6.55	108	6.92	275	6.79	341	5.93	344
2800	6.86	474	6.92	332	6.41	97	6.92	261	6.85	329	6.09	345
3000	6.77	463	6.79	344	6.38	104	6.91	253	6.80	300	5.98	337
3200	6.82	421	6.90	289	6.43	90	6.98	242	6.88	303	6.22	323
3400	6.80	409	6.86	289	6.30	93	6.95	235	6.85	287	6.05	310
3600	6.81	360	6.95	237	6.32	82	6.97	225	6.88	282	6.16	303
3800	6.78	341	6.89	240	6.23	88	6.95	219	6.85	274	6.11	293
4000	6.82	308	6.96	198	6.23	76	6.97	210	6.90	273	6.21	281
4200	6.84	297	6.91	204	6.16	82	6.94	213	6.88	264	6.16	278
4400	6.90	269	7.02	177	6.28	73	6.96	209	6.90	264	6.27	271
4600	6.84	261	6.92	179	6.14	77	6.92	207	6.86	246	6.16	268
4800	6.97	228	6.98	150	6.08	70	6.96	203	6.91	248	6.25	271
5000	6.90	212	6.89	151	5.94	71	6.95	195	6.88	235	6.25	267

cond – conductivity reported in $\mu\text{S}/\text{cm}$ at 25 °C. Control column of experiment 2 also used as the control for experiment 3 as the waste material was identical.

Coating stage leachate chemistry

Column	Cumulative coating solution (ml)	As	Cu	P	SO ₄ ²⁻	Zn
Column A	200	<2.5	<0.5	n.a.	577	<0.5
	2600	<2.5	<0.5	n.a.	58	<0.5
	5000	<2.5	<0.5	n.a.	<4	<0.5
Column B	200	<2.5	<0.5	n.a.	695	<0.5
	2600	<2.5	<0.5	n.a.	192	<0.5
	5000	<2.5	<0.5	n.a.	137	<0.5
Column C	200	<2.5	12.00	n.a.	1104	3.98
	2600	<2.5	1.37	n.a.	328	<0.5
	5000	<2.5	1.02	n.a.	173	<0.5
Column E	200	<2.5	9.16	740	898	2.62
	2600	<2.5	<0.5	2080	166	<0.5
	5000	<2.5	<0.5	422	179	<0.5
Column F	200	<2.5	<0.5	988	944	<0.5
	2600	<2.5	<0.5	4710	209	<0.5
	5000	<2.5	<0.5	760	203	<0.5
Column G	200	3.57	28.00	2150	933	11.60
	2600	<2.5	5.89	4680	109	<0.5
	5000	<2.5	0.80	1220	145	<0.5

Concentrations in mg/l. Fe (0.5 mg/l) and Pb (3 mg/l) below detection in all samples. Detection limits shown in brackets. n.a. – not analysed.

Dissolution stage leachate chemistry

As

Cumulative oxidising solution (ml)	Column A	Column B	Column C	Column E	Column F	Column G
200	764	732	695	356	656	564
800	567	516	466	532	607	468
1600	428	376	307	372	437	390
2000	351	284	265	303	365	315
2600	245	221	213	242	298	307
3200	206	182	195	220	271	281
3800	157	141	166	185	244	262
4400	143	124	156	181	234	221
5000	113	98	125	156	203	215

Concentrations in µg/l.

Cu

Cumulative oxidising solution (ml)	Column A	Column B	Column C	Column E	Column F	Column G
200	99.9	49.2	103.0	116.0	642.0	4740.0
800	51.5	67.4	340.0	64.1	300.0	2360.0
1600	78.8	84.4	115.0	72.8	129.0	449.0
2000	79.4	82.2	124.0	61.1	110.0	438.0
2600	83.9	110.0	112.0	63.2	87.0	430.0
3200	83.6	85.6	109.0	58.3	92.5	646.0
3800	66.7	74.4	129.0	160.0	85.7	301.0
4400	65.4	64.1	116.0	49.3	82.3	298.0
5000	54.5	57.1	128.0	82.8	153.0	293.0

Concentrations in $\mu\text{g/l}$.**Fe**

Cumulative oxidising solution (ml)	Column A	Column B	Column C	Column E	Column F	Column G
200	169		798	<100	780	23400
800	<100		550	<100	747	13500
1600	<100		916	<100	<100	1740
2000	<100		408	<100	<100	1470
2600	<100		214	<100	<100	1480
3200	<100		149	<100	<100	2860
3800	<100		177	183	<100	814
4400	<100		108	<100	<100	937
5000	<100		<100	<100	219	988

Concentrations in $\mu\text{g/l}$.**P**

Cumulative oxidising solution (ml)	Column A	Column B	Column C	Column E	Column F	Column G
200	262.0	215.0	55.1	192.0	399.0	449.0
800	178.0	144.0	25.7	119.0	176.0	170.0
1600	112.0	81.7	13.9	69.3	98.2	88.6
2000	93.9	60.0	10.6	54.0	66.0	64.8
2600	74.7	57.7	7.5	42.1	50.5	56.9
3200	63.6	36.7	6.7	38.3	46.6	53.0
3800	54.0	26.9	5.5	34.0	40.6	43.5
4400	40.2	17.5	5.2	32.9	39.8	43.0
5000	22.4	11.9	3.9	28.3	35.0	37.8

Concentrations in mg/l .

Pb

Cumulative oxidising solution (ml)	Column A	Column B	Column C	Column E	Column F	Column G
200	103.0	42.4	120.0	72.0	496.0	12300.0
800	9.9	23.5	626.0	13.4	292.0	4830.0
1600	11.8	15.8	85.0	21.3	32.4	702.0
2000	21.6	16.6	68.1	15.3	32.9	596.0
2600	15.6	38.8	87.7	14.6	7.3	705.0
3200	22.9	28.2	65.1	16.7	30.9	999.0
3800	18.7	27.3	75.9	180.0	24.3	334.0
4400	21.9	28.7	60.1	15.6	26.8	380.0
5000	32.3	26.1	49.9	75.0	115.0	359.0

Concentrations in µg/l.

Sb

Cumulative oxidising solution (ml)	Column A	Column B	Column C	Column E	Column F	Column G
200	240	249	796	55	46	262
800	242	228	508	78	85	221
1600	178	177	336	75	65	150
2000	252	219	304	93	78	160
2600	205	197	236	87	78	183
3200	265	237	233	102	94	191
3800	219	201	203	100	94	173
4400	245	224	198	113	111	157
5000	204	187	161	107	104	164

Concentrations in µg/l.

SO₄²⁻

Cumulative oxidising solution (ml)	Column A	Column B	Column C	Column E	Column F	Column G
200	452.4	477.4	224.1	200.9	183.8	134.6
800	275.4	261.8	73.7	110.1	100.5	127.9
1600	169.9	143.2	60.2	79.1	66.3	122.9
2000	98.0	95.8	42.0	52.4	42.4	85.9
2600	79.4	79.4	39.9	54.9	37.8	87.6
3200	60.9	58.8	33.6	44.2	29.2	70.9
3800	63.4	53.4	36.7	47.4	32.8	69.5
4400	49.5	44.5	28.5	43.1	25.7	59.5
5000	41.7	41.7	32.0	44.2	28.4	60.9

Concentrations in mg/l.

Zn

Cumulative oxidising solution (ml)	Column A	Column B	Column C	Column E	Column F	Column G
200	44.6	21.6	64.0	70.0	371.0	3190.0
800	16.8	20.2	229.0	28.0	146.0	2320.0
1600	38.4	47.1	77.6	50.0	55.2	662.0
2000	53.8	47.9	97.9	45.7	52.8	553.0
2600	42.8	61.1	94.7	53.4	41.1	514.0
3200	45.8	52.3	108.0	47.7	47.5	712.0
3800	38.7	45.0	148.0	114.0	52.8	368.0
4400	45.6	44.4	144.0	43.6	51.1	349.0
5000	40.4	38.7	190.0	62.3	99.4	339.0

Appendix B5

SEM observations, experiment 1

Coating stage

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column A	Pb phosphate	pincushions of 0.5 μm x 10 μm needles, occasionally coalesced into "carpets" covering areas up to 1000 μm^2	Pb phosphate	heterogeneous, generally covers >75 % of galena surfaces, rare isolated precipitates on anglesite and quartz.
	Cu phosphate	scattered spherical rosettes of ~10 μm diameter, preferentially precipitated in cracks and hollows on chalcopyrite surfaces	Cu–Ca+K, Fe phosphate	cover <5 % of chalcopyrite surfaces, rare on other minerals
	Ca phosphate	agglomerations of very fine grained (<1 μm long) needles and rare botryoids, preferentially precipitated in hollows on grain surfaces	Ca+K, Si, S, Fe phosphate	cover <1 % of grain surfaces, no preferential substrate
	Fe phosphate	thin (<1 μm) amorphous coating with desiccation cracks	Fe+K–Cu phosphate	thin coating covering <1 % of chalcopyrite surfaces
	Zn phosphate	bladed 30 μm x 3 μm crystal precipitates	Zn–Ca–K phosphate	rare precipitate on sphalerite
Column B	phosphate phases identical to those observed in column A but with a slight increase in abundance			

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column C	Fe phosphate	amorphous layered thick (>3 μm) coating with extensive desiccation cracks	Fe–K±Cu phosphate	coat ~95 % of chalcopyrite surfaces, rare and poorly-formed on pyrite and arsenopyrite
	Cu phosphate	spherical rosettes, often coalesced into a coating of radial acicular splays on Fe phosphate-coated chalcopyrite	Cu–Ca–(K) phosphate	coalesced coating formed on <20 % of Fe phosphate-coated chalcopyrite, scattered precipitates on quartz, clays and tetrahedrite
	Pb phosphate	coating of fine-grained pincushions; occasional late, large (100 μm x 1 - 10 μm) acicular crystals	Pb phosphate; large crystals Pb±Ca phosphate	cover 100 % of galena surfaces, rarely on minerals adjacent to galena
	Zn phosphate	radial flow-like agglomerations of very fine-grained (100 nm x 10 nm) acicular crystals often with late, large (100 μm x 10 μm) bladed crystal precipitates	Zn–K±Ca phosphate	cover ~50 % of sphalerite surfaces, always associated with sphalerite although often covers adjacent Fe and Cu phosphates
	Ca phosphate	amorphous and rare botryoidal agglomerations	Ca phosphate	cover <5 % of grain surfaces
	sulphates	euhedral rosettes or splays of crystal precipitates	Pb, Pb-As, Cu, Fe and Ca (gypsum) sulphates	rare isolated precipitates
Column D	phosphate and sulphate phases identical to those observed in column C but with a slight increase in abundance; rare precipitates of Fe and As (scorodite?) were also observed			

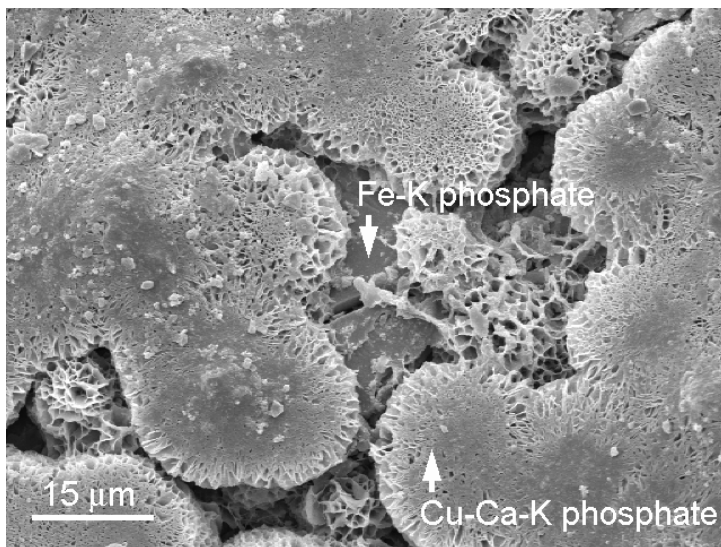
Dissolution stage

Column	Major phases	Habit and morphology	Chemistry	Abundance
Control	metal sulphates	scattered euhedral crystals and rosettes	Pb, Cu, Cu–Zn and Fe sulphates	order of abundance Pb > Cu > Cu–Zn > Fe. All phases <5 % coverage of parent sulphide
	Pb–As sulphate	scattered precipitates of euhedral crystals, often twinned	Pb–As sulphate	heterogeneous abundance from ~5 % to absent, no preferential substrate
Column A	Pb phosphate	fine-grained pincushions; large (30 µm x 5 µm) tabular crystals	Pb phosphate; tabular crystals Pb–Ca phosphate	heterogeneous, generally covers >75 % of galena surfaces, rarely on minerals adjacent to galena; tabular crystals very rare
	sulphates	euhedral radial splays (Ca, Pb); acicular pincushions, hexagonal platelets, tabular crystal (Pb) (Pb–As); rosettes (Cu); acicular crystals (Zn)	Ca (gypsum), Cu, Pb, Pb–As, Zn sulphates	order of abundance Pb > Ca > Cu > Zn. Pb and Ca phases cover <1 % of substrate; Cu and Zn rare
	Fe arsenate	fan-shaped crystal splays	Fe arsenate (scorodite?)	very rare precipitate.
Column B	Pb phosphate phases were identical to column A except that the large tabular crystals were far more abundant and contained no Ca			
	Fe phosphate	thin (<1 µm) amorphous coating with desiccation cracks	Fe–K±(Cu,Ca) phosphate	thin coating covering <1 % of chalcopyrite surfaces
	Cu phosphate	isolated, spherical rosettes of ~10 µm diameter,	Cu–Ca–(K) phosphate	rare precipitates on Fe phosphate-coated chalcopyrite

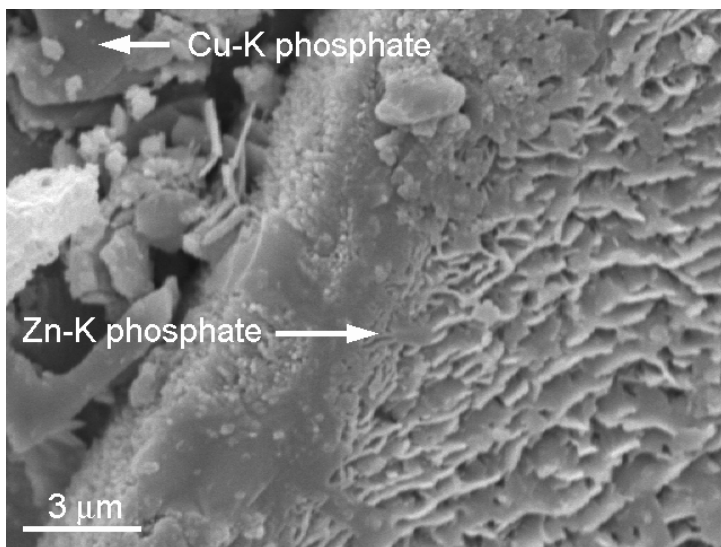
Column	Major phases	Habit and morphology	Chemistry	Abundance
Column B continued	Ca phosphate	very fine-grained granular agglomerations	Ca _± (Si) phosphate	rare precipitates, no preferential substrate
	sulphates	euhedral radial splays (Ca); blocky crystals and rosettes (Cu, Pb-As); very fine platelets (Fe)	Ca (gypsum), Cu, Fe, Pb-As sulphates	Ca covers <1 % of substrate; Cu, Pb-As and Fe rare
Column C	Fe phosphate	amorphous layered thick (>3 µm) coating with extensive desiccation cracks	Fe-K-(Cu) _± (Si, S) phosphate	coats ~95 % of chalcopyrite, cobaltite and stannite surfaces, rare and poorly-formed on pyrite, bournonite and arsenopyrite
	Cu phosphate	spherical rosettes, often coalesced into a coating of radial acicular splays on Fe phosphate coated chalcopyrite; coarser grained (50 µm) when precipitated on quartz	Cu-Ca-(K) phosphate	coalesced coating formed on <10 % of Fe phosphate-coated chalcopyrite; scattered precipitates on quartz, clays and tetrahedrite
	Pb phosphate	coating of fine-grained pincushions; large (30 µm x 5 µm) tabular crystals; rice-shaped granules (10 µm x 3 µm); amorphous coatings	pincushions and large crystals Pb phosphate; granules and amorphous coatings Pb-Ca phosphate	cover 99 % of galena surfaces, rarely on minerals adjacent to galena
	Zn phosphate	agglomerations of fine-grained (10 µm x 1 µm) acicular crystals, large (100 µm x 10 µm) bladed crystals, rice-shaped grains.	acicular and bladed crystals Zn-K phosphate; rice-shaped grains Zn-Ca phosphate	very heterogeneous, covering 0 - 50 % of sphalerite surfaces

Column	Major phases	Habit and morphology	Chemistry	Abundance
Column C continued	sulphates	fine-grained (~1 μm) granules (Pb, Fe); euhedral crystals (Pb-As) acicular (1 μm long) crystals (Cu),	Pb, Pb-As Fe, Cu sulphates	rare precipitates, occasionally with phosphate substrates
Column D	phosphate and sulphate phases identical to those observed in column C but with a slight increase in abundance, excepting the rice-shaped Zn–Ca phosphate grains which were uncommon in column D			

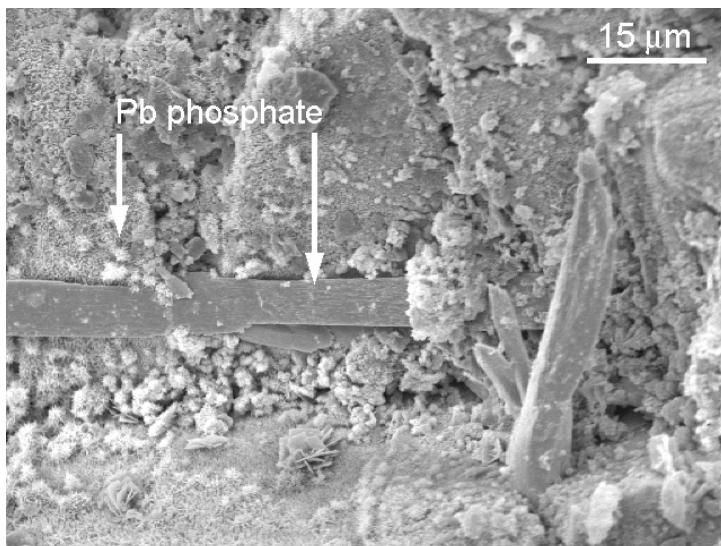
Additional SEM micrographs, experiment 1



Detail of Cu-Ca-K phosphate rosettes precipitated on Fe-K phosphate coating chalcopyrite, column D post-coating stage.



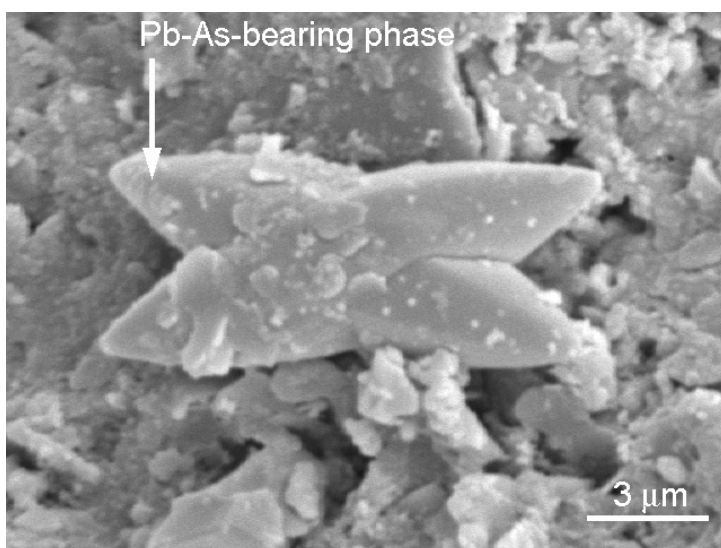
Detail of edge of Zn-K phosphate flow-like agglomeration shown in Figure 3.4b, column C post-coating stage.



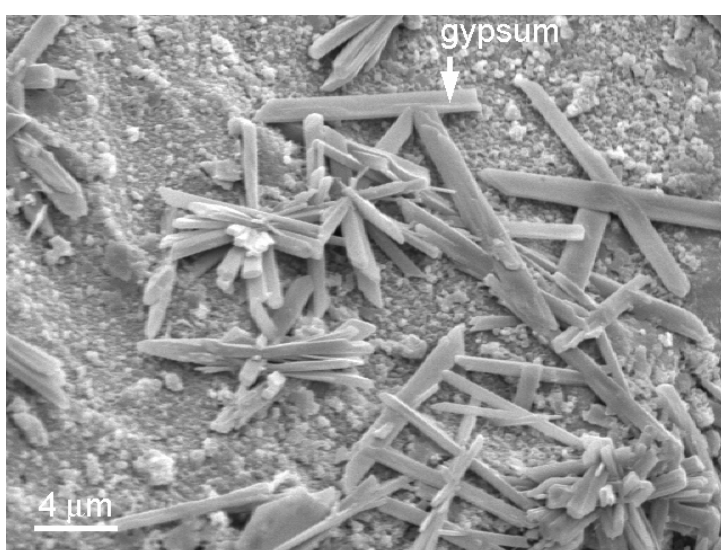
Bladed Pb phosphate crystals precipitated on fine-grained acicular Pb phosphate pincushions, column C post-coating stage.



Detail of acicular Pb phosphate pincushions shown above, column C post-coating stage.



Unidentified twinned Pb-As sulphate crystal, column A post-coating stage.



Radial splays of gypsum on quartz substrate, column B post-dissolution stage.