Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

The role of organic colloids in the sequestration and mobilization of copper within contaminated oxic soils

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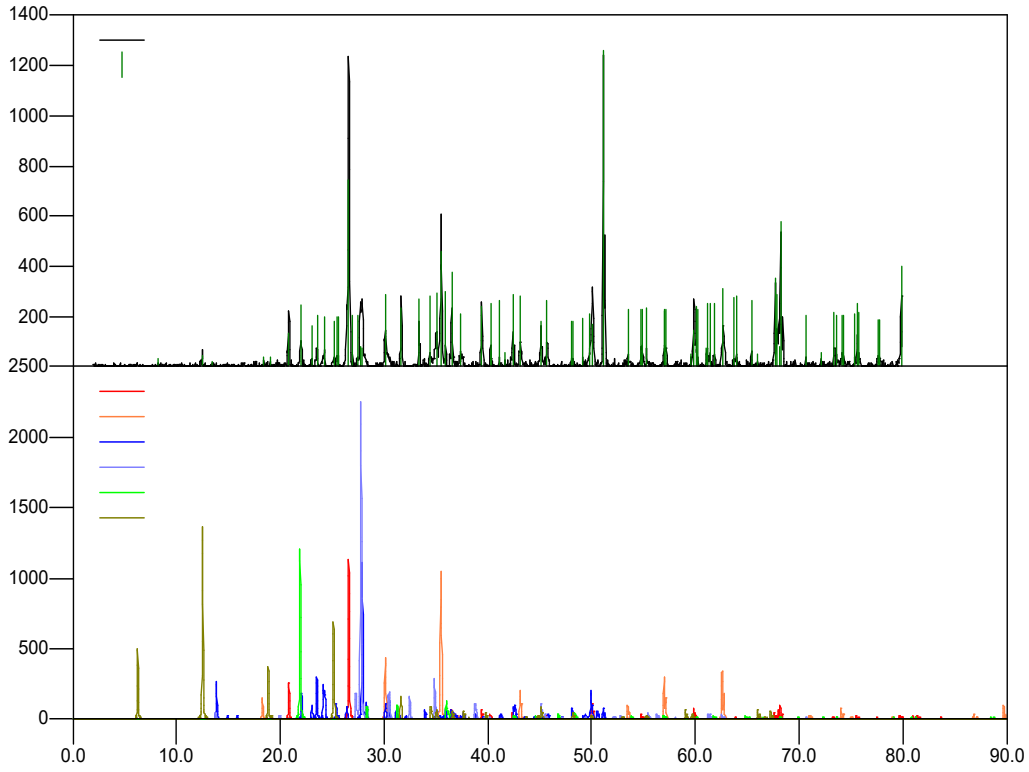
Supplementary Information

Fig. S1a A photographic image of site 7 with the smelter stack in the background

Fig. S1b A photographic image of a wet soil sample (sample 7C) collected at site 7, from which colloids were not extracted for TEM analysis.

Powder X-ray diffraction data for sample 7A



Identification letter, mineral name, formula, pdf-number	
A Quartz, $Si O_2$, 83-539	*B Magnesioferrite, $Mg Fe_2 O_4$,36-398*
C Albite, ordered, $Na Al Si_3 O_8$, 9-466	*D Protoenstatite, $Mg Si O_3$, 74-2017*
E Cristobalite low temperature, $Si O_2$, 76-937	*F Clinochlore-1 , ferroan, $(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$, 29-701*

Peak List

Peak Search Settings

Confidence Threshold	60%
Matched / Total	69 / 79

List of Peaks

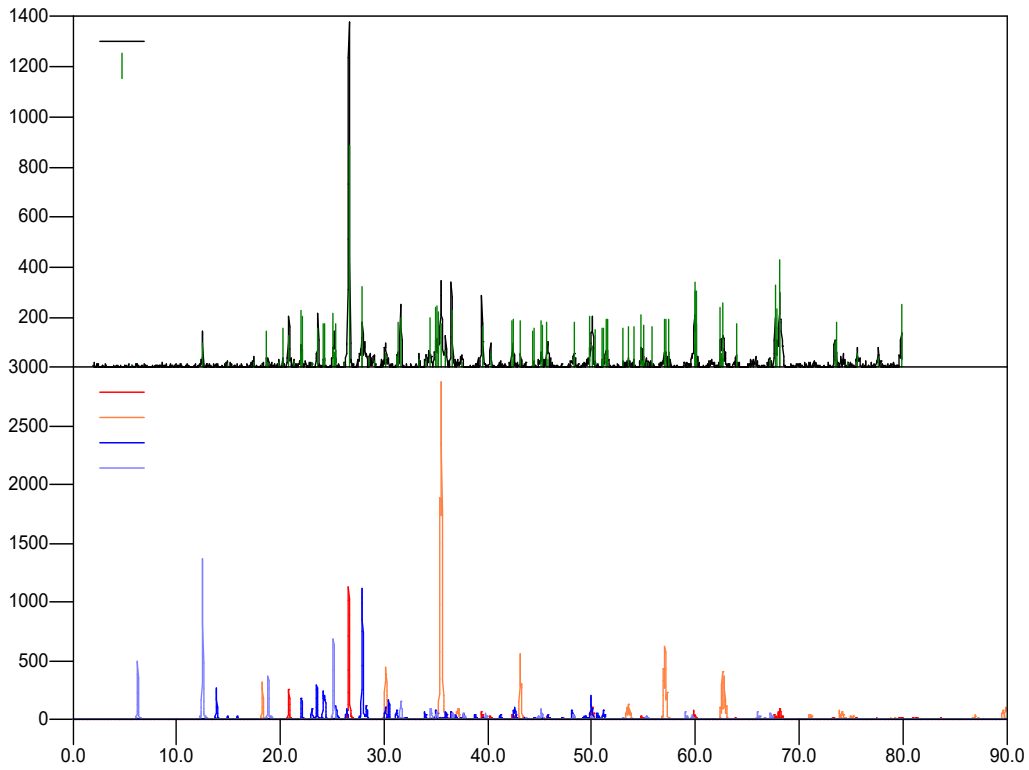
2-Theta	*D-Spacing*	*Intensity*	*Width*	*Confidence*	*Matches*

8.240	10.7219	32	0.035	86.3%	
12.485	7.0840	45	0.044	83.0%	F
13.453	6.5765	24	0.035	60.9%	
18.421	4.8125	37	0.037	72.1%	B
19.004	4.6661	39	0.037	71.0%	D
20.855	4.2558	136	0.061	95.9%	A
21.982	4.0402	246	0.060	100%	CE
23.037	3.8576	161	0.060	100%	C
23.544	3.7756	203	0.060	100%	C
24.274	3.6636	197	0.060	100%	C
25.146	3.5385	182	0.060	100%	F
25.430	3.4996	198	0.060	100%	C
25.552	3.4832	200	0.060	100%	C
26.608	3.3473	747	0.071	100%	A
26.992	3.3006	202	0.060	100%	
27.438	3.2479	205	0.060	100%	
27.735	3.2139	80	0.057	75.1%	D
27.894	3.1959	74	0.058	74.2%	C
30.112	2.9653	288	0.060	100%	BC
31.689	2.8212	235	0.042	100%	DF
33.361	2.6840	269	0.042	99.9%	D
34.396	2.6052	281	0.060	100%	
35.045	2.5584	293	0.060	100%	CF
35.483	2.5280	461	0.039	99.9%	B
35.958	2.4955	297	0.060	100%	CD
36.526	2.4580	378	0.060	100%	AC
37.378	2.4039	212	0.060	100%	C
39.427	2.2836	238	0.044	99.3%	AC

40.268	2.2379	60	0.048	71.1%	AB
40.306	2.2357	254	0.060	100%	AB
41.118	2.1935	263	0.060	100%	C
41.684	2.1648	59	0.034	79.4%	
42.396	2.1303	288	0.060	100%	AC
43.146	2.0949	279	0.060	100%	B
45.113	2.0080	180	0.040	99.4%	DF
45.722	1.9827	261	0.060	100%	AC
48.091	1.8904	181	0.060	100%	C
48.193	1.8867	181	0.060	100%	CF
49.126	1.8530	191	0.060	100%	C
49.795	1.8296	212	0.060	100%	BCD
50.092	1.8195	171	0.059	92.3%	ADF
51.151	1.7843	1259	0.041	100%	C
53.524	1.7107	228	0.060	100%	BD
54.743	1.6749	49	0.035	60.3%	ABD
54.781	1.6743	231	0.060	100%	ABD
54.842	1.6726	231	0.060	100%	ABD
55.329	1.6590	234	0.060	100%	AF
56.992	1.6145	227	0.060	100%	BE
57.073	1.6124	223	0.060	100%	ABE
57.175	1.6098	226	0.060	100%	ADE
59.569	1.5504	49	0.035	65.4%	D
59.891	1.5435	147	0.055	91.4%	AD
60.083	1.5386	239	0.060	100%	DE
60.245	1.5349	231	0.060	100%	E
61.107	1.5152	74	0.042	82.6%	
61.118	1.5150	249	0.060	100%	

61.402	1.5087	249	0.060	100%	DF
61.848	1.4989	254	0.060	100%	DE
62.680	1.4810	311	0.060	100%	B
63.755	1.4586	278	0.060	100%	BD
63.958	1.4544	284	0.060	100%	ABD
65.398	1.4258	266	0.060	100%	E
66.040	1.4138	50	0.035	69.4%	DF
67.707	1.3827	353	0.051	100%	AE
67.929	1.3788	291	0.060	100%	D
68.091	1.3758	83	0.070	71.2%	ADB
68.251	1.3730	576	0.050	100%	ADE
70.639	1.3324	207	0.060	100%	D
72.110	1.3087	54	0.037	64.5%	
73.398	1.2889	214	0.060	100%	A
73.601	1.2859	205	0.060	100%	DE
74.148	1.2777	206	0.060	100%	BD
74.315	1.2753	206	0.060	100%	DB
75.410	1.2595	213	0.060	100%	DB
75.592	1.2569	254	0.060	100%	A
75.755	1.2546	216	0.060	100%	
77.641	1.2287	186	0.060	100%	A
77.722	1.2277	185	0.060	100%	DE
79.877	1.1999	398	0.060	100%	A

Powder X-ray diffraction data for sample 7B



Identification letter, mineral name, formula, pdf-number	
A Quartz, $Si\ O_2$, 83-539	*B Magnetite, syn, $Fe_3\ O_4$, 75-1609*
C Albite, ordered, $NaAlSi_3O_8$, 9-466	***D Clinochlore-1 , ferroan, $(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$, 29-701***

Peak List

Peak Search Settings

Confidence Threshold	70%
Matched / Total	69 / 99

List of Peaks

2-Theta	*D-Spacing*	*Intensity*	*Width*	*Confidence*	*Matches*
5.710	15.4638	9	0.086	73.9%	
12.513	7.0680	97	0.101	100%	D

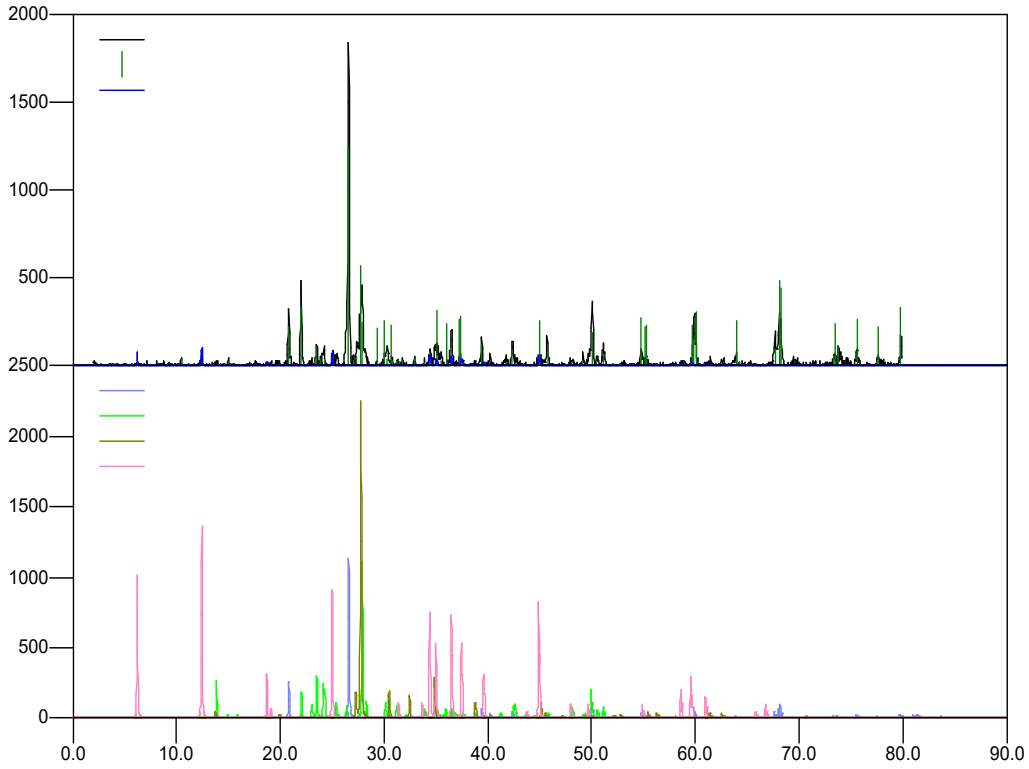
14.865	5.9545	16	0.093	84.9%	C
17.432	5.0832	19	0.098	84.8%	
18.718	4.7367	146	0.120	100%	
18.794	4.7177	20	0.098	83.1%	D
19.895	4.4591	19	0.088	80.2%	
20.219	4.3882	159	0.120	100%	
20.835	4.2599	130	0.103	100%	A
21.276	4.1727	26	0.093	90.6%	B
22.004	4.0361	228	0.120	100%	C
22.038	4.0300	60	0.103	100%	C
22.105	4.0179	205	0.120	100%	C
23.051	3.8551	24	0.100	85.6%	C
23.612	3.7648	160	0.102	100%	C
24.175	3.6784	172	0.120	100%	C
24.276	3.6633	172	0.120	100%	C
25.067	3.5495	217	0.120	100%	D
25.185	3.5332	60	0.106	99.8%	D
25.372	3.5076	178	0.120	100%	C
26.114	3.4095	21	0.136	78.9%	
26.620	3.3459	888	0.104	100%	A
27.907	3.1944	81	0.095	100%	C
27.930	3.1918	324	0.120	100%	C
28.601	3.1185	32	0.094	94.4%	
29.035	3.0728	30	0.106	91.5%	
30.119	2.9647	57	0.112	99.9%	BC
31.253	2.8596	47	0.105	99.4%	C
31.330	2.8528	183	0.120	100%	
31.632	2.8262	196	0.105	100%	D

33.374	2.6826	35	0.094	97.9%	
34.046	2.6311	30	0.096	91.9%	C
34.381	2.6063	197	0.120	100%	
34.989	2.5624	238	0.120	100%	CD
35.121	2.5530	249	0.120	100%	D
35.212	2.5466	220	0.120	100%	
35.508	2.5261	176	0.118	100%	B
35.961	2.4953	67	0.105	99.9%	C
36.519	2.4584	228	0.106	100%	ACD
37.568	2.3922	20	0.092	73.6%	CD
39.453	2.2821	163	0.105	100%	AC
40.254	2.2385	59	0.107	99.9%	A
42.287	2.1355	189	0.120	100%	
42.420	2.1291	29	0.118	89.5%	AC
42.517	2.1244	194	0.120	100%	C
43.132	2.0956	186	0.120	100%	B
43.154	2.0946	27	0.103	90.4%	B
44.317	2.0423	148	0.120	100%	
44.345	2.0410	16	0.091	71.7%	
44.404	2.0385	156	0.120	100%	C
45.116	2.0079	188	0.120	100%	D
45.247	2.0024	170	0.120	100%	CD
45.641	1.9860	182	0.120	100%	A
45.782	1.9802	34	0.114	94.0%	AC
48.279	1.8835	180	0.120	100%	D
48.320	1.8820	28	0.108	89.9%	D
49.805	1.8293	204	0.120	100%	C
50.082	1.8199	85	0.117	100%	ACD

50.403	1.8090	152	0.120	100%	
51.067	1.7870	25	0.085	85.5%	C
51.078	1.7867	156	0.120	100%	C
51.121	1.7853	155	0.120	100%	C
51.360	1.7775	193	0.120	100%	
51.410	1.7759	24	0.161	77.7%	
51.524	1.7723	192	0.120	100%	
53.042	1.7250	155	0.120	100%	D
53.555	1.7097	163	0.120	100%	B
54.040	1.6955	161	0.120	100%	
54.801	1.6738	210	0.120	100%	A
54.882	1.6715	27	0.121	85.0%	A
55.002	1.6681	172	0.120	100%	
55.250	1.6612	21	0.088	81.5%	AD
55.766	1.6471	161	0.120	100%	
57.000	1.6143	194	0.120	100%	B
57.079	1.6123	19	0.106	73.8%	AB
57.123	1.6111	194	0.120	100%	AB
57.406	1.6038	19	0.090	74.6%	
57.439	1.6030	190	0.120	100%	
59.925	1.5423	341	0.120	100%	A
59.971	1.5412	93	0.139	100%	A
60.041	1.5396	303	0.120	100%	
60.076	1.5388	308	0.120	100%	
62.442	1.4861	242	0.120	100%	B
62.490	1.4851	55	0.097	87.9%	B
62.602	1.4826	257	0.120	100%	B
62.678	1.4810	41	0.093	80.0%	B

63.964	1.4543	178	0.120	100%	A
63.973	1.4541	20	0.085	72.4%	A
67.136	1.3932	26	0.080	75.4%	
67.687	1.3831	328	0.120	100%	A
67.878	1.3797	232	0.120	100%	
68.120	1.3754	428	0.120	100%	A
68.149	1.3749	157	0.109	100%	A
73.419	1.2889	104	0.093	100%	A
73.598	1.2859	182	0.120	100%	
74.735	1.2696	23	0.078	75.9%	
75.622	1.2568	54	0.090	98.0%	A
77.655	1.2288	38	0.080	91.6%	A
79.870	1.2000	253	0.120	100%	A

Powder X-ray diffraction data for sample 5F



Identification letter, mineral name, formula, pdf-number	
A Quartz, Si O_2, 83-539	***B Albite, ordered, Na Al Si_3 O_8, 9-466***
C Protoenstatite, Mg Si O_3, 74-2017	***D Clinochlore-1 , manganoan, (Mg_3Mn_2Al $Si_3AlO_{10}(OH)_8$, 45-1321***

Peak List

Peak Search Settings

Confidence Threshold	60%
Matched / Total	52 / 73

List of Peaks

2-Theta	*D-Spacing*	*Intensity*	*Width*	*Confidence*	*Matches*
6.186	14.2770	11	0.088	75.6%	D
6.922	12.7586	12	0.077	70.8%	

7.214	12.2437	12	0.090	79.8%	
10.454	8.4552	38	0.098	99.8%	
12.445	7.1068	48	0.101	99.9%	D
14.993	5.9039	30	0.090	96.8%	B
15.374	5.7586	14	0.091	66.7%	
18.768	4.7243	17	0.081	70.2%	D
20.815	4.2640	224	0.106	100%	A
22.007	4.0356	334	0.105	100%	B
23.512	3.7807	109	0.104	100%	B
23.830	3.7308	40	0.084	95.1%	
24.257	3.6661	39	0.086	88.1%	B
25.105	3.5442	49	0.094	98.1%	D
26.596	3.3489	1246	0.105	100%	A
27.039	3.2949	28	0.133	85.6%	
27.391	3.2534	58	0.107	97.5%	C
27.772	3.2096	572	0.120	100%	C
27.882	3.1972	246	0.144	100%	B
29.318	3.0438	213	0.120	100%	
30.033	2.9729	258	0.120	100%	
30.330	2.9445	36	0.117	87.5%	
30.718	2.9082	236	0.120	100%	
30.789	2.9017	31	0.093	88.3%	
31.259	2.8591	27	0.097	84.8%	B
31.517	2.8363	22	0.071	74.6%	BD
31.780	2.8134	28	0.087	87.2%	
32.934	2.7174	40	0.098	96.9%	
33.897	2.6424	18	0.090	68.3%	B
34.427	2.6029	41	0.113	94.4%	D

34.916	2.5675	42	0.111	89.8%	BCD
35.161	2.5502	318	0.120	100%	
35.218	2.5462	25	0.090	67.7%	
35.550	2.5232	32	0.097	85.9%	
36.050	2.4893	239	0.120	100%	B
36.073	2.4878	22	0.091	73.0%	B
36.503	2.4595	114	0.113	100%	ABD
37.249	2.4119	264	0.120	100%	
37.411	2.4018	282	0.120	100%	BD
39.418	2.2841	122	0.107	100%	A
40.212	2.2408	23	0.095	76.0%	AC
41.741	2.1621	23	0.084	74.5%	
42.390	2.1306	90	0.114	100%	A
44.992	2.0132	256	0.120	100%	D
45.066	2.0100	24	0.103	76.4%	C
45.742	1.9819	90	0.105	100%	AB
48.142	1.8886	17	0.084	64.8%	B
49.183	1.8510	31	0.099	88.2%	B
50.086	1.8197	194	0.121	100%	AC
50.525	1.8049	22	0.147	74.3%	AB
51.176	1.7835	66	0.132	99.8%	B
54.764	1.6748	48	0.116	97.2%	AC
54.803	1.6737	275	0.120	100%	ACD
55.177	1.6632	224	0.120	100%	A
55.235	1.6616	34	0.089	93.6%	A
55.283	1.6603	231	0.120	100%	A
59.666	1.5484	229	0.120	100%	CD
59.873	1.5435	152	0.112	100%	AC

60.083	1.5386	309	0.120	100%	C

Fig. S2 XRD patterns, identified minerals, two-theta values, d-spacings and matches of observed d-spacing to minerals for the samples 5A, 7A and 7B, respectively.

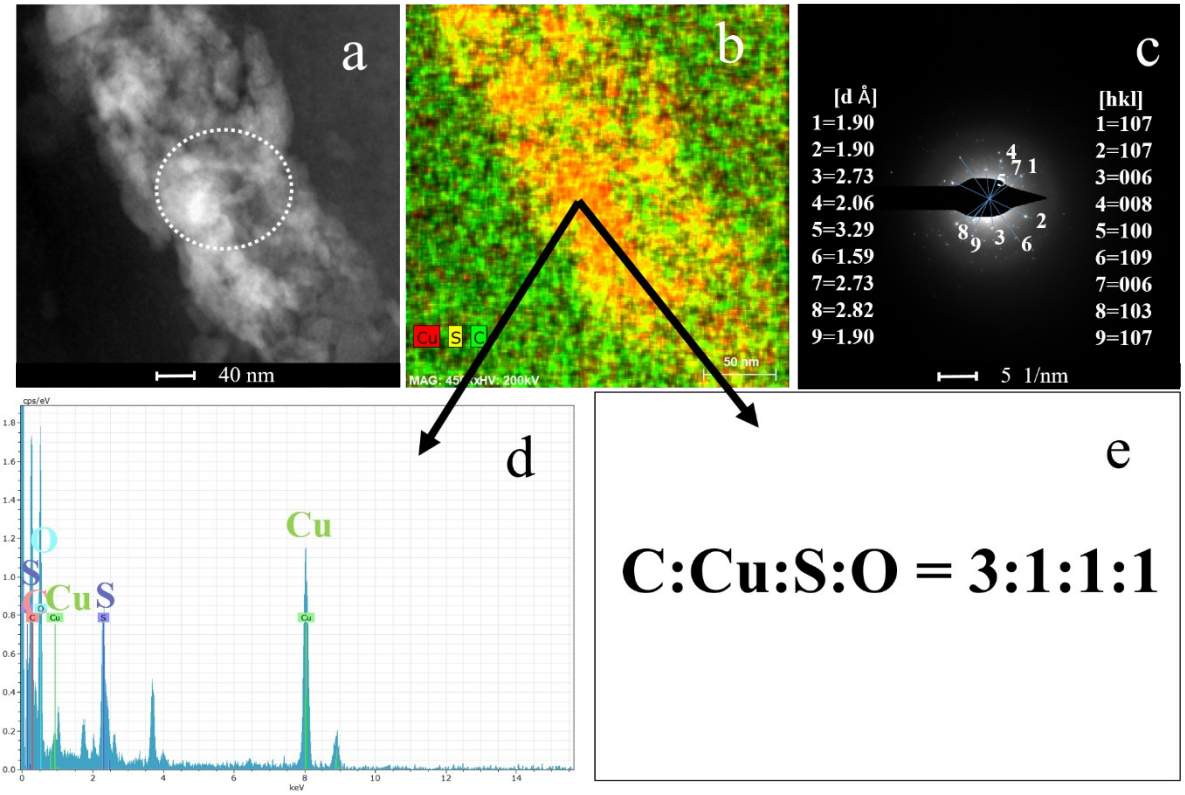


Fig. S3 Identification process of covellite: (a) STEM image and (b) STEM-EDS chemical distribution maps for Cu (red), S (yellow) and C (green); (c) selected area electron diffraction pattern (SAED) of area highlighted by white and black dashed lines in (a) indicating that all the of the observed d-spacings correspond to covellite. (d) STEM-EDS spectrum and (e) C, Cu, S and O ratio obtained from EDS spectrum indicating the presence of a sulfide rather than sulfate (as sulfates depict O : S ratios larger than 4 when semi-quantified with STEM-EDS)

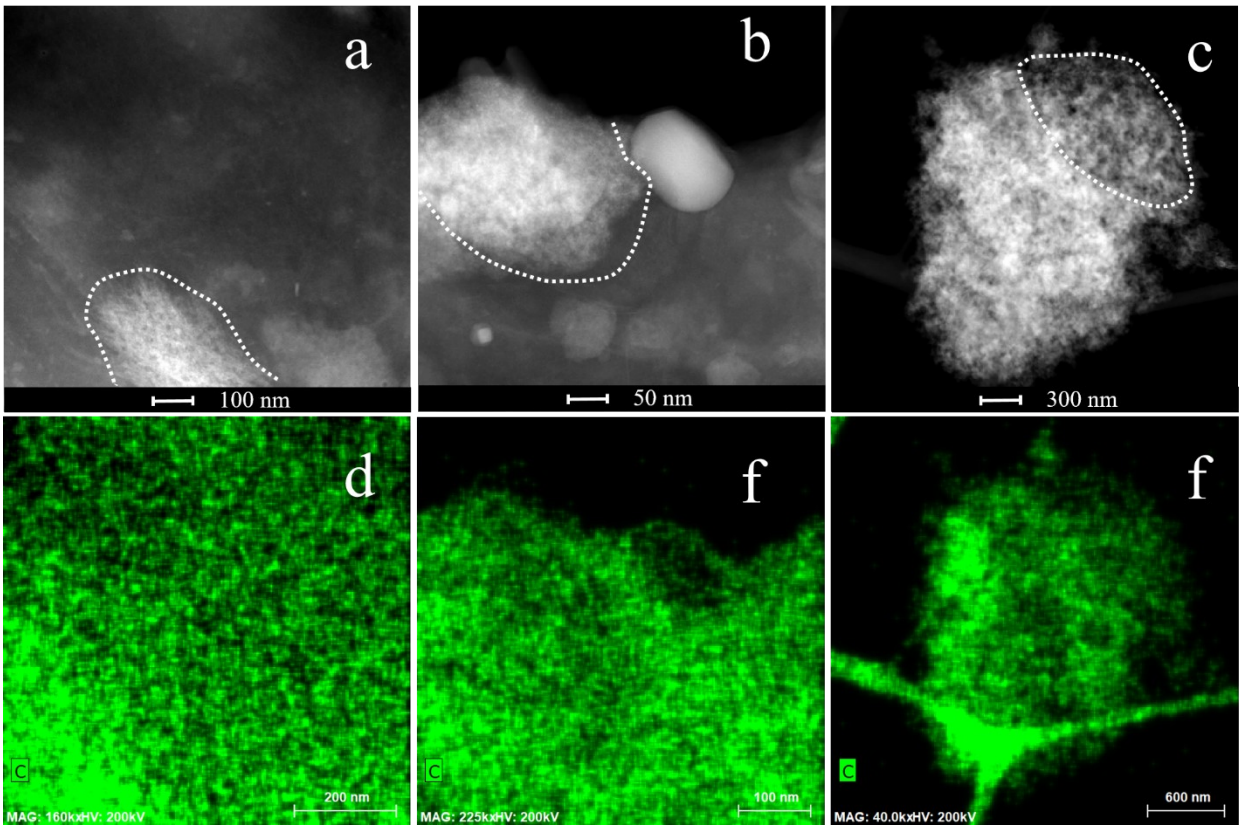


Fig. S4 Morphology of organic colloids: (a-c) STEM images and (d-f) STEM-EDS chemical distribution maps for C (green); (a-c) nanopores or porous zones are visible within organic colloids (highlighted with white dashed lines).

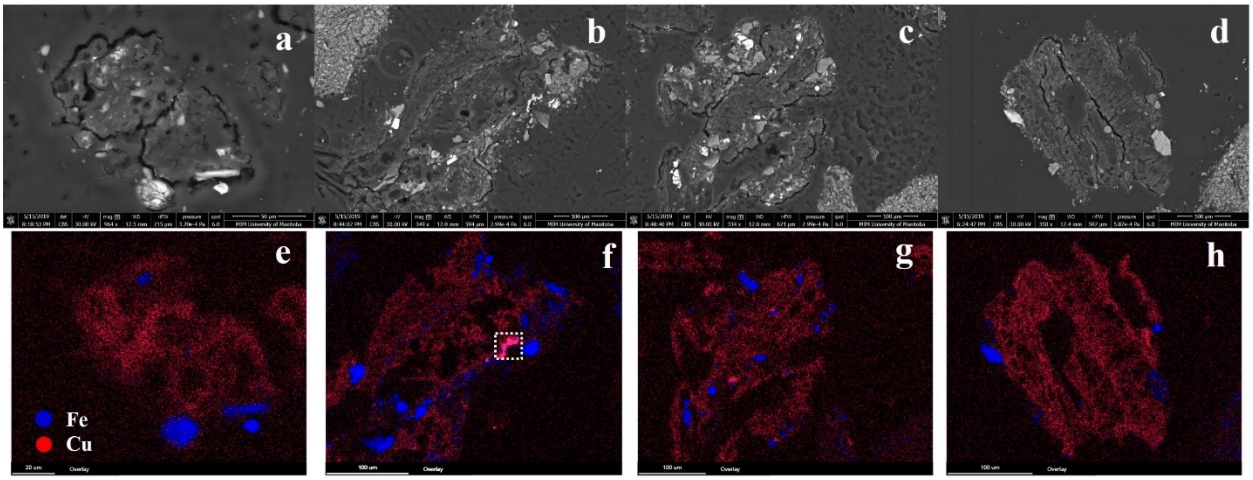


Fig. S5 (a-d) SEM images in backscattering mode (BSE) of organic particles from sample 5A and (e)-(h) their corresponding SEM-EDS chemical distribution maps for Fe (blue) and Si (red). The maps indicate that Cu is homogenously distributed within the OM particles, whereas Fe is concentrated within certain regions.

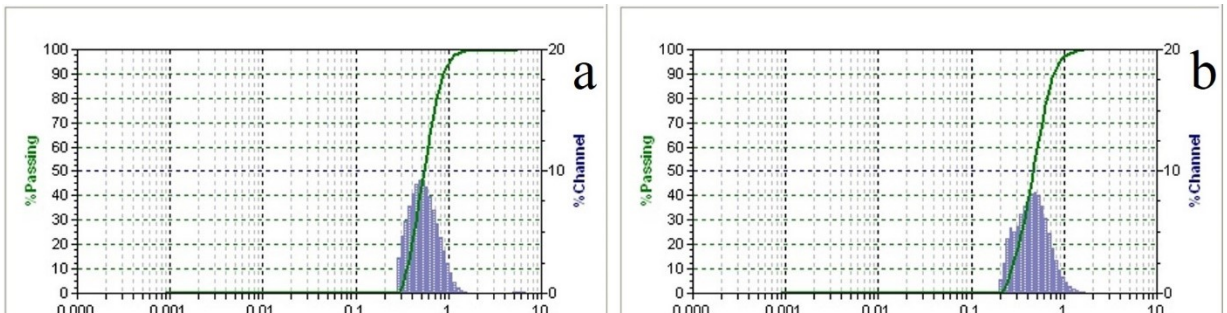


Fig. S6 Dynamic light scattering plots indicating the average particular size of sample (a) 5A and (b) 7A.

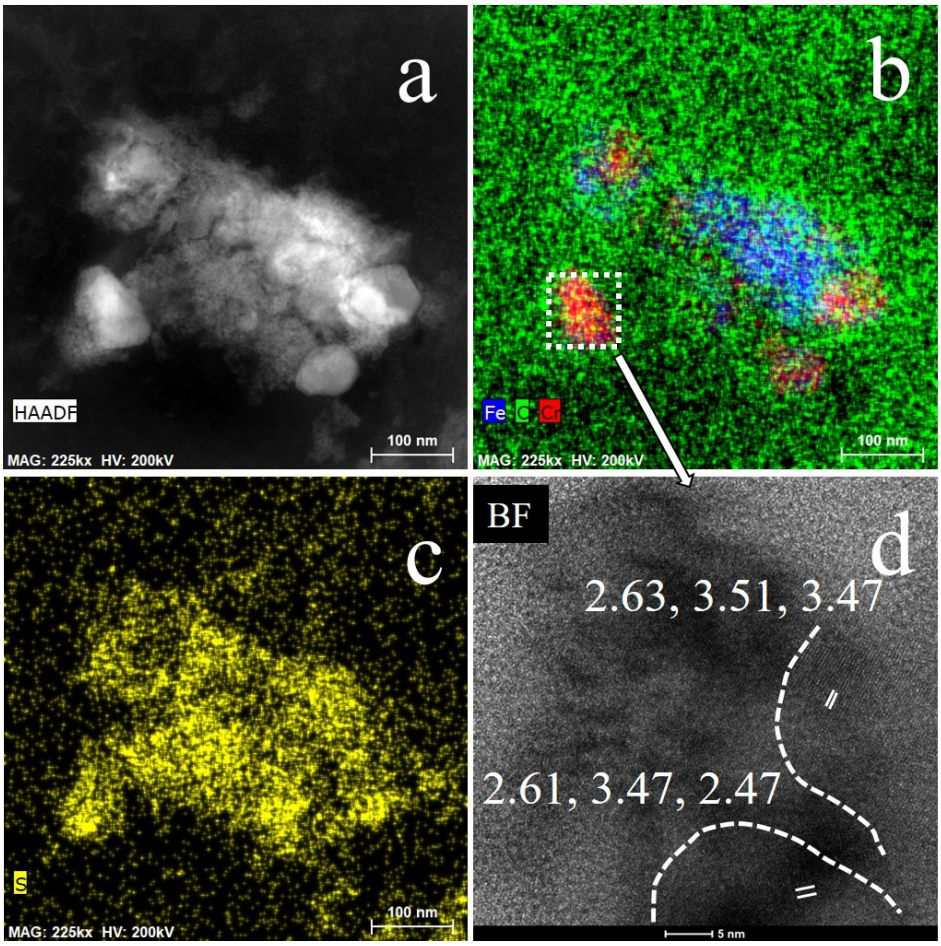


Fig. S7 (a)-(d) Almost euhedral $(Fe,Cr)_2(SO4)_3$ nanoparticles located within organic colloids : (a) STEM image, (b) STEM-EDS chemical distribution maps for Fe (blue), Cr (red) and C (green) and (c) for S (yellow), (d) high-resolution TEM images indicating characterizing lattice fringes (highlighted with solid white lines) within nanodomains $(Fe,Cr)_2(SO4)_3$;all d-spacings are given in [Å].

75

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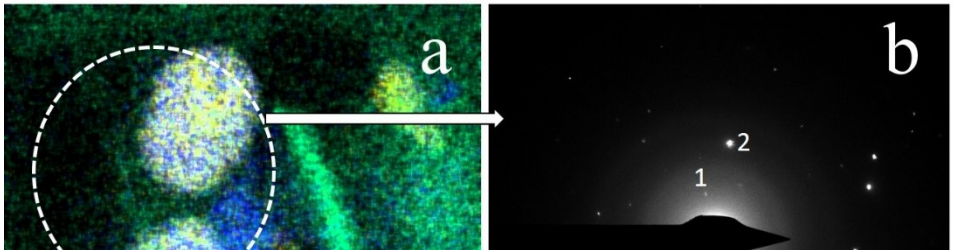

Fig. S8 (a)-(b) Almost euhedral Cr-bearing hematite (Hem) nanoparticles: (a) STEM-EDS chemical distribution maps for Fe (blue), Cr (yellow) and C (green) and (b) selected area diffraction pattern (SAED) of area highlighted by white dashed line in (a).

78

79

80

81

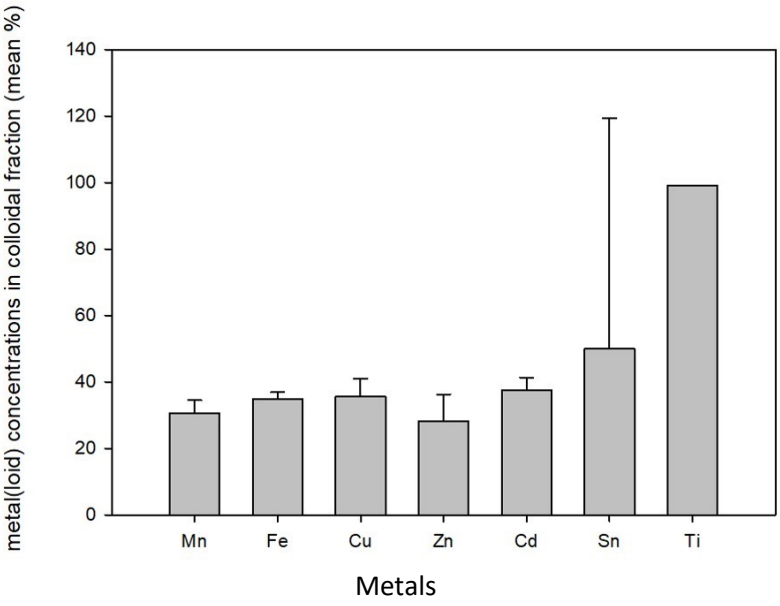

Fig. S9 The proportions of the metals in the colloidal fraction (mean %) with respect to their total concentrations in the leachate.

82

83

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Table. S1 Trace metal(loid) concentrations in all collected samples around the Horne smelter in Rouyn Noranda.

	Trace metal concentration [mgkg^{-1}]							Distance to smelter complex [km]
Sample	Ag	Co	Cu	Pb	Sb	Sn	Zn	
1A	18.8	273	2860	1760	28.4	>90	263	3.5
1B	1.4	68.5	854	226	2.2	8.9	118	3.5
1C	19.2	143	4140	909	25.1	72.3	363	3.5
2A	5.1	296	5320	3830	26.1	>90	773	3.1
2B	2.6	154	789	378	4.8	21.5	83	3.1
2C	9.6	81.3	6120	2100	12.5	57.0	707	3.1
3A	8.8	125	2040	2170	13.7	>90	420	2.9
3B	2.7	123	1010	719	4.7	25.3	255	2.9
3C	1.4	275	523	176	2.1	7.9	516	2.9
4A	9.2	105	2850	602	12.9	29.1	656	2.9
4B	11.3	84.6	3420	836	14.6	36.1	507	2.9
4C	0.5	81.4	131	52.0	1.4	3.3	169	2.9
5A	21.9	174	7970	3100	32.9	>90	1470	1.8
5B	23.4	115	6920	1690	35.4	64.5	1520	1.8
6A	8.1	117	3420	495	10.1	24.8	615	1.2
6B	6.4	81.8	1740	927	15.6	32.4	246	1.2
6C	19.8	118	6540	1460	18.3	44.4	692	1.2
6F	12.8	99.2	3730	609	26.7	32.1	1150	1.2
7A	7.4	184	2690	1260	49.0	>90	4230	1.8
7B	7.3	88.0	3830	2023.9	42.6	>90	2178	1.8
7C	5.3	118	1900	875.1	38.9	>90	1480	1.8
Average	10	138	3276	1248	20	33	887	