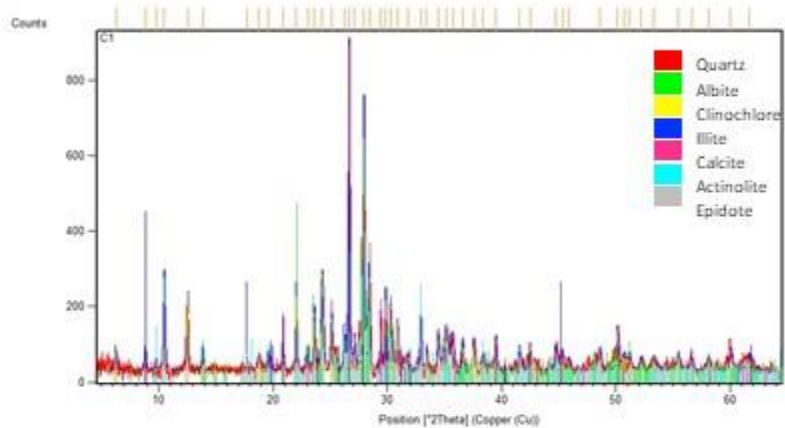


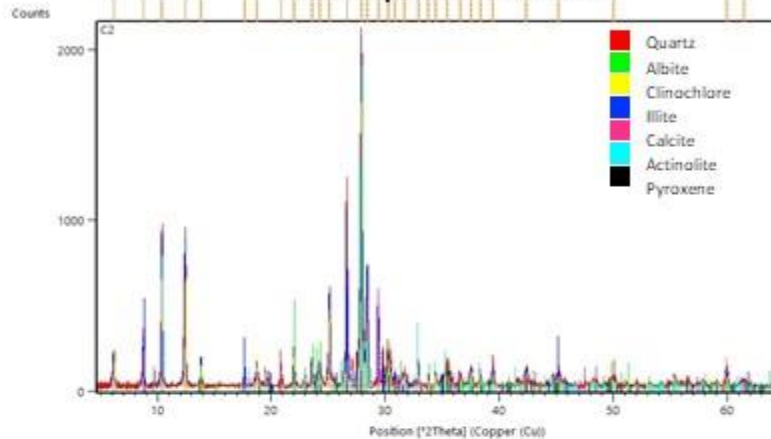
# Supplementary Data A

X-ray diffraction pattern from samples collected at  
site A and B tailings sites

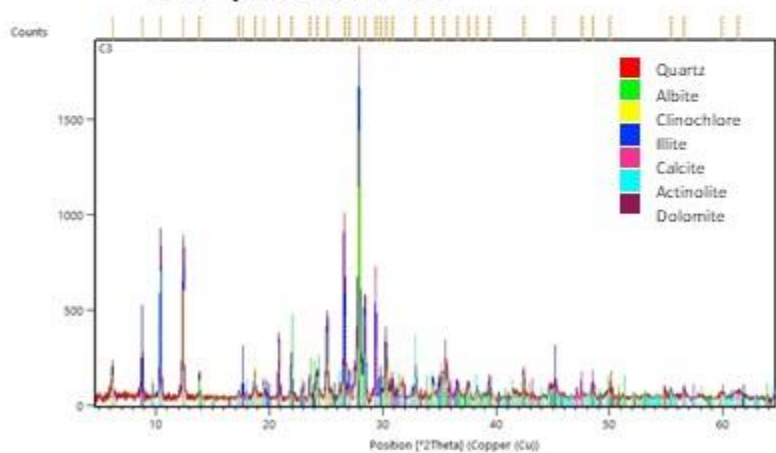
Sample No. A-1



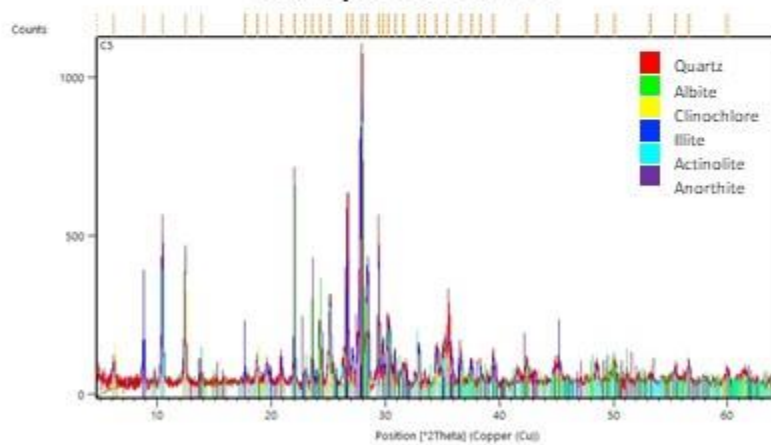
Sample No. A-2



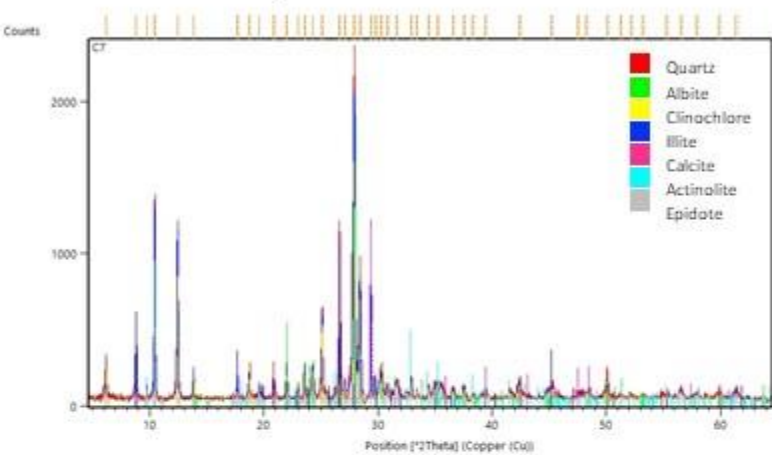
Sample No. A-3



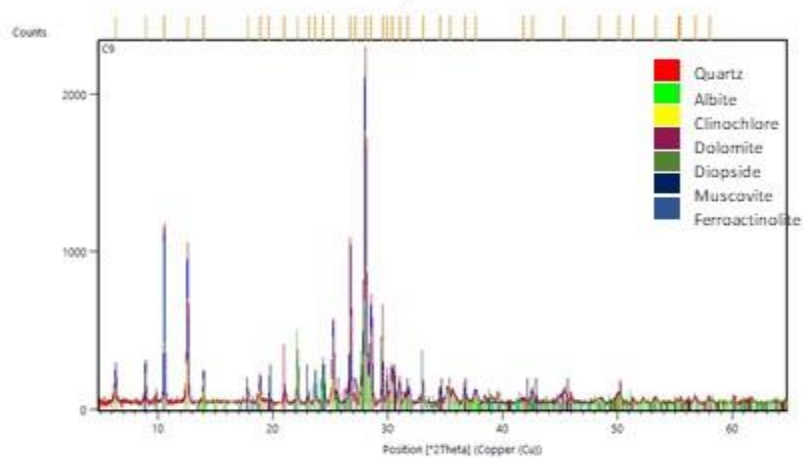
Sample No. A-5



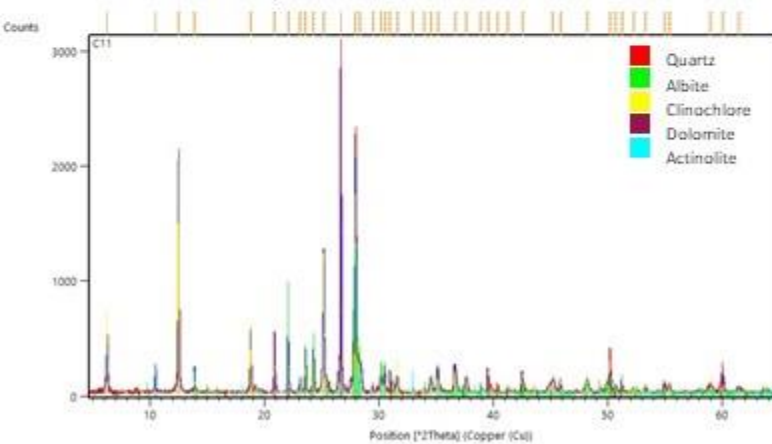
Sample No. A-7



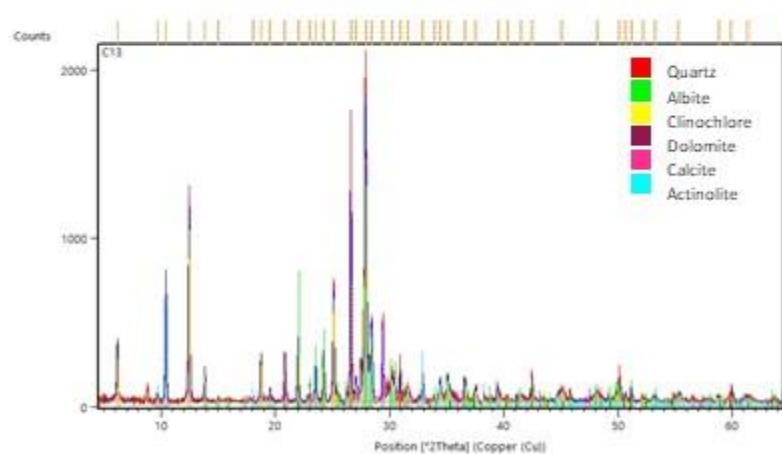
Sample No. A-9



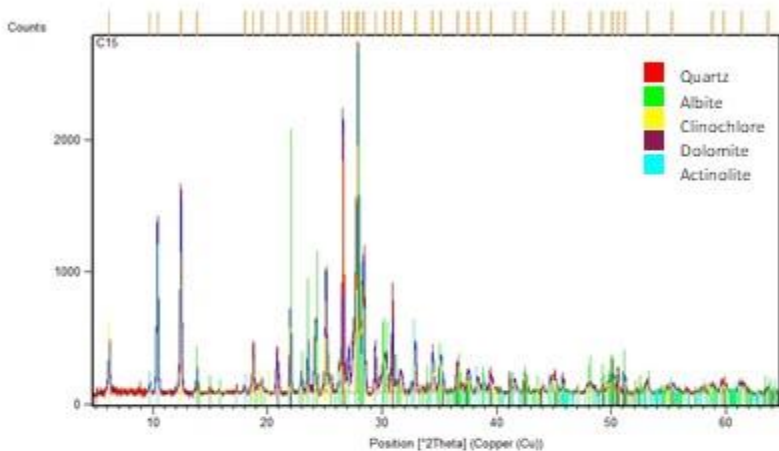
Sample No. A-11



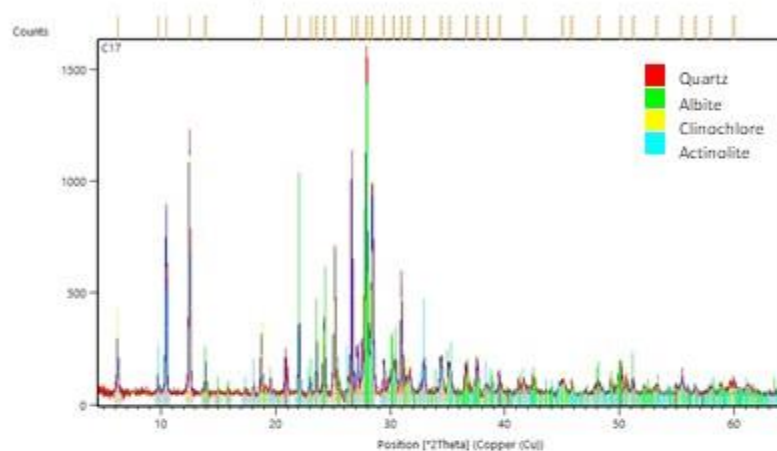
Sample No. A-13



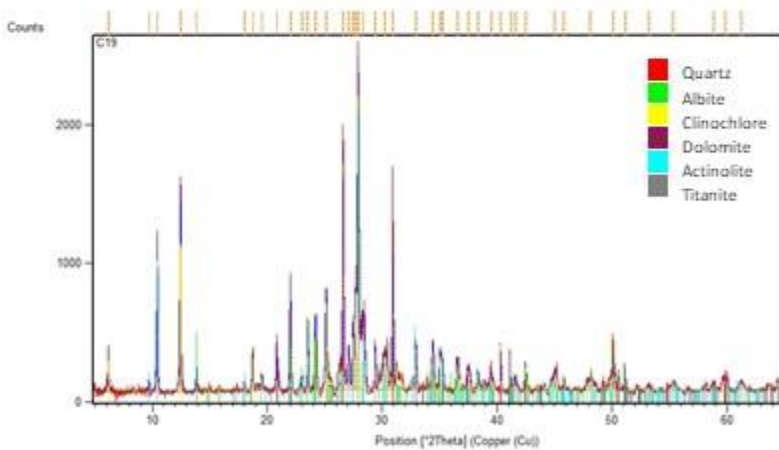
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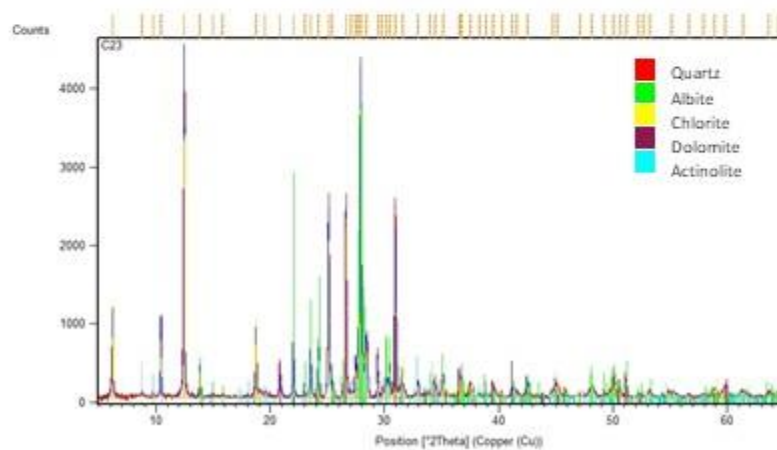
### Sample No. A-17



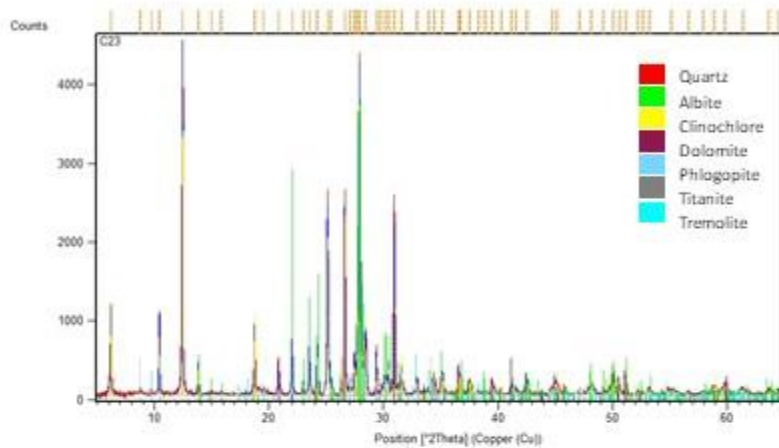
### Sample No. A-19



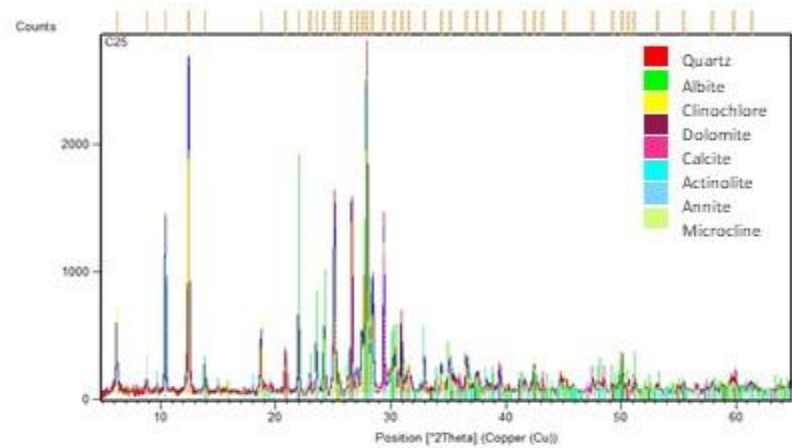
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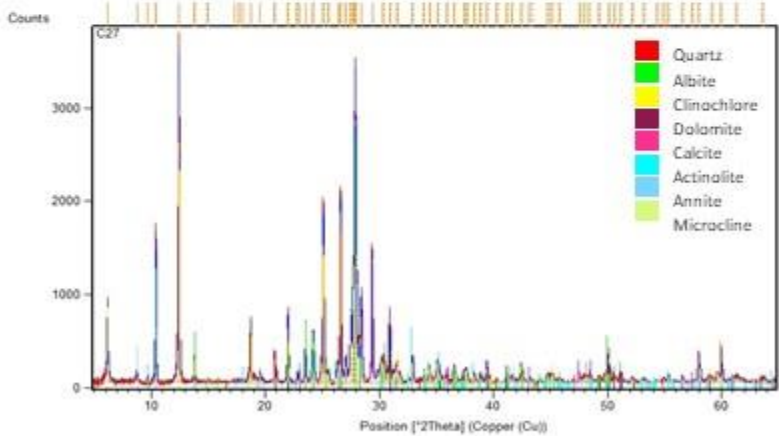
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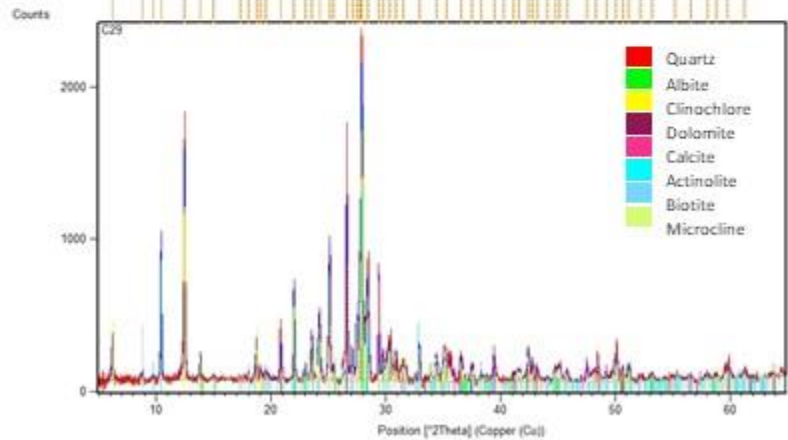
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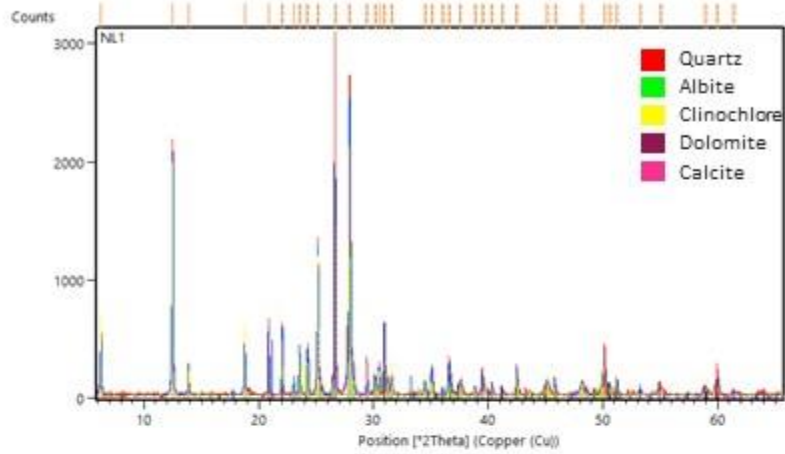
### Sample No. A-27



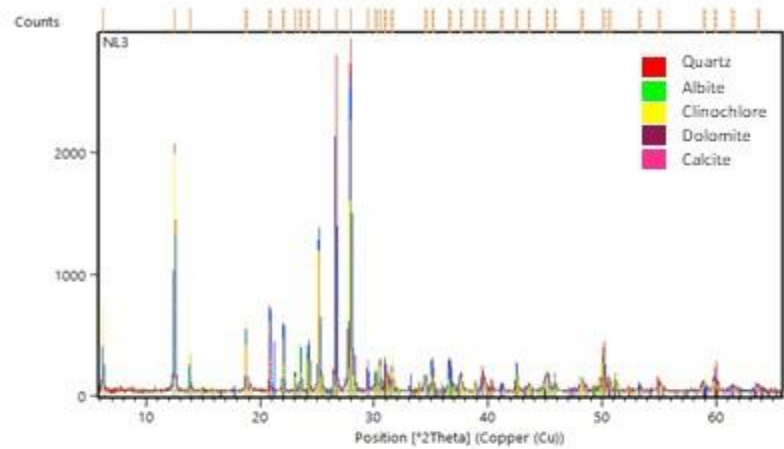
### Sample No. A-29



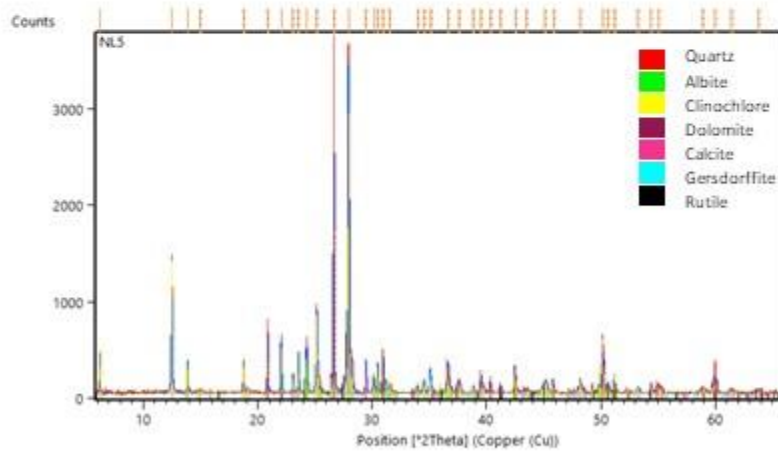
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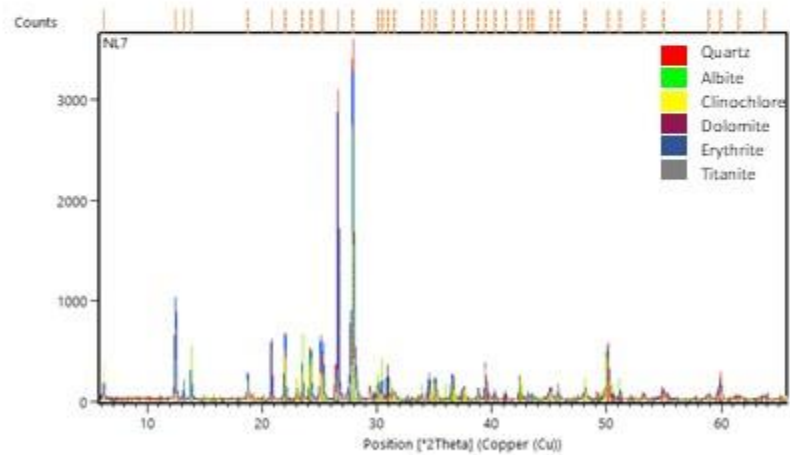
### Sample No. B-3



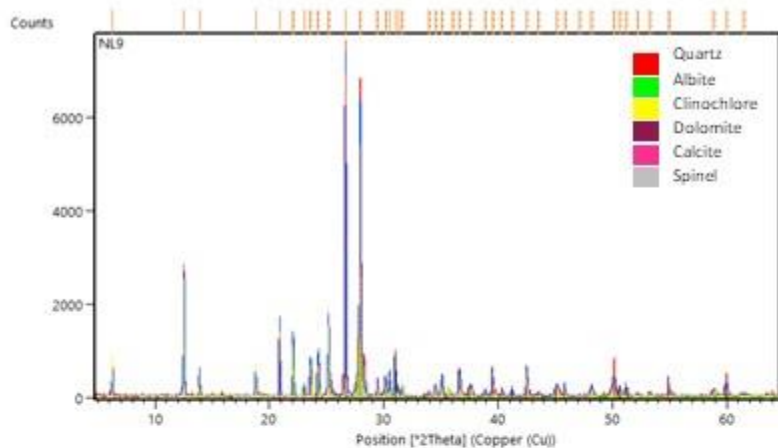
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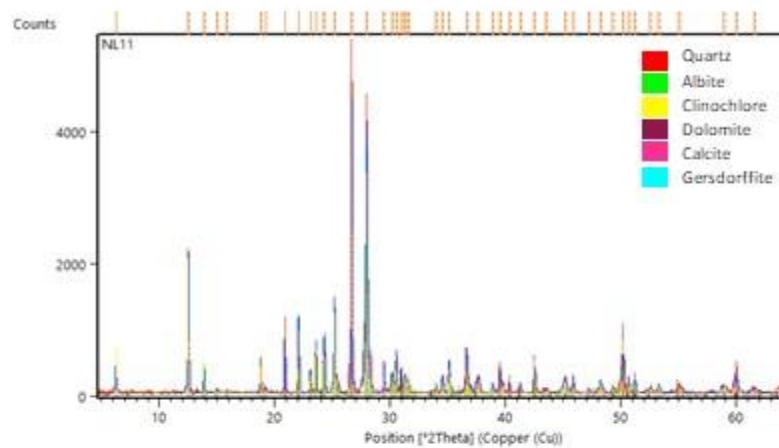
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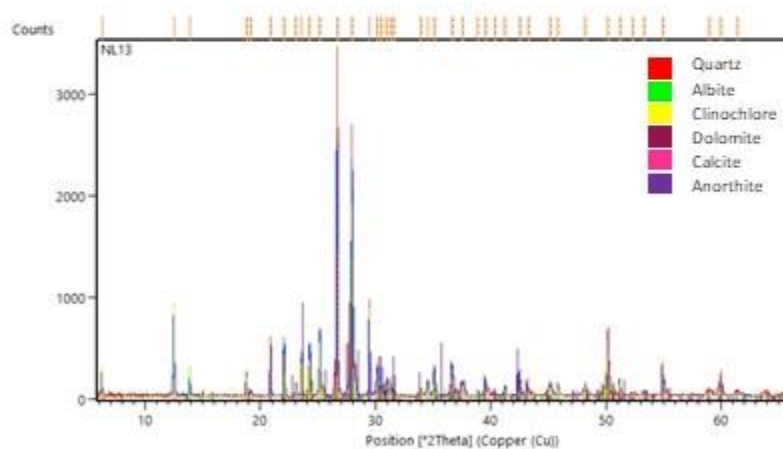
### Sample No. B-9



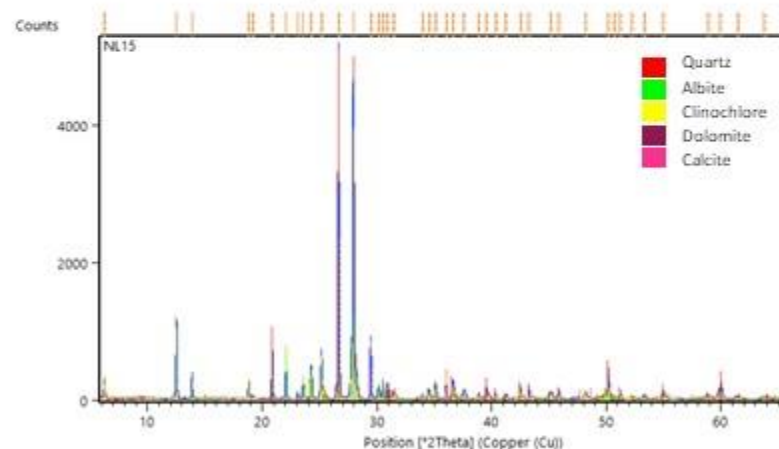
### Sample No. B-11



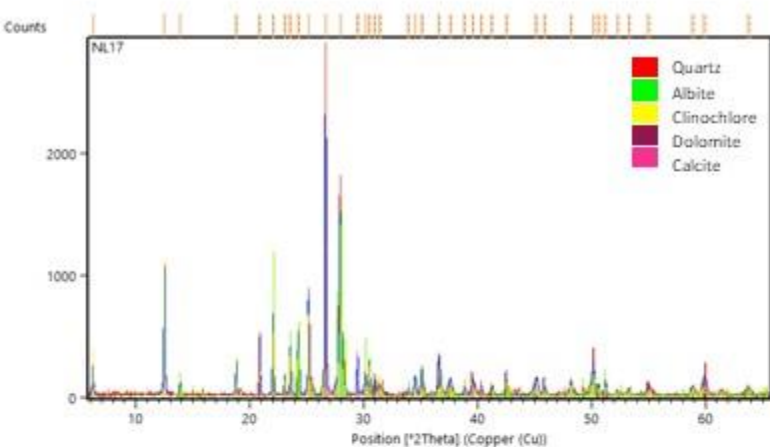
### Sample No. B-13



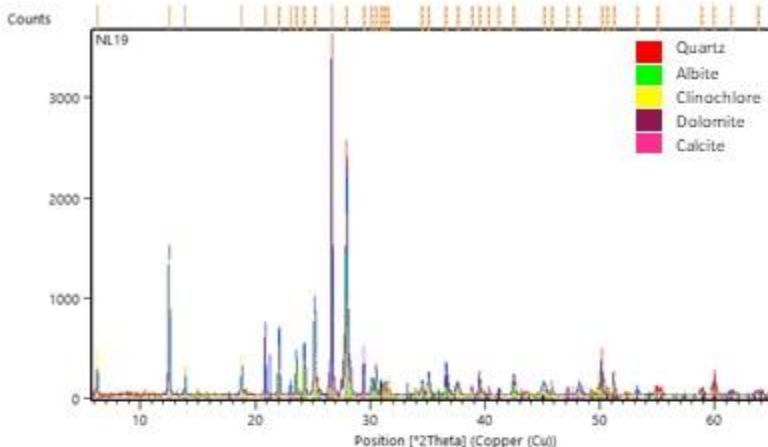
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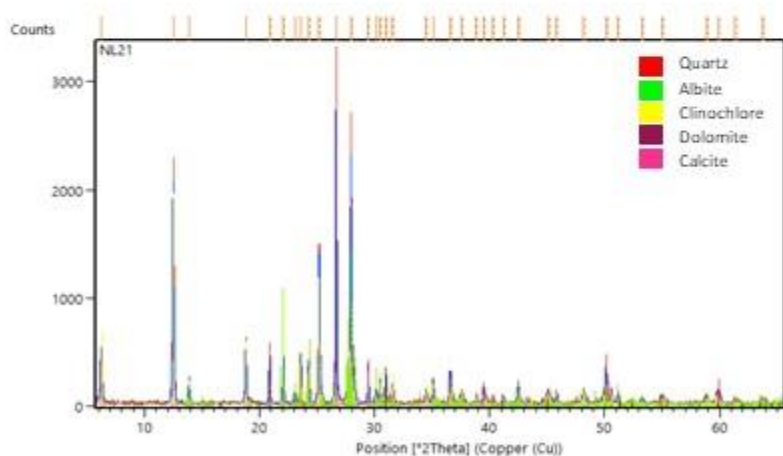
Sample No. B-17



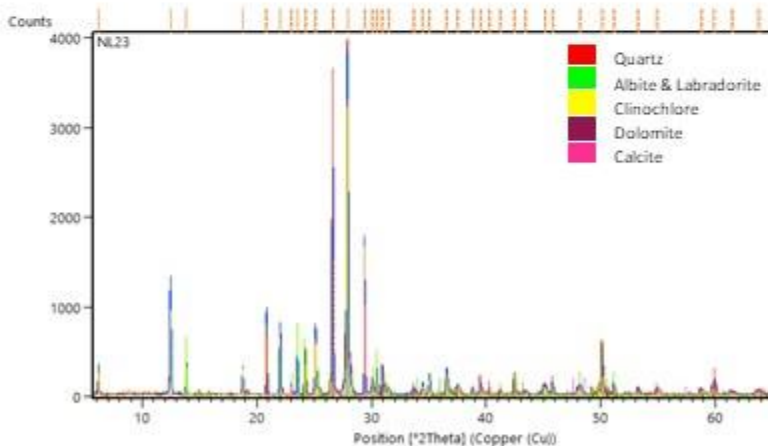
Sample No. B-19



Sample No. B-21

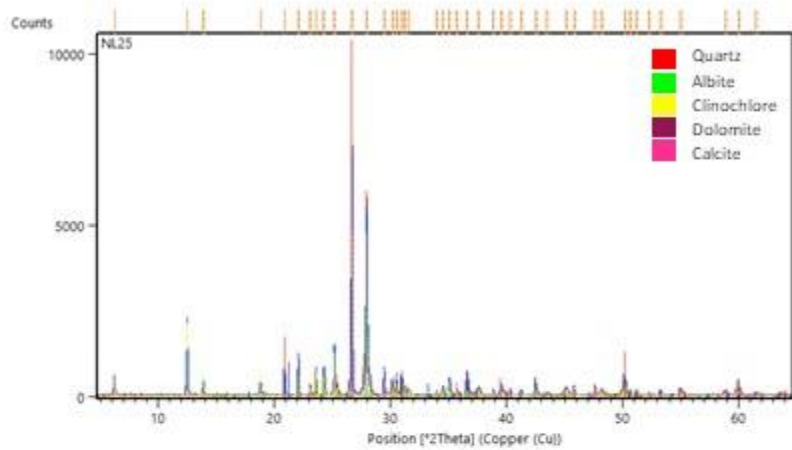


Sample No. B-23

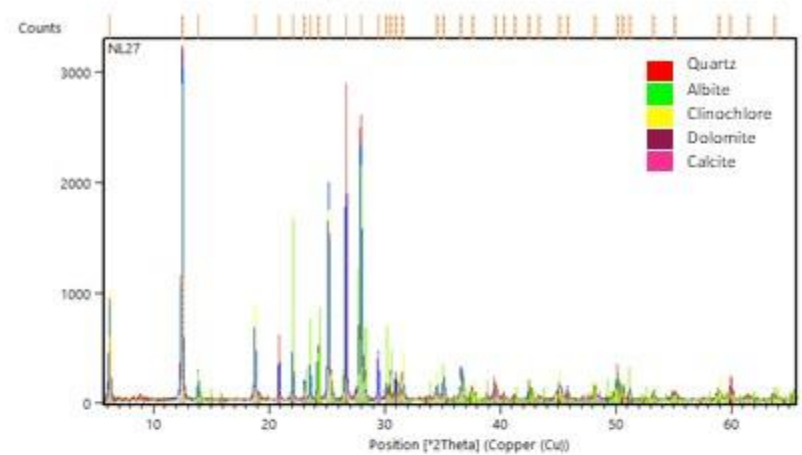




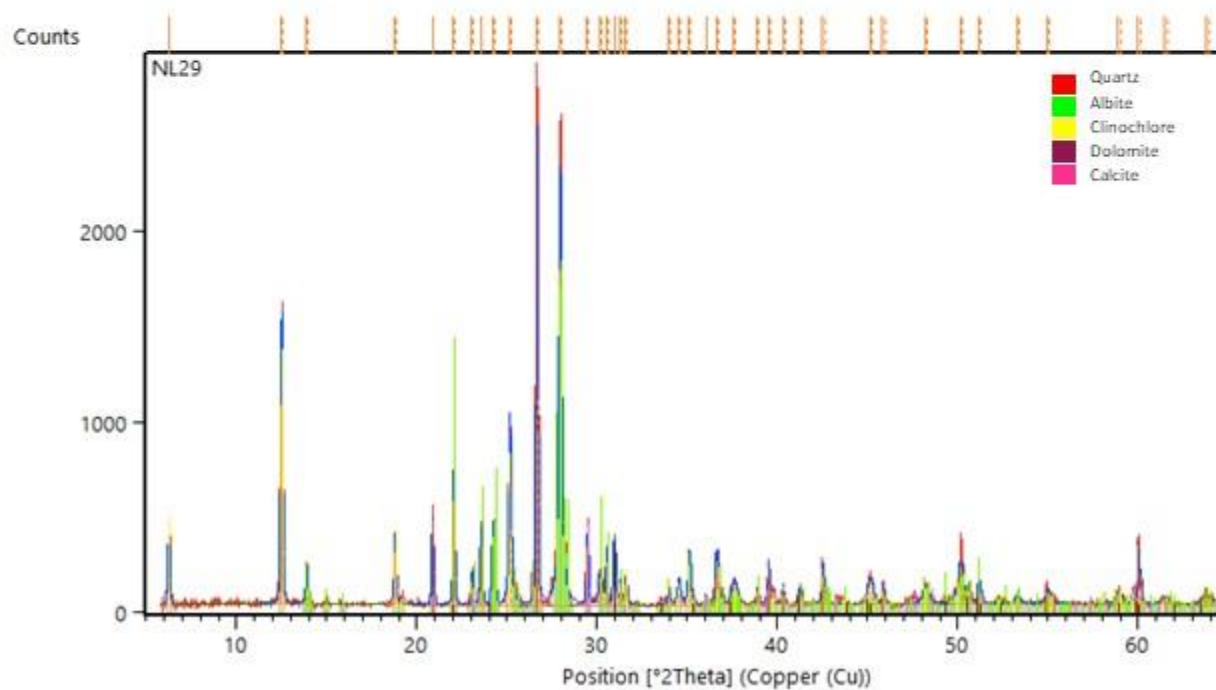
### Sample No. B-25



### Sample No. B-27

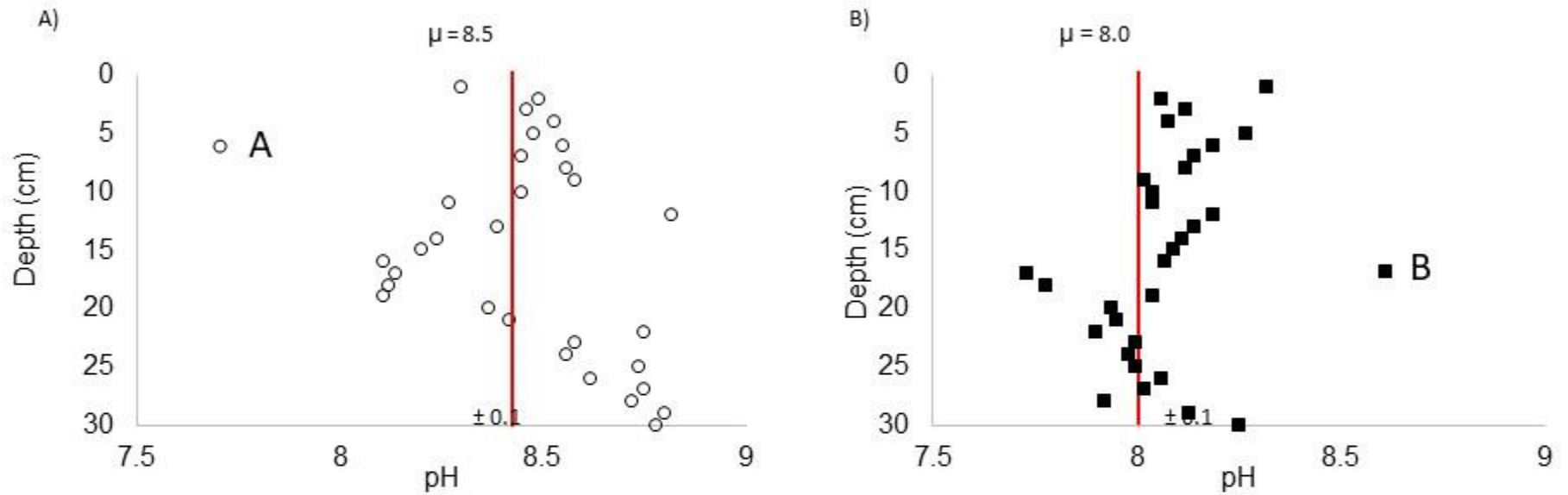


### Sample No. B-29



# Supplementary data B

Change of contact pH with depth



A and B: Plot of contact pH value versus depth for the two depth profiles

# Supplementary data C

## Chemical composition of the tailing samples, Nipissing low grade mine tailings

FINAL RESULTS wt% or (mg/Kg)																					
ELRFS LABEL	Ag	Al	As	Ca	Co	Cu	Fe	Hg	K	Mn	Mo	Na	P	Pb	Sb	Se	Ti	V	Zn	Zr	
Units	ppm	wt%	wt%	wt%	ppm	ppm	wt%	ppm	wt%	ppm	ppm	wt%	ppm	ppm	ppm	ppm	wt%	ppm	ppm	ppm	
NL = Nipissing- low tailings site																					
NL-1	4.19	7.78	0.313	2.37	937	414	5.32	1	0.587	906	1.5	3.62	577	396	333	2.81	0.424	155	318	101	
NL-2	6.91	8.22	0.303	2.45	1020	411	6.06	4.29	0.58	1020	1.5	3.63	651	467	328	3.06	0.46	172	388	106	
NL-3	6.95	7.61	0.268	2.25	936	375	5.54	3.52	0.562	928	1.5	3.43	595	416	268	2.4	0.437	158	317	102	
NL-4	6.41	7.38	0.296	2.19	997	396	5.53	4.7	0.514	926	1.5	3.38	578	455	278	2.49	0.429	156	329	99.1	
NL-5	8.67	7.74	0.344	2.31	1070	485	5.28	2.6	0.519	895	1.5	3.71	562	429	250	1.24	0.446	150	326	106	
NL-6	6.61	7.42	0.376	2.23	1040	560	4.88	4.51	0.463	841	1.5	3.62	496	442	245	2.13	0.407	137	314	94.1	
NL-7	5.82	7.24	0.411	2.2	1170	562	5	6.34	0.5	865	1.5	3.5	522	447	254	1.79	0.437	139	345	101	
NL-8	8.11	7.57	0.428	2.33	1090	661	5.14	2.57	0.462	909	1.5	3.67	510	526	283	2.82	0.423	143	319	97.7	
NL-9	14.5	7.76	0.868	2.08	2340	834	4.93	1	0.465	847	5.35	4	512	673	370	1.7	0.47	137	449	113	
NL-10	9.47	7.37	0.838	1.875	2190	761.5	4.73	1.93	0.4515	811	6.385	3.825	533	589	343	1.4675	0.4925	132.5	409.5	113	
NL-11	8.88	7.64	1.03	2.18	2720	882	5.04	1	0.469	861	8.25	3.93	587	777	423	1.64	0.503	137	478	125	
NL-12	10.1	7.32	0.506	2.27	1140	615	4.64	1	0.472	825	3.58	3.68	480	540	261	0.991	0.446	133	291	97.6	
NL-13	14.1	7.85	0.56	2.51	1270	663	5.4	1	0.505	946	3.75	3.73	536	642	321	1.95	0.468	153	356	105	
NL-14	12.3	7.61	0.471	2.19	1080	541	4.79	1	0.522	843	6.23	3.84	471	478	236	1.47	0.468	141	335	101	
NL-15	12.8	7.61	0.616	2.25	1490	681	4.99	1	0.513	871	6.93	3.76	524	588	285	1.29	0.488	143	391	110	
NL-16	9.24	7.38	0.463	2.39	1150	609	5.5	1	0.493	948	1.5	3.3	566	761	318	1.72	0.432	156	374	93.3	
NL-17	5.96	6.32	0.508	2.05	1280	614	5.22	8.96	0.481	904	3.19	2.88	559	730	309	1.18	0.437	146	396	94.7	
NL-18	11.5	7.41	0.524	2.25	1420	638	5.26	2.17	0.49	933	3.16	3.41	560	745	290	1.07	0.44	149	426	94.8	
NL-19	13	7.61	0.558	2.41	1190	735	5.52	1	0.51	948	3.31	3.53	548	902	363	0.3	0.445	154	332	97.9	
NL-20	7.88	7.04	0.503	2.23	1180	672	5.11	1	0.472	877	3.11	3.25	506	807.5	323.5	0.7675	0.3945	139.5	345.5	87.35	
NL-21	5.11	7.22	0.543	2.36	1210	746	5.38	2.43	0.482	942	3.27	3.22	559	896	382	1.73	0.398	148	472	89.3	
NL-22	11.2	7.42	0.613	2.35	1410	858	5.48	6.52	0.509	951	4.33	3.24	581	951	432	1.57	0.415	150	495	94.6	
NL-23	9.53	7.50	0.597	2.59	1260	750	5.45	1	0.485	956	3.42	3.45	595	1040	383	0.3	0.435	152	502	98.3	
NL-24	10	7.84	0.406	2.67	982	529	6.81	1	0.5	1100	1.5	3.18	658	856	401	1.6	0.435	191	438	97.7	
NL-25	13.9	7.93	0.65	2.69	1470	900	6.02	4.9	0.519	1050	4.34	3.53	646	1140	440	1.08	0.454	167	583	101	
NL-26	11.6	8.04	0.547	2.65	1390	701	6.27	1	0.544	1060	3.12	3.67	660	964	387	1.16	0.477	176	445	106	
NL-27	6.99	7.02	0.375	2.56	1150	443	5.92	9.92	0.504	1010	1.5	3.1	663	445	298	0.893	0.458	164	275	96.4	
NL-28	6.1	7.28	0.39	2.51	979	503	6.57	9.6	0.482	1060	1.5	2.92	634	832	388	1.42	0.416	181	403	93.5	
NL-29	6.16	6.42	0.341	2.33	1080	360	4.84	5.06	0.457	846	1.5	3.07	564	285	226	1.29	0.418	134	190	88.3	
NL-30	7.06	7.44	0.5	2.785	1680	412.5	5.895	2.325	0.668	1034	3.91	3.9	753.5	276.5	243	1.55	0.5635	161.5	220.5	122.5	

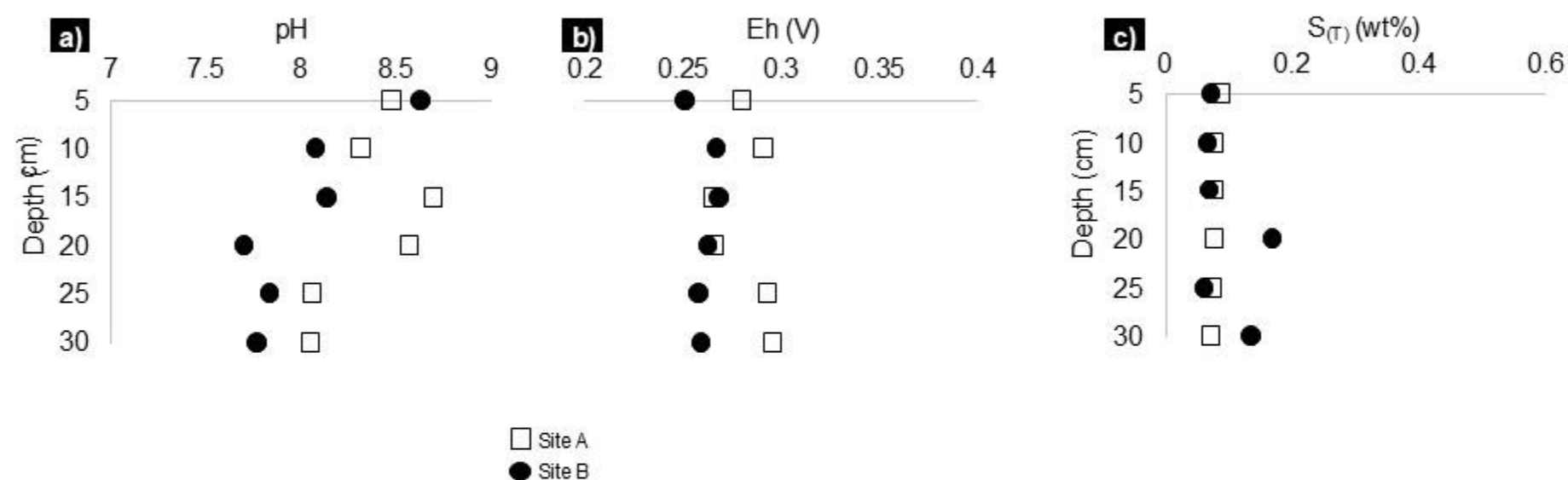
# Supplementary data C

## Chemical composition of the tailing samples, Crosswise lake mine tailings

FINAL RESULTS (mg/Kg)																					
ELRFS LABEL	Ag	Al	As	Ca	Co	Cu	Fe	Hg	K	Mn	Mo	Na	P	Pb	Sb	Se	Ti	V	Zn	Zr	
C = Crosswise Lake tailings site	ppm	wt%	wt%	wt%	ppm	ppm	wt%	ppm	wt%	ppm	ppm	wt%	ppm	ppm	ppm	ppm	wt%	ppm	ppm	ppm	
C-1		53	10.40	0.214	11.8	922	236	10	1	1.61	2550	1.5	2.11	542	84	35.5	1.34	0.554	314	135	97
C-2		6.52	5.30	0.161	6.31	699	175	7.53	1	1.19	1900	1.5	1.28	327	67.2	23.8	1.96	0.491	207	92.2	63.5
C-3		4.61	6.37	0.144	7.03	780	184	7.63	1	1.24	1920	1.5	1.51	321	51.1	24.1	0.824	0.451	227	84.2	59.7
C-4		2.37	6.77	0.125	7.19	725	191	7.85	1	1.3	2040	1.5	1.66	329	50.9	19.8	2.24	0.492	247	94.5	60.3
C-5		3.42	7.05	0.0975	7.07	616	181	7.58	1	1.25	1970	1.5	1.8	303	50.4	17.5	1.26	0.47	245	90.9	59.9
C-6		4.44	7.48	0.108	7.68	674	189	8.27	1	1.39	2140	1.5	1.95	342	54.9	19.1	3.29	0.535	265	97.4	65.3
C-7		4.16	6.63	0.115	6.68	579	187	7.73	1	1.28	1870	1.5	1.69	358	61.5	14.7	1.45	0.463	245	104	58.4
C-8		4.01	7.01	0.0967	6.81	525	178	7.67	1	1.24	1860	1.5	1.95	376	67	13.1	1.56	0.493	263	106	62.3
C-9		4.53	7.18	0.0796	5.38	452	169	7.86	1	1.08	1710	1.5	2.56	571	67	10.4	1.84	0.651	269	130	81.3
C-10		5.4	7.90	0.196	2.44	1100	134.5	7.63	1	0.74	1093.5	1.5	2.885	748	67	13.35	2.79	0.524	202.5	130.5	110.5
C-11		3.5	8.03	0.209	1.03	1280	93.4	6.76	1	0.57	695	1.5	3.14	805	67	11.3	1.76	0.404	155	103	113
C-12		5.32	8.36	0.186	1.73	1140	113	7.38	1	0.676	930	1.5	3.2	792	67	12.4	2.13	0.464	186	117	111
C-13		6.13	7.47	0.166	4.33	471	160	7.31	1	1.12	1720	1.5	3.05	801	67	14	1.15	0.65	249	184	103
C-14		5.69	7.17	0.285	6.21	641	221	9.41	1	1.56	2750	1.5	2.45	882	67	20.8	1.31	0.732	329	304	87.6
C-15		5.14	6.58	0.276	5.23	581	350	9.9	1	1.21	2870	1.5	2.61	1230	67	22.5	1.61	0.826	342	433	92.4
C-16		4.81	6.51	0.251	4.84	547	288	8.75	1	0.999	2560	1.5	2.54	1120	67	19.6	1.24	0.733	319	402	81.8
C-17		5.61	5.23	0.197	4.09	303	247	8.71	1	1.31	2400	1.5	2.7	1100	67	19.3	2.71	0.989	293	329	102
C-18		5.17	7.07	0.196	4.75	325	228	8.41	1	1.18	2370	1.5	3.28	1050	67	17.8	0.663	0.909	319	316	93.6
C-19		5.48	7.05	0.244	4.79	478	254	8.87	1	1.18	2430	1.5	3.2	1080	67	21.5	2.35	0.93	323	348	98.9
C-20		5.68	8.04	0.417	1.585	2120	173	8.01	10	6.295	1185	1.5	3.13	951.5	67	23.4	2.635	0.5015	205.5	439.5	122
C-21		3.1	7.80	0.259	2.68	1150	148	7.72	1	0.913	1530	1.5	3.01	841	67	23	1.64	0.573	251	283	87.9
C-22		4.4	8.10	0.201	4.95	586	181	8.71	1	1.26	2200	1.5	3.06	856	67	27.4	1.11	0.743	338	247	69.6
C-23		4.86	7.67	0.229	4.85	636	213	9.01	1	1.23	2250	1.5	2.83	865	67	32.2	1.27	0.732	340	283	69.9
C-24		5.83	9.04	0.262	6.19	865	247	11.2	1	1.45	2760	1.5	3.17	1060	67	43.1	2.14	0.81	406	335	84.4
C-25		5.92	8.94	0.121	6.61	465	131	10.3	1	1.53	2540	1.5	3.26	1020	67	25.1	1.75	0.807	360	178	81.5
C-26		2.87	7.37	0.0479	5.11	225	73.8	7.61	1	1.23	1860	1.5	2.7	727	67	13	1.29	0.625	262	109	63.2
C-27		4.01	5.52	0.0484	4.56	233	128	7.44	1	1.23	1800	1.5	1.95	757	67	13.2	2.26	0.65	241	118	64.7
C-28		4.38	6.77	0.0534	5.13	251	85.3	7.86	1	1.27	1920	1.5	2.46	783	67	14.7	1.71	0.674	262	115	68.9
C-29		4.38	7.11	0.0449	5.15	221	101	7.73	1	1.25	1890	1.5	2.6	731	67	14.4	1.66	0.659	260	113	67.7
C-30		4.71	6.82	0.0647	5.54	281	168.5	8.685	1	1.27	2180	1.5	2.38	873.5	67	19.7	1.197	0.8	282.5	138.5	73.7

## Supplementary data D

Chemical data from two additional profiles at site A and B sampled by Courchesne et al. 2019



**S13** Additional geochemical data of site A and B from Courchesne et al. (2021)

(a) Contact pH, (b) Eh and (c) total sulfur

# Supplementary Data E

**S 14** Visual Minteq calculations using the pore water chemistry C17 from Percival, J.B., Kwong, Y.T.J. Dumaresq, C.G., Michel, F.A. (2004) Transport and attenuation of arsenic, cobalt and nickel in an alkaline environment (Cobalt, Ontario) Geological Survey of Canada Open File 1680 and the thermodynamic data for  $\text{FeOHCO}_3$  with  $\log K = 10.76$  from Grivé, M., Duro, L., Bruno, J. (2014) Fe(III) mobilisation by carbonate in low temperature environments: Study of the solubility of ferrihydrite in carbonate media and the formation of Fe(III) carbonate complexes Applied Geochemistry 49, 57–67.

H+1	0
Ag+1	98.0
Al+3	364.7
As(V)	114800.0
Ba+2	14.2
Ca+2	40800.0
Cd+2	2.36
Co+2	3721.0
Cr(III)	16.57
Cu+2	1291.0
Fe+3	879.0
Hg(II)	226.6
Mg+2	3503.0
Mn+2	10.97
Mo(VI)	479.8
Na+1	283900.0
Ni+2	1035.0
P (PO4)	418.0
Pb+2	3091.0
Rb+1	25.58
S (SO4)	159000.0
Sb(V)	2949.0
Si (H4SiO4)	11590.0
Sr+2	144.0
Ti(IV)	54.4
V(V)	78.6
W(VI)	2.28
Zn+2	12.85

pH = 8

Total concentrations  
 $\mu\text{g L}^{-1}$

**S 15** Assumption 1: pore water in equilibrium with calcite,  
Ionic strength = 0.0216

Output data for Fe-species:

Concentration Activity Log activity

Species	Concentration	Activity	Log activity
Fe(CO <sub>3</sub> ) <sub>3</sub>	2.4938E-10	6.8728E-11	-10.163
Fe(OH) <sub>2</sub> <sup>+</sup>	1.4844E-08	1.2864E-08	-7.891
Fe(OH) <sub>3</sub> (aq)	7.1953E-10	7.2312E-10	-9.141
Fe(OH) <sub>4</sub> <sup>-</sup>	1.6644E-09	1.4423E-09	-8.841
Fe(SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	1.163E-18	1.0078E-18	-17.997
Fe <sup>+3</sup>	2.6266E-18	7.2388E-19	-18.14
Fe <sub>2</sub> (OH) <sub>2</sub> <sup>+4</sup>	6.6086E-23	6.6839E-24	-23.175
Fe <sub>3</sub> (OH) <sub>4</sub> <sup>+5</sup>	7.0018E-28	1.9516E-29	-28.71
FeH <sub>2</sub> PO <sub>4</sub> <sup>+2</sup>	1.9065E-20	1.0751E-20	-19.969
FeHPO <sub>4</sub> <sup>+</sup>	3.3779E-14	2.9272E-14	-13.534
FeOH <sup>+2</sup>	1.2254E-12	6.9106E-13	-12.16
FeOHCO <sub>3</sub>	0.000015722	0.000015801	-4.801
FeSO <sub>4</sub> <sup>+</sup>	3.5786E-17	3.1011E-17	-16.508

Output data for Fe-minerals:

Mineral log IAP Sat. index

Mineral	log IAP	Sat. index
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (s)	-44.135	-40.401
FeAsO <sub>4</sub> ·2H <sub>2</sub> O(s)	-25.031	-4.831
Ferrihydrite	5.859	2.659
Ferrihydrite (aged)	5.859	3.169
Goethite	5.859	5.368

Species distribution for Fe<sup>3+</sup>-species:

FeOHCO <sub>3</sub>	99.889
Fe(OH) <sub>2</sub> <sup>+</sup>	0.094
Fe(OH) <sub>4</sub> <sup>-</sup>	0.011

## S16 Assumption 2: pore water in equilibrium with CO<sub>2</sub> atmosphere

Ionic strength = 0.0216

Output data for Fe-species:

Concentration Activity Log activity

Fe(CO <sub>3</sub> ) <sub>3</sub>	1.2177E-10	3.4655E-11	-10.46
Fe(OH) <sub>2</sub> <sup>2+</sup>	2.0807E-08	1.8095E-08	-7.742
Fe(OH) <sub>3</sub> (aq)	1.0125E-09	1.0172E-09	-8.993
Fe(OH) <sub>4</sub> <sup>-</sup>	2.333E-09	2.0289E-09	-8.693
Fe(SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	1.848E-18	1.6072E-18	-17.794
Fe <sup>3+</sup>	3.5781E-18	1.0183E-18	-17.992
Fe <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup>	1.2351E-22	1.3226E-23	-22.879
Fe <sub>3</sub> (OH) <sub>4</sub> <sup>5+</sup>	1.7827E-27	5.4326E-29	-28.265
FeH <sub>2</sub> PO <sub>4</sub> <sup>2+</sup>	2.9558E-20	1.6909E-20	-19.772
FeHPO <sub>4</sub> <sup>+</sup>	5.2935E-14	4.6037E-14	-13.337
FeOH <sup>2+</sup>	1.6994E-12	9.7212E-13	-12.012
FeOHCO <sub>3</sub>	0.000015715	0.000015789	-4.802
FeSO <sub>4</sub> <sup>+</sup>	5.3408E-17	4.6448E-17	-16.333

Output data for Fe-minerals:

Mineral	log IAP Sat. index	
FeAsO <sub>4</sub> ·2H <sub>2</sub> O(s)	-24.877	-4.677
Ferrihydrite	6.007	2.807
Ferrihydrite (aged)	6.007	3.317
Goethite	6.007	5.516

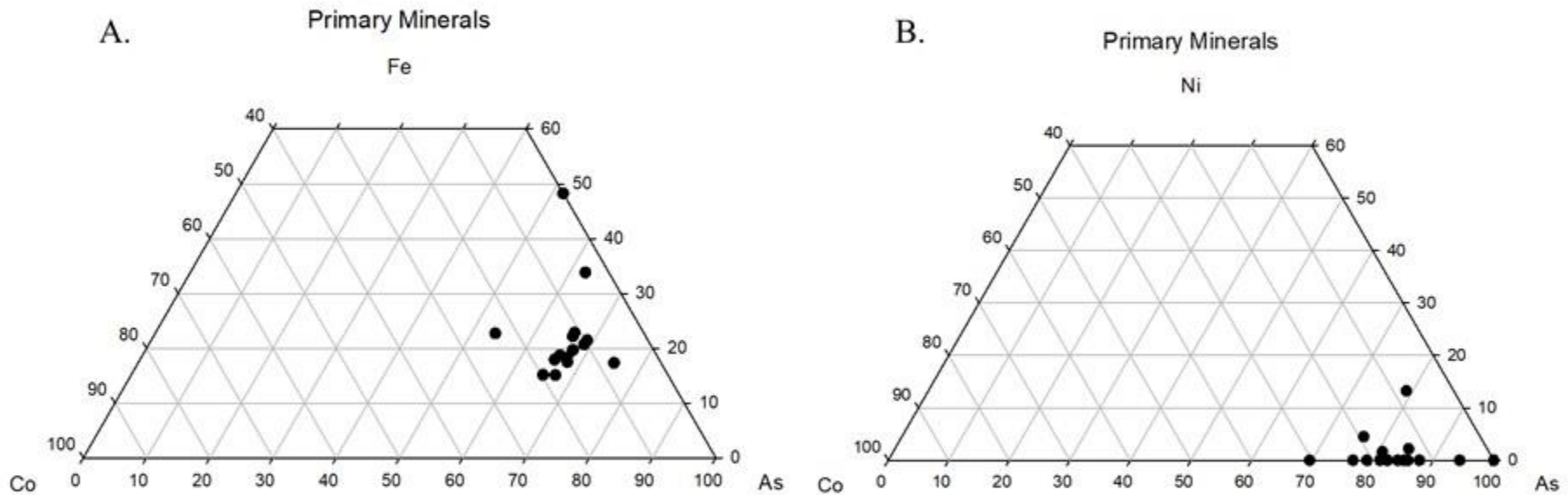
Species distribution for Fe<sup>3+</sup>-species:

FeOHCO <sub>3</sub>	99.847
Fe(OH) <sub>2</sub> <sup>2+</sup>	0.132
Fe(OH) <sub>4</sub> <sup>-</sup>	0.015



## Supplementary data F

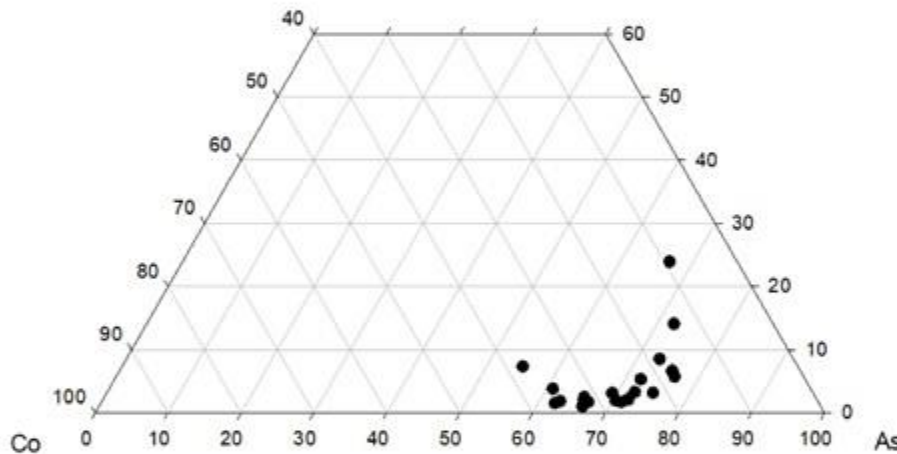
Composition of the arsenides (primary minerals) characterized with SEM



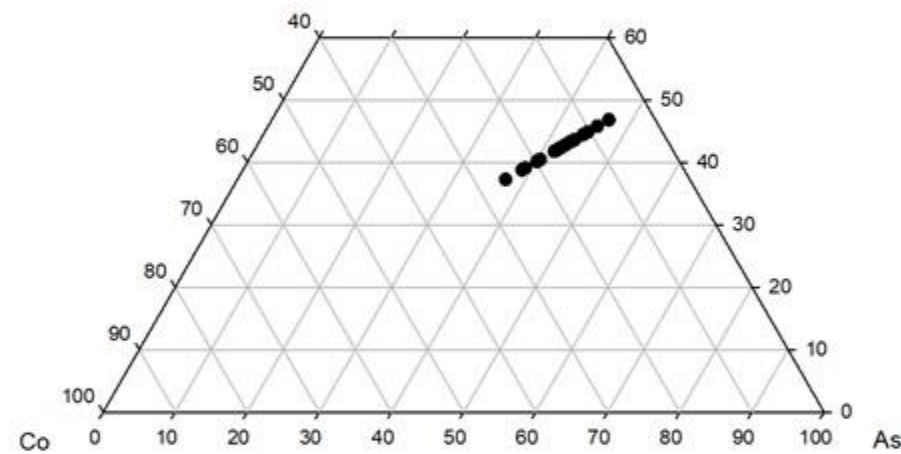
S17 Triangle diagrams depicting the proportions of A. Co vs. Fe vs. As and B. Co vs. Ni vs. As

# Composition of the arsenate cements characterized with SEM

A. Secondary Minerals  
Fe



B. Secondary Minerals  
Ni



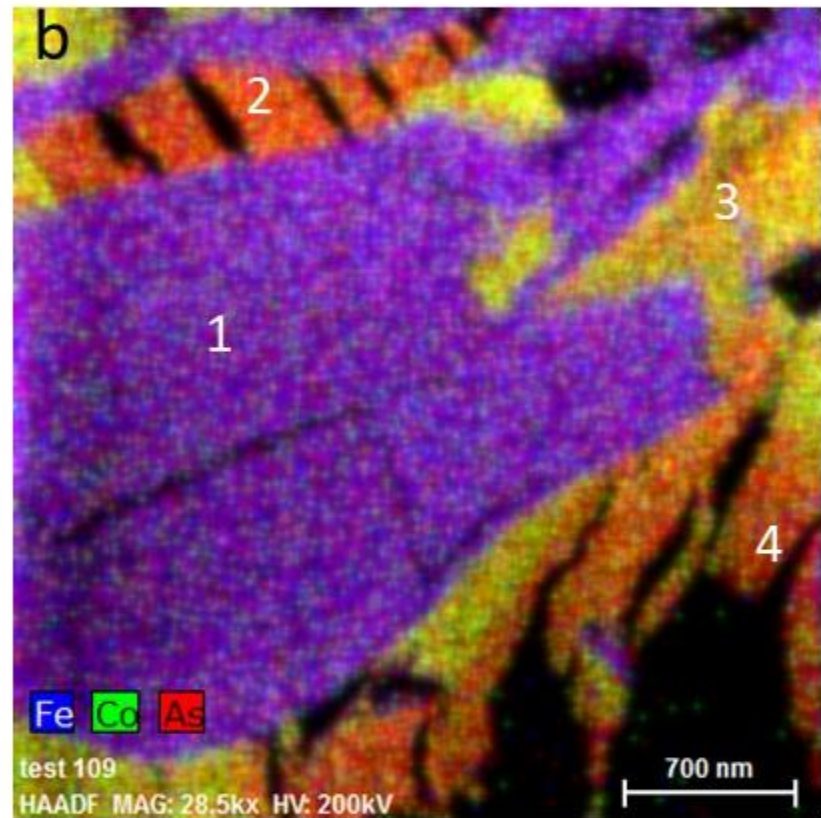
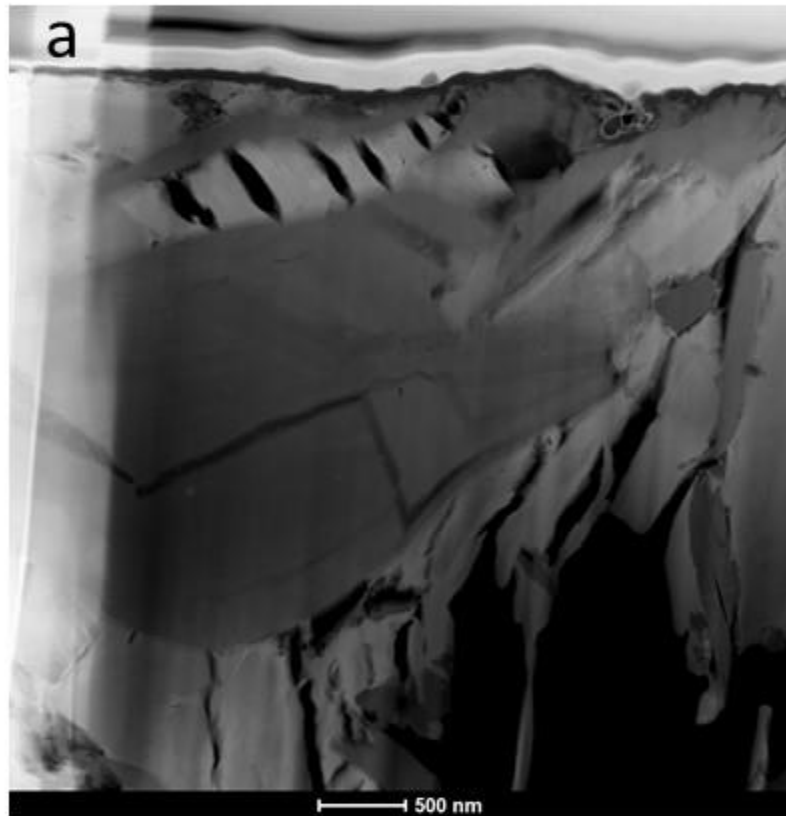
**S18** Triangle diagrams depicting the proportions of A. Co vs. Fe vs. As and B. Co vs. Ni vs. As

Supplementary data G  
Selected Area diffraction pattern,  
Fast Fourier Transformation pattern of lattice fringes  
and semi-quantitative chemical analyses  
for the major phases identified in the FIB section

Note that the concentrations for Oxygen are not listed in all chemical analyses

Area #1

Minerals of the arsenohopeite group and chlorite group



(a) STEM-EDS and (b) chemical distribution map for Fe (blue), Co (green) and As (red) for area 1; the chemical analyses listed in S17 are numbered from 1 to 4.

# Semi-quantitative chemical analyses for the areas numbered 1 to 4 in S16b

## 1

Spectrum: 1

Element	Series	Net un.	C norm.	C Atom.	C Error (3 Sigma)
		[wt.%]	[wt.%]	[at.%]	[wt.%]
Magnesium	K-series 3621	9.02	9.02	7.97	1.00
Aluminium	K-series 3805	10.16	10.16	8.09	1.12
Iron	K-series 5019	17.98	17.98	6.92	1.89
Silicon	K-series 4833	12.68	12.68	9.70	0.63
Oxygen	K-series 17462	50.16	50.16	67.33	4.73
Total:		100.00	100.00	100.00	

## 2

Spectrum: 1

Element	Series	Net un.	C norm.	C Atom.	C Error (3 Sigma)
		[wt.%]	[wt.%]	[at.%]	[wt.%]
Oxygen	K-series 1514	32.35	32.35	67.36	3.91
Iron	K-series 6	0.18	0.18	0.11	0.30
Arsenic	L-series 1118	32.69	32.69	14.54	10.49
Zinc	L-series 1286	29.77	29.77	15.16	9.47
Nickel	K-series 90	2.67	2.67	1.51	1.01
Cobalt	K-series 81	2.34	2.34	1.32	0.93
Total:		100.00	100.00	100.00	

## 3

Spectrum: 1

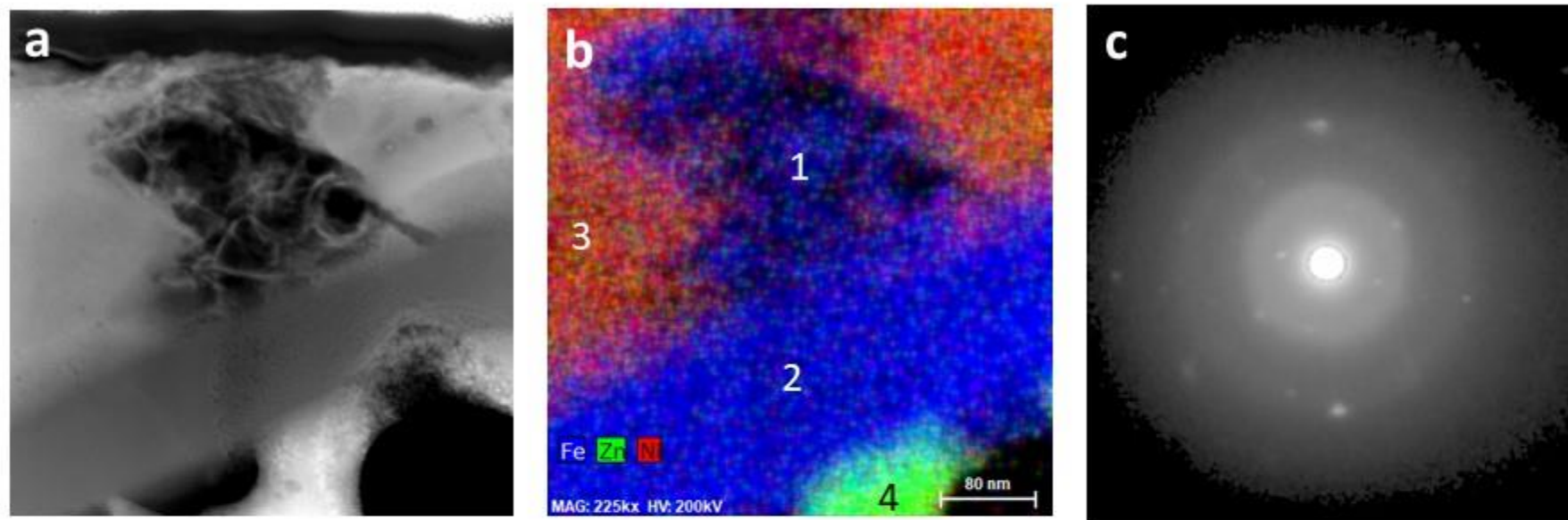
Element	Series	Net un.	C norm.	C Atom.	C Error (3 Sigma)
		[wt.%]	[wt.%]	[at.%]	[wt.%]
Oxygen	K-series 2536	33.50	33.50	67.77	3.69
Iron	K-series 7	0.11	0.11	0.07	0.21
Arsenic	L-series 1727	31.22	31.22	13.48	9.82
Zinc	K-series 558	12.14	12.14	6.01	2.06
Nickel	K-series 727	13.24	13.24	7.30	2.05
Cobalt	K-series 551	9.79	9.79	5.37	1.68
Total:		100.00	100.00	100.00	

## 4

Spectrum: 1

Element	Series	Net un.	C norm.	C Atom.	C Error (3 Sigma)
		[wt.%]	[wt.%]	[at.%]	[wt.%]
Oxygen	K-series 1061	30.49	30.49	65.28	4.00
Iron	K-series 0	0.00	0.00	0.00	0.00
Arsenic	L-series 784	30.83	30.83	14.09	10.13
Zinc	K-series 686	32.42	32.42	16.98	5.01
Nickel	K-series 80	3.13	3.13	1.83	1.24
Cobalt	K-series 82	3.14	3.14	1.83	1.23
Total:		100.00	100.00	100.00	

# Occurrence of a mineral with the tsumcorite-group $A_1M_2(XO_4)_2(OH,H_2O)_2$ structure type



S21 (a) STEM-EDS image, (b) chemical distribution map for Fe (blue), Zn (green) and Ni (red), c SAED pattern and d observed d spacings with (hkl) indices of a mineral of the tsumcorite group in an alteration halo (1) within an Co-Ni-arsenate mineral with the vivianite structure type (3) and in close association of a mineral of chlorite group (2) and Zn-arsenate (4); the chemical analyses for (1)-(4) are listed in S22

**d** tsumcorite-group  
 $A_1M_2(XO_4)_2(OH,H_2O)_2$

D-spacing [Å]	(hkl)
4.6	(111)
2.85	(220)
1.59	(430)

# Semi-quantitative chemical analyses of the areas depicted in S20b

Spectrum: 1      **1**

Element	Series	Net uncorr. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Iron	K-series 1951	25.72	25.72	28.05	3.05
Cobalt	K-series 190	2.70	2.70	2.79	0.75
Nickel	K-series 191	2.79	2.79	2.89	0.77
Zinc	K-series 90	1.56	1.56	1.45	0.62
Silicon	K-series 357	3.44	3.44	7.45	0.63
Arsenic	L-series 2819	40.77	40.77	33.14	12.61
Aluminium	K-series 110	1.07	1.07	2.43	0.40
Calcium	K-series 1147	12.51	12.51	19.01	1.71
Lead	M-series 439	9.45	9.45	2.78	6.02
Total:		100.00	100.00	100.00	

Spectrum: 1      **2**

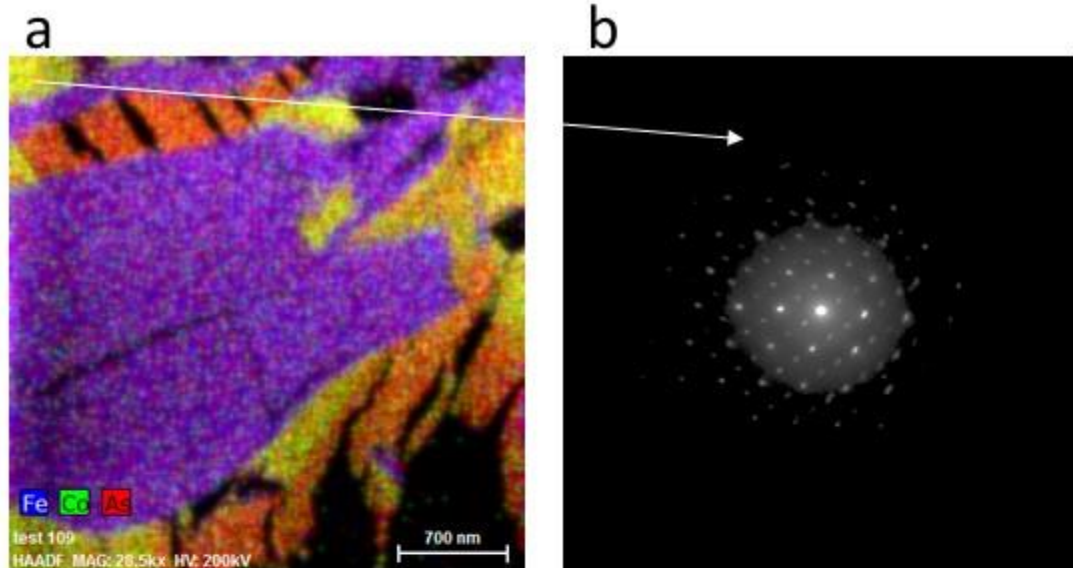
Element	Series	Net uncorr. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Magnesium	K-series 3210	20.25	20.25	27.07	2.19
Aluminium	K-series 2647	17.91	17.91	21.57	2.00
Silicon	K-series 4025	26.76	26.76	30.96	1.37
Iron	K-series 3862	35.07	35.07	20.40	3.71
Total:		100.00	100.00	100.00	

Spectrum: 1      **3**

Element	Series	Net uncorr. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Iron	K-series 254	2.29	2.29	2.64	0.58
Zinc	K-series 415	4.92	4.92	4.84	0.97
Nickel	K-series 1790	17.79	17.79	19.47	2.17
Cobalt	K-series 2614	25.36	25.36	27.65	2.86
Arsenic	L-series 4719	46.61	46.61	39.97	14.27
Silicon	K-series 125	0.86	0.86	1.96	0.31
Calcium	K-series 291	2.17	2.17	3.48	0.53
Total:		100.00	100.00	100.00	

Spectrum: 1      **4**

Element	Series	Net uncorr. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Cobalt	K-series 132	5.18	5.18	6.01	1.59
Nickel	K-series 106	4.21	4.21	4.91	1.45
Zinc	L-series 1385	43.45	43.45	45.47	13.74
Iron	K-series 49	1.74	1.74	2.13	0.89
Arsenic	L-series 1145	45.42	45.42	41.48	14.53
Total:		100.00	100.00	100.00	



**c**

D-spacing [Å]	(hkl)
5.21	(210)
3.45	(221)
3.63	(240)

Co-Ni-As-rich mineral with the arsenohopeite structure type

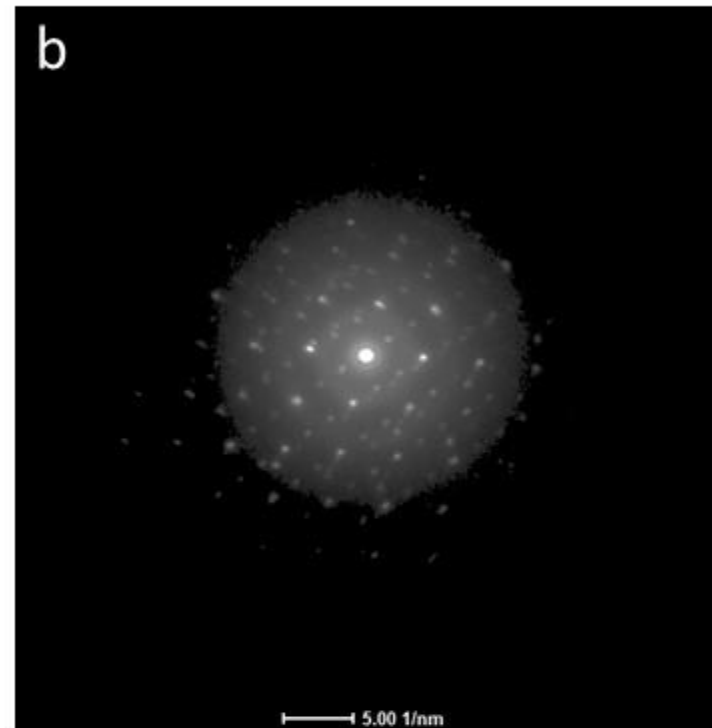
**d**

SpectralArea2		Colour = yellow (ZnCo Ni map)			
Element	Series	Net unkn. (wt%)	C norm. (wt%)	C atom. (at%)	C Error (3 sigma) (wt%)
Oxygen	K	36.93	36.93	70.86	4.79
Arsenic	L	32.13	32.13	13.17	10.67
Cobalt	K	17.61	17.61	9.17	3.36
Nickel	K	10.04	10.04	5.25	2.45
Zinc	L	3.29	3.29	1.54	1.64
Total		100	100	99.99	

**S23** Chemical distribution maps for Fe (blue), Co (green) and As (red) of area 1, (b) SAED pattern (c) d-spacing and (hkl) indices and (d) semi-quantitative chemical analysis of a Co-Ni-rich mineral with arsenohopeite structure type



Mineral of the chlorite group  $(\text{Mg,Fe})_5\text{Al}(\text{AlSi}_3\text{O}_{10})\text{OH}_8$

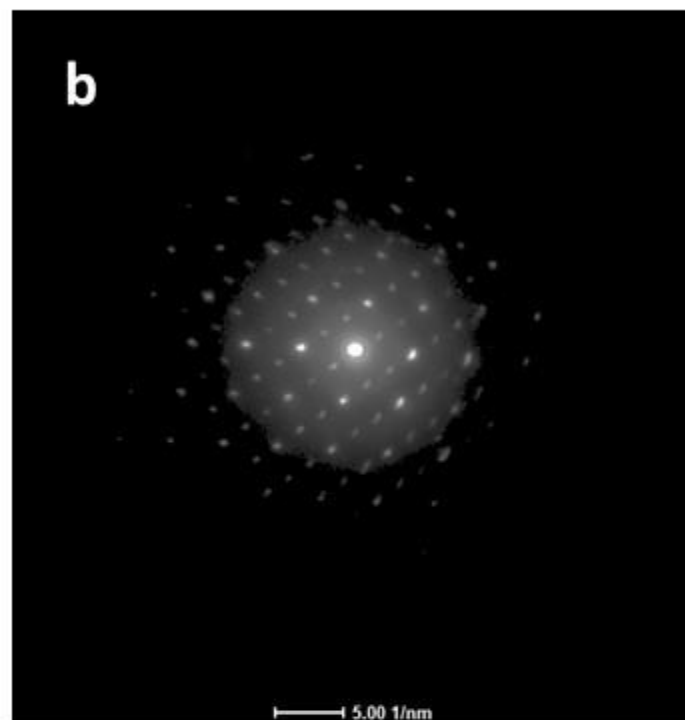
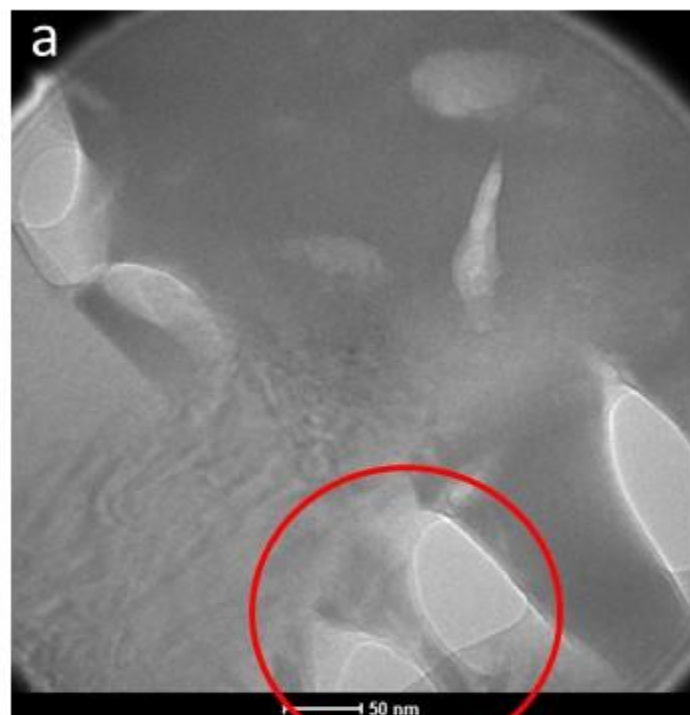


**C**

D-spacing [Å]	(hkl)
3.45	(-1 -1 3)
1.68	(-1 -3 7)
3.90	(-1 -1 3)
2.44	(-1 -3 3)

S24 (a) TEM image, (b) SAED pattern and © selected d-spacings and (hkl) for a mineral of the chlorite group in area 1; the area from which the SAED pattern was recorded is encircled in (a).

## Co-Ni-rich arsenate with the Arsenohopeite structure type

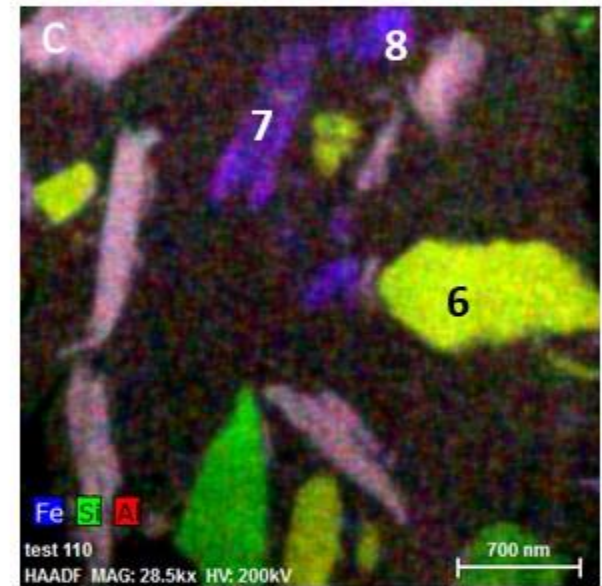
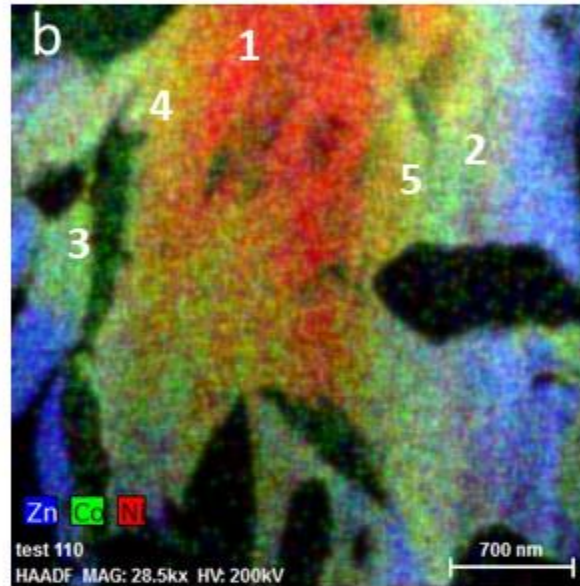
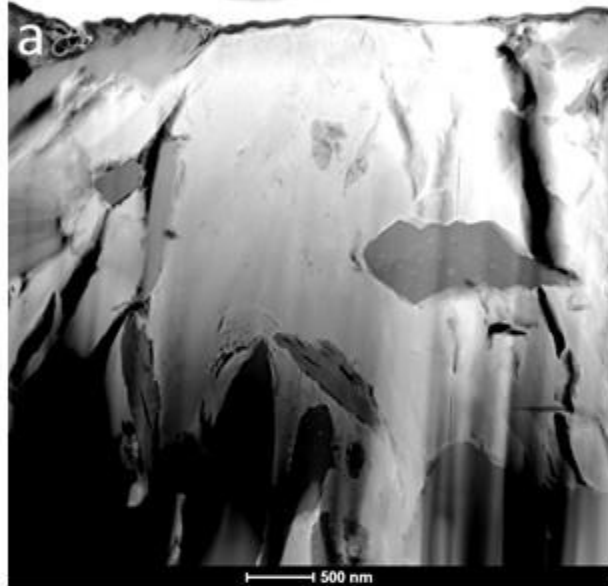


**C**

D-spacing [Å]	(hkl)
5.15	(2 1 0)
3.63	(2 4 0)
2.43	(2 7 0)
2.58	(4 2 0)

S25 (a) TEM image, (b) SAED pattern and (c) selected d-spacings and (hkl) mineral with the arsenohopeite structure type in area 1; the area from which the SAED pattern was recorded is encircled in (a).

## Area #2



Minerals of the vivianite group  
Scorodite  
Albite  
Minerals of the chlorite group

S26 (a) STEM-EDS image and (b)-(c) chemical distribution for (b) Zn (blue), Co (green) and Ni (red) and (c) Fe (blue), Si (green) and Al (red) of area 2; semi-quantitative chemical analyses for the phases numbered (1)-(8) are given in S24 and S25.

1

Q2	1 Element	Series	Net un.	C norm.	C Atom.	C Error(3 Sigma)
			[wt.%]	[wt.%]	[at.%]	[wt.%]
Ni~As						
	Oxygen	K-series 1751	35.83	35.83	69.19	4.20
	Nickel	K-series 963	27.37	27.37	14.40	3.83
	Arsenic	L-series 1118	31.58	31.58	13.02	10.14
	Manganese	K-series 114	2.82	2.82	1.59	0.96
	Calcium	K-series 105	2.25	2.25	1.73	0.80
	Zinc	L-series 7	0.15	0.15	0.07	0.28
	Total: 100.00 100.00 100.00					

3

Q2	3 Element	Series	Net un.	C norm.	C Atom.	C Error(3 Sigma)
			[wt.%]	[wt.%]	[at.%]	[wt.%]
Co=Ni						
Co+Ni=As						
CoNiZn-AsO	Oxygen	K-series 1312	34.18	34.18	67.96	4.25
	Calcium	K-series 37	1.01	1.01	0.81	0.61
	Manganese	K-series 80	2.54	2.54	1.47	1.01
	Nickel	K-series 354	12.81	12.81	6.94	2.55
	Zinc	K-series 154	6.65	6.65	3.24	1.90
	Arsenic	L-series 851	30.57	30.57	12.98	9.99
	Cobalt	K-series 347	12.25	12.25	6.61	2.46
	Total: 100.00 100.00 100.00					

2

Q2	2 Element	Series	Net un.	C norm.	C Atom.	C Error(3 Sigma)
			[wt.%]	[wt.%]	[at.%]	[wt.%]
Zn+Co+Ni>As						
	Oxygen	K-series 1491	31.69	31.69	66.07	3.84
	Calcium	K-series 32	0.80	0.80	0.67	0.51
	Manganese	K-series 46	1.18	1.18	0.72	0.65
	Nickel	K-series 198	5.85	5.85	3.33	1.51
	Zinc	K-series 717	25.29	25.29	12.90	3.87
	Arsenic	L-series 1014	29.80	29.80	13.27	9.63
	Cobalt	K-series 186	5.38	5.38	3.05	1.43
	Total: 100.00 100.00 100.00					

4

Q2	4 Element	Series	Net un.	C norm.	C Atom.	C Error(3 Sigma)
			[wt.%]	[wt.%]	[at.%]	[wt.%]
Ni>>Co+Zn						
	Oxygen	K-series 1629	40.28	40.28	73.19	4.78
	Calcium	K-series 48	1.23	1.23	0.89	0.65
	Manganese	K-series 81	2.44	2.44	1.29	0.97
	Nickel	K-series 547	18.79	18.79	9.31	3.16
	Zinc	L-series 25	0.66	0.66	0.29	0.58
	Arsenic	L-series 841	28.76	28.76	11.16	9.41
	Cobalt	K-series 233	7.84	7.84	3.87	1.87
	Total: 100.00 100.00 100.00					

S27 Semi-quantitative Chemical analysis for the areas numbered in S23b and c

5

5		Element	Series	Net un.	C norm.	C Atom.	C Error(3 Sigma)
Q2		[wt.%]	[wt.%]	[at.%]	[wt.%]		
CoNi-AsO		Oxygen	K-series1633	35.76	35.76	69.61	4.25
		Calcium	K-series 31	0.80	0.80	0.62	0.51
		Manganese	K-series 42	1.13	1.13	0.64	0.64
		Nickel	K-series 463	14.09	14.09	7.47	2.53
		Zinc	L-series 383	9.17	9.17	4.37	3.28
		Arsenic	L-series 979	29.63	29.63	12.31	9.59
		Cobalt	K-series 317	9.42	9.42	4.98	1.97
		Total: 100.00 100.00 100.00					

6

Albite		Element	Series	Net un.	C norm.	C Atom.	C Error(3 Sigma)
		[wt.%]	[wt.%]	[at.%]	[wt.%]		
		Silicon	K-series4920	32.84	32.84	23.57	1.51
		Aluminium	K-series1572	10.68	10.68	7.98	1.33
		Sodium	K-series1220	7.11	7.11	6.23	0.96
		Oxygen	K-series6810	49.37	49.37	62.21	4.87
		Total: 100.00 100.00 100.00					

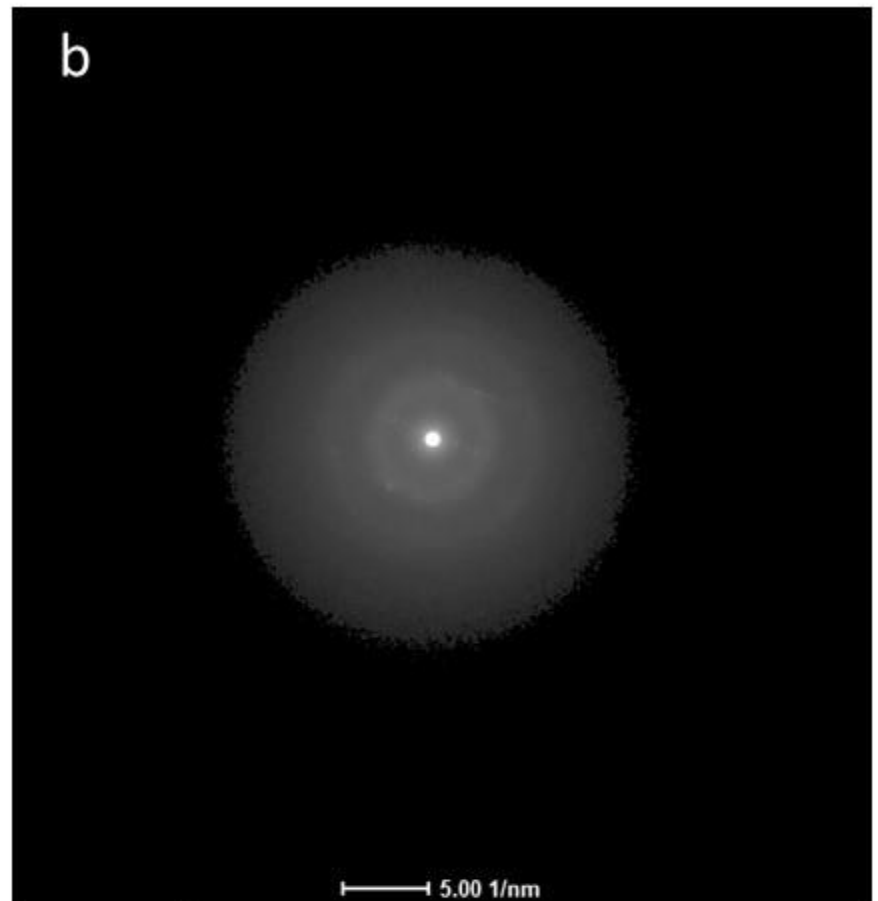
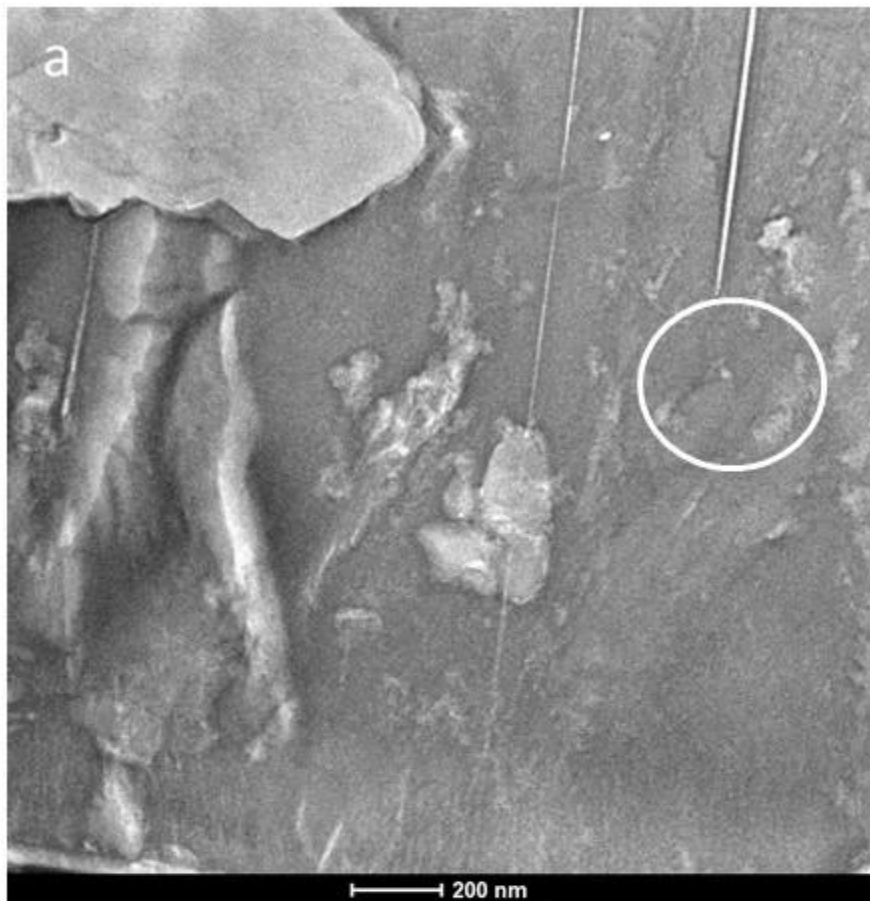
8

8		Element	Series	Net un.	C norm.	C Atom.	C Error(3 Sigma)
FeNi-AsO		[wt.%]	[wt.%]	[at.%]	[wt.%]		
		Oxygen	K-series1558	39.47	39.47	72.59	4.72
		Magnesium	K-series 0	0.00	0.00	0.00	0.00
		Iron	K-series 388	12.35	12.35	6.51	2.37
		Nickel	K-series 392	13.79	13.79	6.91	2.63
		Arsenic	L-series 931	32.56	32.56	12.79	10.57
		Zinc	K-series 10	0.48	0.48	0.22	0.54
		Calcium	K-series 50	1.35	1.35	0.99	0.69
		Total: 100.00 100.00 100.00					

7

7		Element	Series	Net un.	C norm.	C Atom.	C Error(3 Sigma)
Fe-AsO		[wt.%]	[wt.%]	[at.%]	[wt.%]		
		Oxygen	K-series898	33.99	33.99	66.48	4.65
		Iron	K-series 593	28.20	28.20	15.80	4.58
		Arsenic	L-series631	32.89	32.89	13.73	11.01
		Aluminium	K-series 45	1.62	1.62	1.88	0.81
		Titanium	K-series 29	1.22	1.22	0.80	0.80
		Calcium	K-series 19	0.85	0.85	0.66	0.66
		Cobalt	K-series 24	1.23	1.23	0.66	0.89
		Total: 100.00 100.00 100.00					

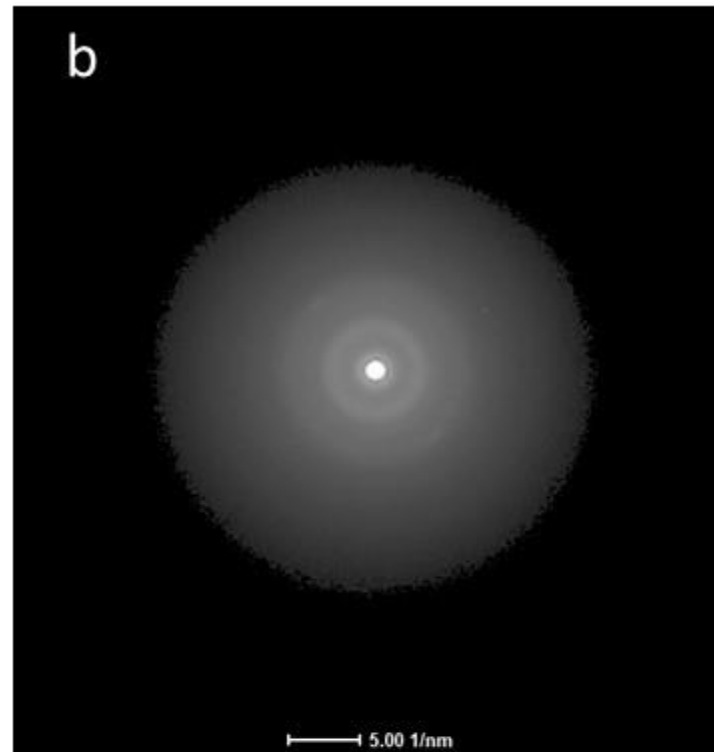
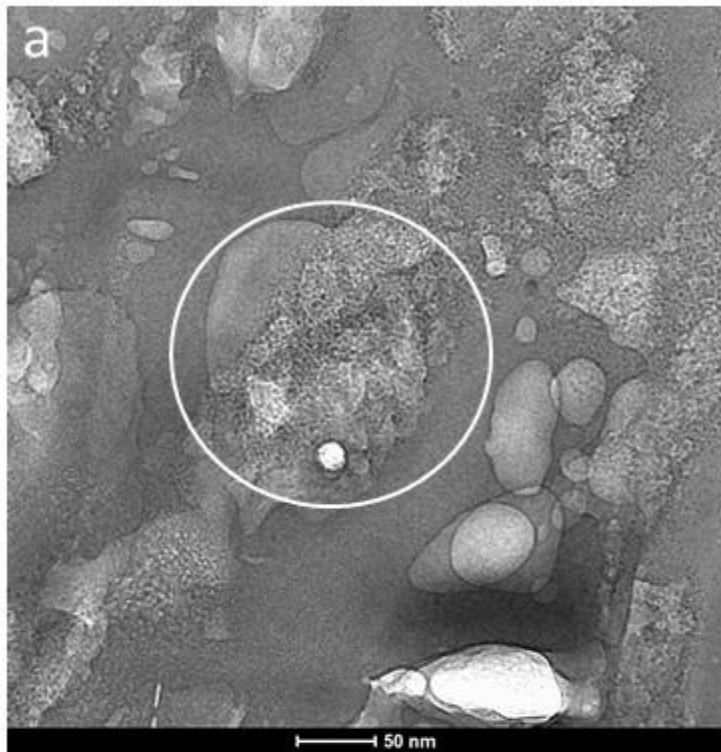
S28 Semi-quantitative chemical analysis for the areas numbered in S23b and c



**C**

<b>Co-Ni-arsenate of the vivianite group</b>	
D-spacing [Å]	(hkl)
2.66	(0 4 1)
3.86	(-2 0 1)

**S29** (a) TEM image and (b) SAED pattern of a selected area in area 2 (encircled in (a)); (c) corresponding d-spacing and (hkl) of a Co-Ni-arsenate of the vivianite group

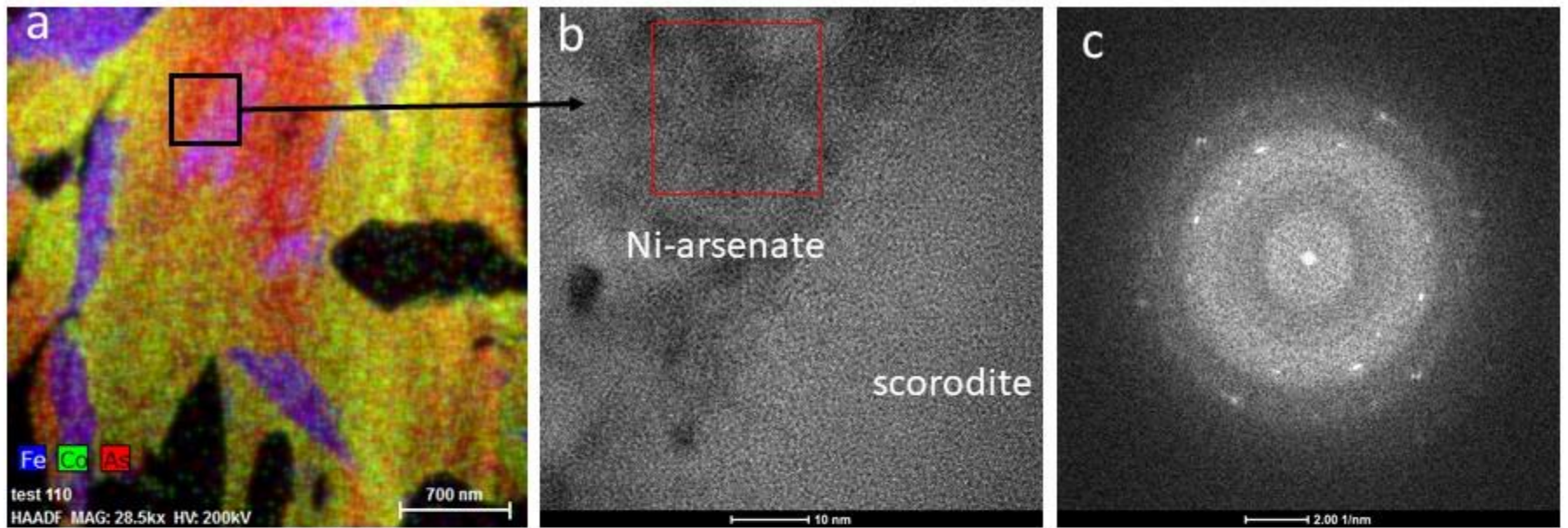


Co-Ni-rich arsenate with of the vivianite group

**c**

D-spacing [Å]	(hkl)
3.40	(-2 2 1)
1.62	(-5 5 1)
3.28	(-1 3 1)
2.45	(-4 0 1)

**S30** (a) TEM image and (b) SAED pattern from a selected area (encircled in (a)) and (c) d-spacings and (hkl) indices of a Co-Ni-rich arsenate of the vivianite group

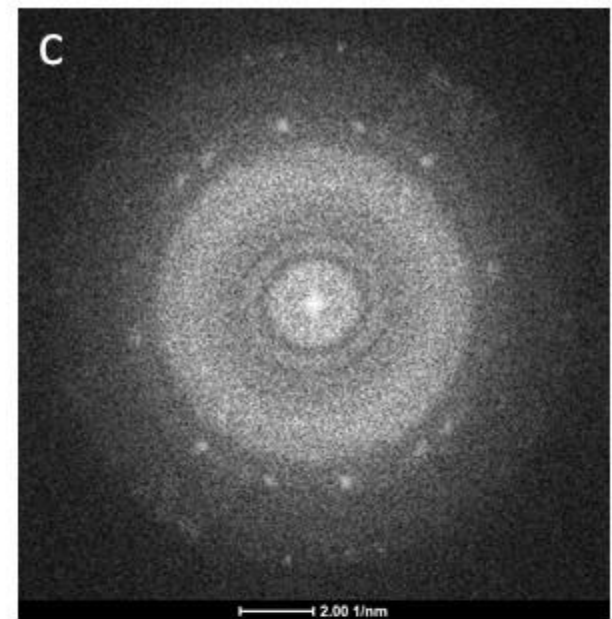
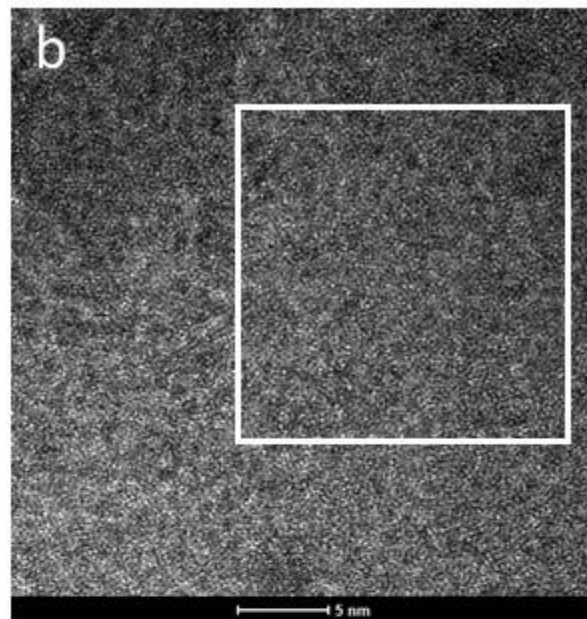
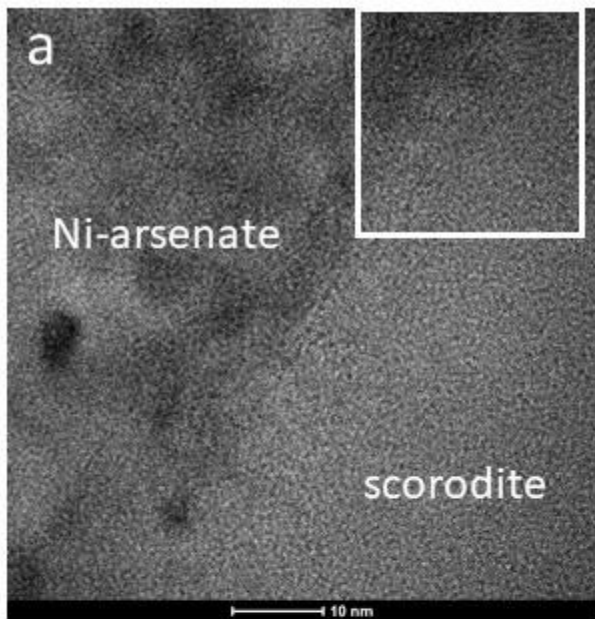


**d**

Ni-arsenate-bearing minerals of the vivianite group	
D-spacing [Å]	(hkl)
2.64	(330)
1.88	(202)
2.40	(-401)
1.90	(202)
1.97	(-441)

**S31** (a) Chemical distribution map for Fe (blue), Co (green) and As (red) for area 2; (b) TEM of the interface between a Ni-arsenate of the vivianite group and scorodite (indicated with a black box in (a)); (c) FFT pattern of a selected area in (b) (indicated with a red box) and (d) D-spacings and (hkl) indices of a Ni-arsenate mineral of the vivianite group

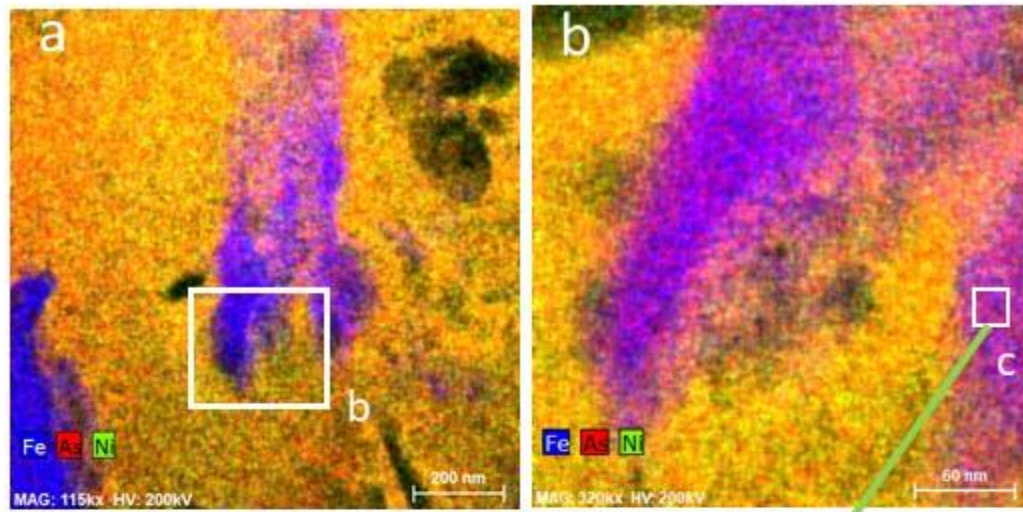




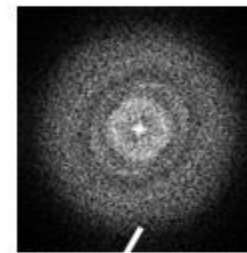
d

Scorodite $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$	
D-spacing	hkl index
5.66	(1 1 1)
2.48	(2 3 1)
1.97	(5 1 1)

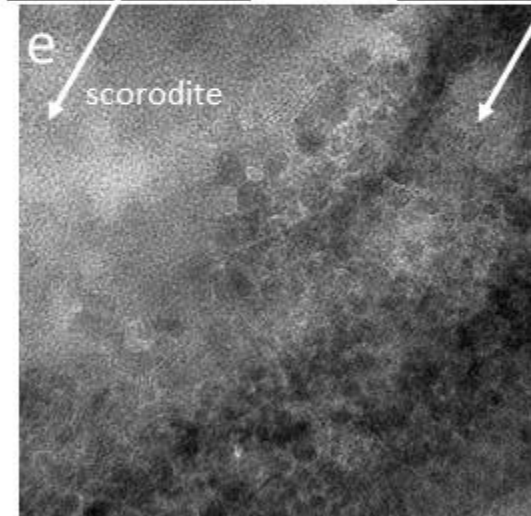
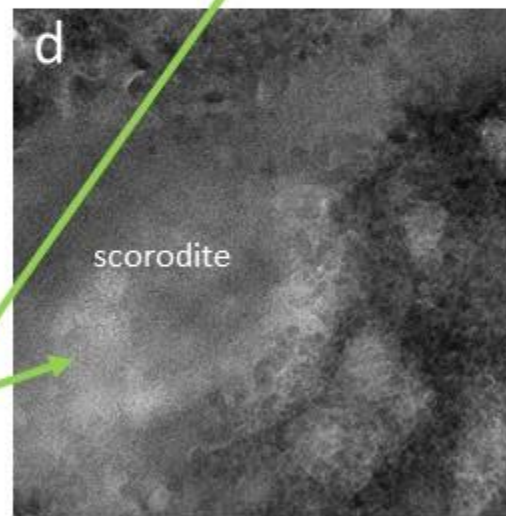
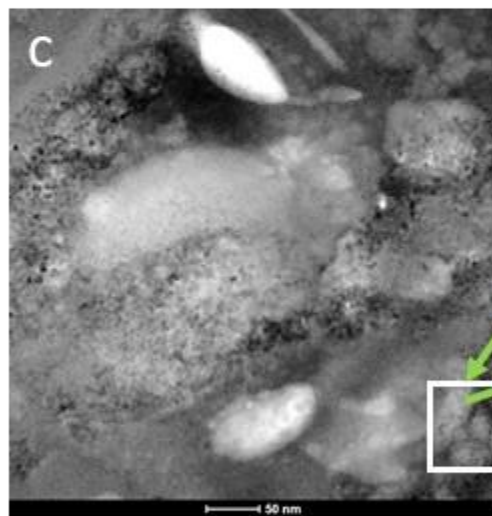
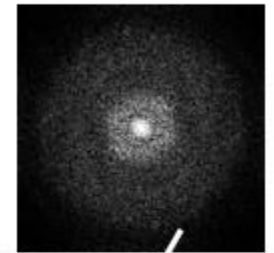
**S32** (a) TEM of the interface between a Ni-arsenate of the vivianite group and scorodite (b) High-Resolution TEM of a selected area in (a) (indicated with a white box in (a)); (c) FFT pattern of a selected area in (b) (indicated with a white box) and (d) corresponding d-spacings and (hkl) indices of scorodite



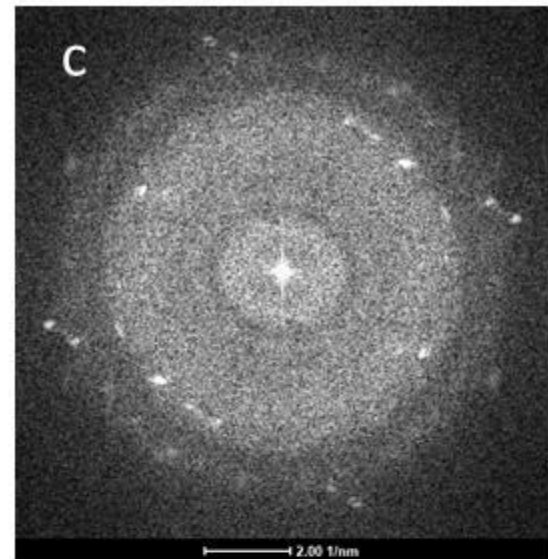
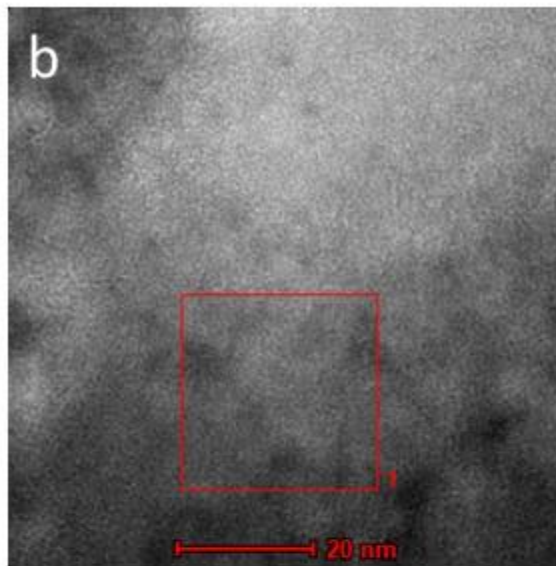
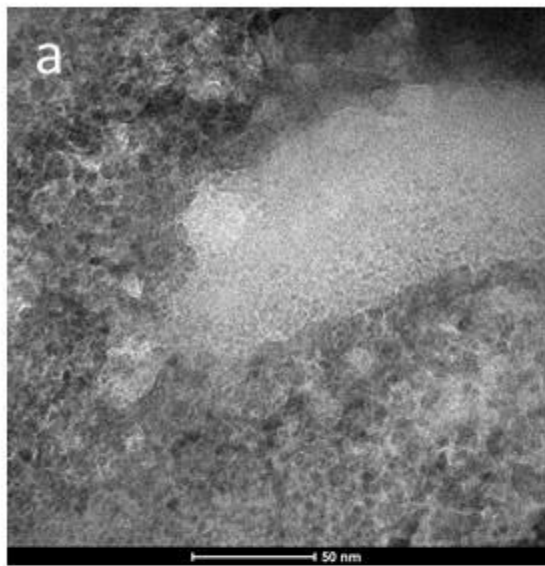
D=5.6 (111)  
scorodite



D=7.9 (110)  
vivanite



**S33** (a)-(b) STEM-EDS chemical distribution maps for Fe (blue), As (red) and Ni (green) and (c)-(e) TEM images of the replacement of scorodite by (Co, Ni)-arsenates of the vivianite group; the areas shown in (b), (c) and (d) are indicated with squares in (a), (b) and (c), respectively; (e) FFT pattern from areas composed of scorodite and a mineral of the vivianite group.

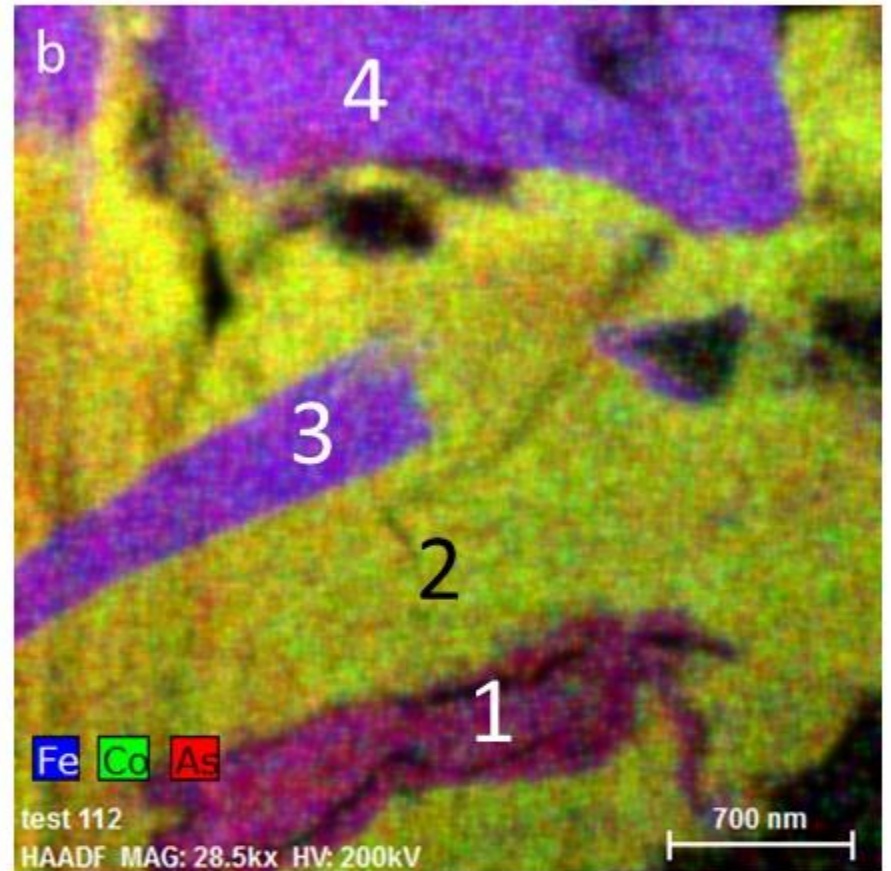
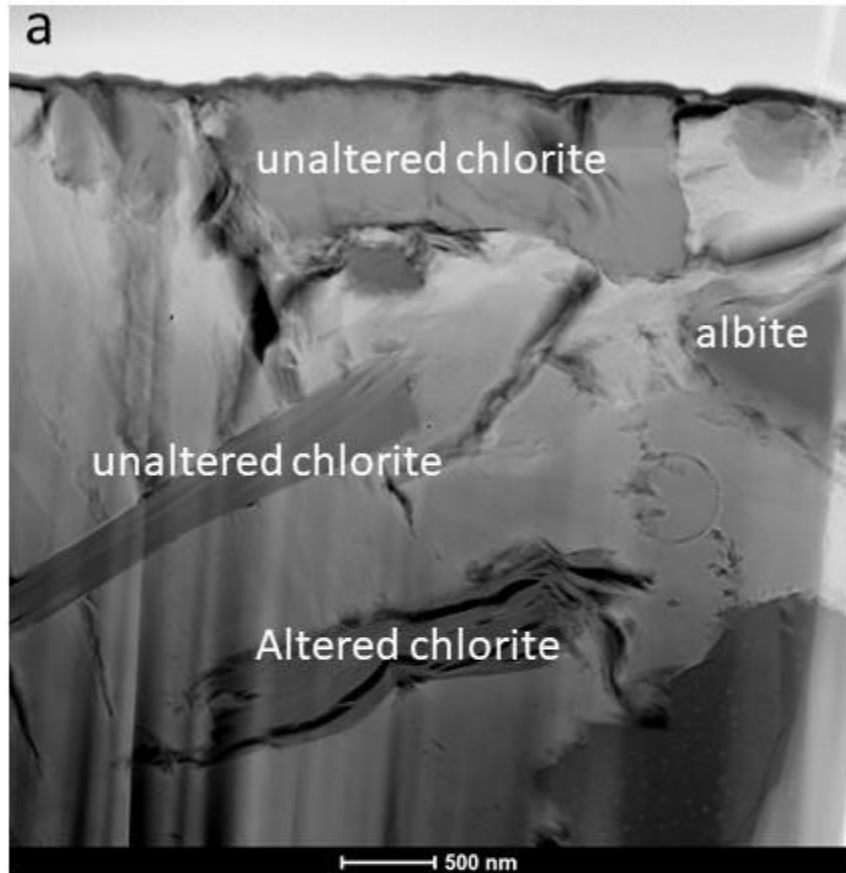


e

Arsenate-bearing minerals of the vivianite group	
D-spacing	hkl Index
2.65	(330)
3.03	(201)
1.96	(510)
1.79	(261)

**S34** (a)-(b) TEM images and (c) FFT pattern for the area indicated with a red square in (b); (e) Table listing the observed d-spacing in the FFT pattern, which are characteristic for those observed for a mineral of the vivianite group.

## Area #4



S35 (a) STEM-EDS image and (b) chemical distribution for (b) Fe (blue), Co (green) and As (red); semi-quantitative chemical analyses for the chlorite numbered (1)-(4) are given in S33.

Spectrum: 1 **1**

Element	Series	Net uncorr. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (3 Sigma) [wt.%]
Nickel	K-series 433	21.17	21.17	13.39	3.86
Iron	K-series 423	18.71	18.71	12.44	3.45
Aluminium	K-series 189	6.23	6.23	8.57	1.56
Silicon	K-series 812	26.39	26.39	34.89	2.91
Magnesium	K-series 508	15.66	15.66	23.92	2.59
Calcium	K-series 59	2.12	2.12	1.97	0.99
Arsenic	L-series 200	9.72	9.72	4.82	3.90
-----					
Total:		100.00	100.00	100.00	

Spectrum: 1 **2**

Element	Series	Net uncorr. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (3 Sigma) [wt.%]
Arsenic	L-series 3377	32.30	32.30	27.21	9.97
Zinc	K-series 698	8.03	8.03	7.75	1.29
Nickel	K-series 2693	25.91	25.91	27.86	2.90
Cobalt	K-series 3255	30.60	30.60	32.77	3.32
Iron	K-series 151	1.31	1.31	1.48	0.44
Calcium	K-series 258	1.86	1.86	2.93	0.48
-----					
Total:		100.00	100.00	100.00	

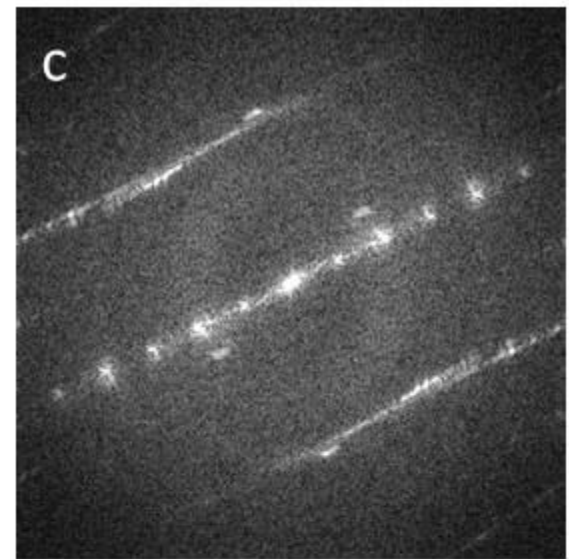
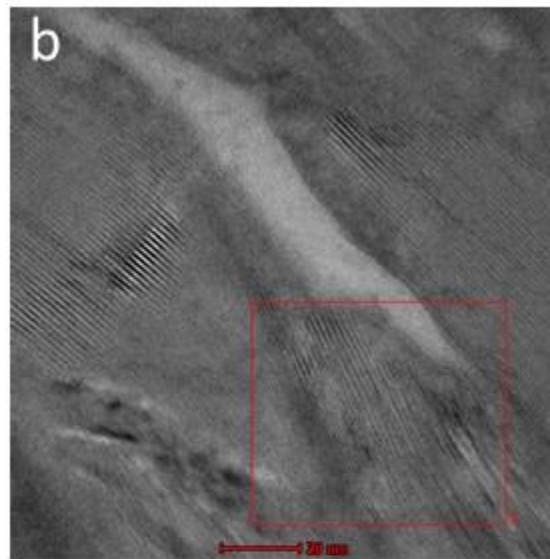
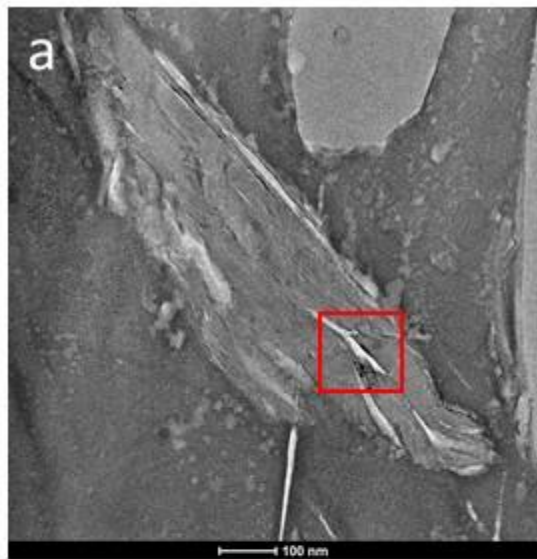
Spectrum: 1 **3**

Element	Series	Net uncorr. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (3 Sigma) [wt.%]
Arsenic	L-series 41	1.46	1.46	0.72	1.00
Iron	K-series 1575	50.44	50.44	33.13	6.18
Magnesium	K-series 555	12.34	12.34	18.62	2.00
Aluminium	K-series 646	15.41	15.41	20.95	2.37
Silicon	K-series 867	20.35	20.35	26.58	2.19
-----					
Total:		100.00	100.00	100.00	

Spectrum: 1 **4**

Element	Series	Net uncorr. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (3 Sigma) [wt.%]
Arsenic	L-series 387	4.23	4.23	2.12	1.56
Iron	K-series 5024	49.98	49.98	33.53	5.11
Silicon	K-series 2527	18.41	18.41	24.56	1.20
Aluminium	K-series 2137	15.84	15.84	22.00	1.84
Magnesium	K-series 1670	11.54	11.54	17.79	1.42
-----					
Total:		100.00	100.00	100.00	

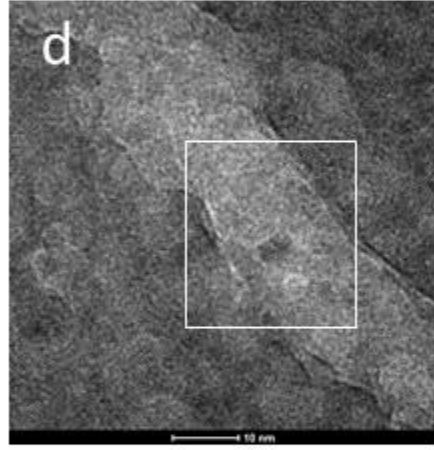
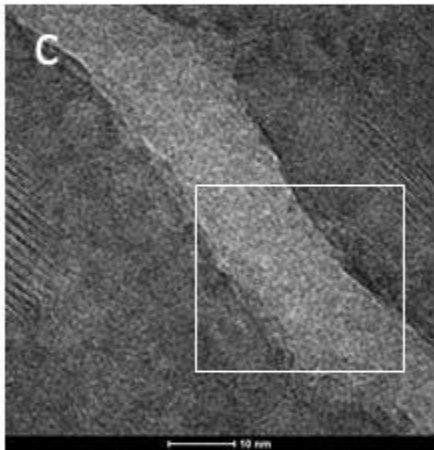
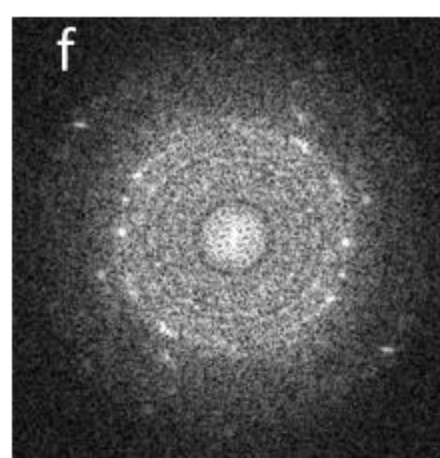
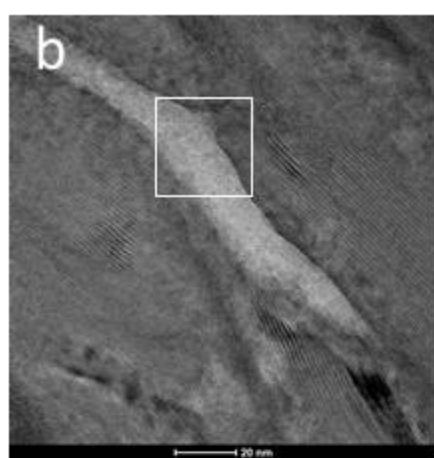
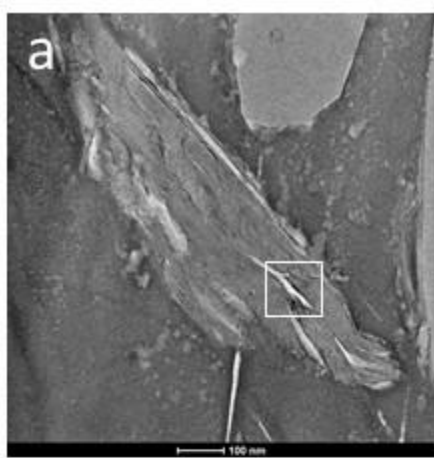
**S36** Semi-Quantitative Chemical analysis for the chlorite grains indicated in S32



**S37** (a)-(b) TEM images of the interior of an altered clinochlore crystal; the area shown in (b) is indicated with a red square in (a); a red square in (b) indicates the area from which the FFT pattern in (c) has been taken; (c) FFT pattern of the area indicated in (b); (d) d-spacings measured in the FFT pattern shown in (c).

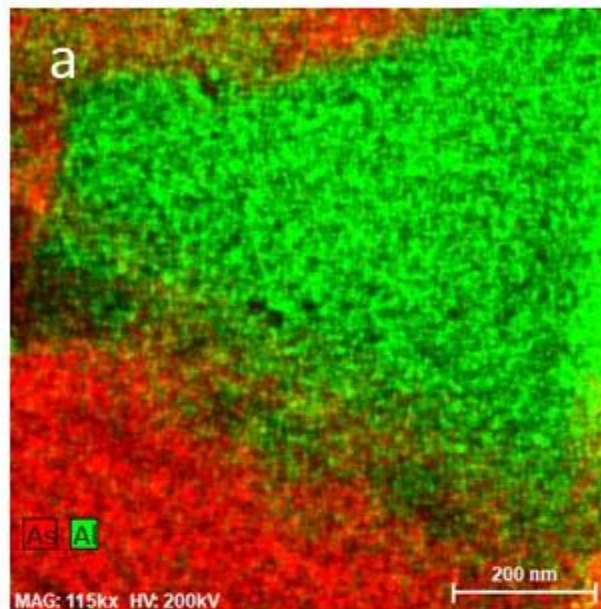
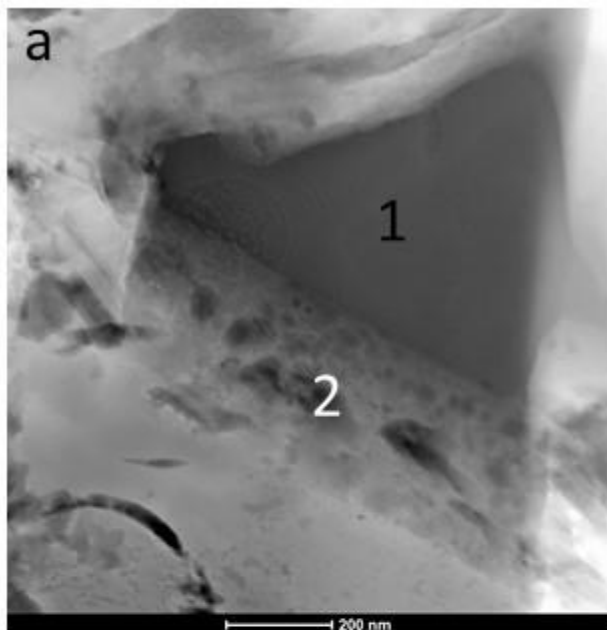
**e**

Clinochlore $(\text{Mg,Fe})_5\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$	
D-spacing	(hkl)
14.4	(001)
7.20	(002)
4.80	(003)
3.60	(004)
2.90	(005)
4.33	(021)
3.25	(0-23)
2.75	(024)



g Arsenohopeite structure type	
D-spacing [Å]	(hkl)
4.90	(011)
4.11	(230)
3.50	(240)

S38 (a)-(d) TEM images of the interior of clinochore crystals containing (Co, Ni)-arsenates nanoparticles with the arsenohopeite structure type; the areas shown in (b), (c) and (d) are indicated with white squares in (a), (b) and (c), respectively; the area from where the FFT pattern in (f) was taken is indicated with a white square in (d); (f) FFT pattern from the area shown in (d); (g) d-spacings measured in the FFT pattern.



Spectrum: 1      **1**

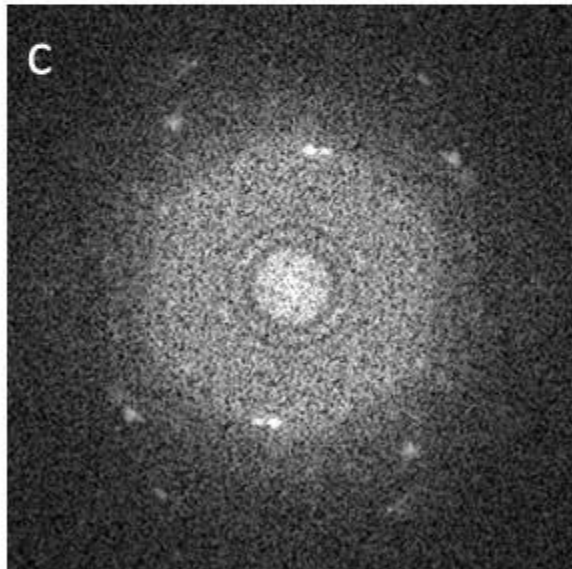
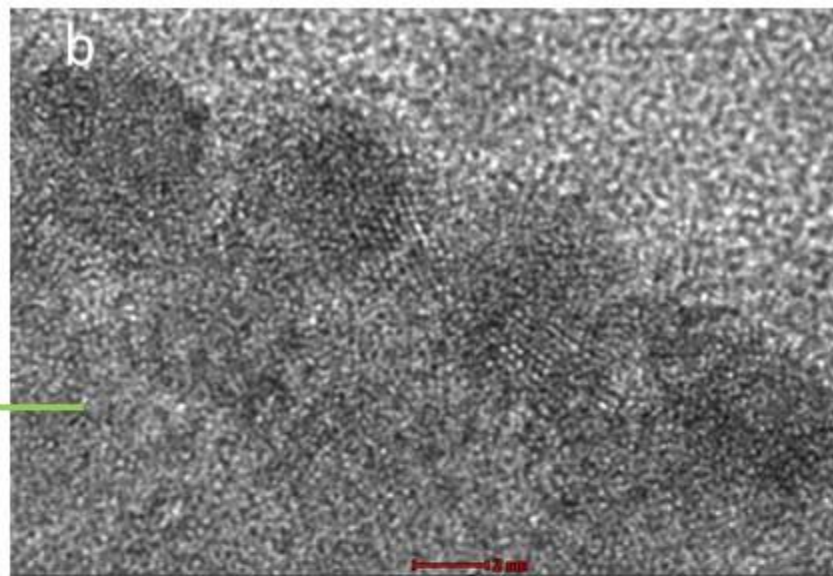
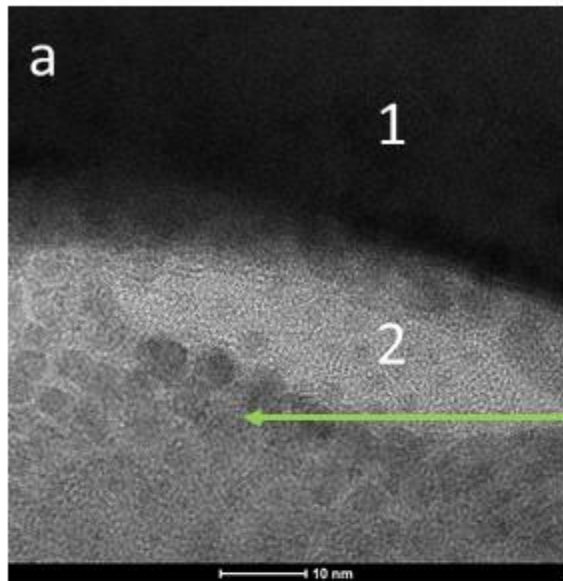
Element	Series	Net un.	C norm.	Atom. C	Error (3 Sigma)	
		[wt.%]	[wt.%]	[at.%]	[wt.%]	
Sodium	K-series	391	14.18	14.18	16.67	2.57
Aluminium	K-series	484	20.48	20.48	20.50	3.44
Silicon	K-series	1573	65.34	65.34	62.84	5.12
Total:		100.00	100.00	100.00		

Spectrum: 1      **2**

Element	Series	Net un.	C norm.	Atom. C	Error (3 Sigma)	
		[wt.%]	[wt.%]	[at.%]	[wt.%]	
Iron	K-series	1867	3.46	3.46	2.82	0.48
Cobalt	K-series	9732	19.48	19.48	15.00	1.94
Nickel	K-series	9672	19.82	19.82	15.33	1.97
Zinc	K-series	2472	6.06	6.06	4.20	0.75
Arsenic	L-series	10239	20.86	20.86	12.64	6.38
Silicon	K-series	14209	19.31	19.31	31.20	0.57
Aluminium	K-series	4579	6.33	6.33	10.65	0.71
Sodium	K-series	2880	3.41	3.41	6.73	0.44
Calcium	K-series	824	1.27	1.27	1.43	0.26
Total:		100.00	100.00	100.00		

**S39** (a) TEM STEM-EDS and (b) chemical distribution map for As (red) and Al (green) of a reaction rim around albite, the areas from where the semi-quantitative analyses (1) and (2) were taken are indicated in (a).





d

Minerals of the vivianite structure type	
D-spacing [Å]	(hkl)
6.71	(020)
2.60	(330)
2.03	(260)

S40 (a)-(b) TEM images of the reaction rim on the surface of albite; labelled “1” and (2) in (a), respectively; the area shown in (b) is indicated with a green arrow in (a); (c) FFT pattern of the area shown in (b); (d) d-spacings measured in the FFT pattern in (c).