Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.
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Supporting information: A. sampling sites and bulk chemical and mineralogical composition of the soil samples Figs. S1-S6, Table S1; **B.** SEM-BSE images of *MSC* and *MOM (*Figs. S7-S10); **C.** TEM. SAED and STEM-EDS images of all identified phases (S11-S28); **D.** Table S29, Point of zero charges for selected phases identified in this study.

Supplementary data A

Sampling sites Figure S1 and S2

Bulk mineralogical composition Figures S3-S6

Bulk composition Table S1

Figure S1, Sampling site North, May 2016

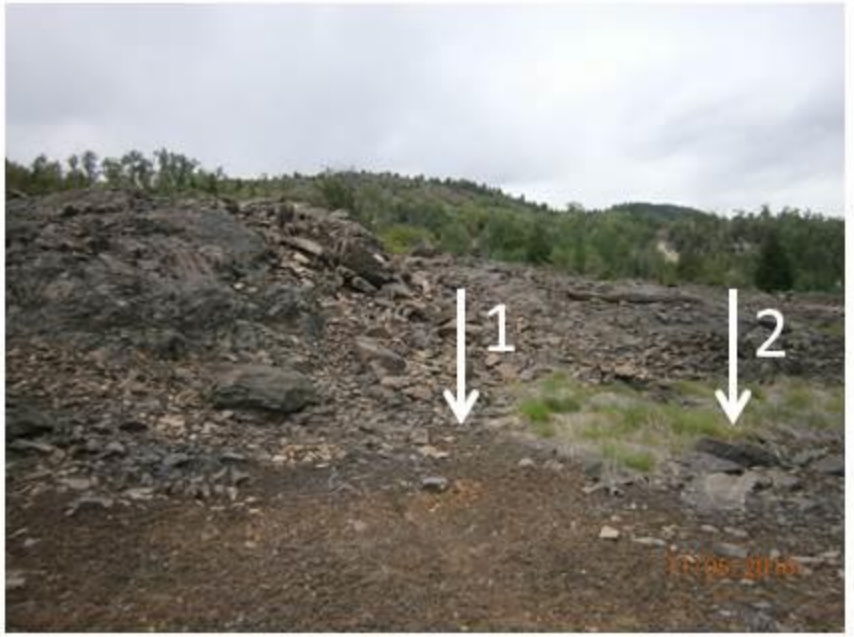
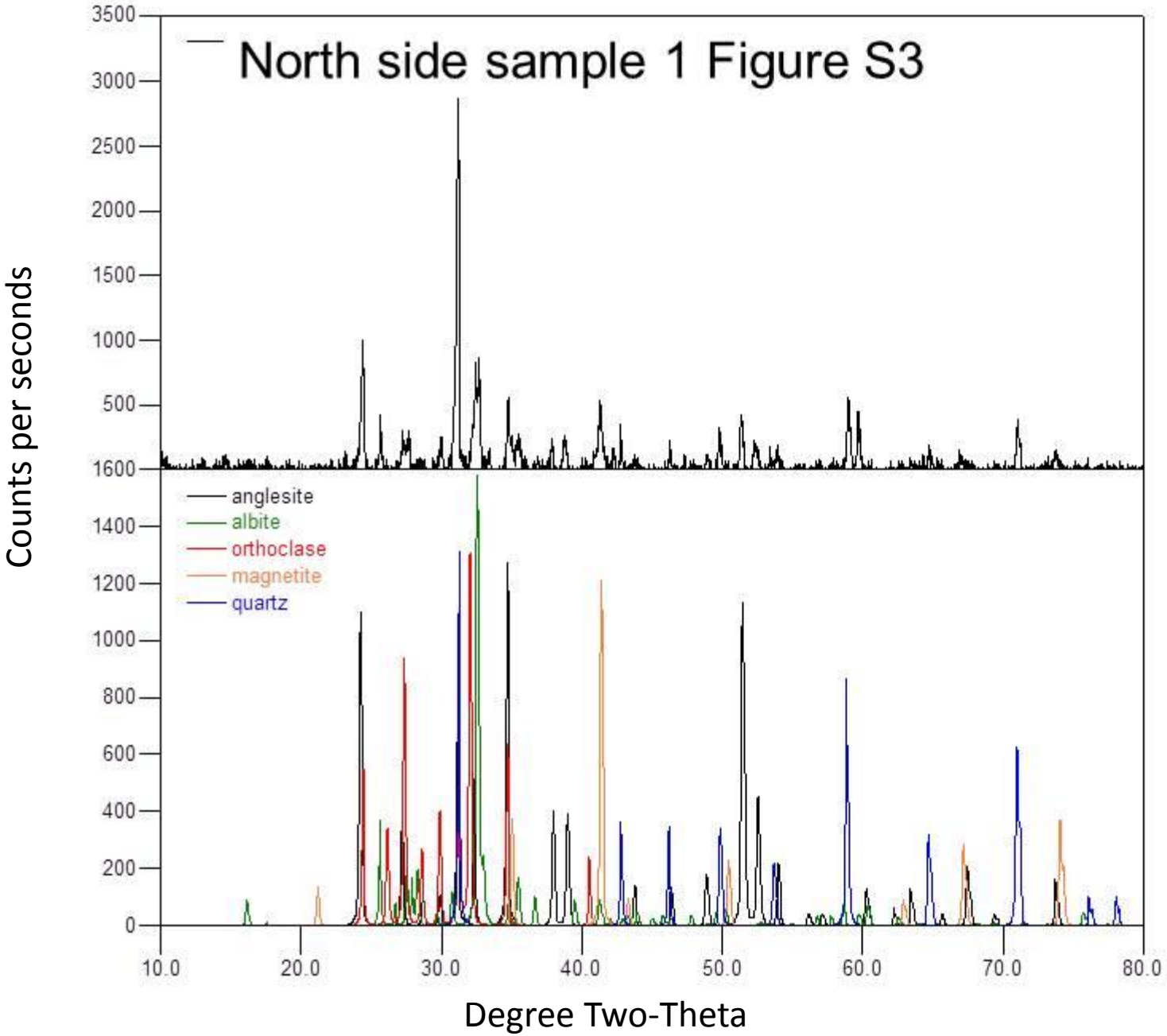
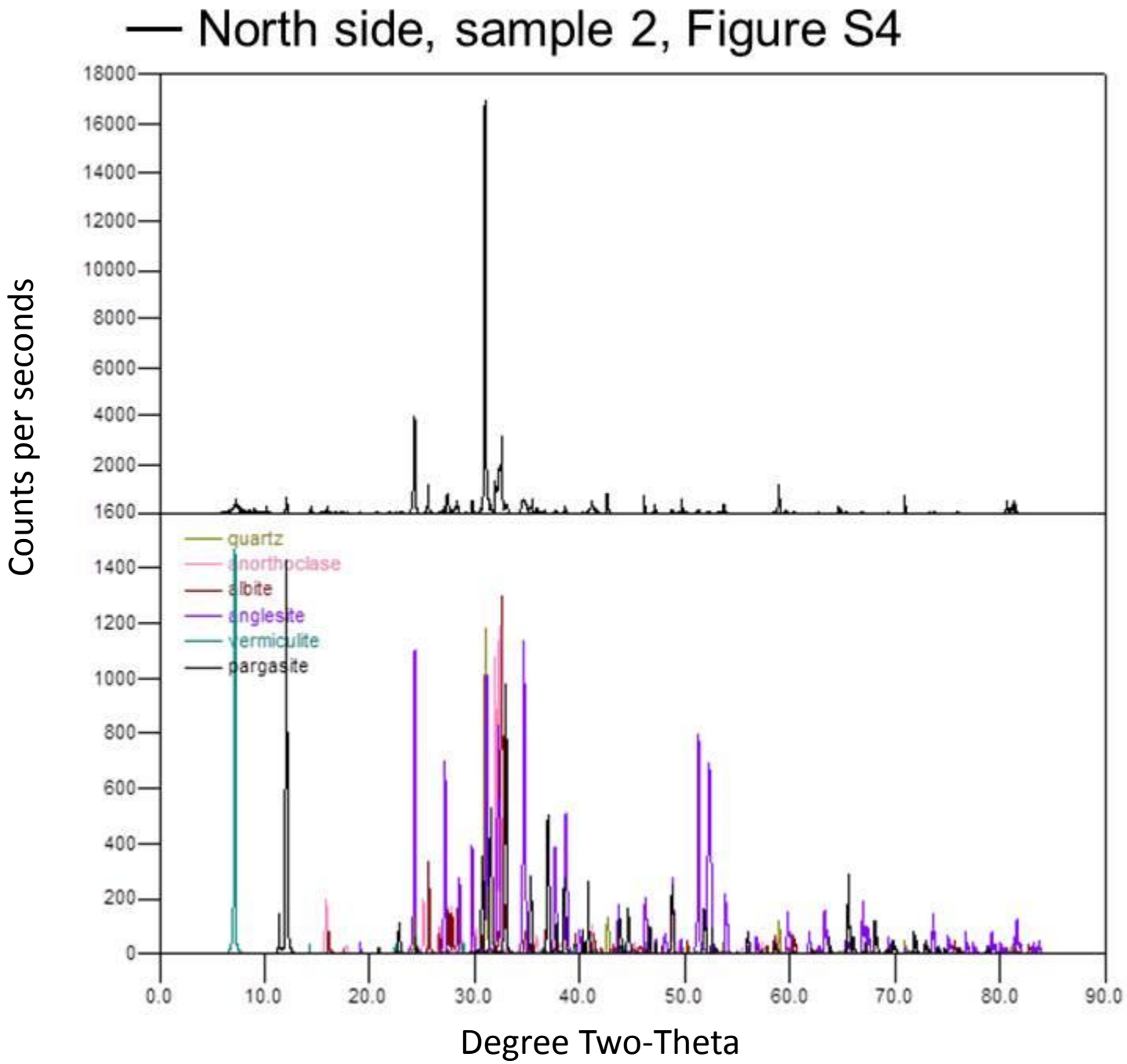
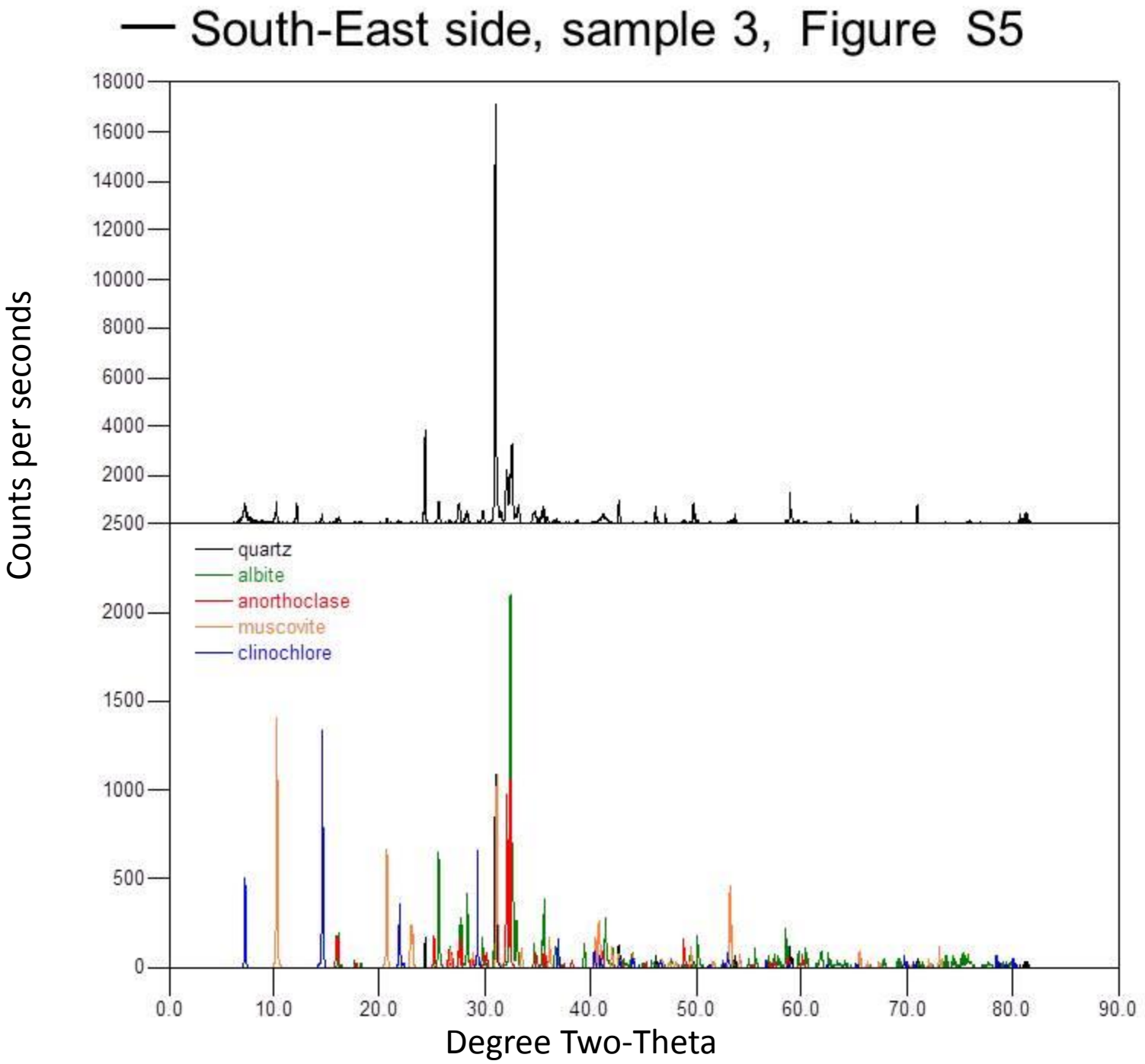


Figure S2, Sampling site South East, May 2016


North side sample 1 Figure S3
Counts per seconds
Degree Two-Theta
anglesite
albite
orthoclase
magnetite
quartz
3500
3000
2500
2000
1500
1000
500
1600
1400
1200
1000
800
600
400
200
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0


— North side, sample 2, Figure S4
Counts per seconds
Degree Two-Theta
quartz
anorthoclase
albite
anglesite
vermiculite
pargasite
18000
16000
14000
12000
10000
8000
6000
4000
2000
1600
1400
1200
1000
800
600
400
200
0
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0


— South-East side, sample 3, Figure S5
Counts per seconds
18000
16000
14000
12000
10000
8000
6000
4000
2000
2500
2000
1500
1000
500
0
quartz
albite
anorthoclase
muscovite
clinochlore
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
Degree Two-Theta

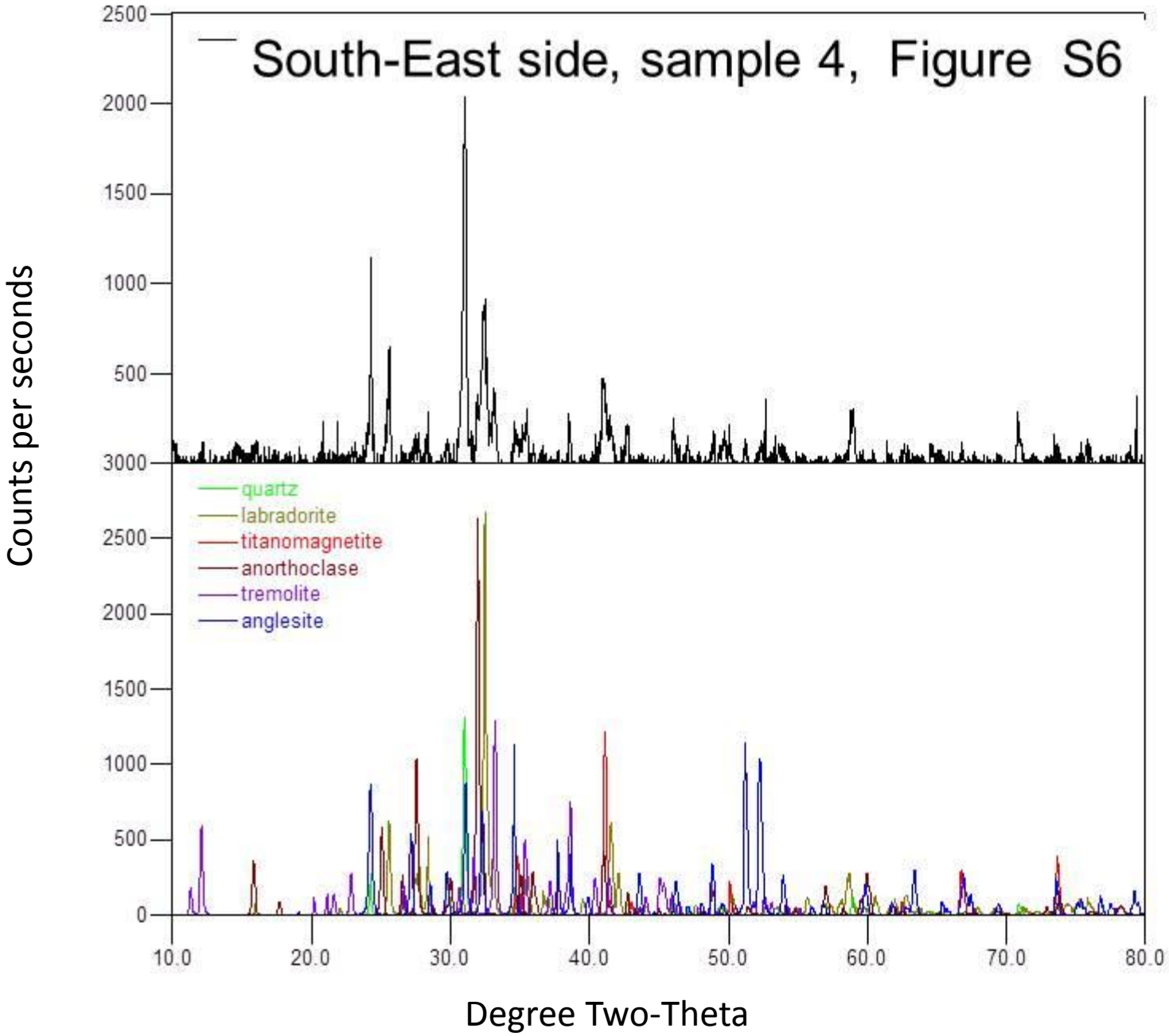

South-East side, sample 4, Figure S6
Counts per seconds
Degree Two-Theta
quartz
labradorite
titanomagnetite
anorthoclase
tremolite
anglesite
2500
2000
1500
1000
500
3000
2500
2000
1500
1000
500
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0

Table S1. Bulk chemical analysis

Analyte:	Al	As	B	Ba	Bi	Ca	Cd	Ce	Co	Cs	Cu	Fe
Unit:	%	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	%
Sample Description RDL:	0.01	30	20	0.5	0.1	0.05	0.2	0.1	0.5	0.1	5	0.01
North site 1	5.78	843	28	1050	35	1.27	28.5	61	19.4	2.7	566	3.66
North site 2	6.11	820	24	1130	32.7	1.36	35.5	53	10.3	3.2	610	3.75
South East site 3	6.6	440	21	950	17.5	1.51	24.2	61	10.2	3.2	450	3.6
South East site 4	6.32	470	23	1060	20.2	1.42	23.1	76	23.3	3	465	3.47

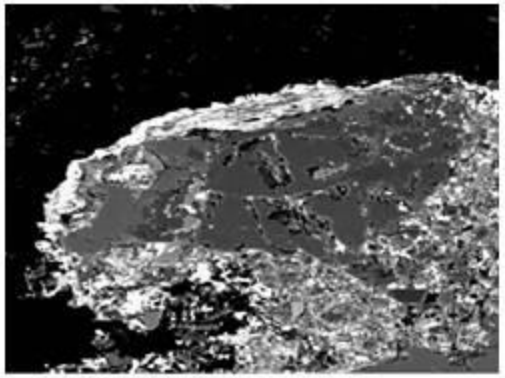
Analyte:	K	Mg	Mn	P	Pb	S	Sb	Si	Sn	Sr	Ti	Zn
Unit:	%	%	ppm	%	ppm	%	ppm	%	ppm	ppm	%	ppm
Sample Description RDL:	0.05	0.01	10	0.01	5	0.01	0.1	0.01	1	0.1	0.01	5
North site 1	1.4	0.61	590	0.34	16600	0.32	766	22.6	146	343	0.33	3520
North site 2	1.62	0.71	695	0.37	14000	0.26	720	21.5	125	382	0.38	3850
South East site 3	1.61	0.72	745	0.44	8800	0.21	440	23.2	112	352	0.35	2440
South East site 4	1.55	0.67	638	0.48	10100	0.24	360	21.9	80	375	0.38	2590

Supplementary data B1

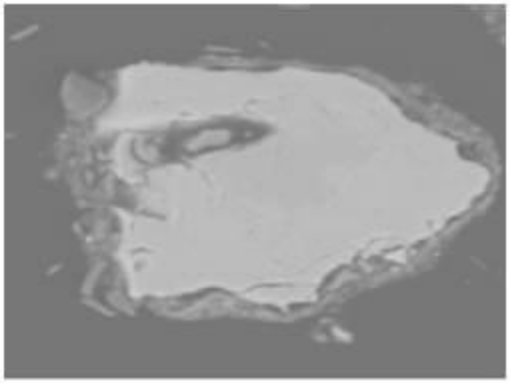
SEM-BSE images of Mineral surface coatings

Figures
S7 North site
S8 South East site

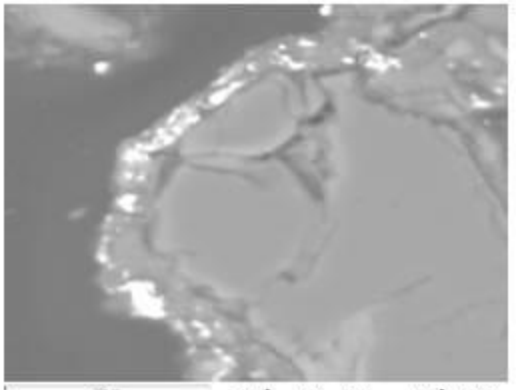
Elements are listed if their concentrations are above 1 at%;



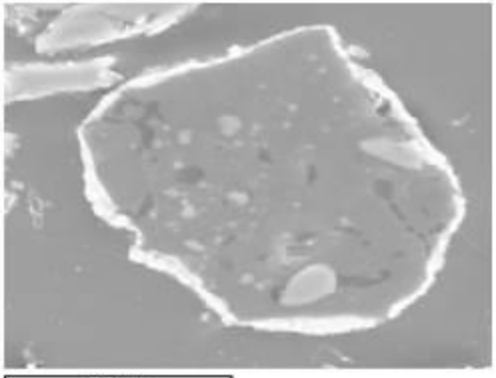
Pb-S-Al-Si



Fe-Al-Si



Pb-S-Na-Al-Si



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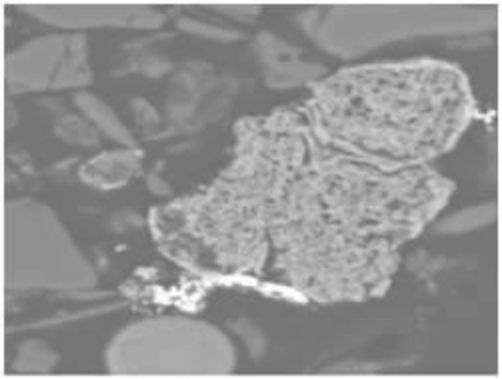

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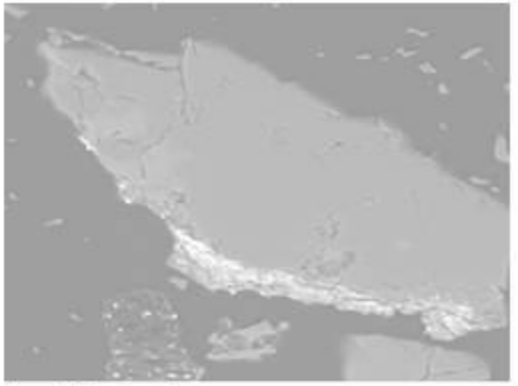

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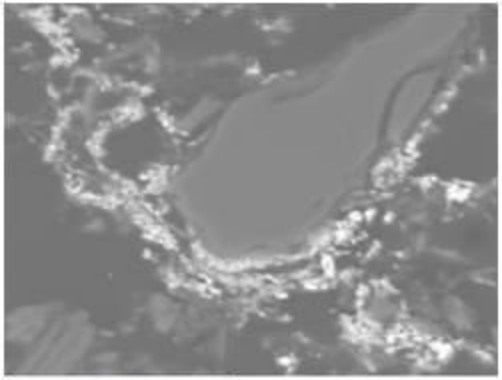

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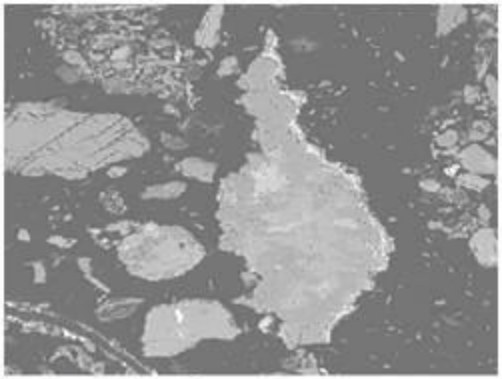

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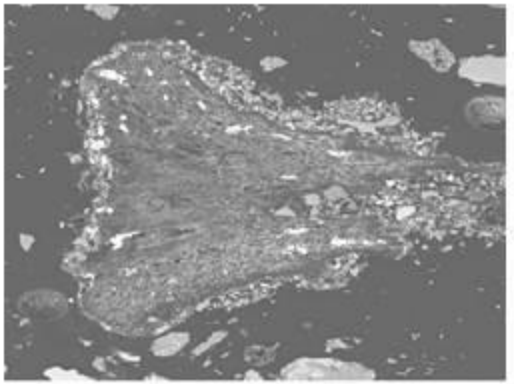
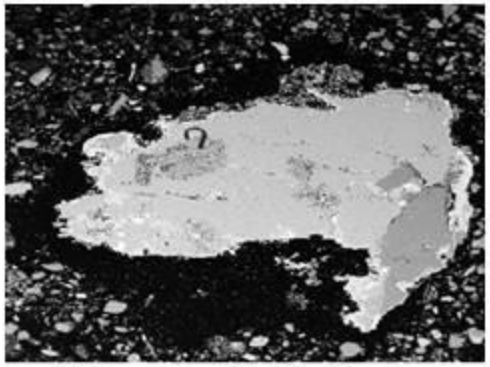


Pb-S-Na-Al-Si

S7



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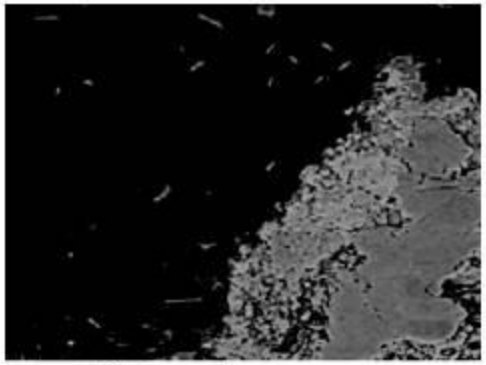

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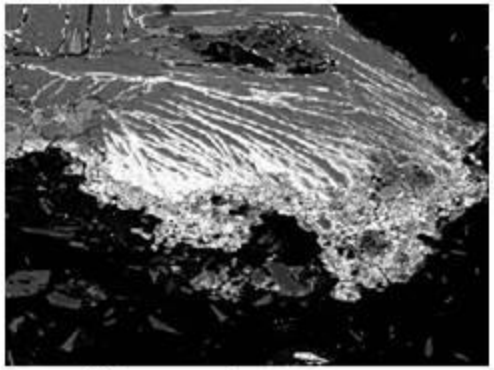
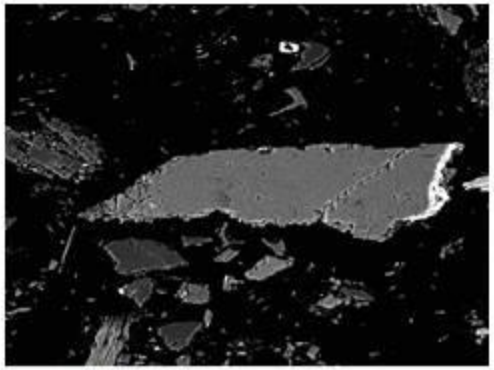


Pb-Zn-Si



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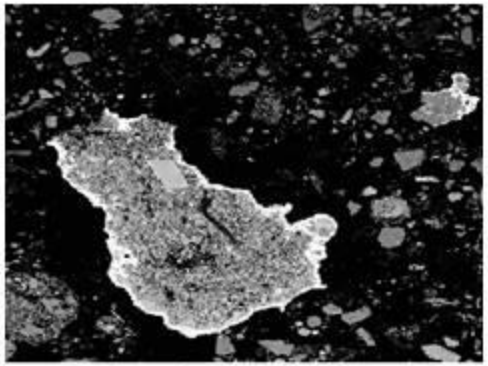

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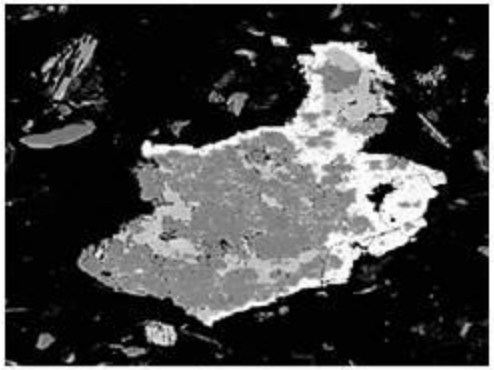

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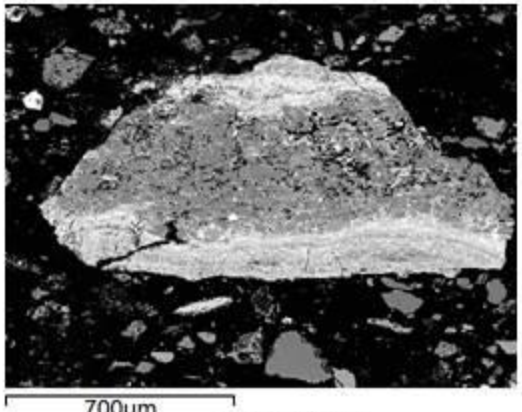

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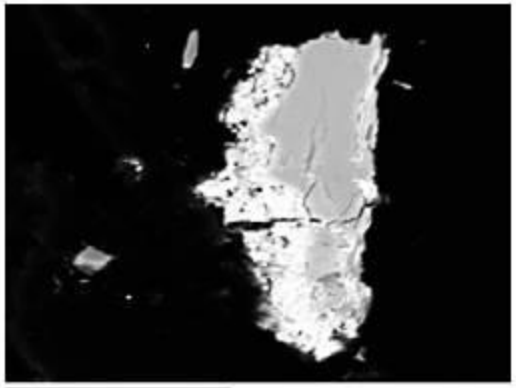
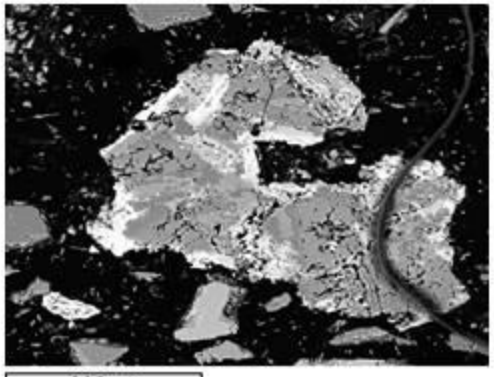


Pb-S-Zn-Fe-Ti-Si

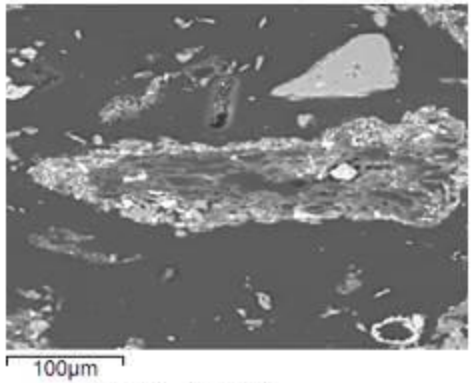


Pb-S-Si

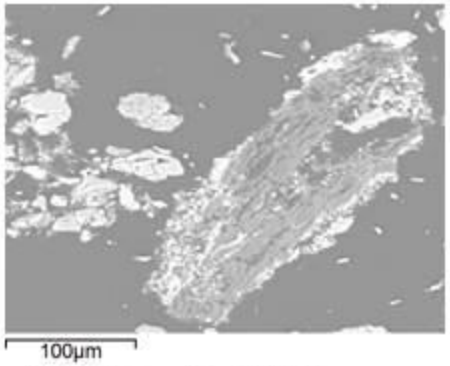
S8

Supplementary data B2
SEM-BSE images of (partly) mineralized organic features in the soils at both sampling sites

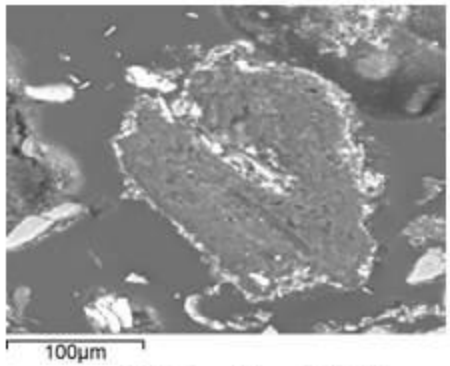
Figures
S9 North site
S10 North site / South-East site
All MOM are mainly composed of C, O and most likely H.
Other elements are only listed if their concentrations are above 1 at%



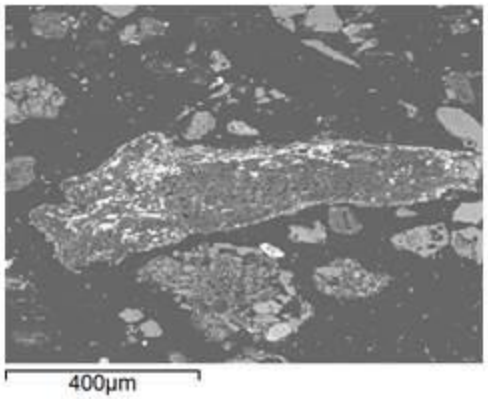
Ba-S-Al-Si



Pb-S-Fe-P-Al-Si



K-Mg-Fe-Al-Si



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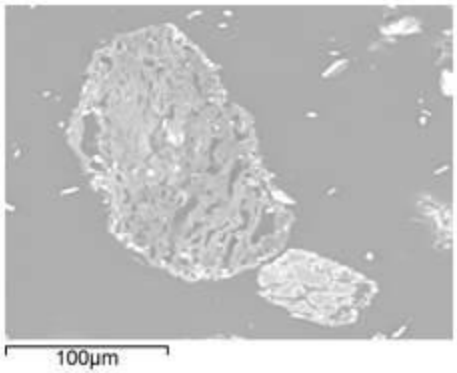

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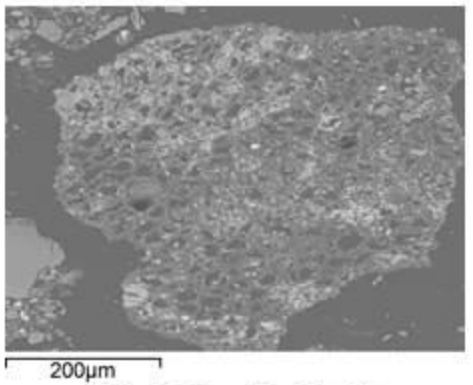

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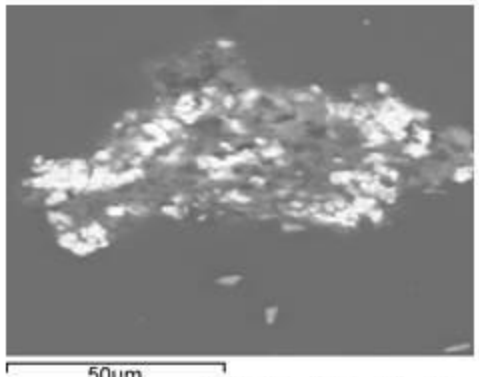

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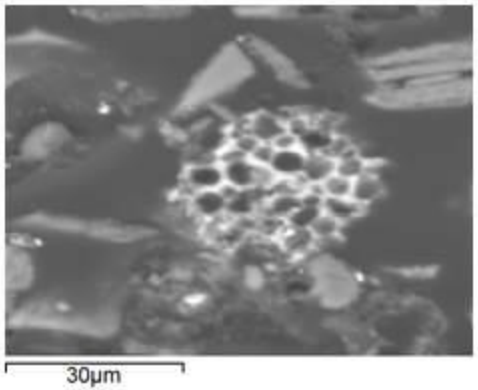
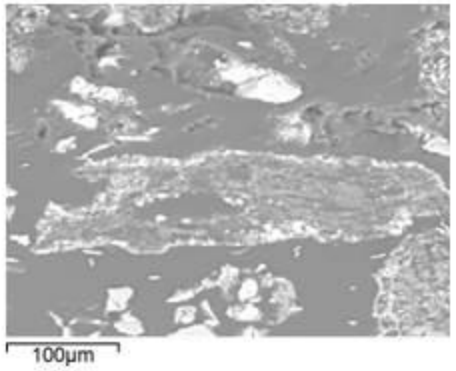
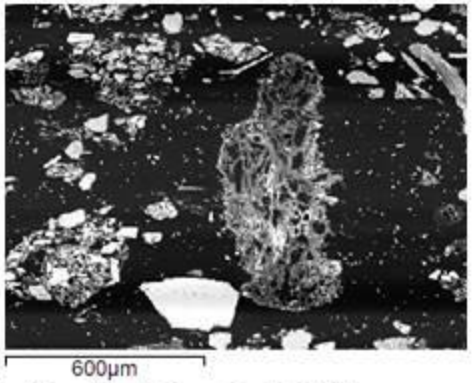


Fe-S-Ca-P-Al-Si



Fe-As-P-Al-Si



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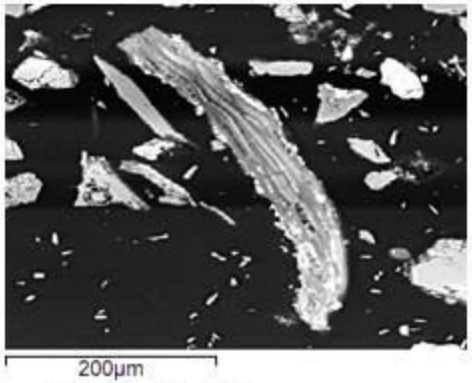

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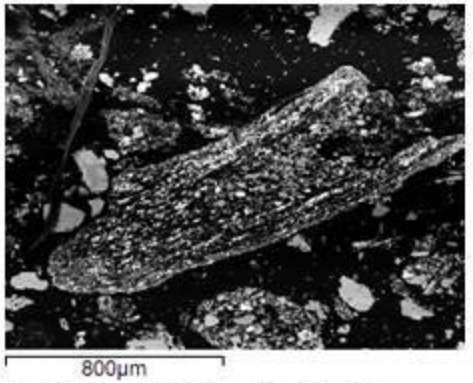
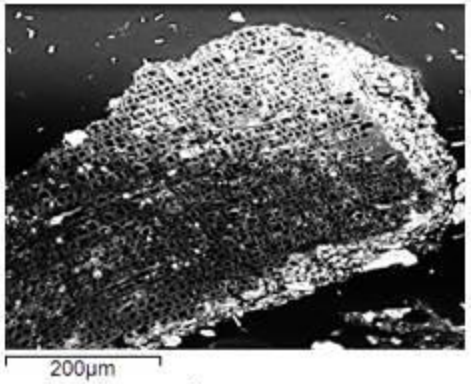
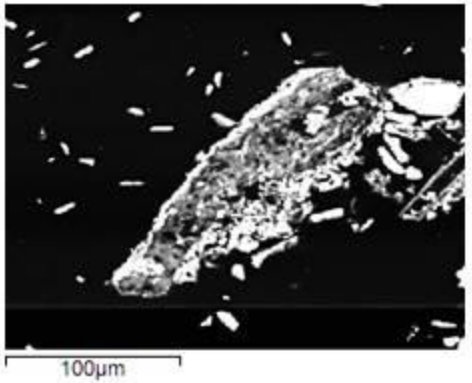


Pb-S-Ca-K-Na-P-Al-Si

NE-site



Fe-P-Al-Si



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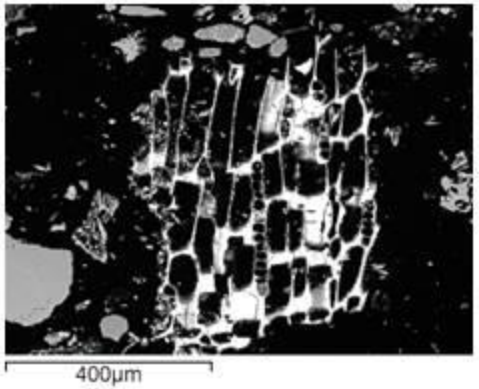
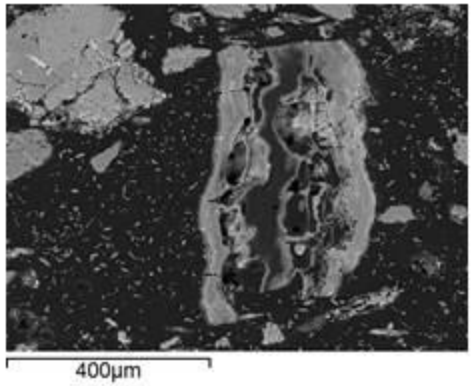
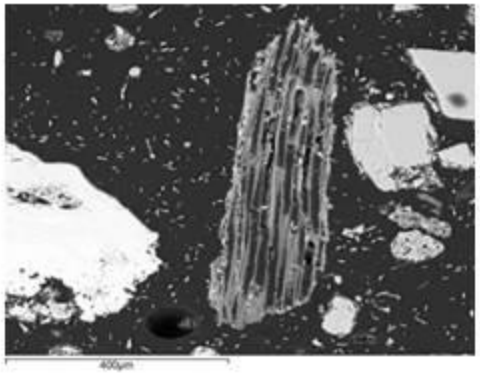


Pb-S-Fe-Al-Si

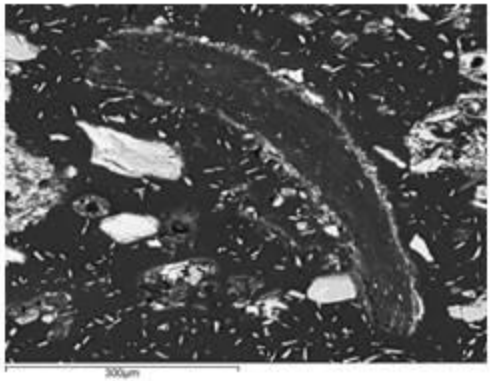
SE-site



Pb



Pb-Fe-Al-P-Si

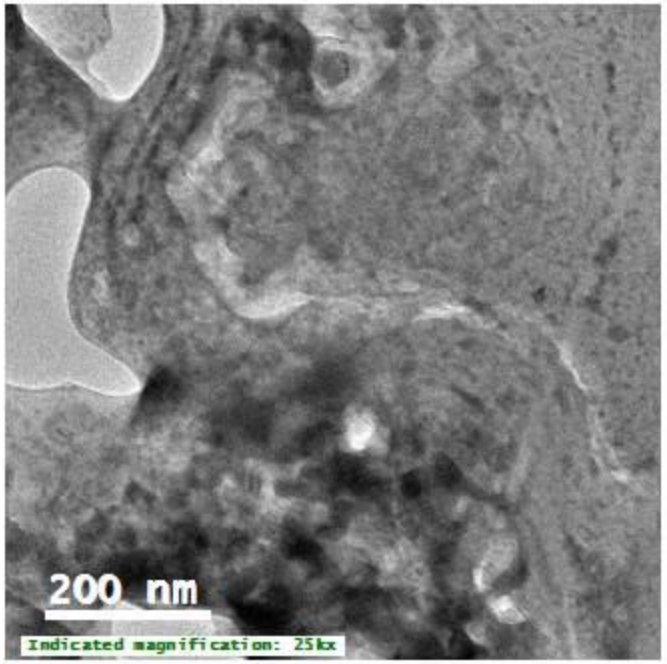


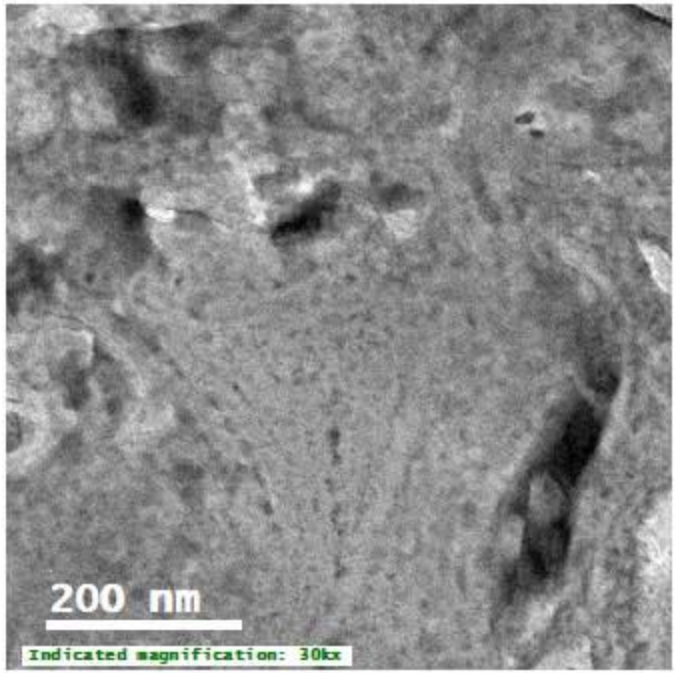
Zn-S-Al-Si

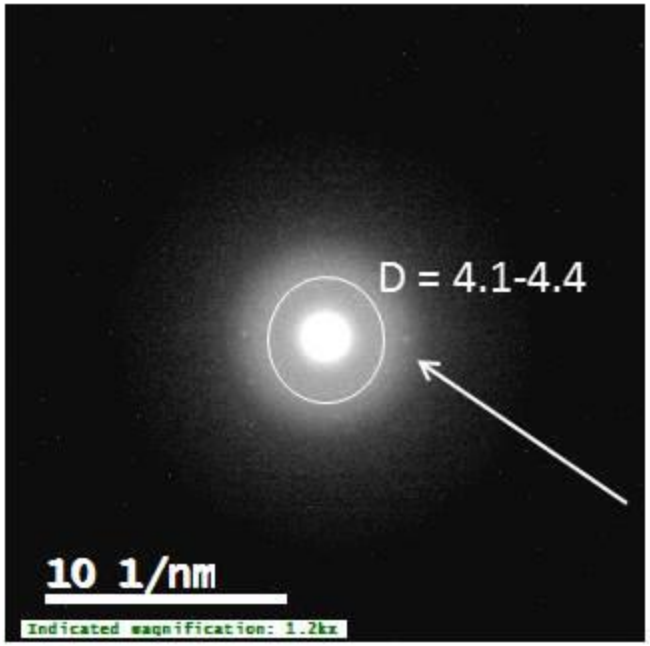
S10

Supplementary data C1

Nano-phases TEM images and diffraction pattern for the mineral surface coating





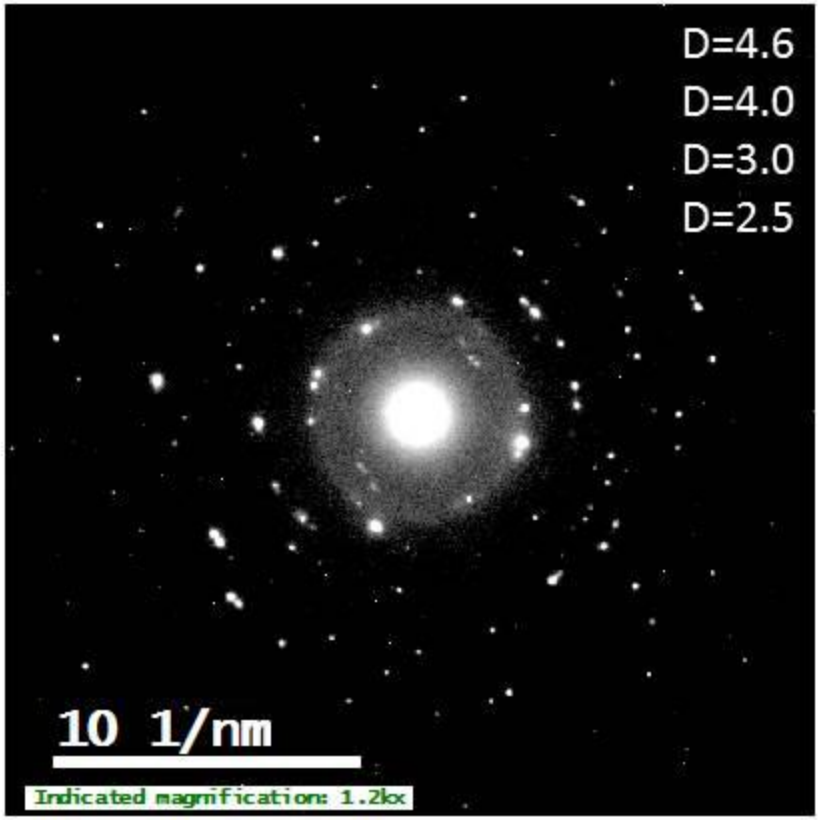


Silica matrix

Broad peak between d = 4.1 and 4.4 Å
characteristic for Opal A/C/CT

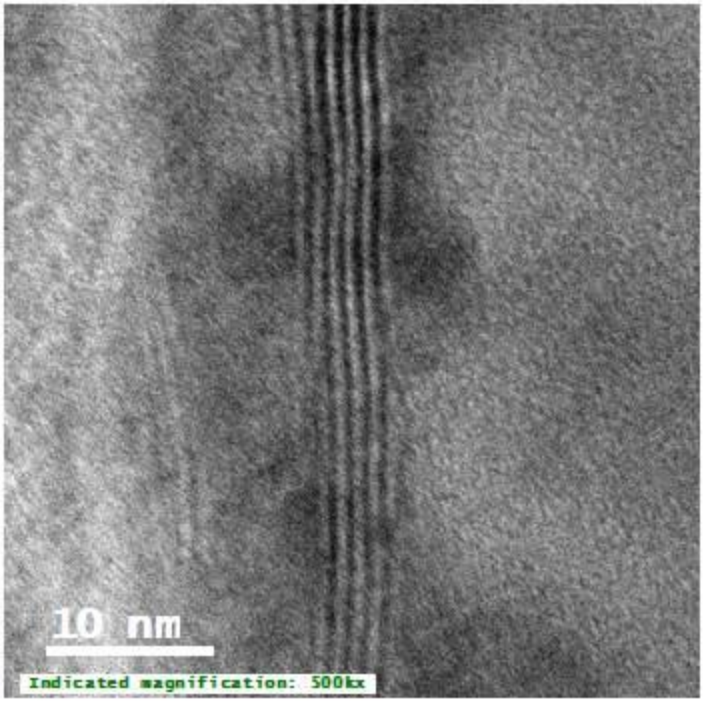
Diffraction spots for anglesite nanoparticles

S11

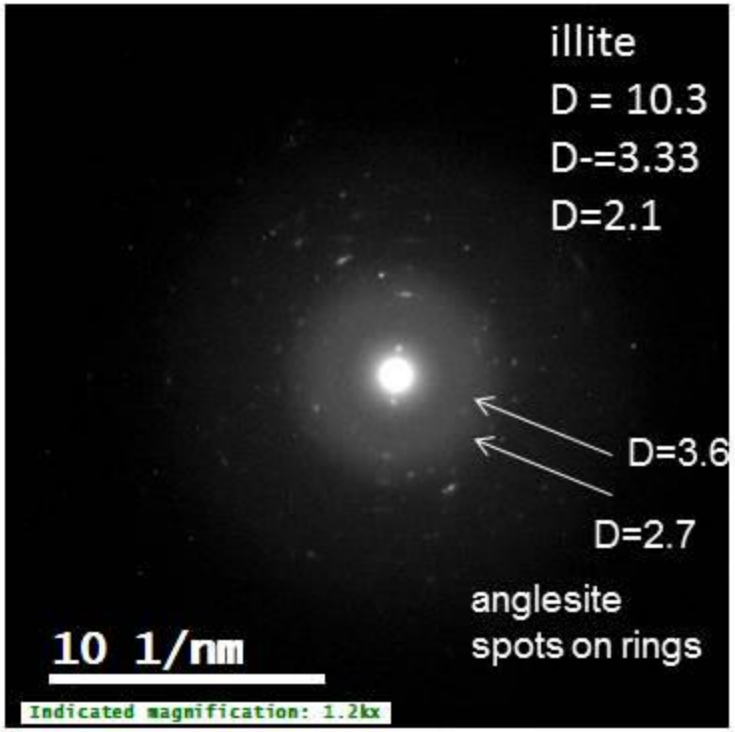


Fluorapatite, (Ca+Pb) : P : F = 5 : 3 : 1

Ca: Pb = 10 : 1



Illite+
Nanoparticles
of anglesite

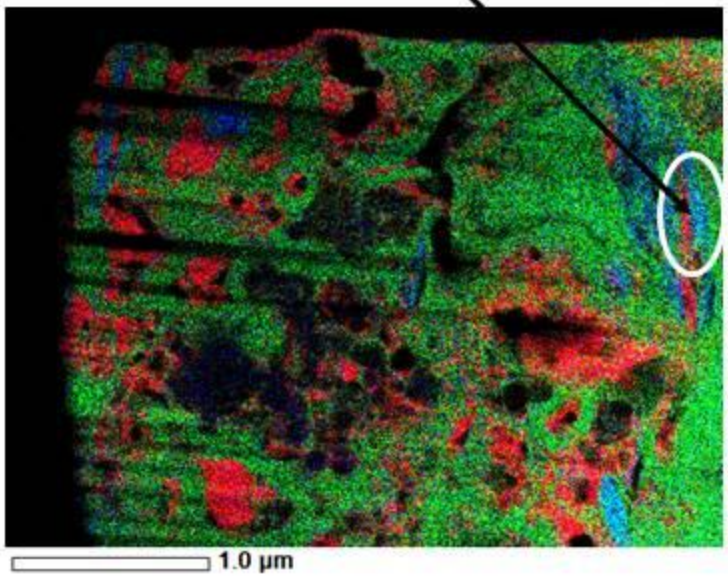


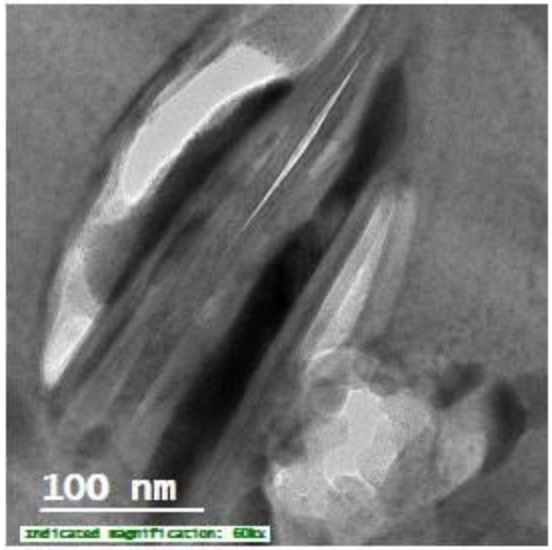
K: Al: Si = 1: 3: 7

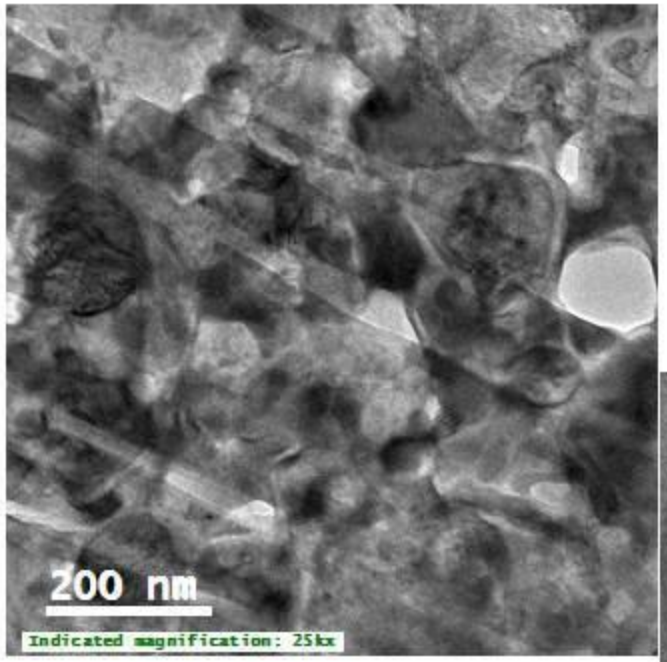
S13

Si: green
Al: Blue
Pb: red

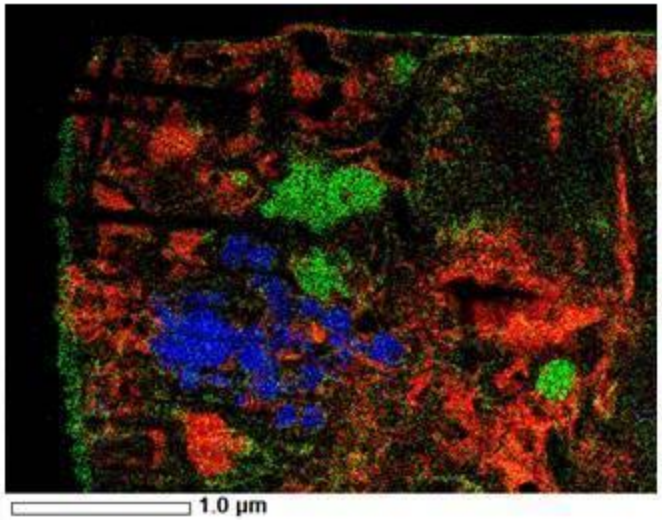
Parallel growth of anglesite
on the surface of illite



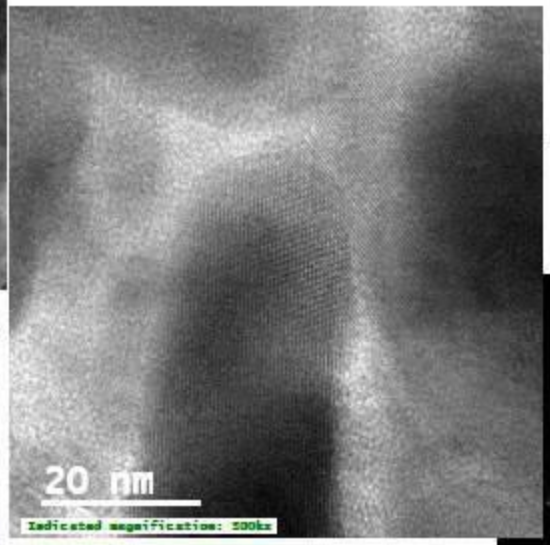


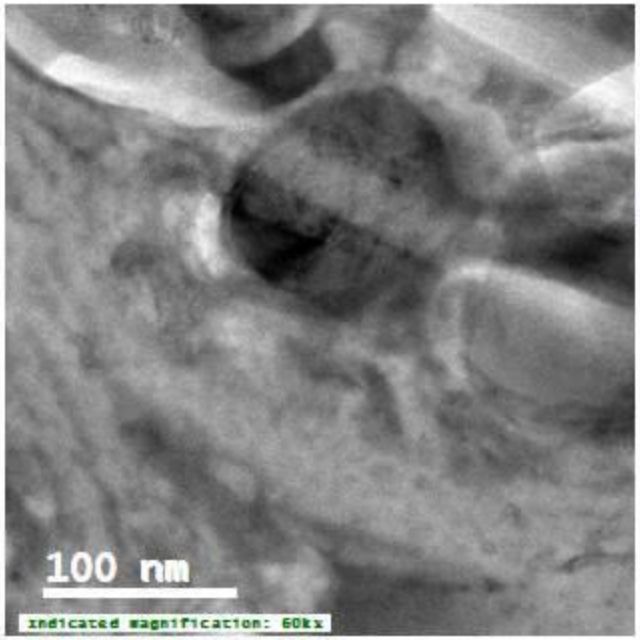


Pb: red
P: green
Zn: blue

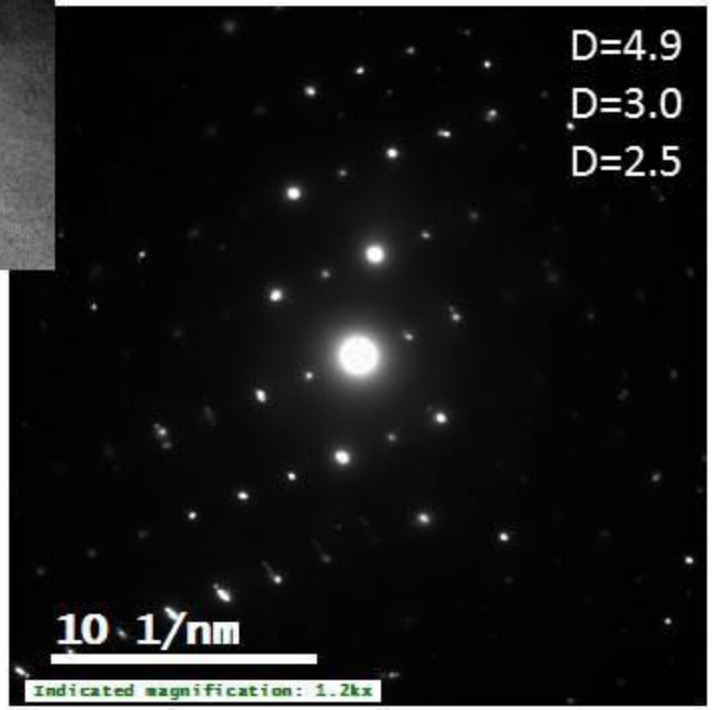


Blue crystals: Zn : Fe = 1:2

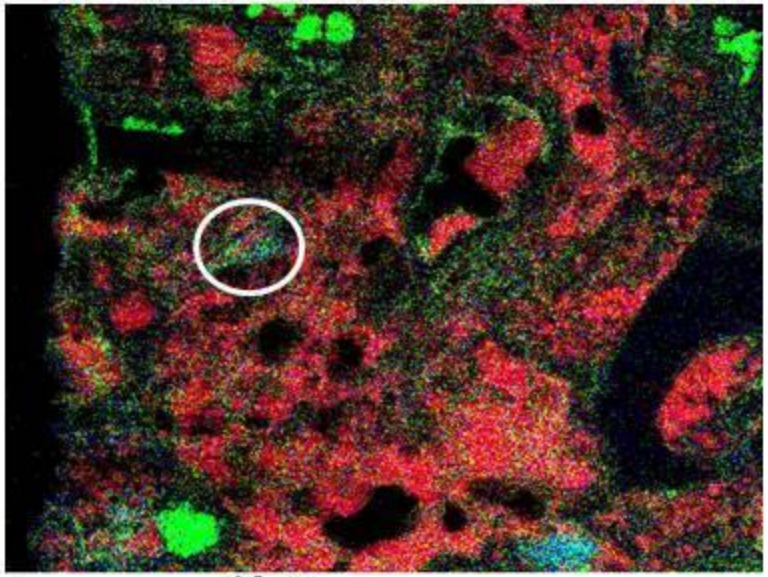




Detrital rounded grains of Franklinite, $ZnFe_2O_4$



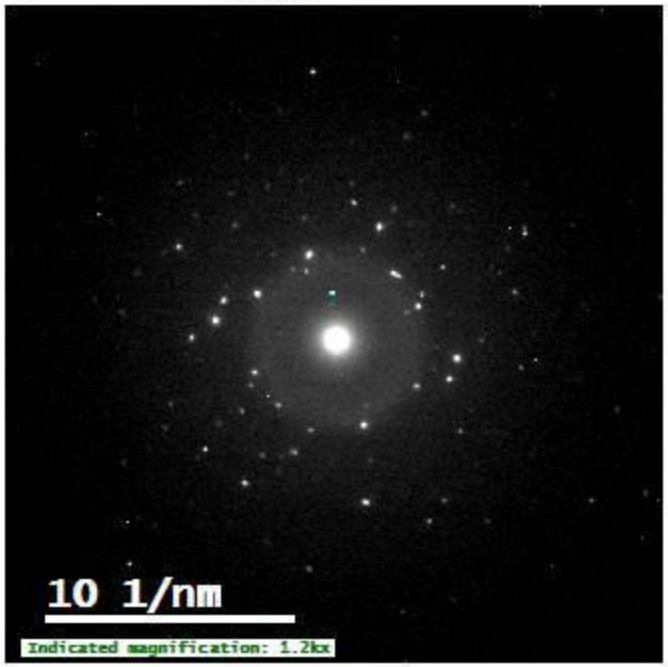
S14



Pb: red
Fe: green
As: blue

Fe : (As+S) = 1: 1

Tsumcorite Group

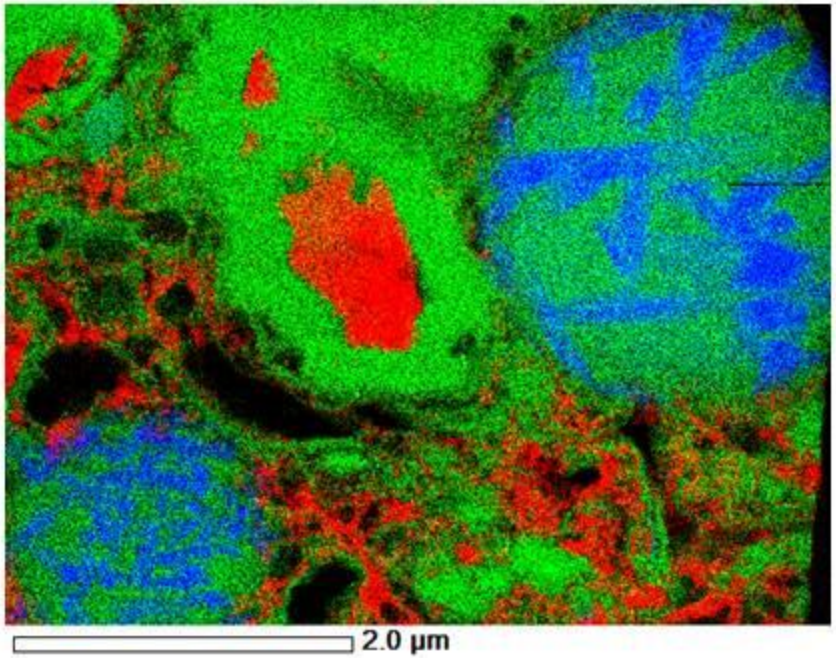


D=6.86
D=3.4
D=2.8
D=2.5

Formula: $AM(XO_4)_2(OH,H_2O)_2$
A group of complex phosphates, arsenates, vanadates and sulphates with a complicated crystal chemistry (symmetry either triclinic or monoclinic, depending on various ordering schemes).

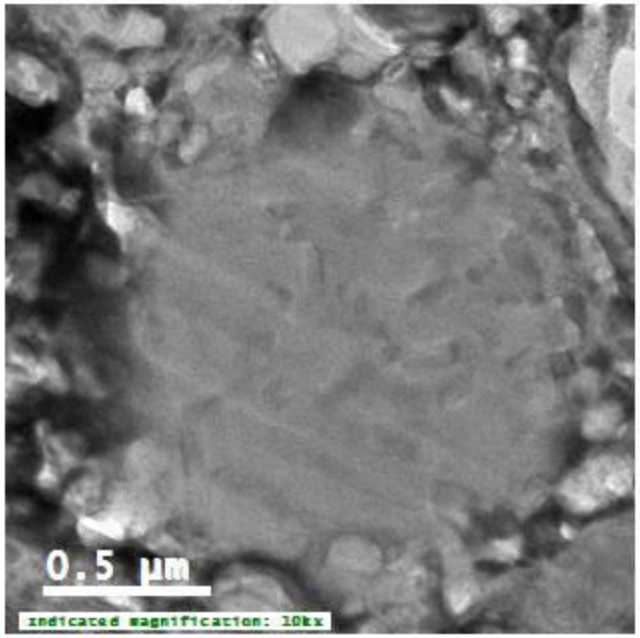
In the general formula given above, A is typically Pb or Ca, rarely Bi, M is typically Fe^{3+} Mn, Cu, Zn, Co or Ni and X is typically P, As or V

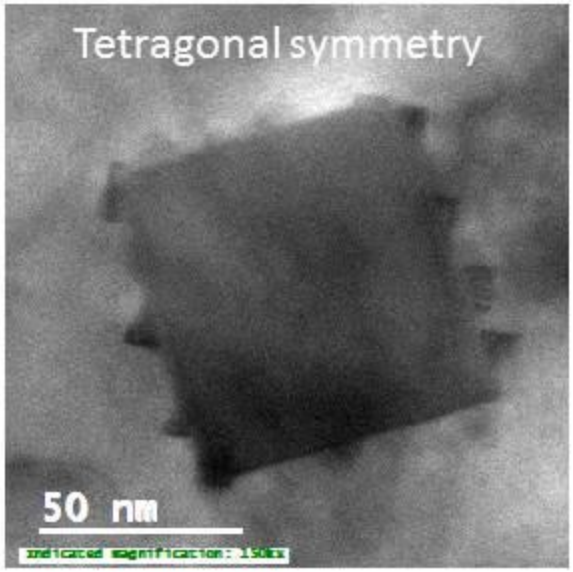
andalusite crystals (blue) in spherical quartz grains (green)

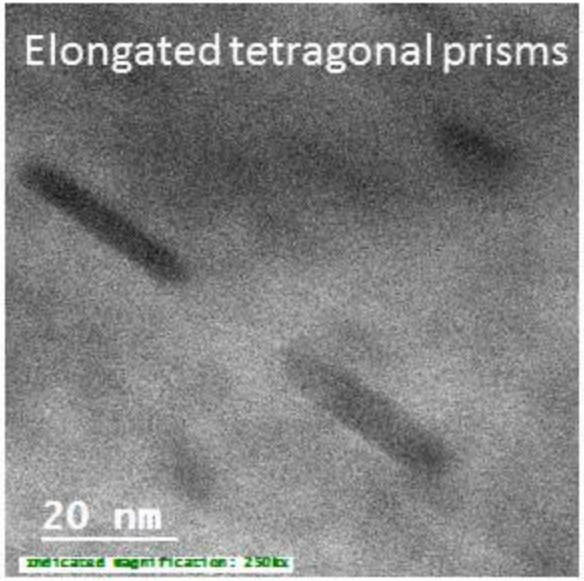


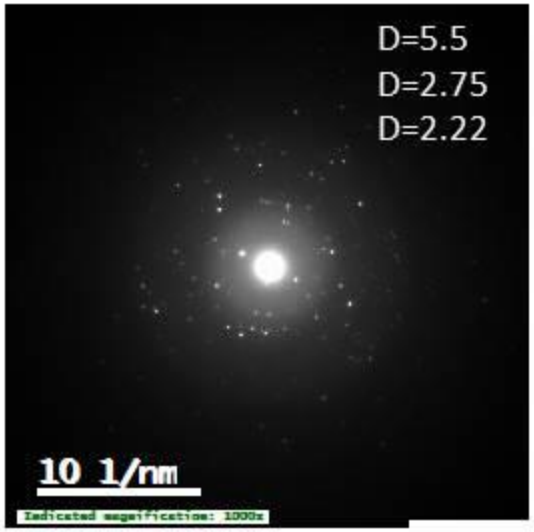
Pb: red
Si: green
Al: blue

Blue crystals:
Al : Si = 2 : 1

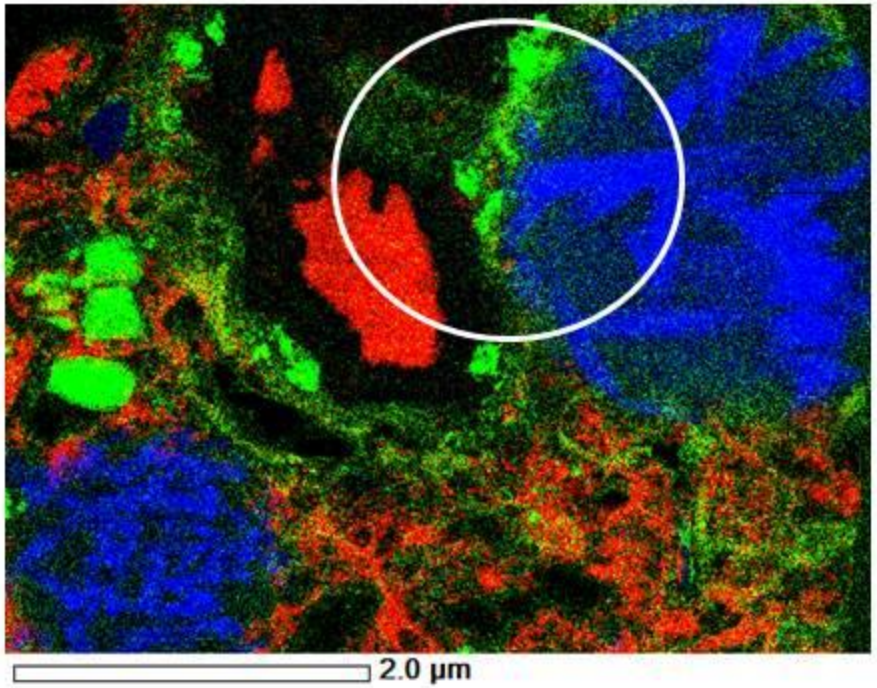


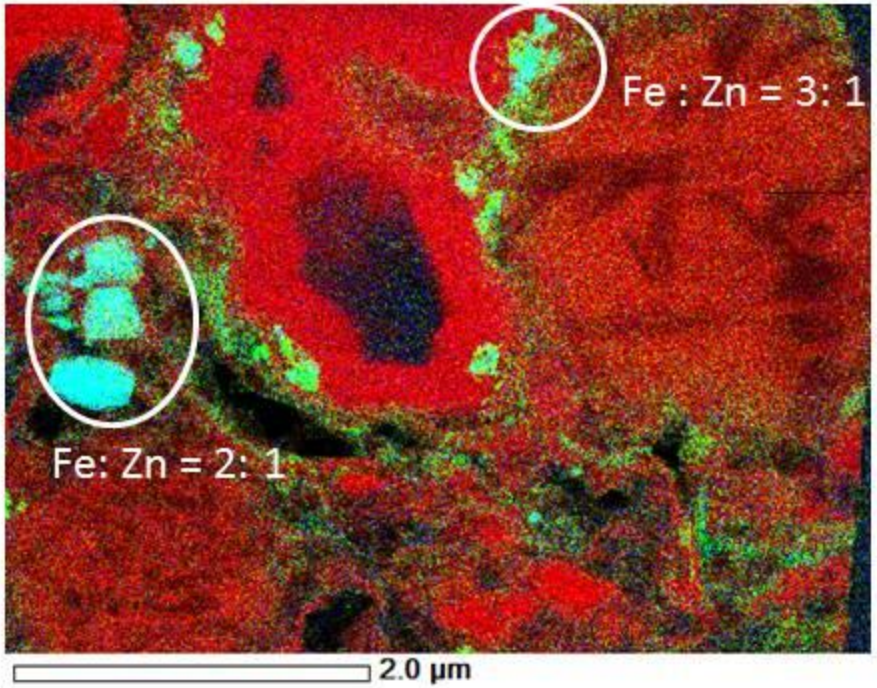


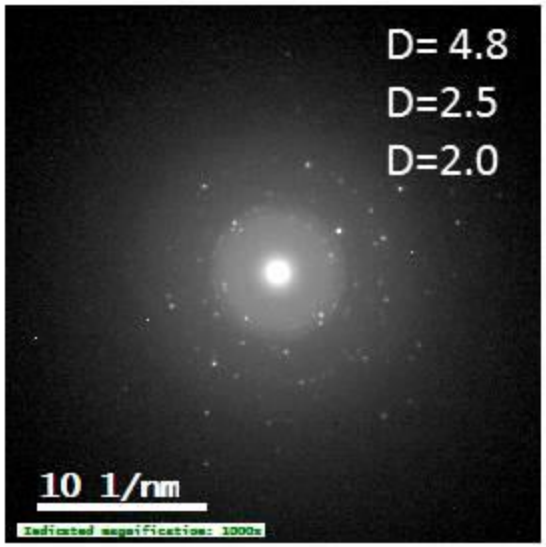




S16



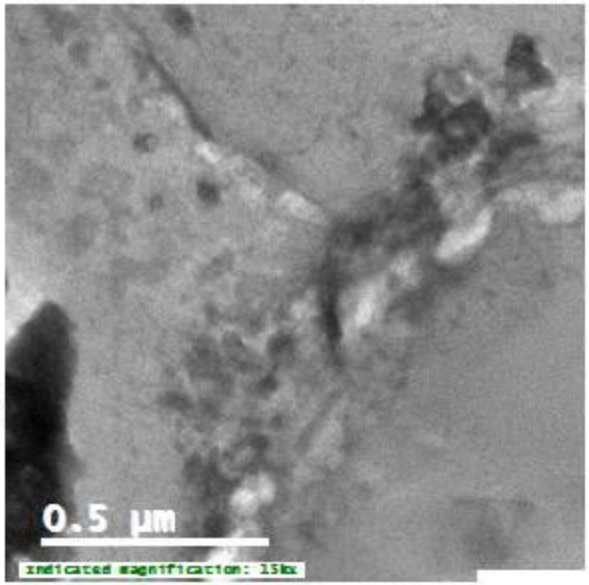


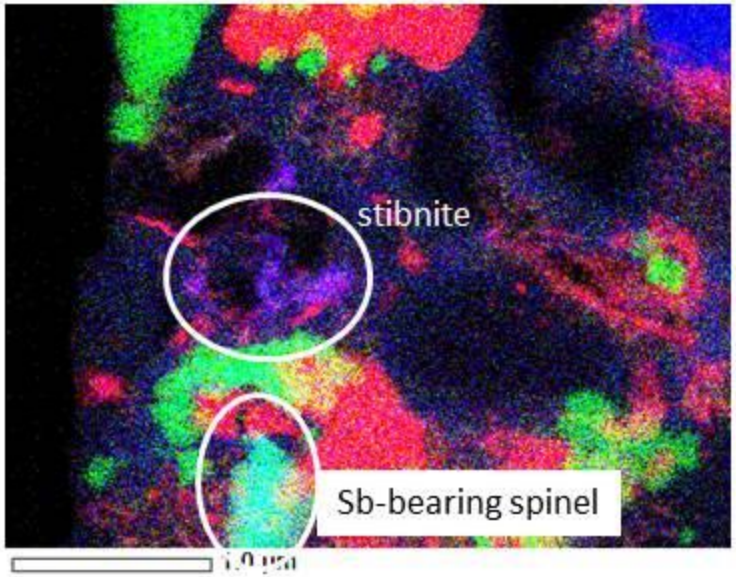


Fe: green
Al: blue
Pb: red

Fe: green
Zn: blue
Si: red

Zn-bearing spinels:
Franklinite
and Zn-magnetite
Fe: Zn ratios vary between
2 : 1 and 3 : 1





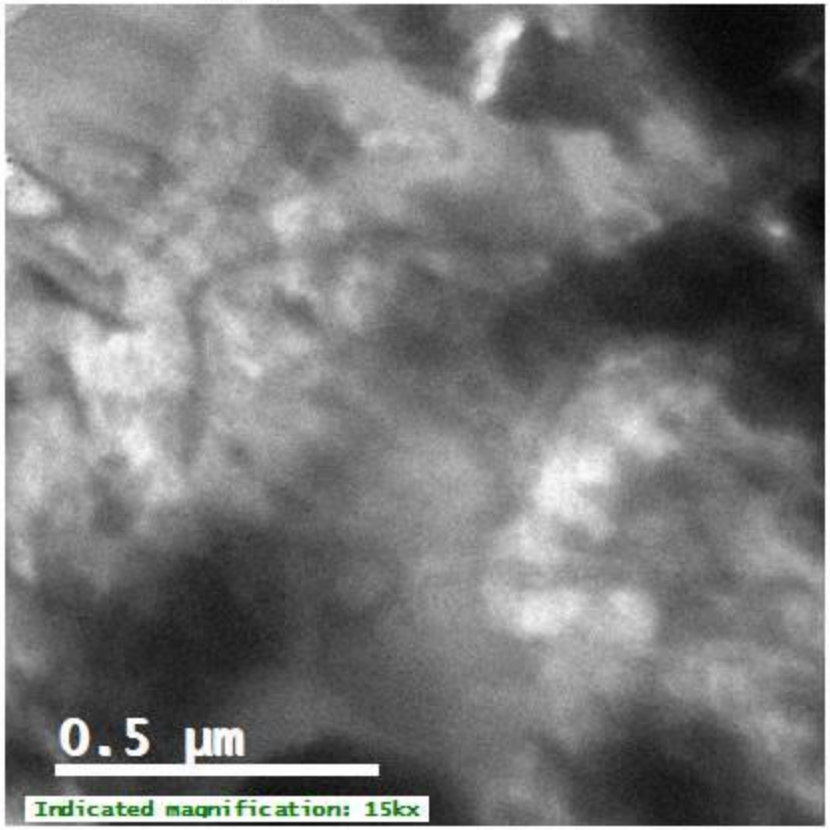
Pb: red
Zn: green
Sb: blue

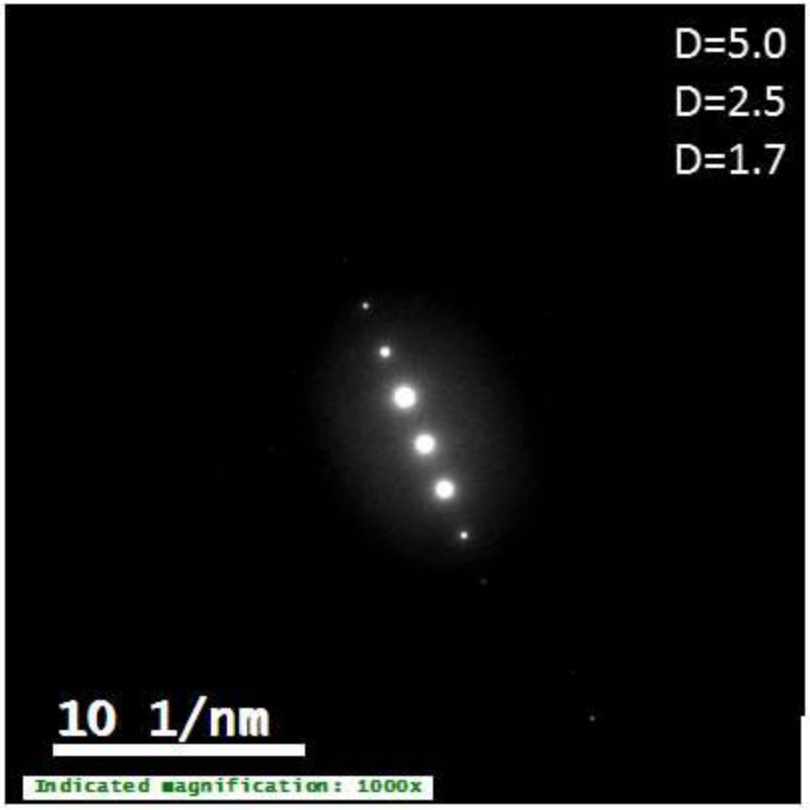
Mixture of various spinels

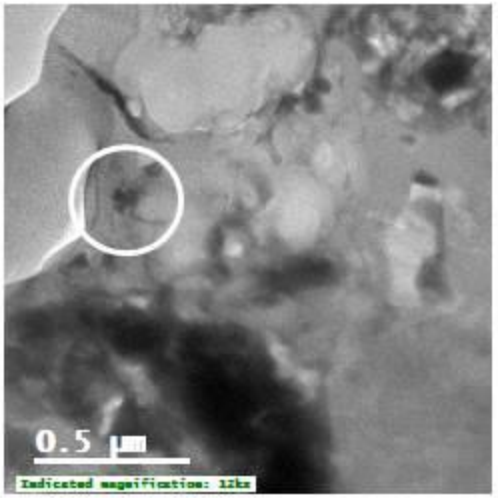
Fe : Zn : Sb = 4 : 7 : 2

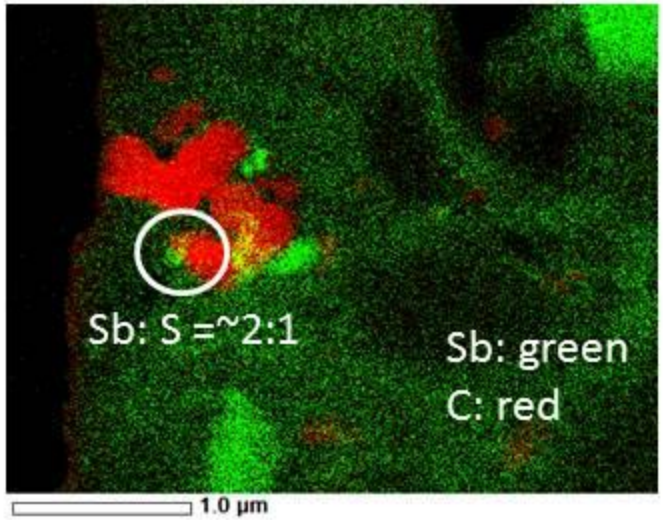
Possible Sb-spinel:

Zn-Sb(V) spinel $Zn_7Sb_2O_{12}$





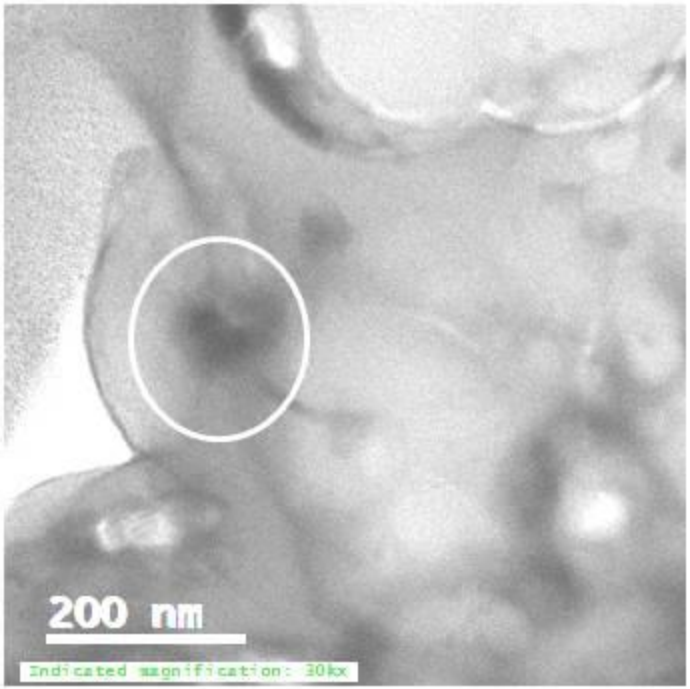


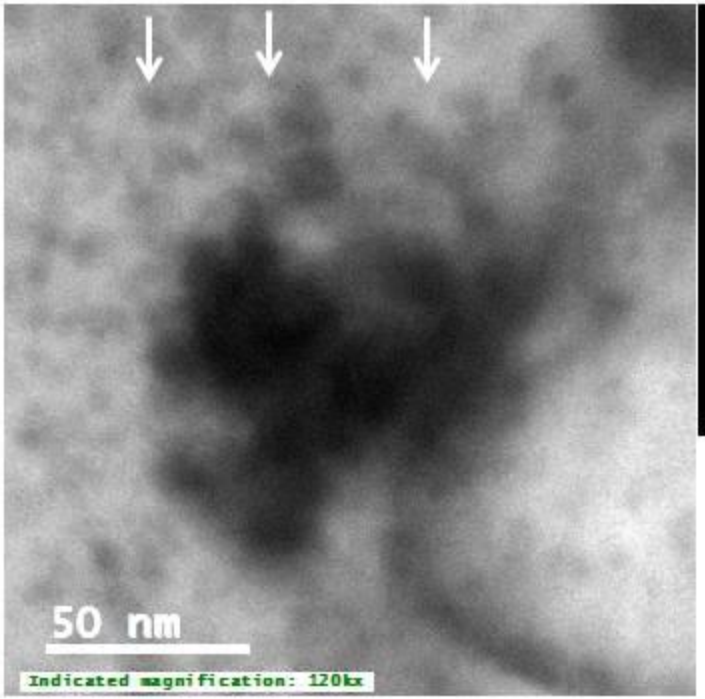


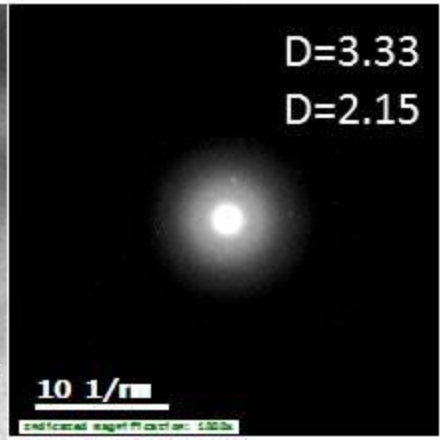
carbonaceous material

material (red) with Sb-bearing nanoparicles inclusions (green)

Unidentified Sb-bearing Nanoparticles



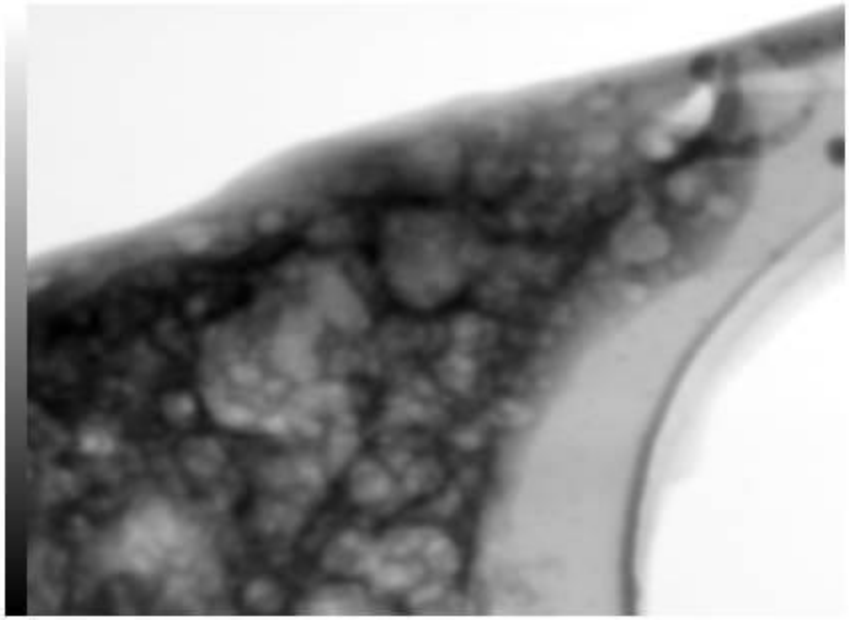


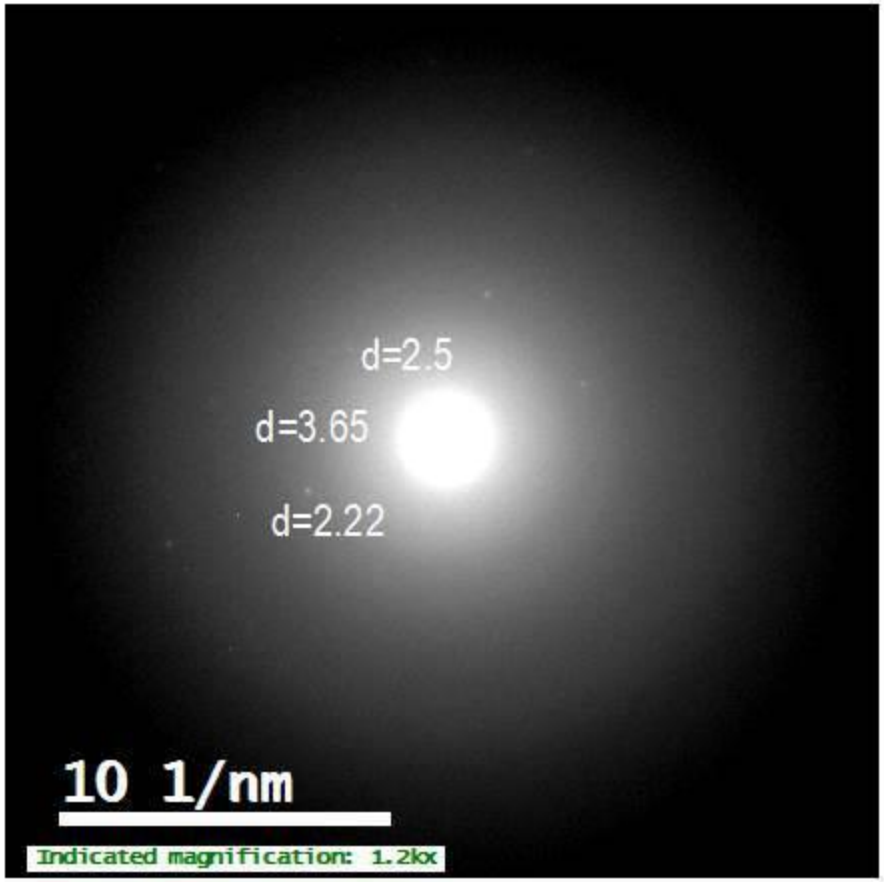


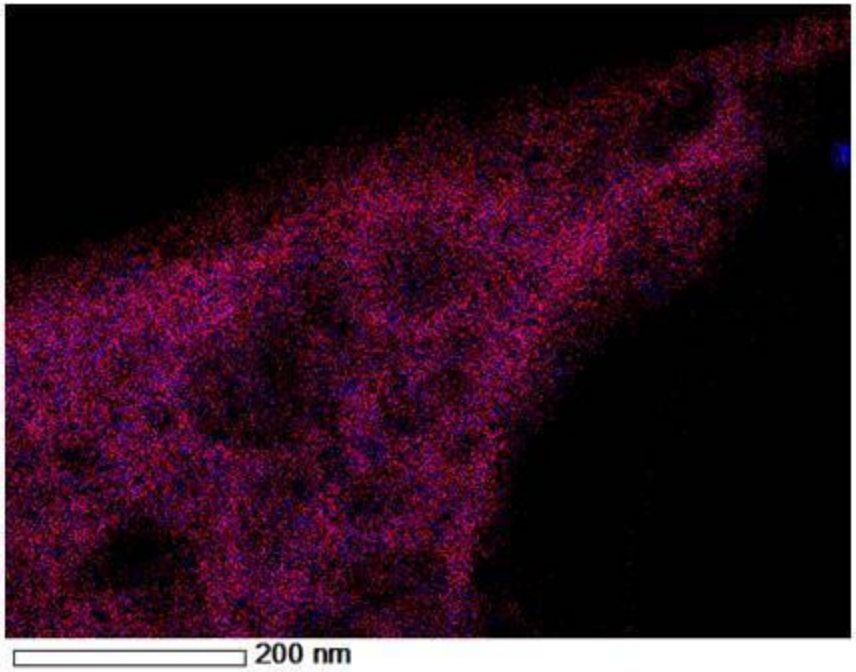
Supplementary data C1

TEM, SAED and EDS-STEM images of nano-size phases in the mineralized organic matter

All listed elemental ratios are given as atomic ratios



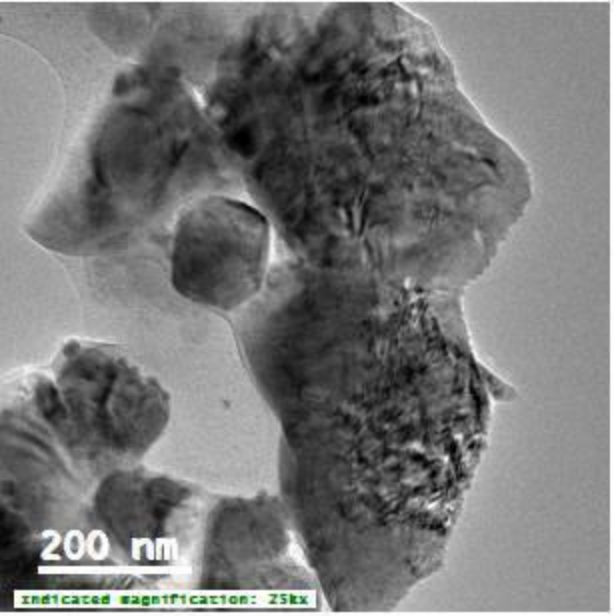


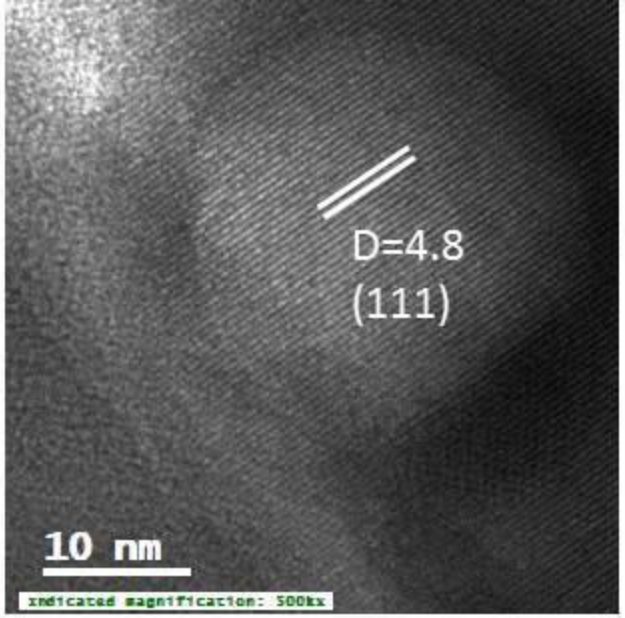


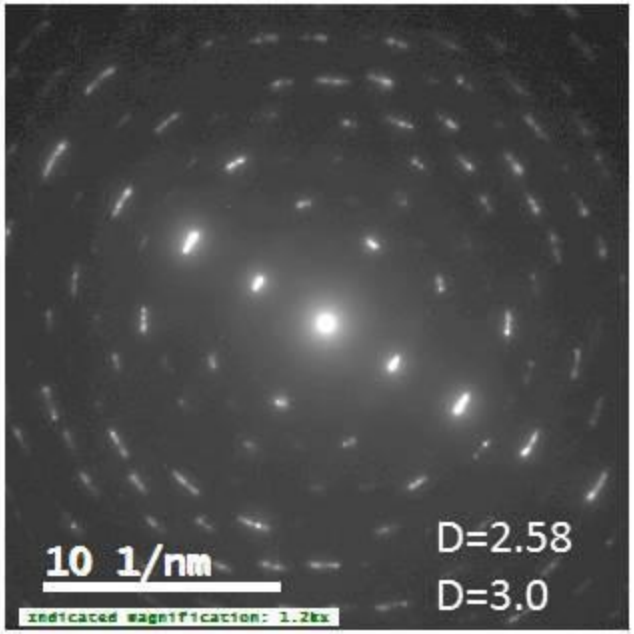
P in red
Pb in blue

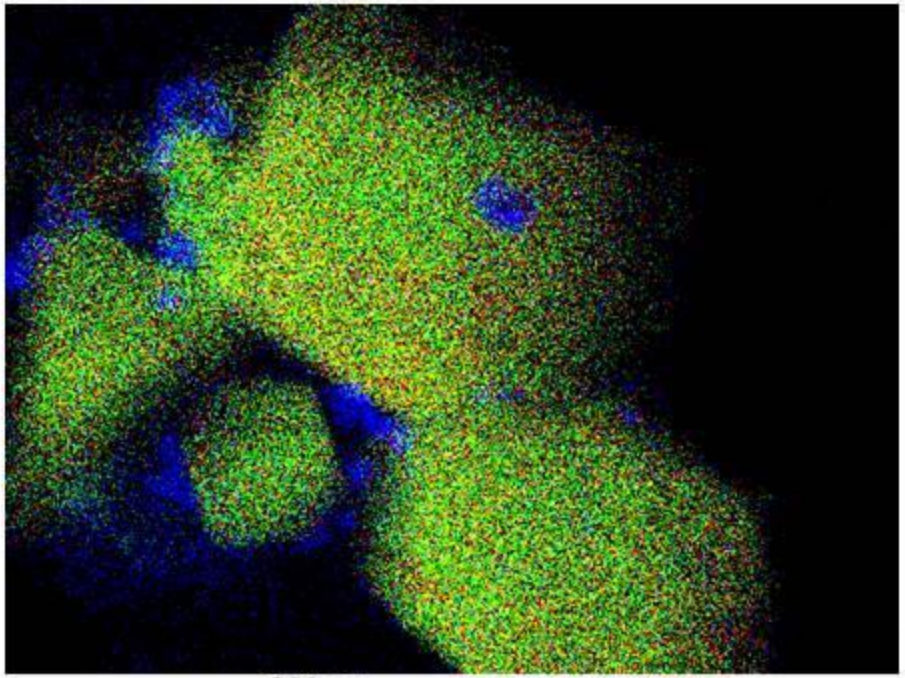
Kintoreite,
mineralized organic matter

P : As = 3 : 1 – 4 : 1
Fe : Al = 3 : 1 – 4 : 1
(P + As) : Pb = 3 : 1









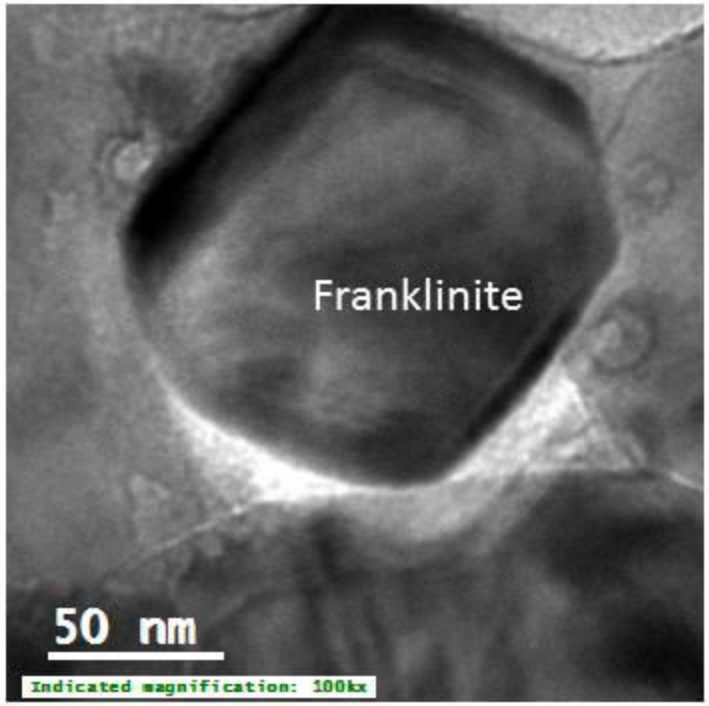
Franklinite with anglesite nanoparticles in the mineralized organic matter

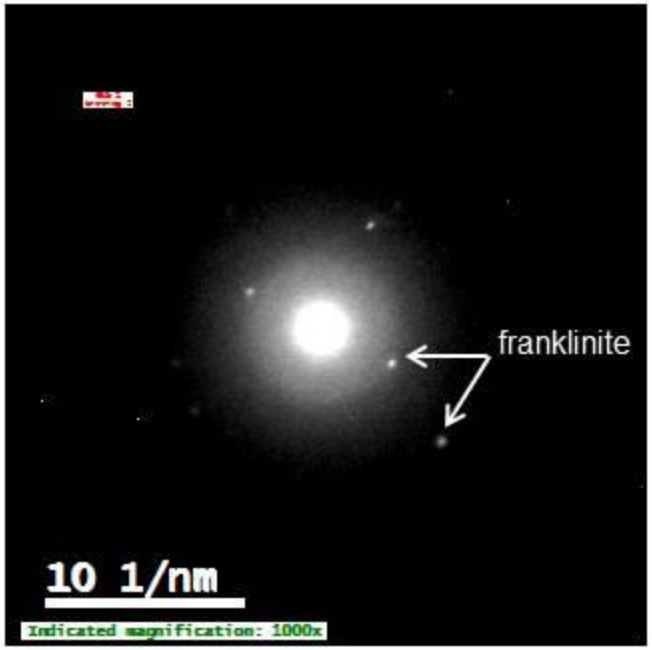
Zn in red Zn : (Al + Fe) = 1 : 2

Fe in green

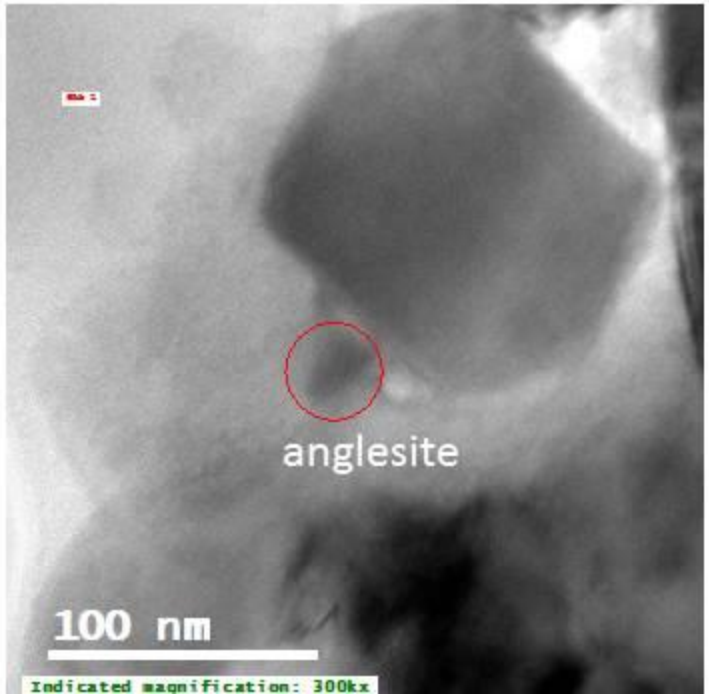
Pb in blue

S21

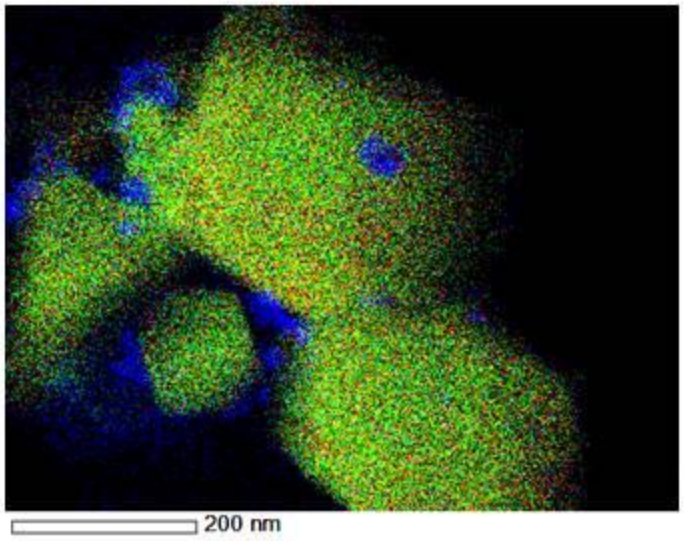




Anglesite spots
D=5.4
D=3.8
D=1.4



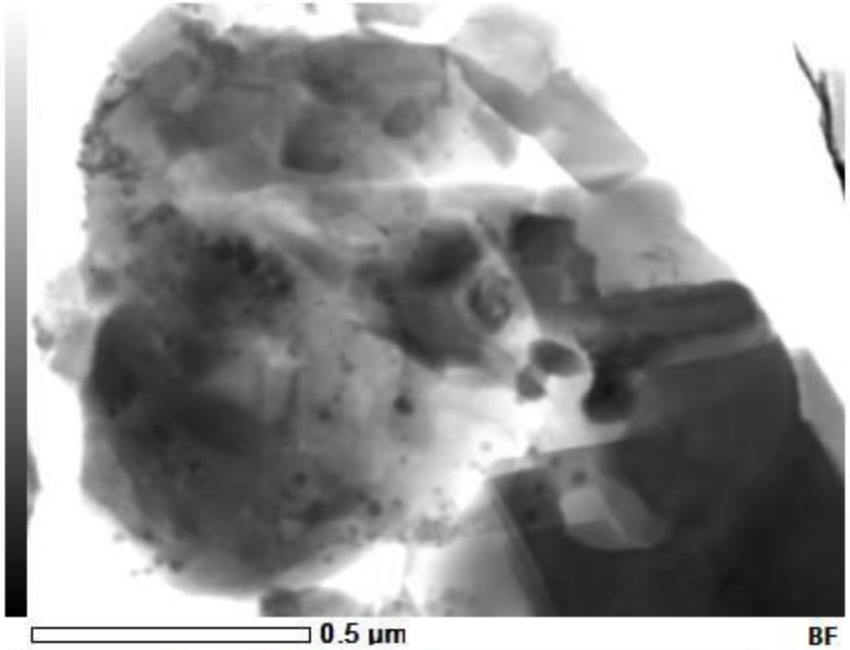
Nano-diffraction of anglesite nanoparticles
on the surface of franklinite with spots belong to franklinit

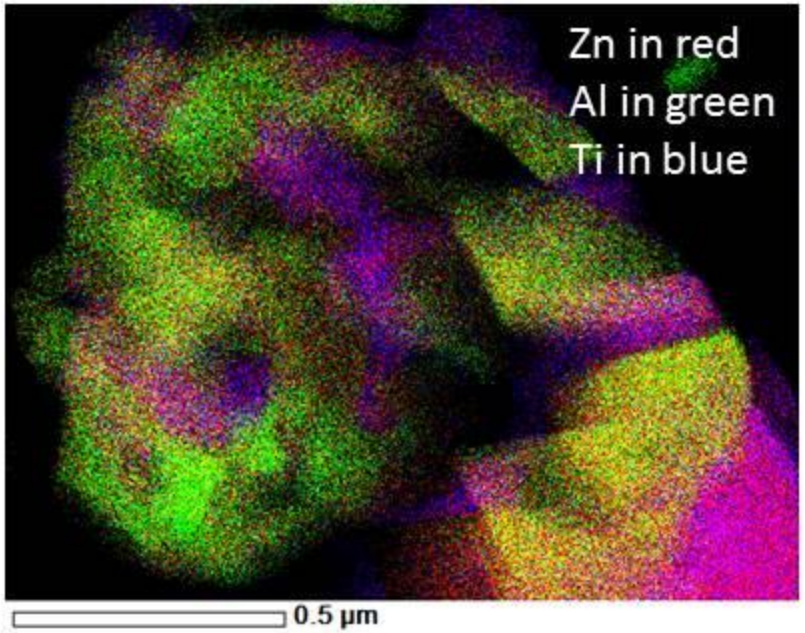


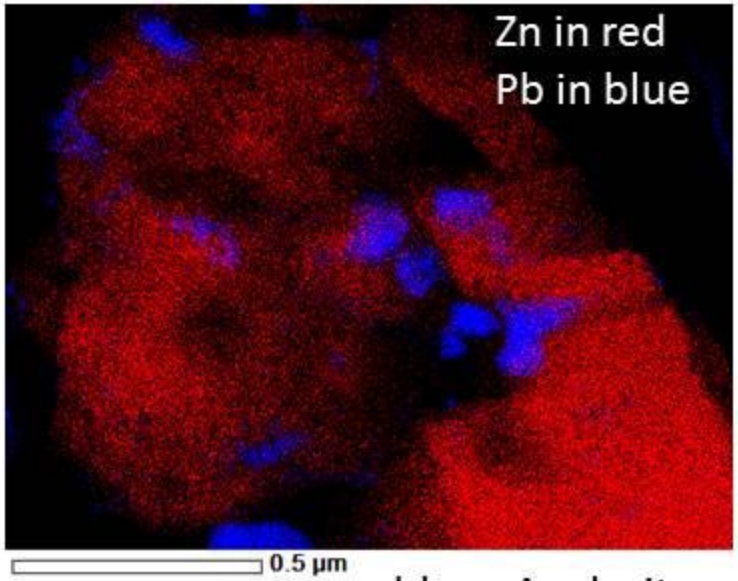
Blue: nanoparticles
of anglesite
Pb : S = 1 ; 1

S22

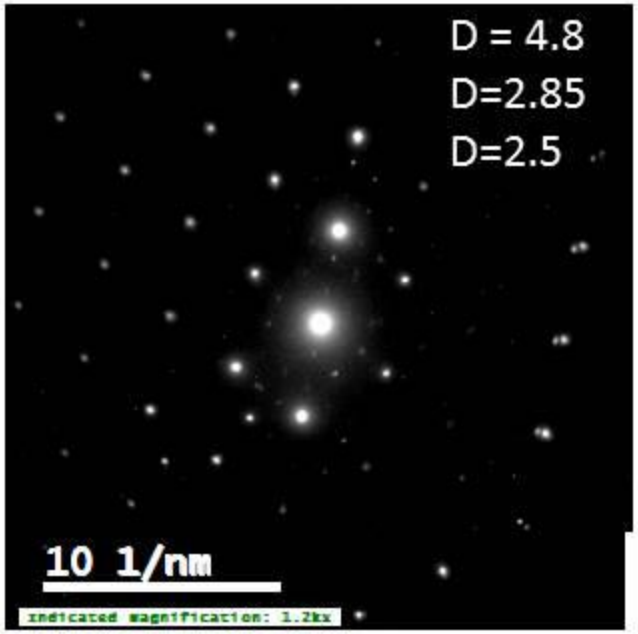
Intergrowth of crystals of gahnite (Zn : Al =1:2, yellow/green) and a Zn-Al-Ti-(hydr)oxide phase (Zn : Al = 4: 1; violet) SAED pattern display most commonly diffraction spots of both phases





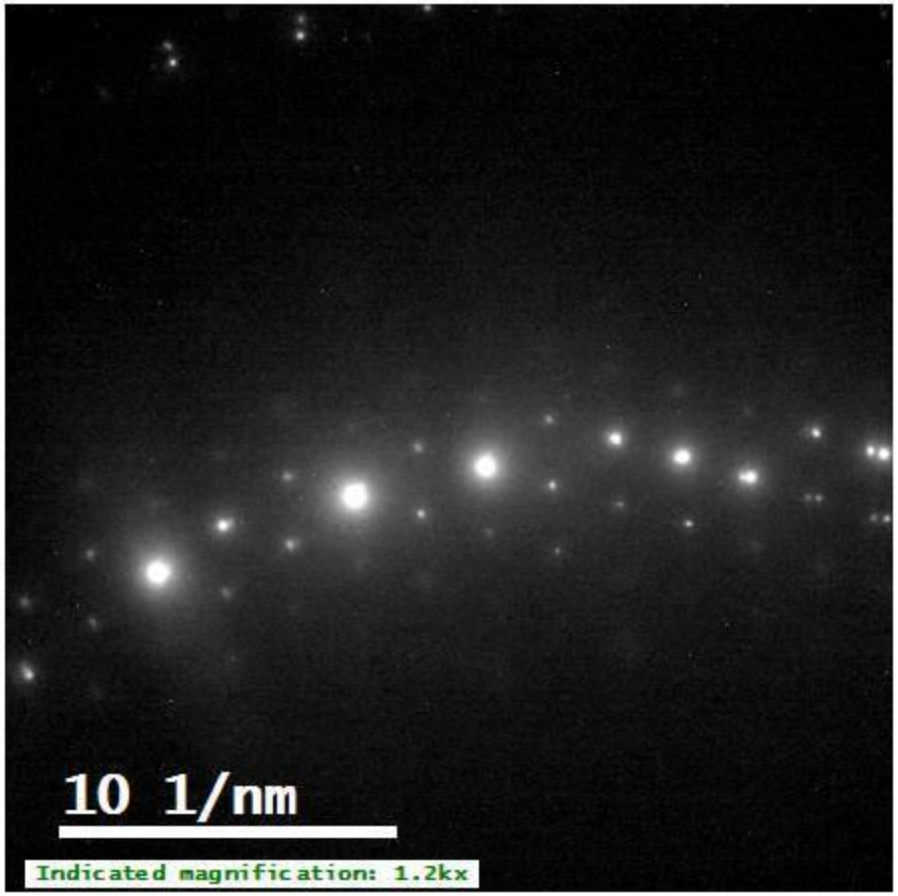


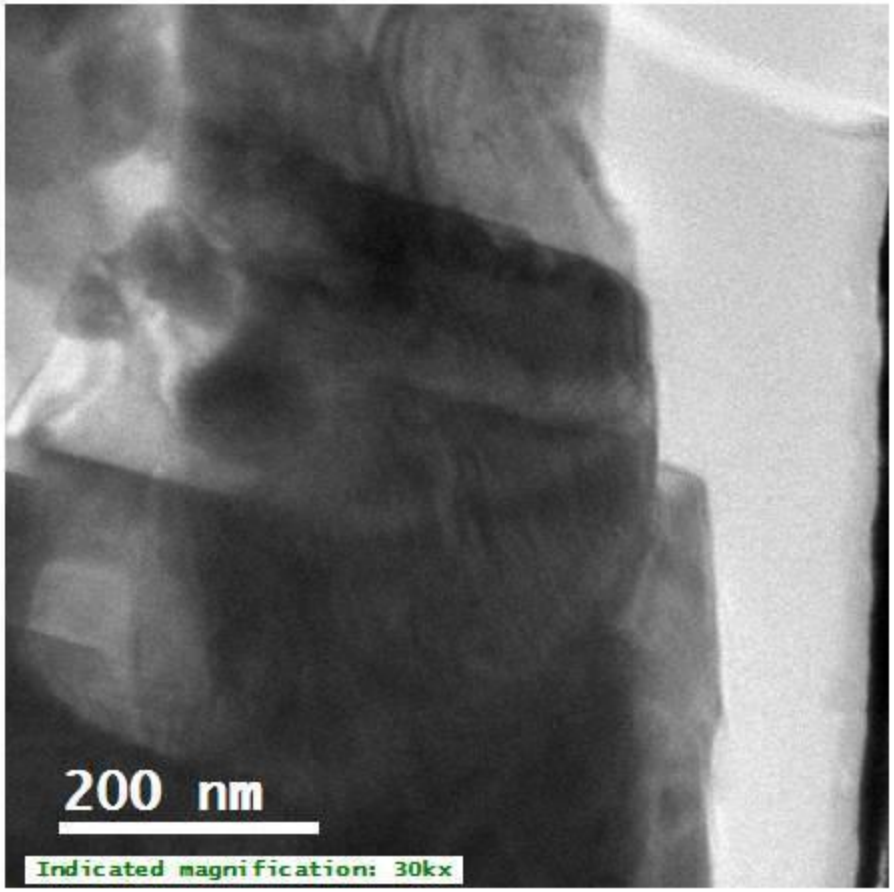
Diffraction pattern of Gahnite, $ZnAl_2O_4$



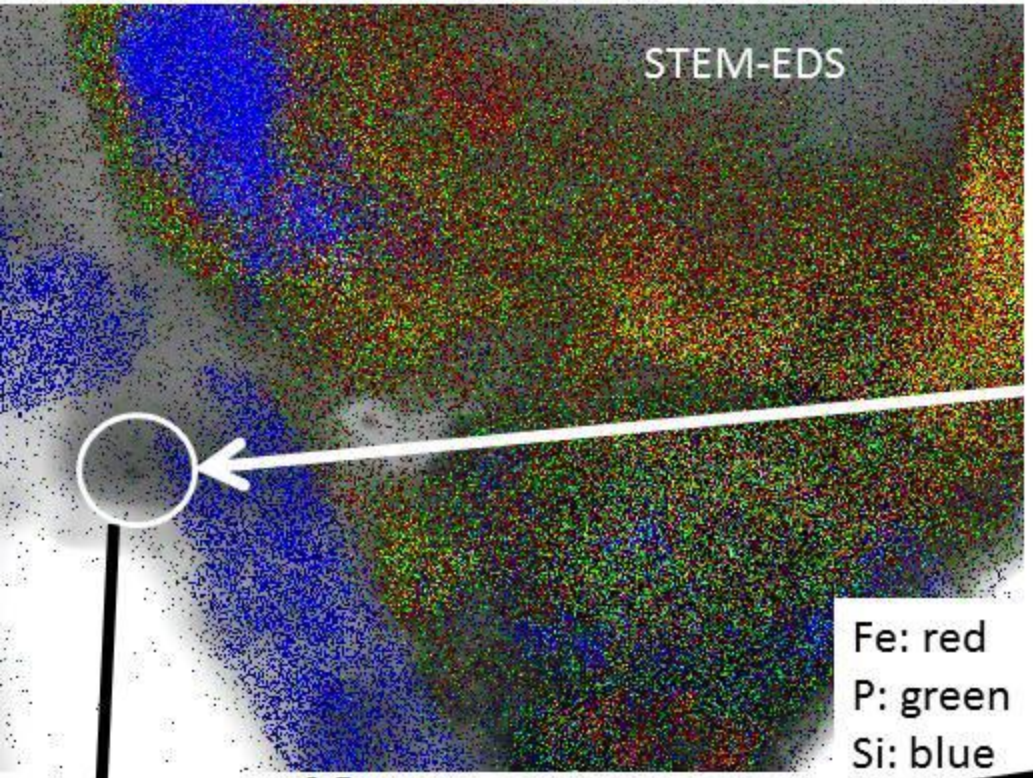
blue: Anglesite nanoparticles

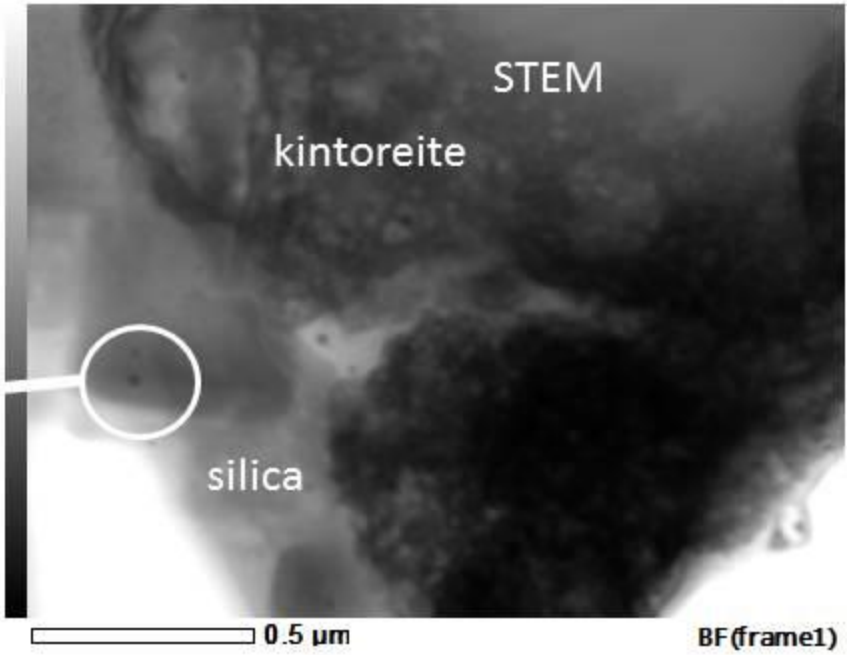
S23

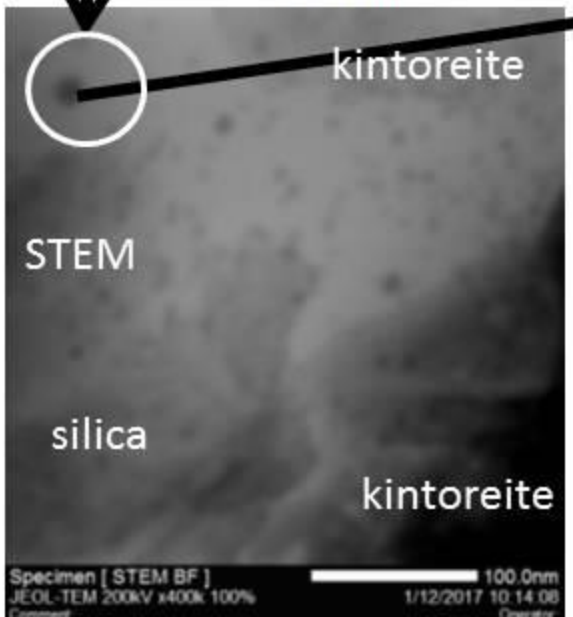


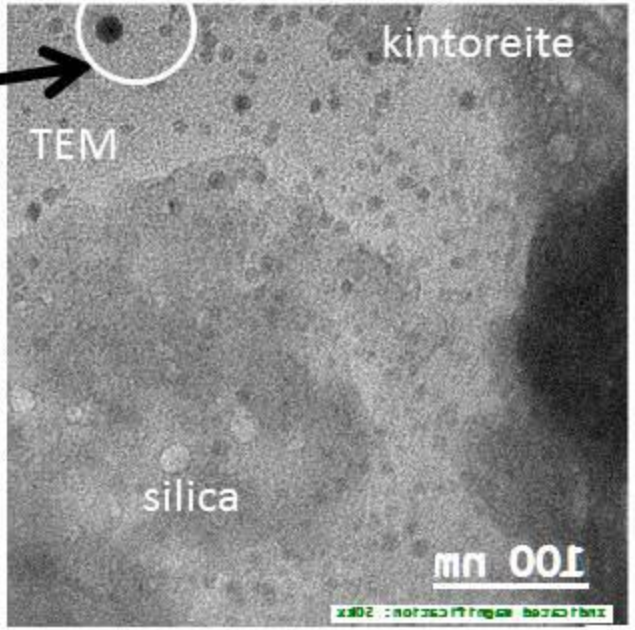


The Zn-Al –Ti oxides in this sections are composed of hydroxides with mainly Zn.
The latter layers are decorated with tetrahdra or OH groups
and have characteristics d-spacings of d = 7.65 and d = 4.0



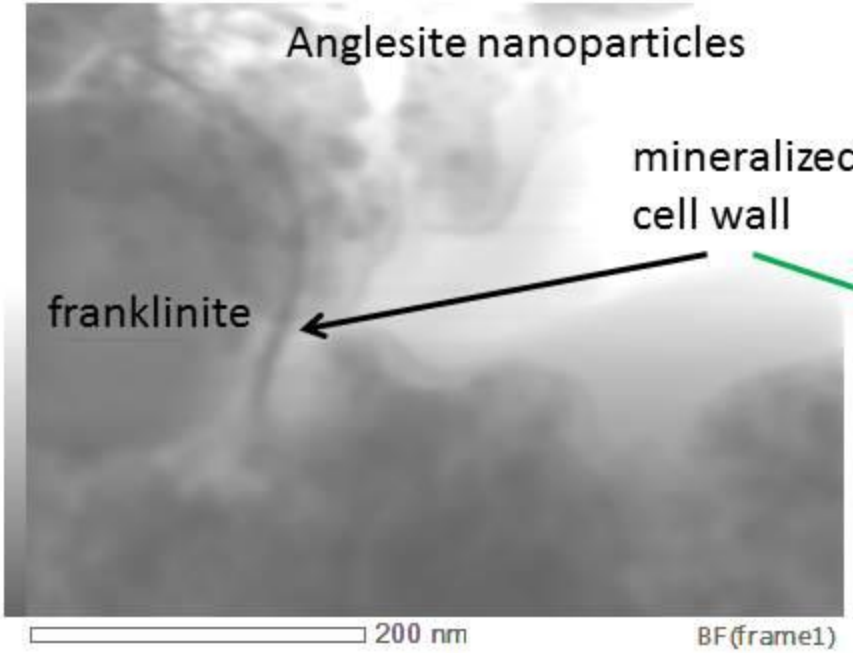


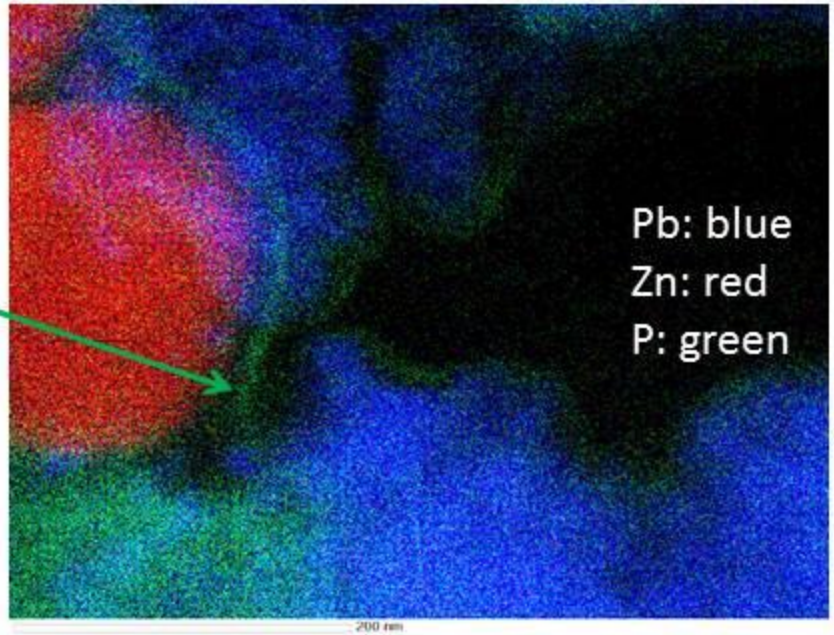


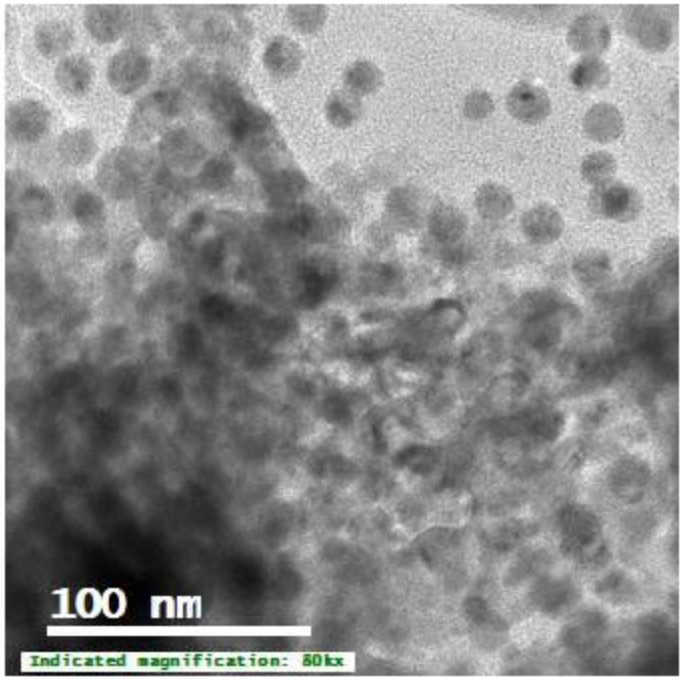


Pb-Fe-Al-P-As
Nanoparticles in
silica matrix
and close to kintoreite
Pb : (Al+Fe) : (P+As) ~
1 0 : 14: 8

S25

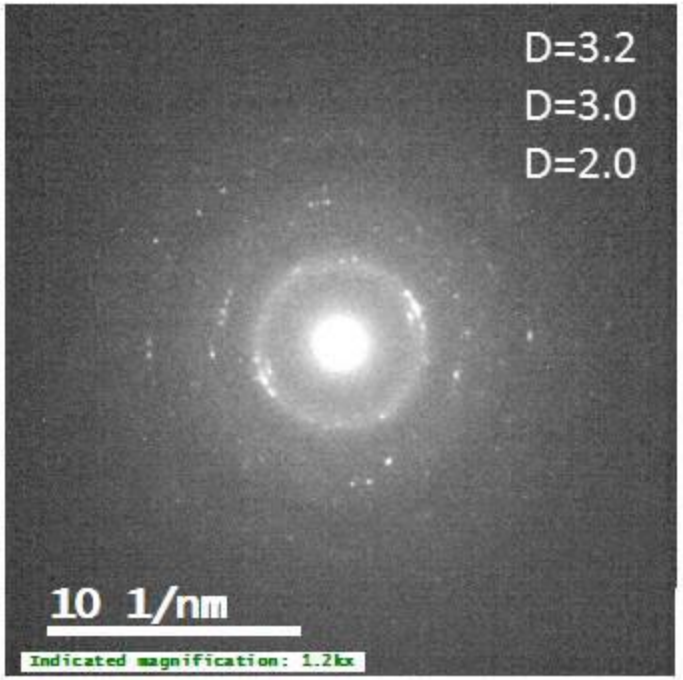


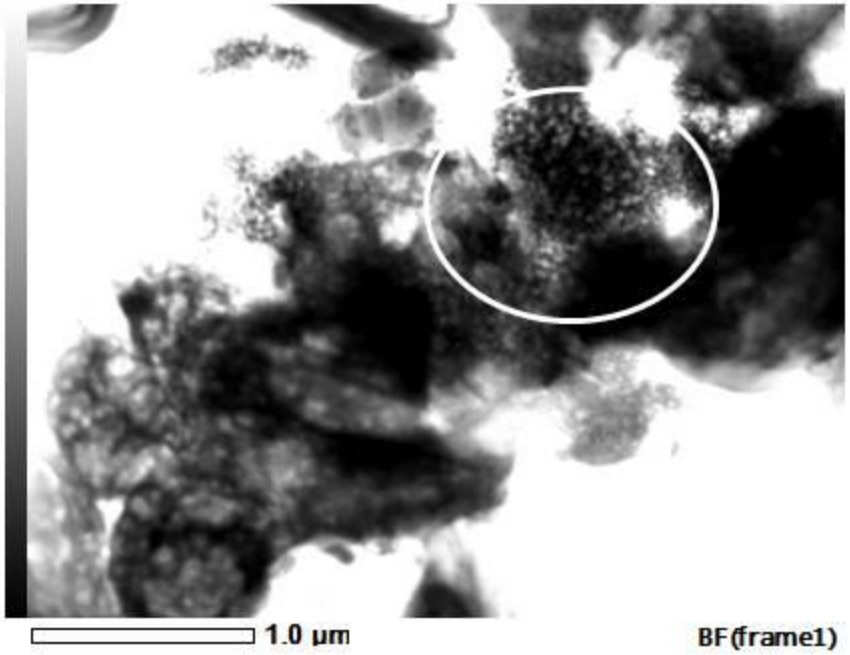


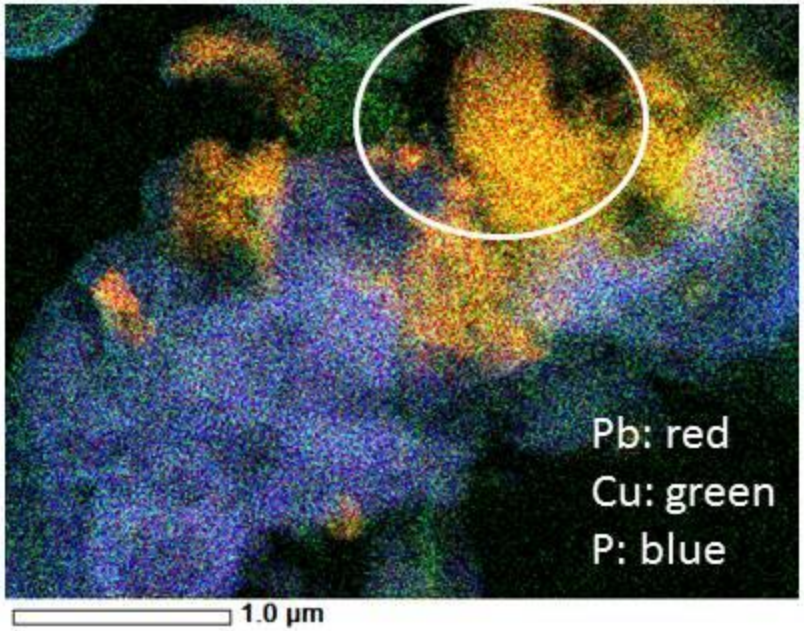


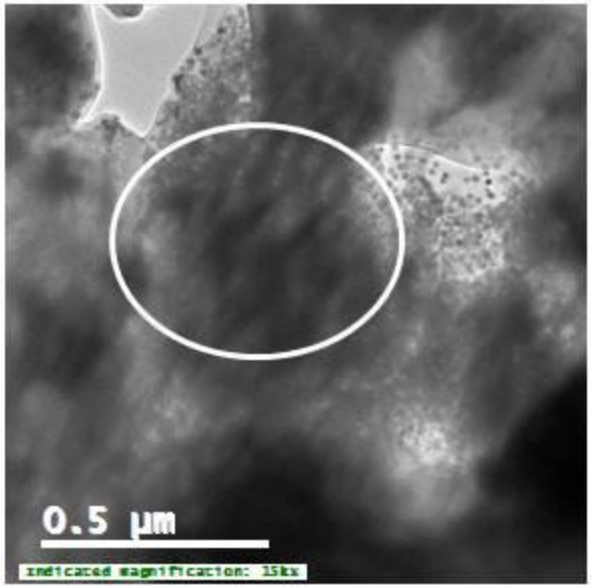
Anglesite
Nanoparticles

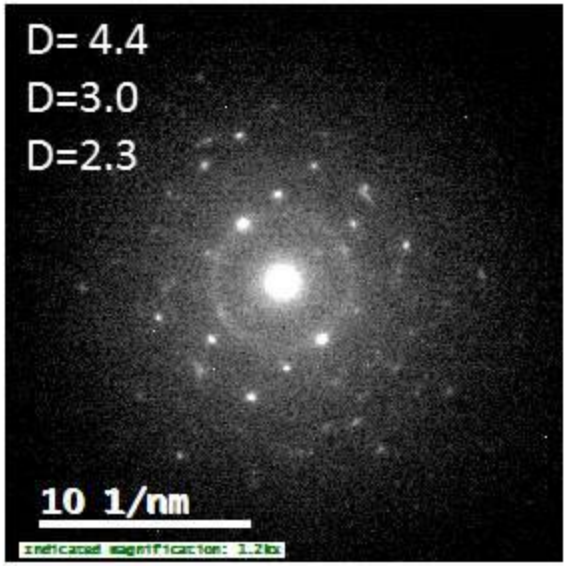
Pb : S ~ 1 : 1





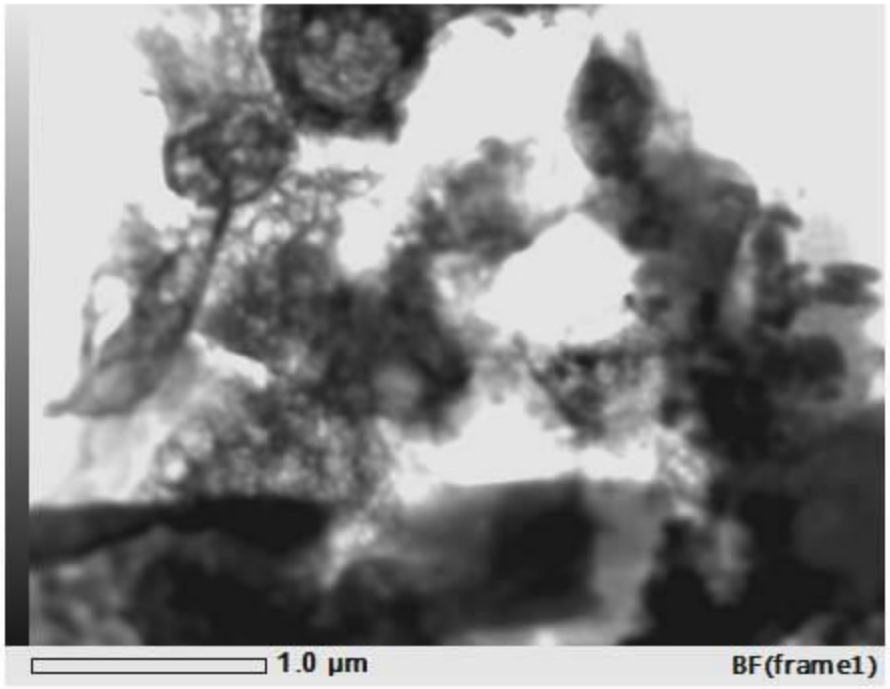


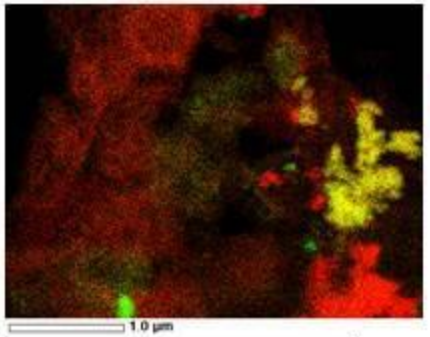




Intergrowth of linarite PbCu(OH)2(SO4) (Yellow, Cu : S ~ 1: 1) with kintoreite (blue)

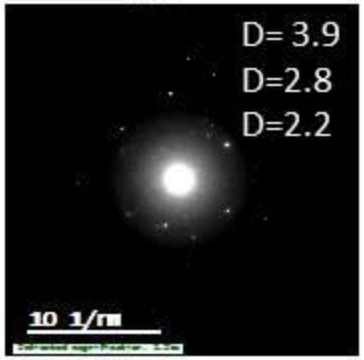
S28





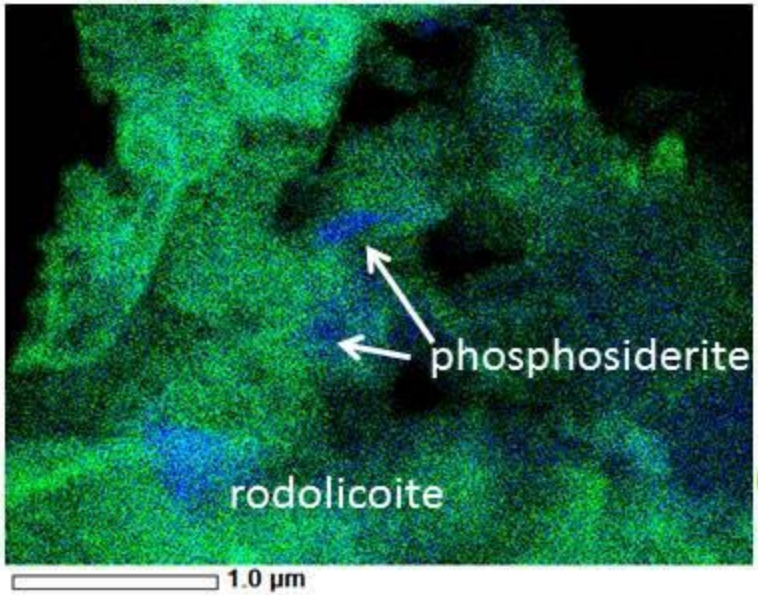
Pb

Ti



yellow Pb : Ti ~ 1: 1

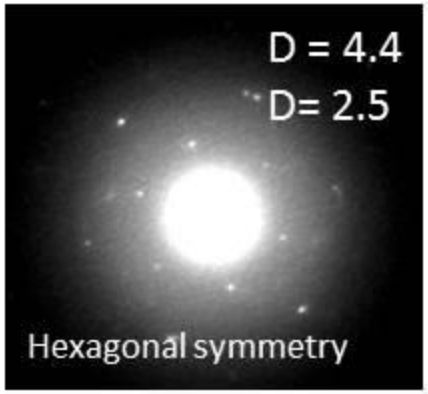
macedonite, $PbTiO_3$



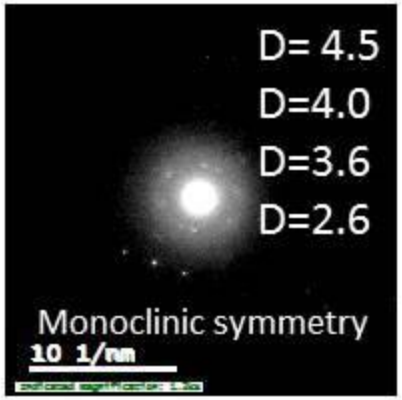
As

P

As : P ~ 2 : 1



Blue:
rodolicoite
$Fe(PO_4)$



Blue:
phosphosiderite,
$Fe(PO_4)(H_2O)_2$

Fe : (As+P) ~ 1 : 1

Supplementary data D, Table S29

Selected minerals identified in the MSC and MOM and their point of zero charge

Mineral	Point of zero charge
anglesite	**4** [3]
Synthetic hydroxyapatite	**7.7-8.1** [1]
Kintoreite	**~3-6**
$Fe_3(PO_4)_3$	**3.3** [5]
$Fe_3(PO_4)_2 (H_2O)_8$	**4..0-5.6** [1]
$FePO_4$(am)	**3** [4]
Al-rich spinel	**9** [1]
(amorphous $MgAl_2O_4$)	
Fe-rich spinel	**6.2-8.5** [1]
(magnetite)	
hydrous silica	**4.1** [1]
(listed as precipitated silica)	
illite	**2.5** [1]
Quartz	**2-3** [2]

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