

Selected Area Diffraction and Fast
Fourier Transformation pattern of
particulate 1 and surroundings

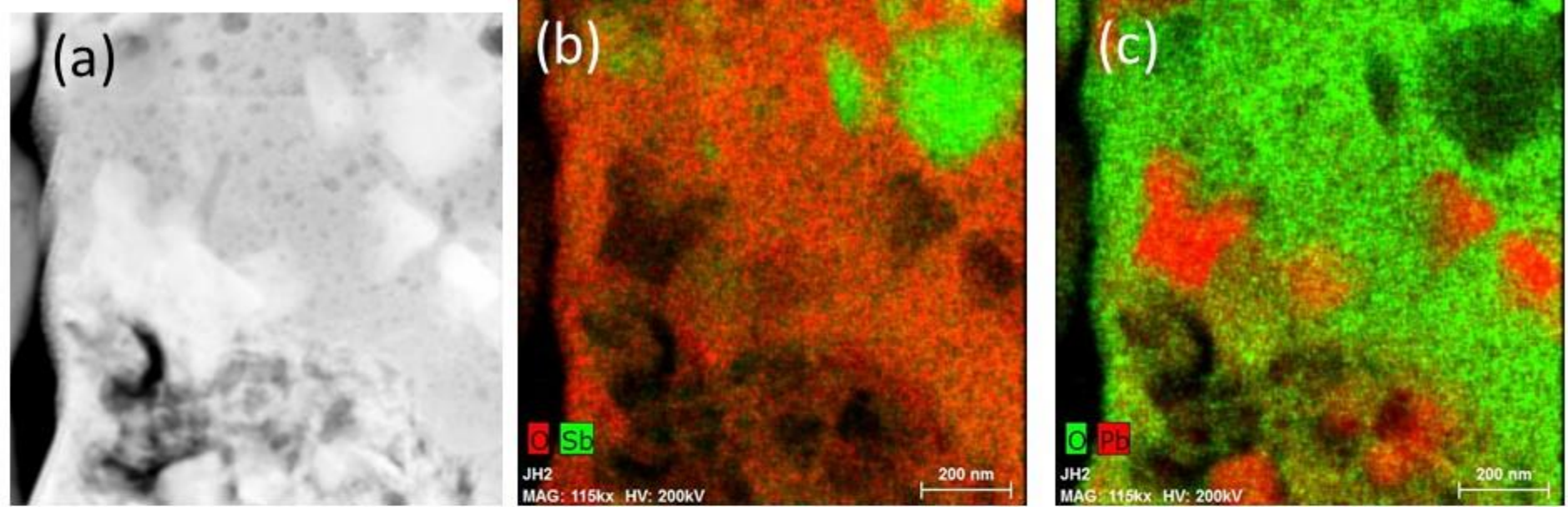


Figure S1. (a) STEM image and (b)-(c) chemical distribution maps for (b) Sb in green and O in red and (c) O in green and Pb in red, indicating the presence of metallic Pb and Sb, diffraction data was not conclusive to identify the metallic phases

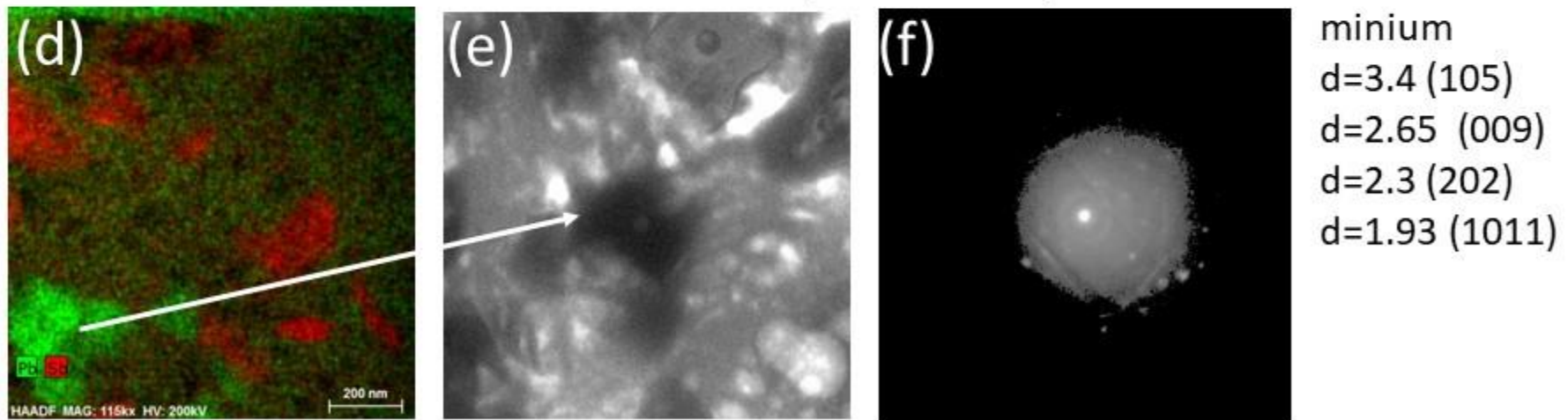


Figure S1. (d) Chemical distribution of Pb (green) and Sb (red), (e) TEM image and (f) SAED pattern indicating the occurrence of angular minium crystals in a hydrocerussite matrix.

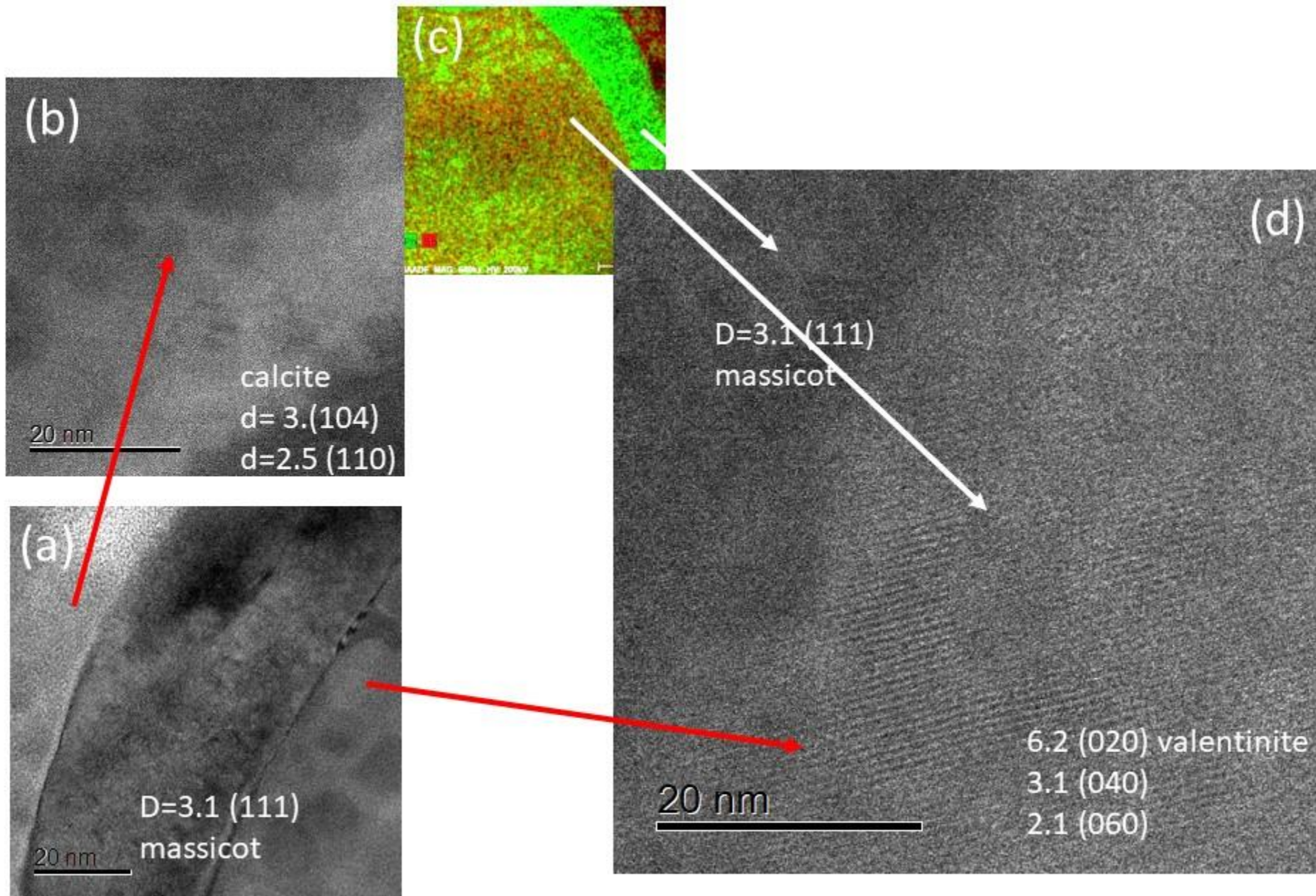


Figure S2. (a) TEM image of massicot-enriched rim and its surrounding; (b) TEM image of the area outside of the particulate indicating the occurrence of nano-domains of calcite; (c) STEM-EDS chemical distribution map for Pb (green) and Sb (red); (d) TEM image indicating the occurrence of nano-domains of valentinite in Sb-rich areas; arrows in red and white indicate the location of areas imaged in high-resolution mode relative to those recorded at lower magnification.

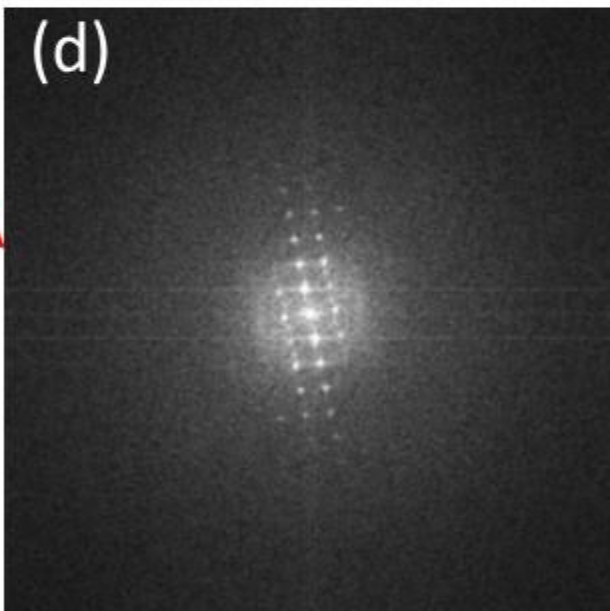
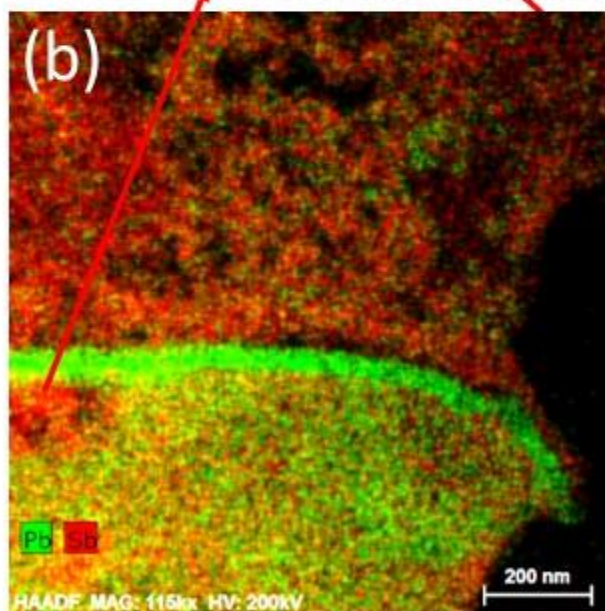
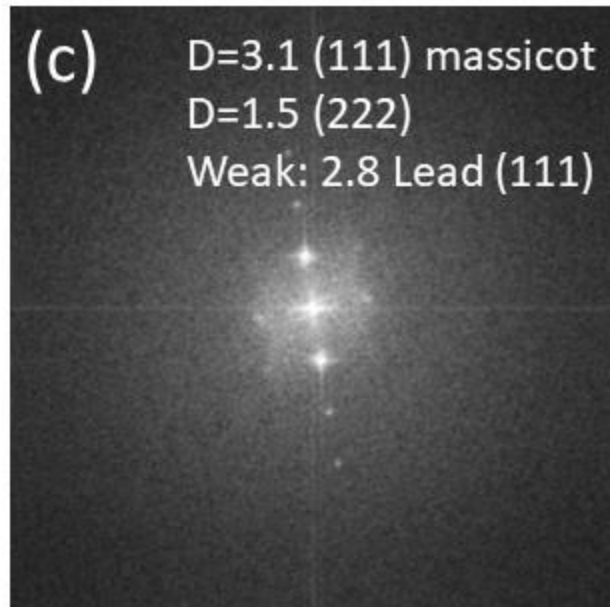
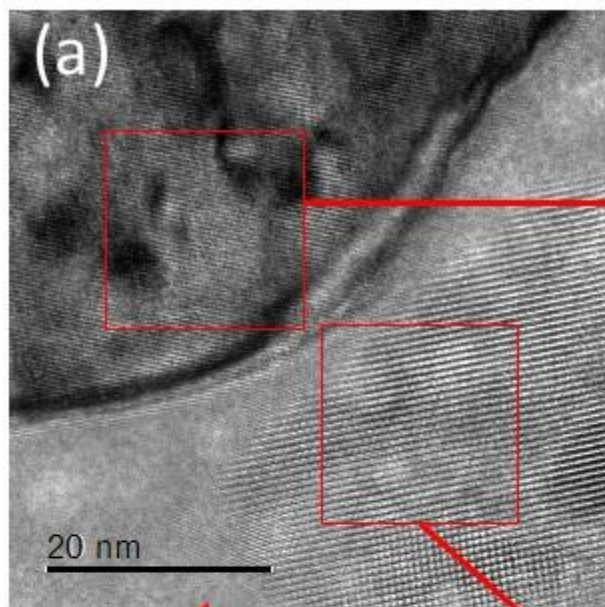
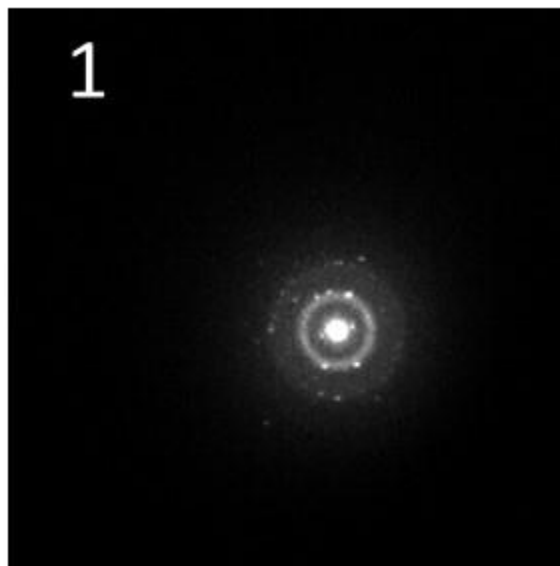
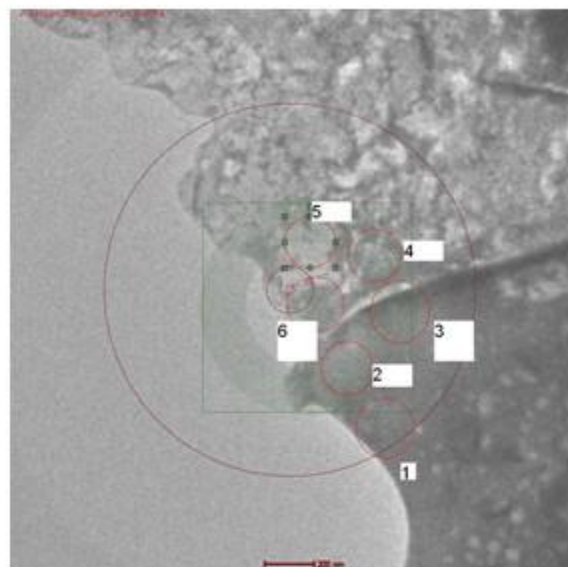
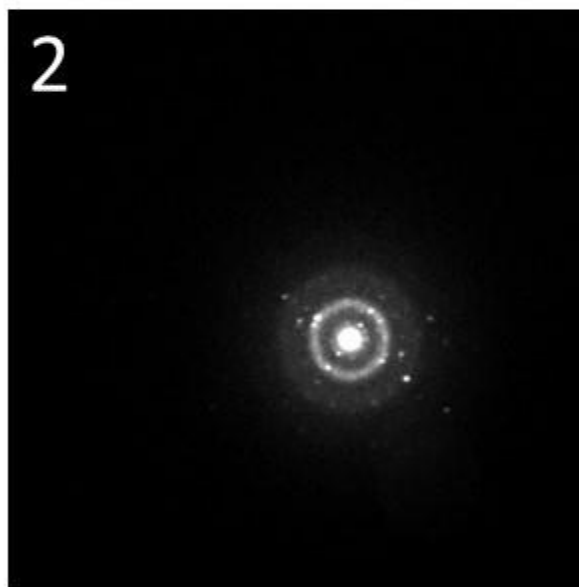
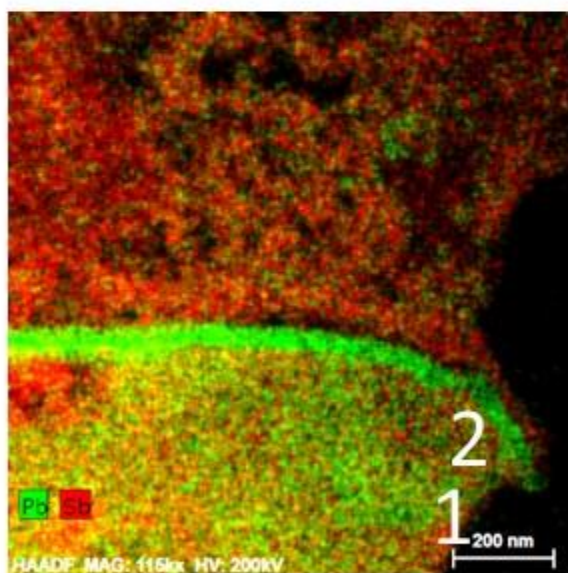


Figure S3 (a) TEM image and (b) EDS-STEM image of a Sb-rich area along the massicot-rich of particulate; (c) and (d) FFT pattern taken from selected areas indicating the presence of massicot and valentinite (location of the areas indicated with squares and arrows)



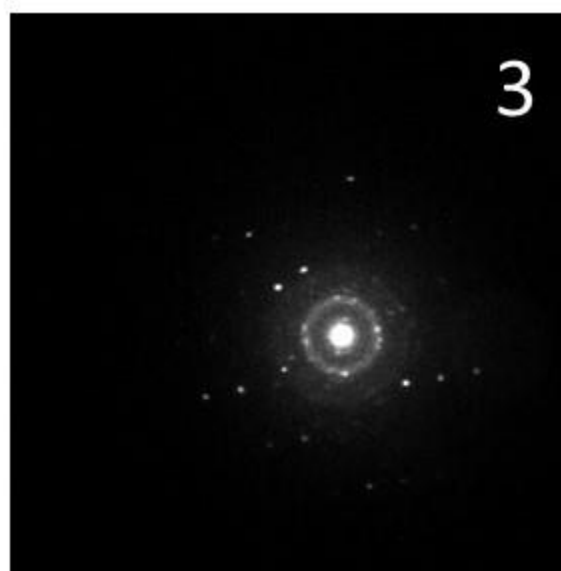
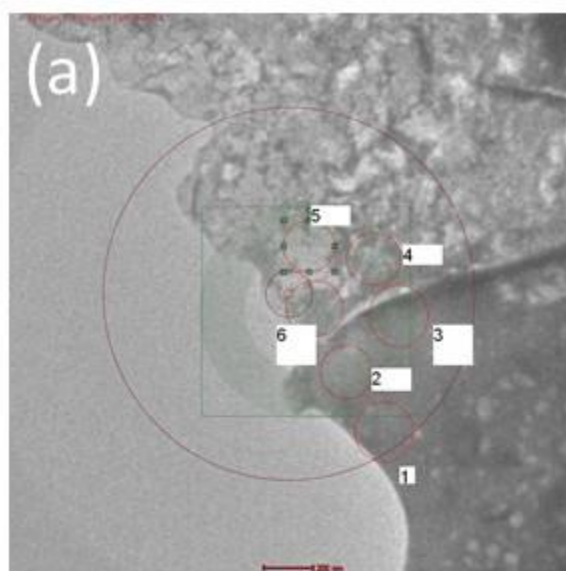
Valentinite
 $D=6.2$ (020)
 $D=3.1$ (040)
 Ring: 3.1 masicot (111)
 $D=2.7$ (002)
 $D=1.5$ (080)



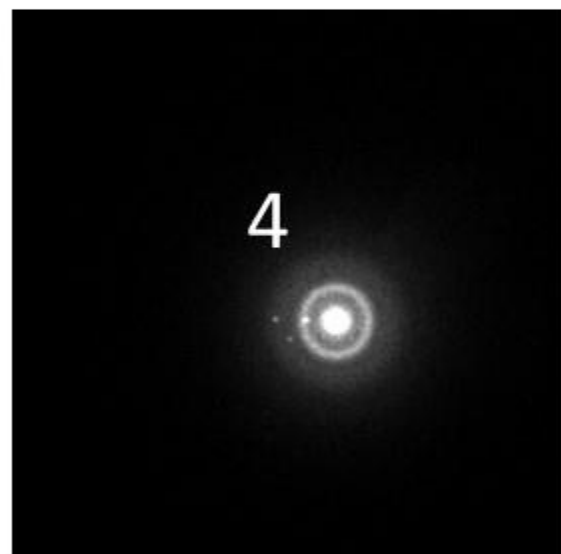
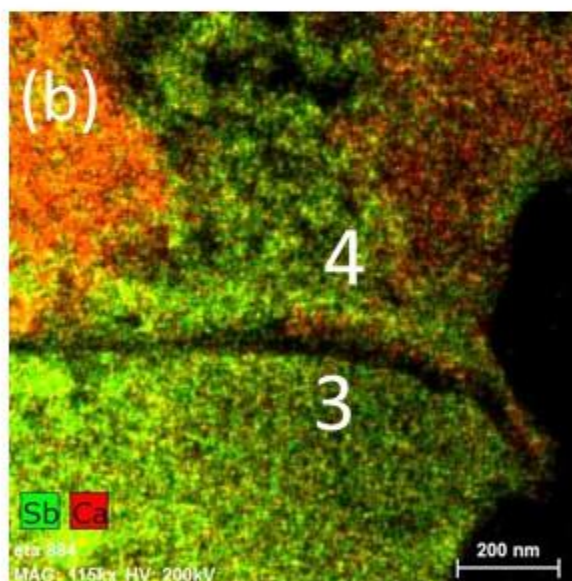
Metallic lead
 $D=2.8$ (111)
 $D=1.4$ (222)

 valentinite
 $D=6.2$ (020)
 $D=3.1$ (040)
 $D=2.1$ (220)

Figure S4. (a) TEM image and (b) EDS-STEM chemical distribution maps for Pb (green) and Sb (red) for a selected area in the interior of particulate 1; “1” and “2” are SAED pattern recorded at the positions “1” and “2” indicated in the Figures (a) and (b)

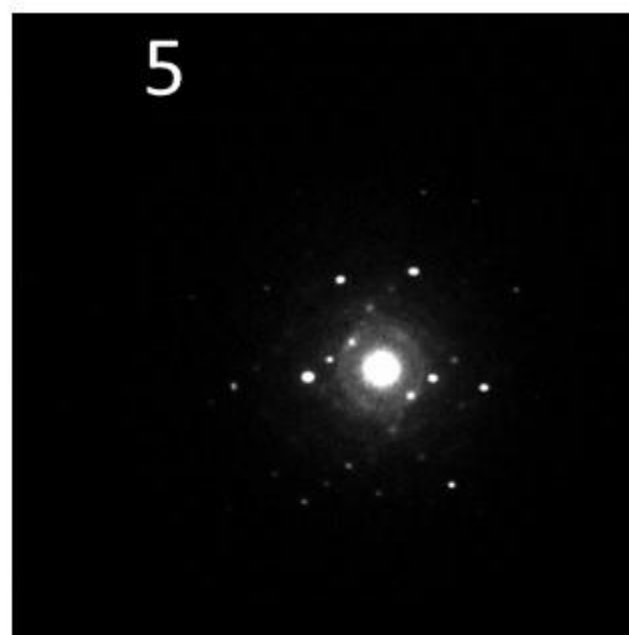
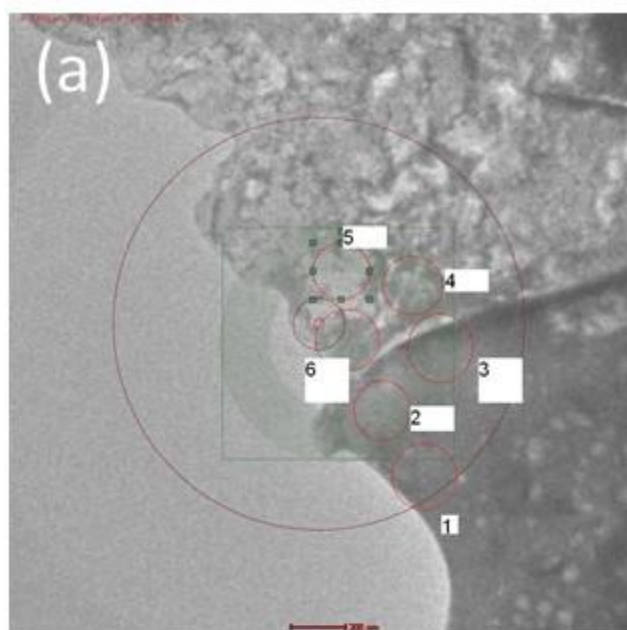


D=6.2 valentinite (020)
 D=3.1 valentinite (040)/massicot
 D=2.92 massicot (200)
 D=2.76 valentinite (020)/massicot

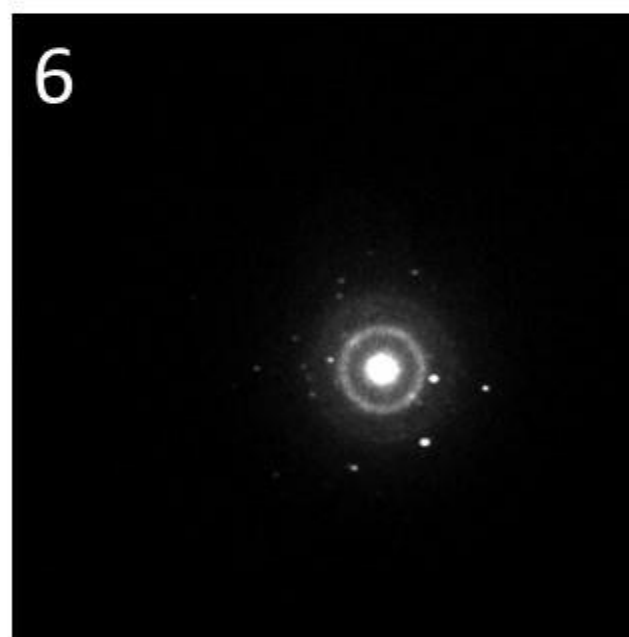
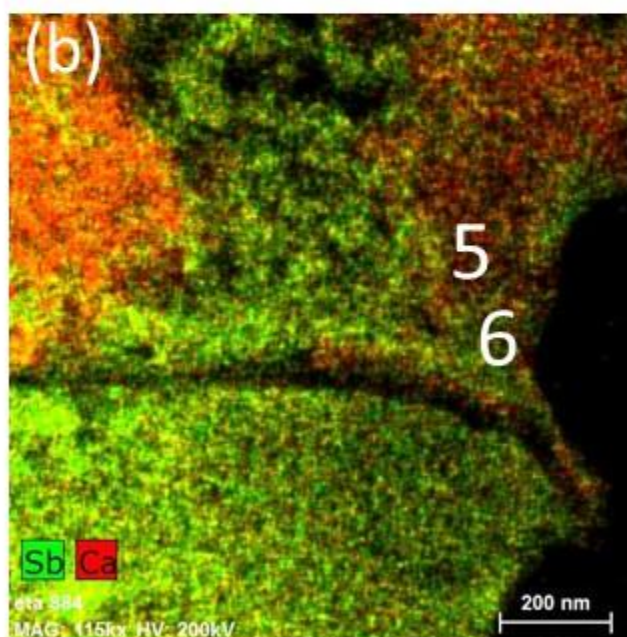


valentinite
 D=3.5 (111)
 D=1.8 (222)
 Ring : 3.15
 Massicot (111)

Figure S5. (a) TEM image and (b) EDS-STEM chemical distribution maps for Sb (green) and Ca (red) for a selected area in the interior and exterior of particulate 1; “1” and “2” are SAED pattern recorded at the positions “1” and “2” indicated in the Figures (a) and (b)

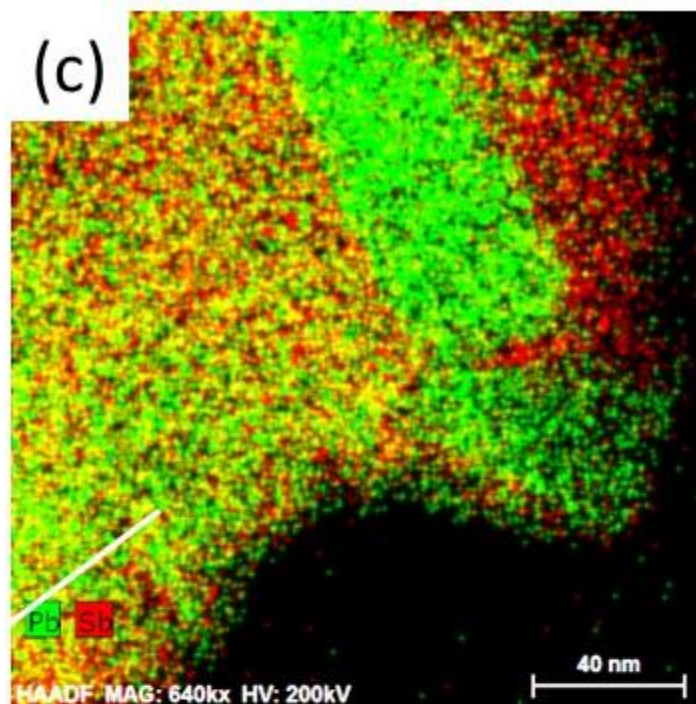
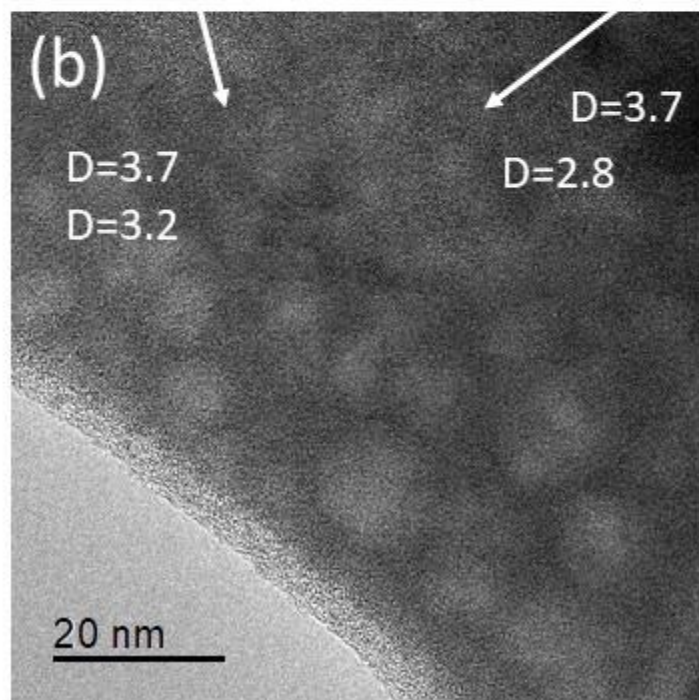
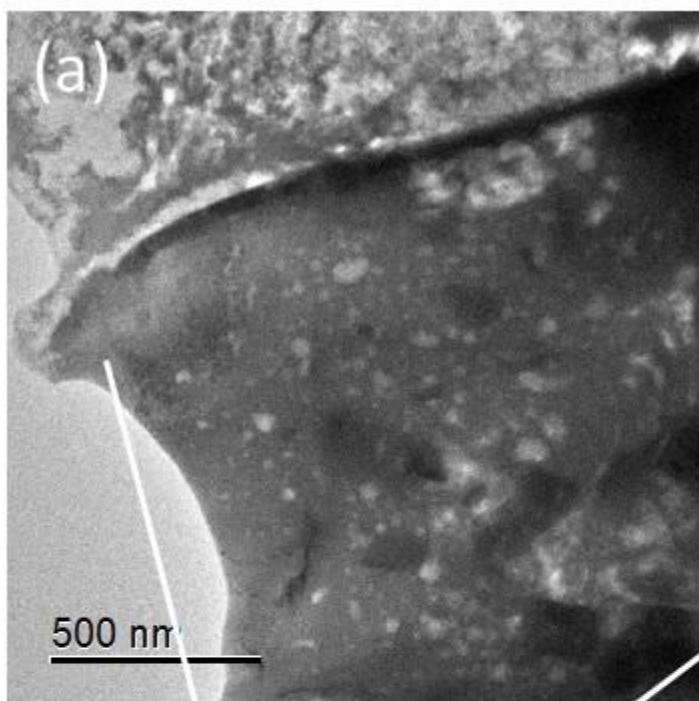


aragonite
 D= 3.4 (111)
 D=2.9 (002)
 D=2.3 (031)
 D=2.2 (022)
 D=1.9 (041)
 Diffuse ring: 3.1



valentinite
 D=3.1 (040)
 D=2.1 (060)
 Ring: 3.1
 (111)
 massicot

Figure S6. (a) TEM image and (b) EDS-STEM chemical distribution maps for Sb (green) and Ca (red) for a selected area in the interior and exterior of particulate 1; "1" and "2" are SAED pattern recorded at the positions "1" and "2" indicated in the Figures (a) and (b)



hydrocerussite
 $d=3.6$ (014)
 $d=3.3$ (015)
 Metallic Pb
 $d=2.8$ (111)

Figure S7. (a)-(b) TEM images and (b) EDS-STEM chemical distribution maps for Pb (green) and Sb (red) for a selected area in the interior of particulate 1; d-spacings for lattice fringes are indicated in (b) and listed below (b);

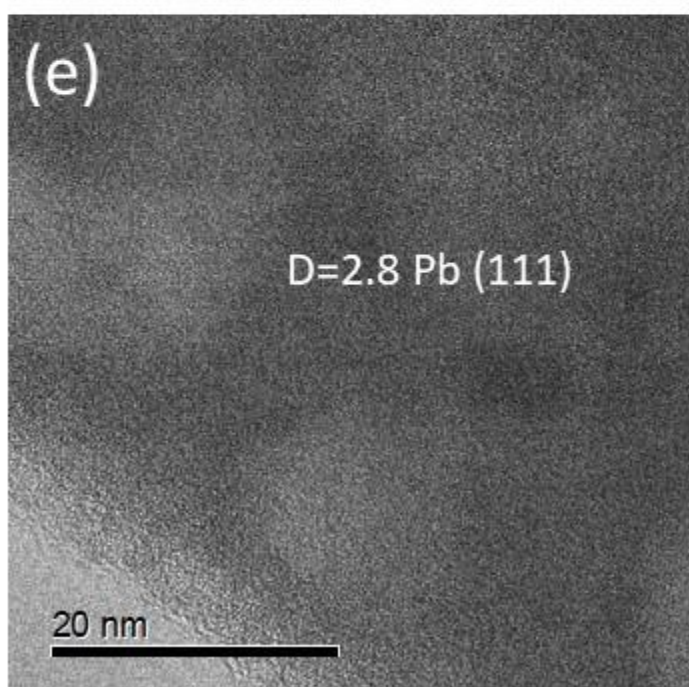
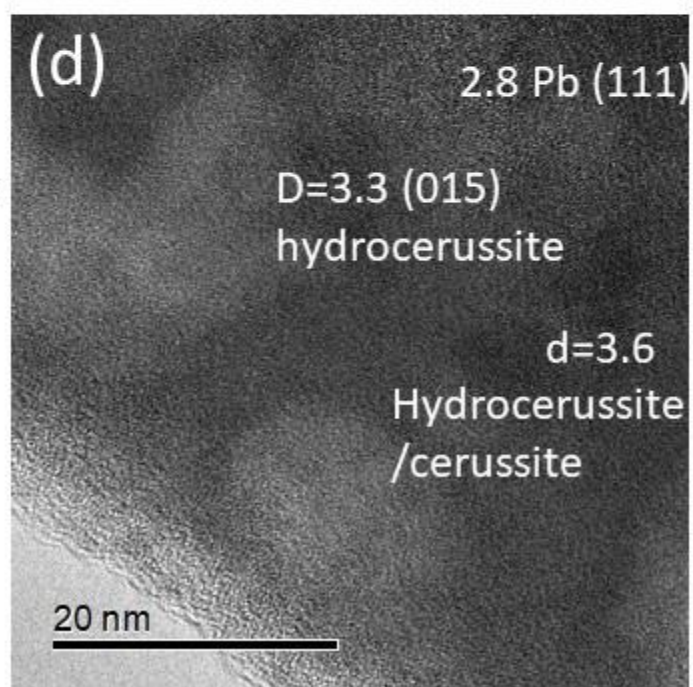
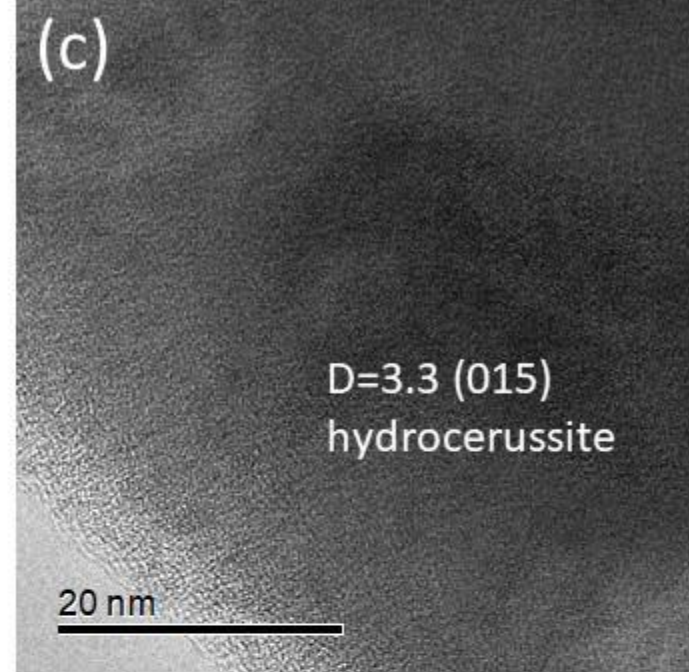
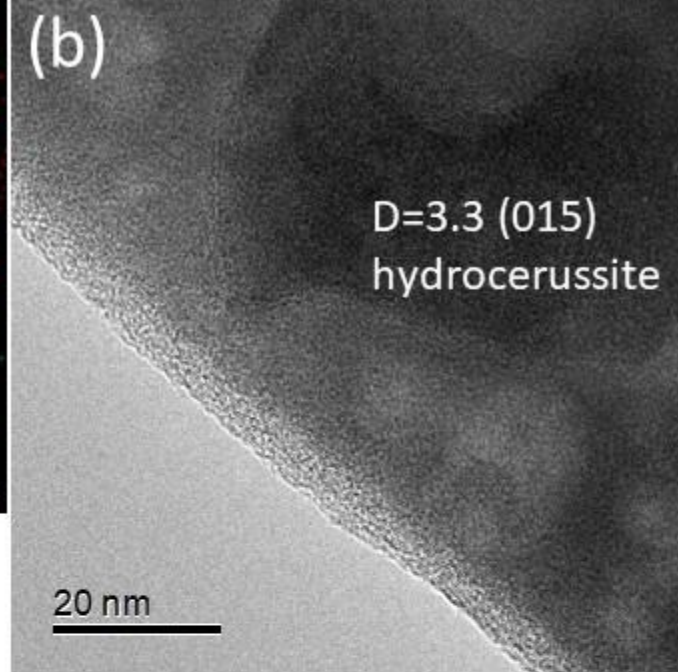
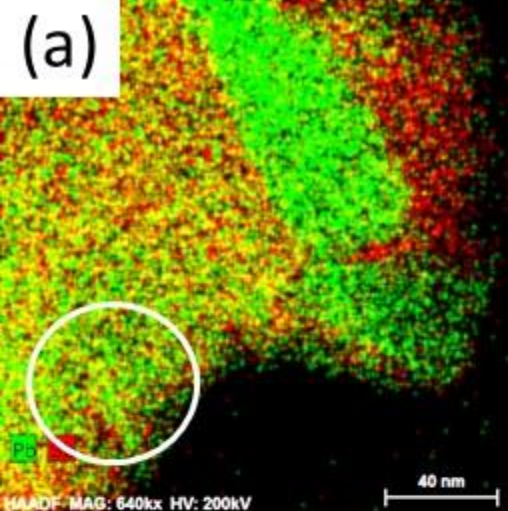


Figure S8. (a) EDS-STEM chemical distribution maps for Pb (green) and Sb (red) and (b)-(c) TEM images for a selected area in the interior of particulate 1; d-spacings for lattice fringes are indicated in (b)-(e);

(a)

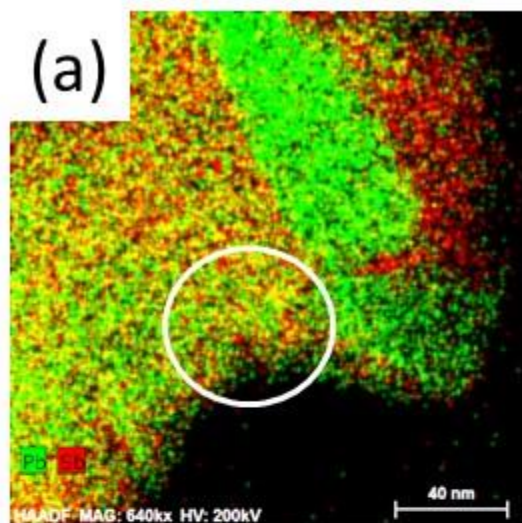


Figure S9. (a) EDS-STEM chemical distribution maps for Pb (green) and Sb (red) and (b)-(c) TEM images for a selected area in the interior of particulate 1; d-spacings for lattice fringes of metallic Pb and hydrocerussite are indicated in (b)-(c);

D=2.8 Pb (111)
D=2.5 Pb (200)

(b)

Metallic Pb

D=2.8 Pb (111)

D=2.8 Pb (111)

D=2.8
Pb (111)
D=2.5
Pb (200)

20 nm

(c)

D=2.8
Pb (111)

D=2.5
Pb (200)

D=3.3 (015)
hydrocerussite

20 nm

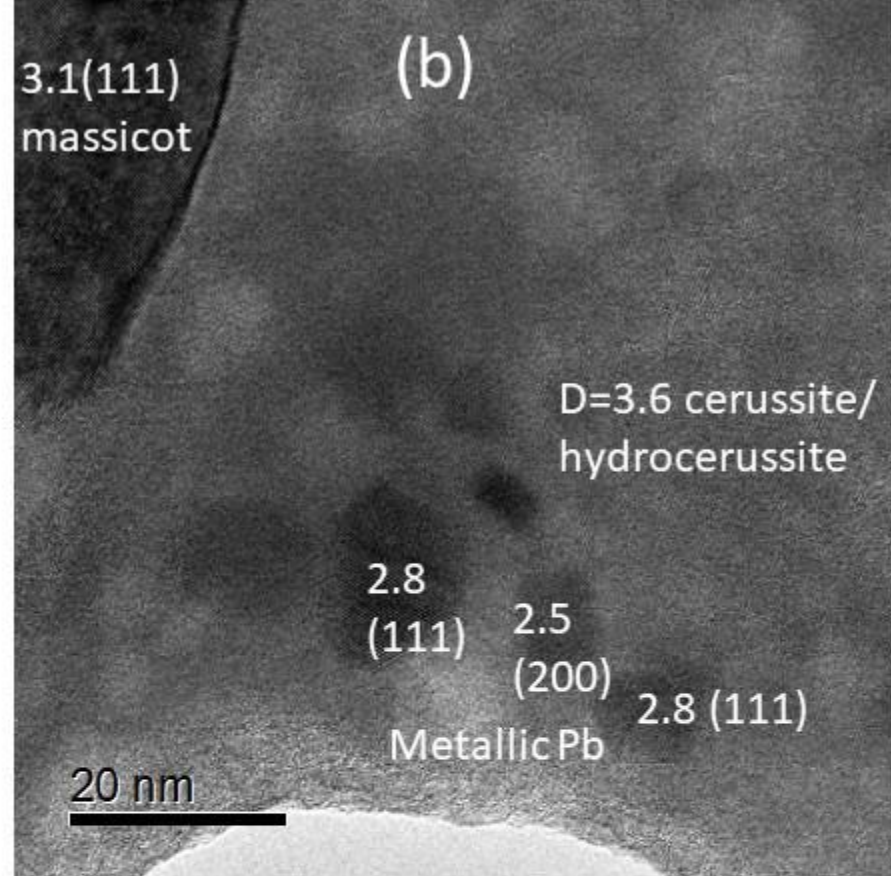
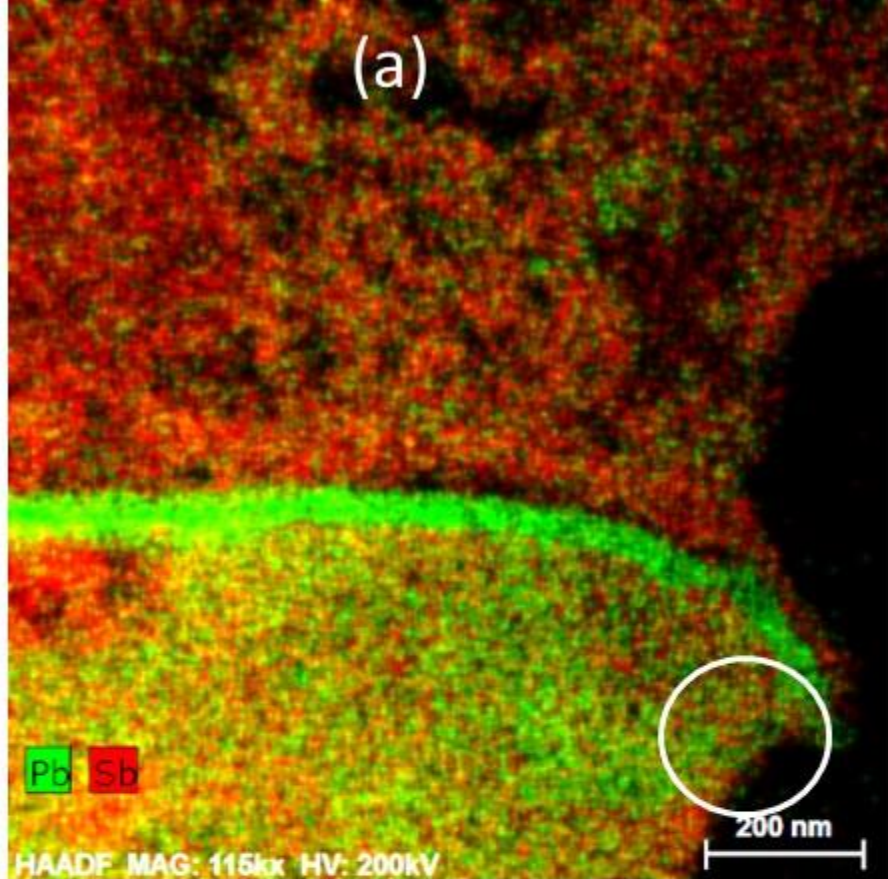


Figure S10. (a) EDS-STEM chemical distribution maps for Pb (green) and Sb (red) and (b) TEM image for a selected area in the interior of particulate 1; d-spacings for lattice fringes of metallic Pb and hydrocerussite are indicated in (b);

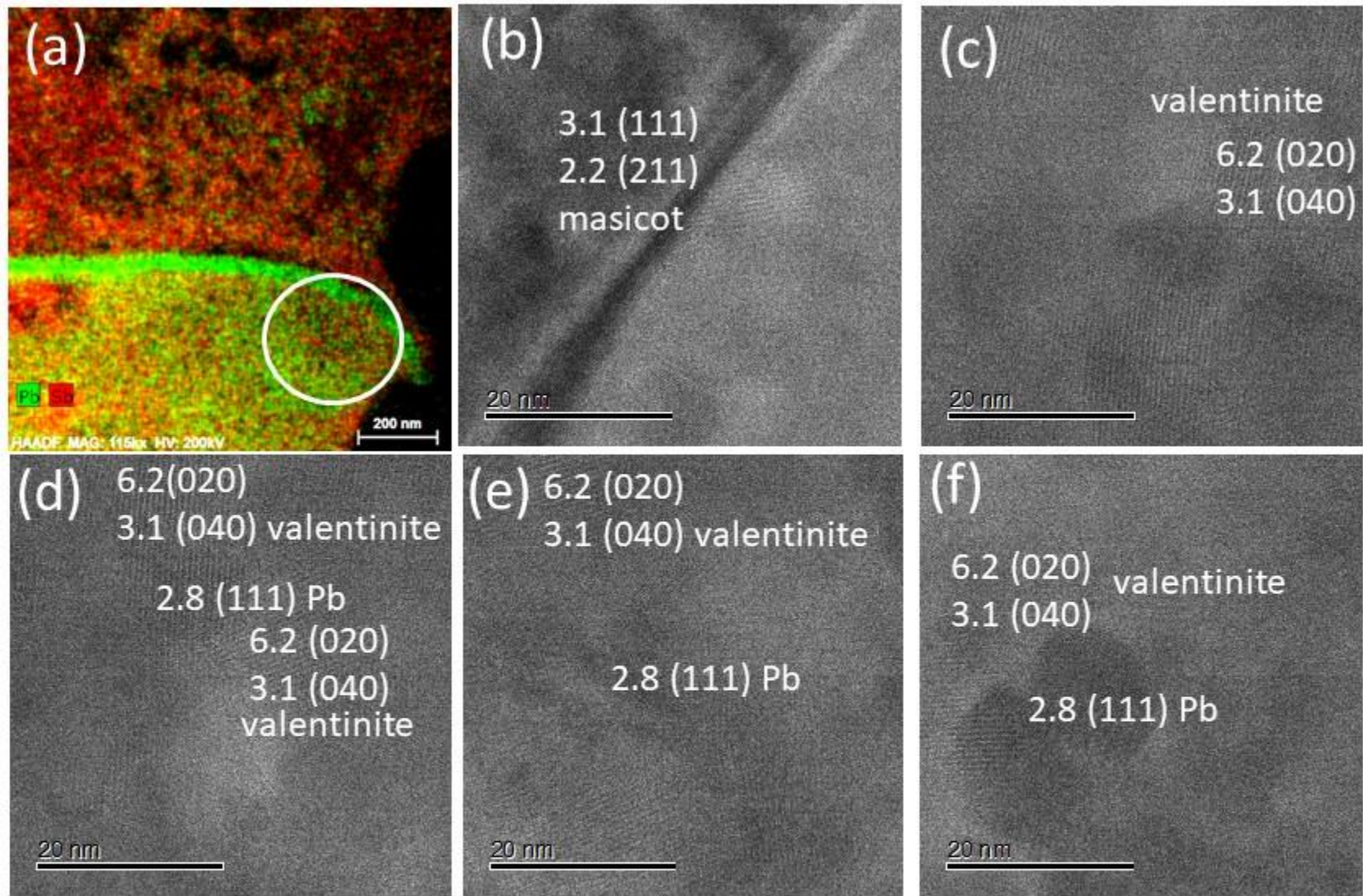


Figure S11. (a) EDS-STEM chemical distribution maps for Pb (green) and Sb (red) and (b)-(f) TEM image for a selected area in the interior of particulate 1 (encircled in (a)); d-spacings for lattice fringes of metallic Pb and valentinite are indicated in (b)-(f);

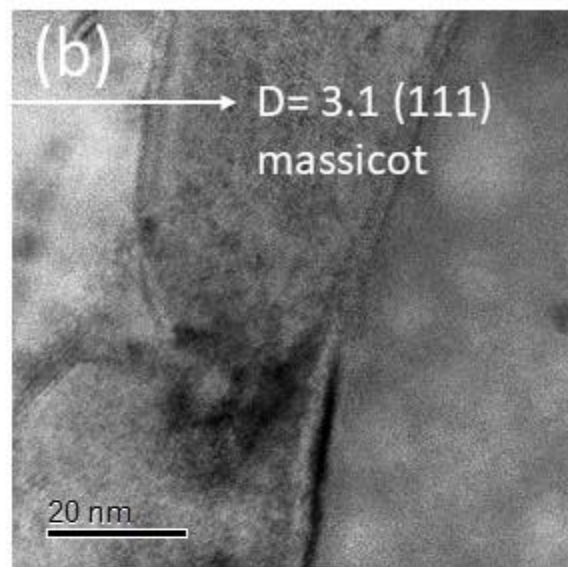
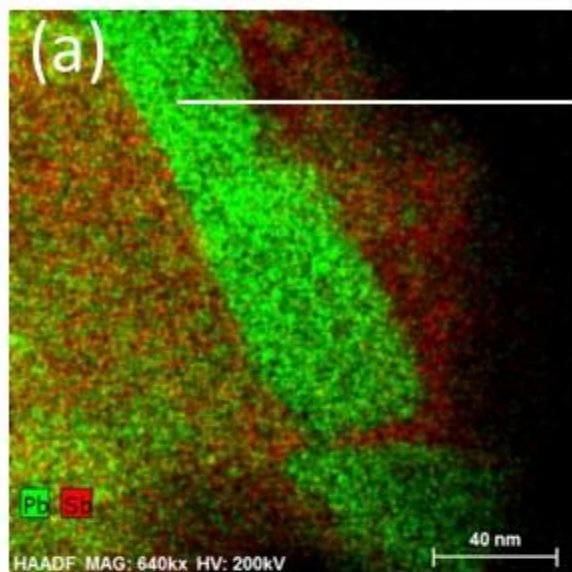


Figure S12. (a) EDS-STEM chemical distribution maps for Pb (green) and Sb (red) and (b) TEM images for a selected area in the rim of particulate 1; d-spacings for lattice fringes of massicot are indicated in (b);

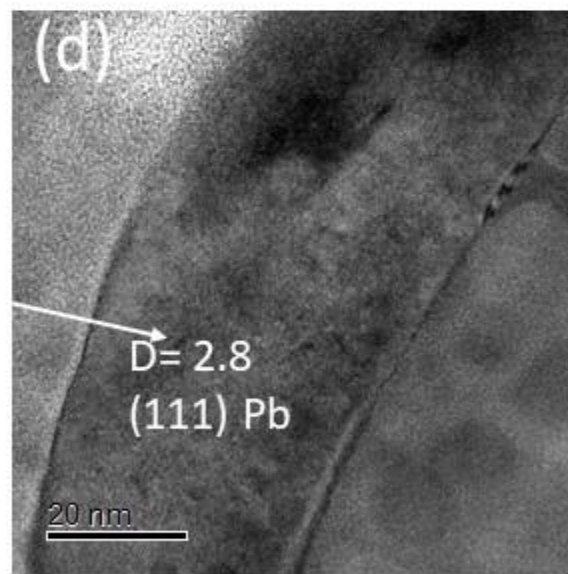
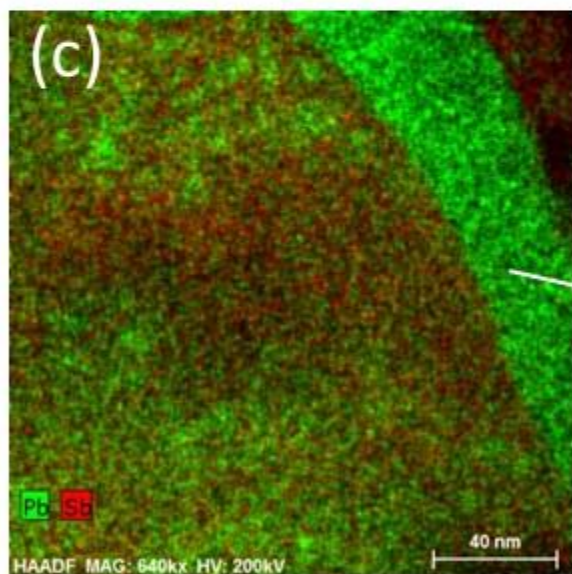


Figure S12. (c) EDS-STEM chemical distribution maps for Pb (green) and Sb (red) and (x)TEM images for a selected area in the rim of particulate 1; d-spacings for lattice fringes of metallic Pb are indicated in (d);

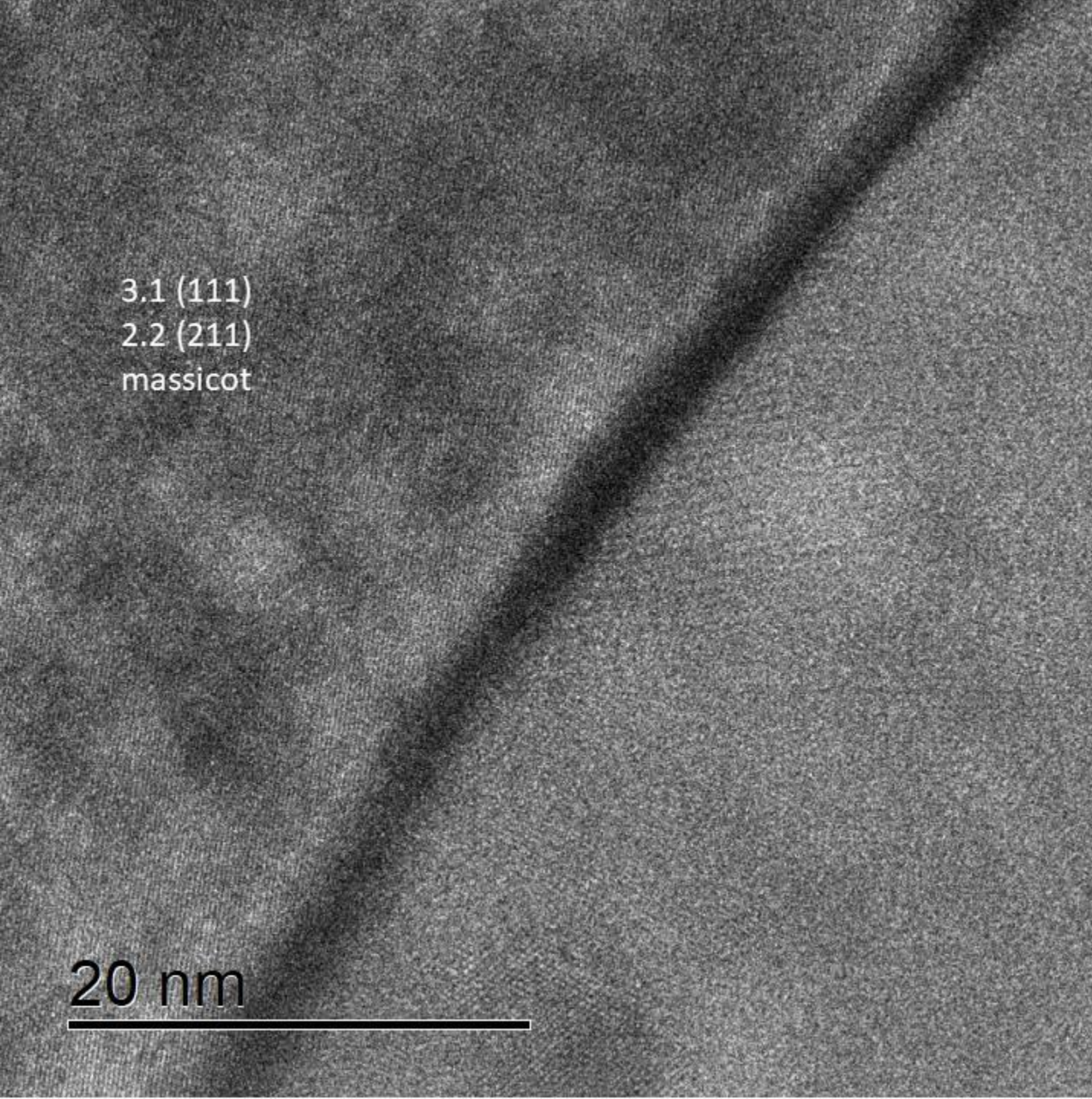


Figure S13.
High resolution TEM of
lattice fringes of massicot
in the rim of particulate 1.

3.1 (111)
2.2 (211)
massicot

20 nm

Selected Area Diffraction and Fast
Fourier Transformation pattern of
particulate 2 and surroundings

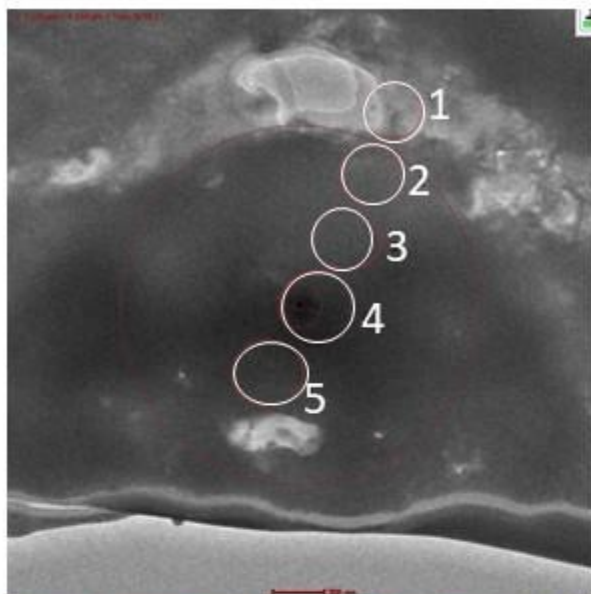
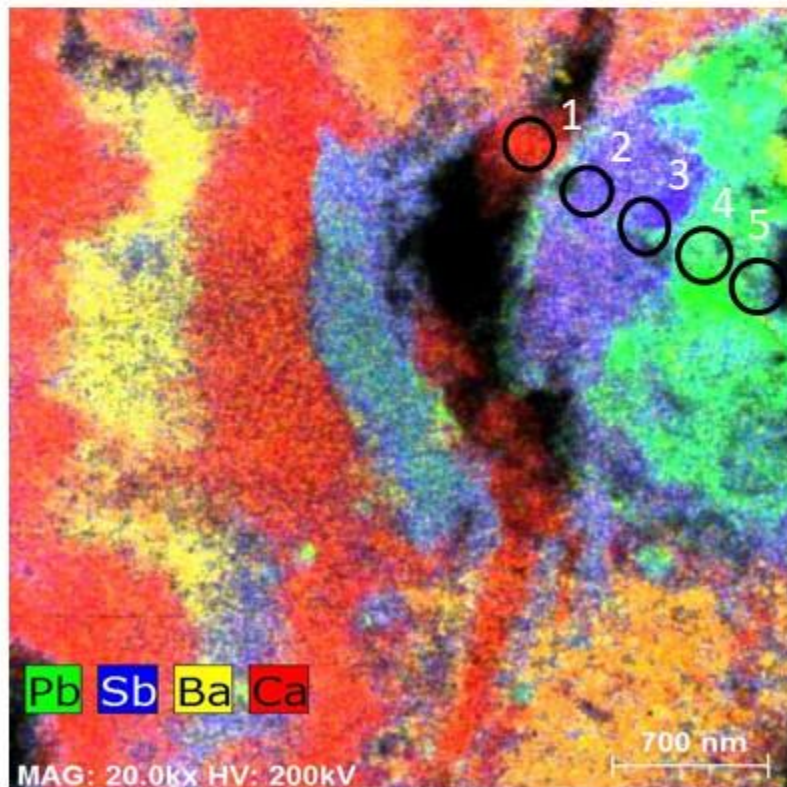


Figure S14. (a) TEM image and (b) EDS-STEM chemical distribution maps for Pb (green), Sb (blue), Ba (yellow) and Ca (red) for particulate 2 and vicinity; five locations for which SAED pattern were recorded are indicated with white and black circles (see S15)



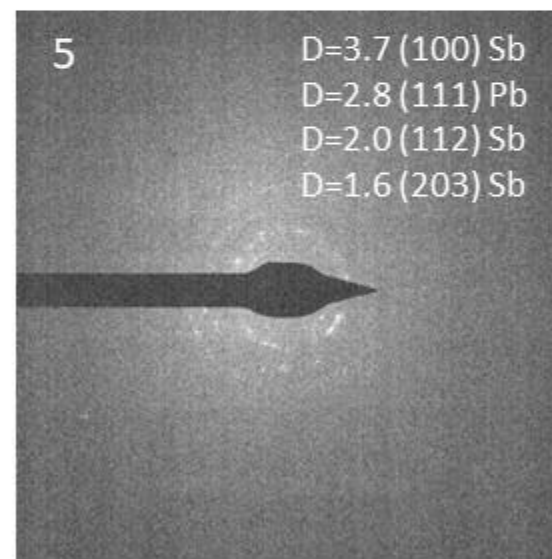
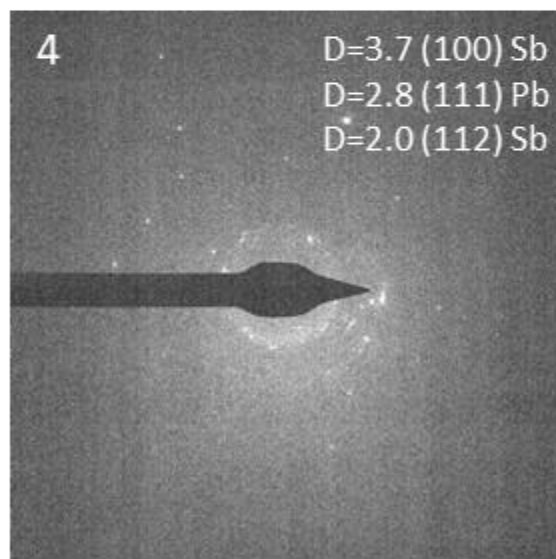
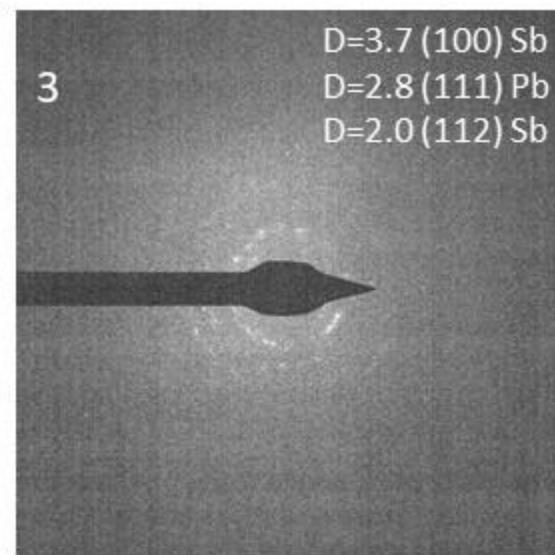
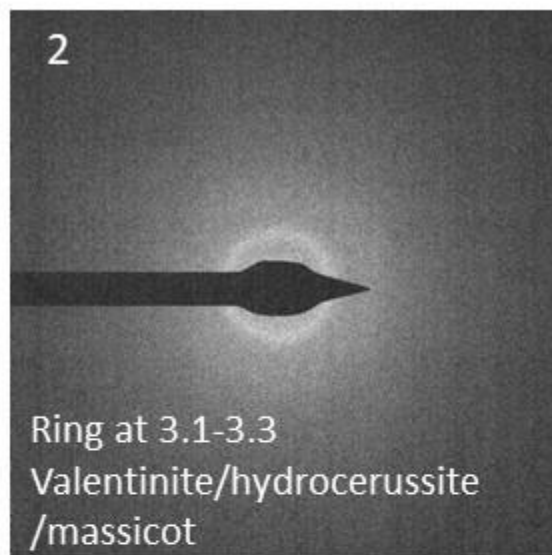
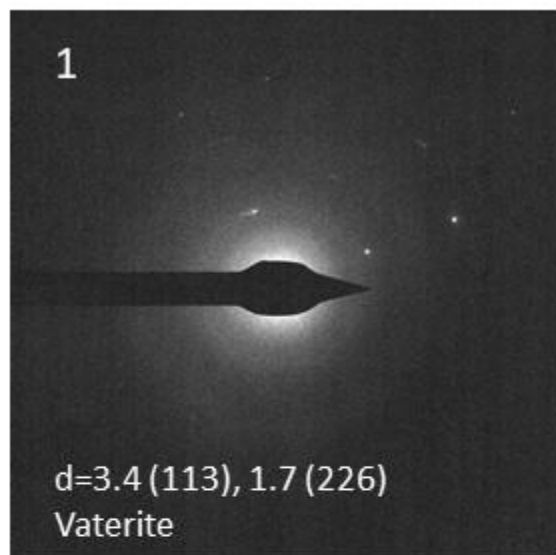


Figure S15. SAED pattern for locations (1)-(5) indicated in S14; d-spacings and names of the corresponding Phases are listed.

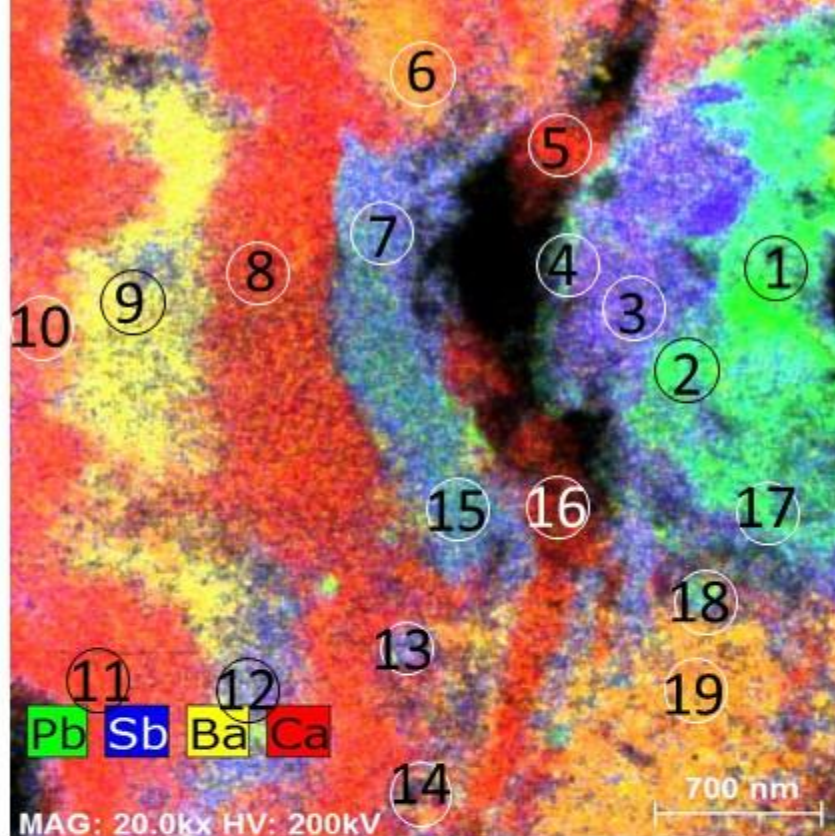
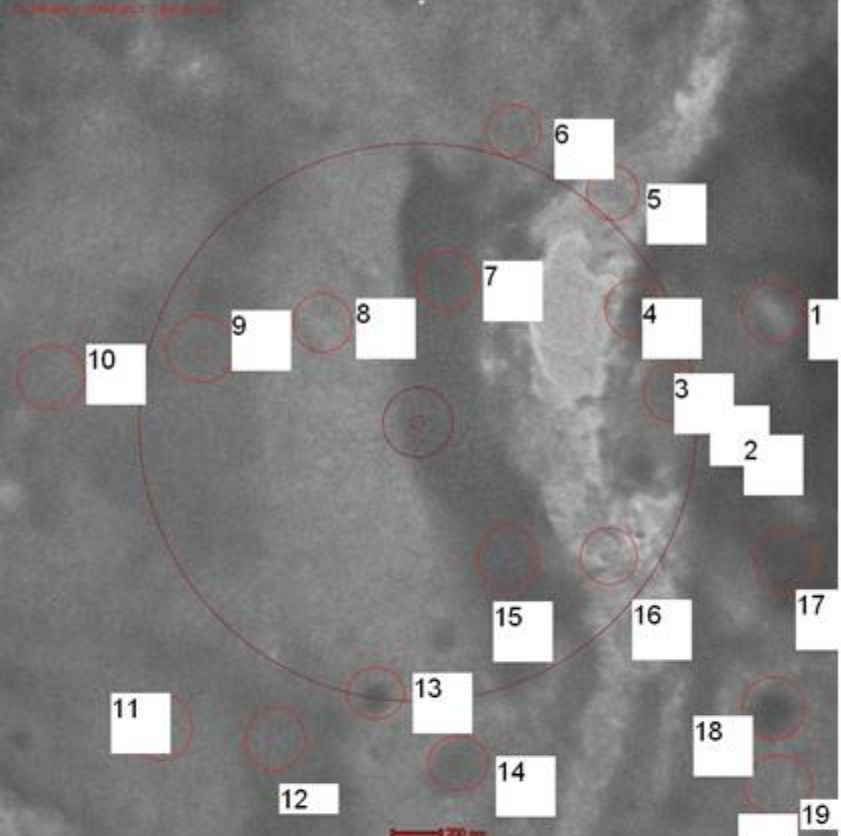


Figure S16. (a) TEM image and (b) EDS-STEM chemical distribution maps for Pb (green), Sb (blue), Ba (yellow) and Ca (red) for particulate 2 and vicinity; five locations for which SAED pattern were recorded are indicated with white and black circles (see S15)

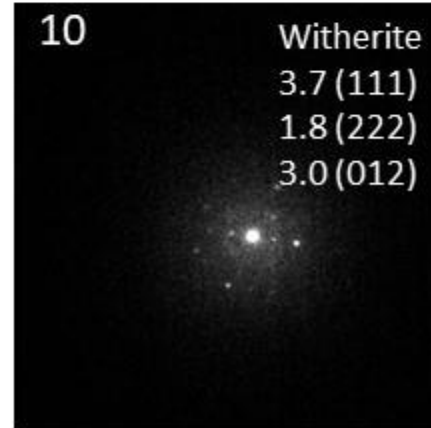
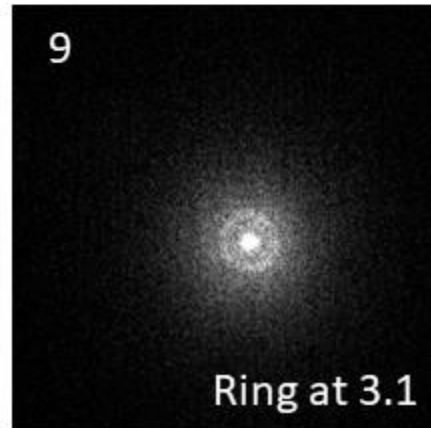
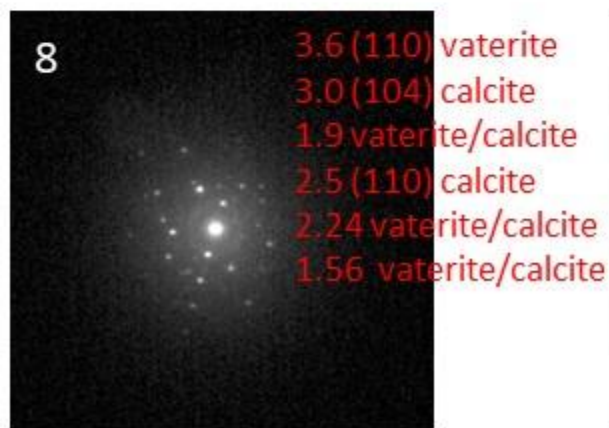
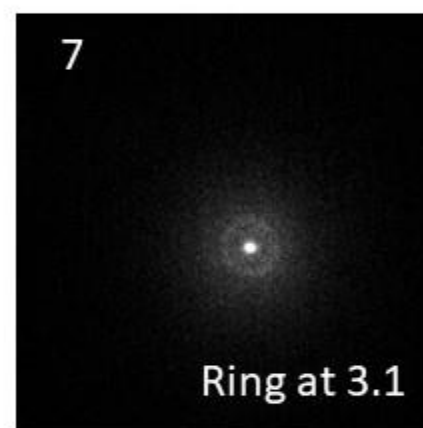
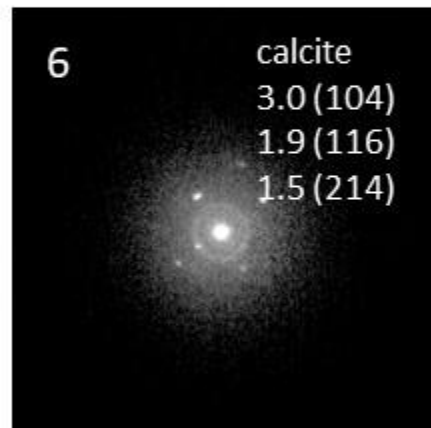
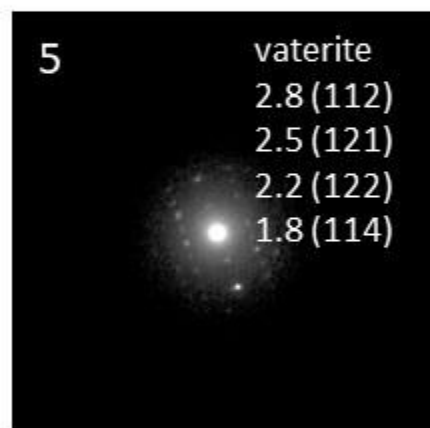
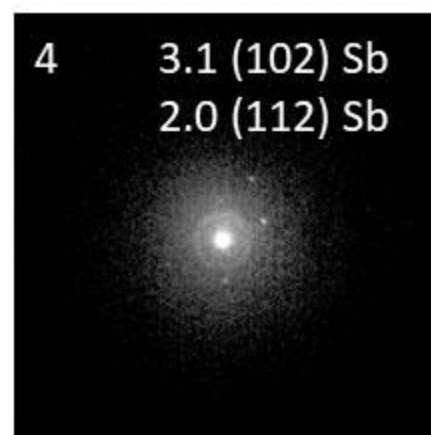
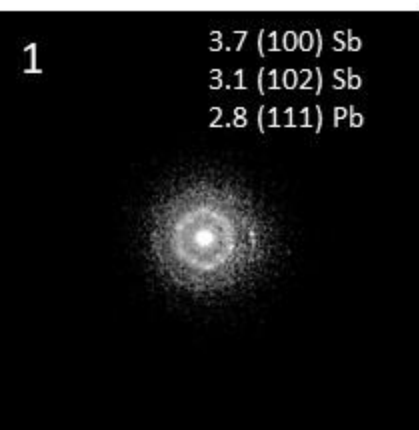


Figure S17.
SAED pattern
For the locations
1-10 indicated
In S14; d-
spacings and
phases are listed
In the
corresponding
pattern

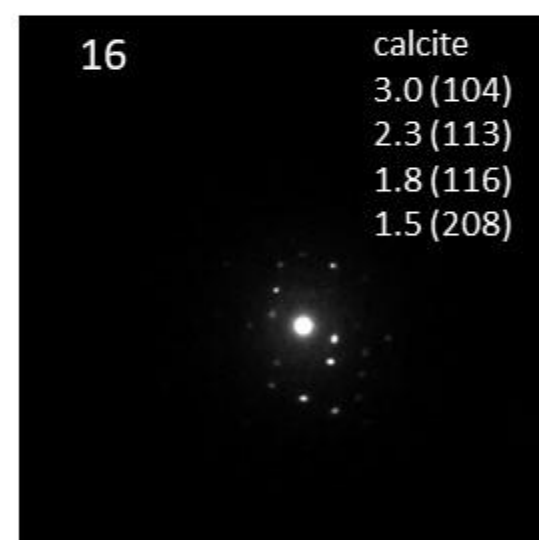
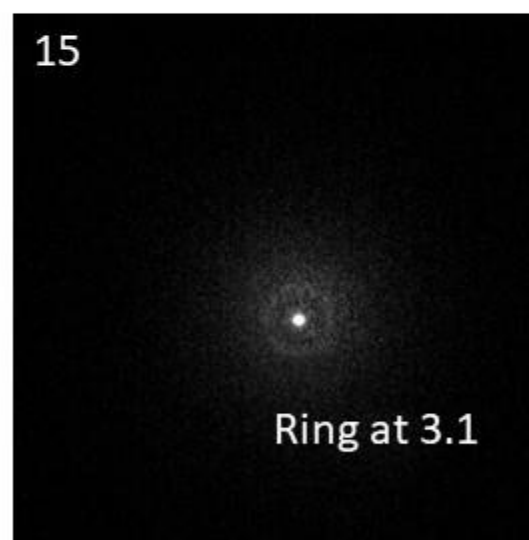
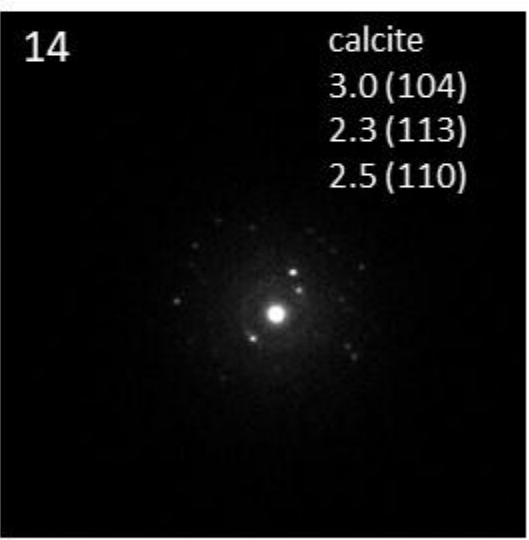
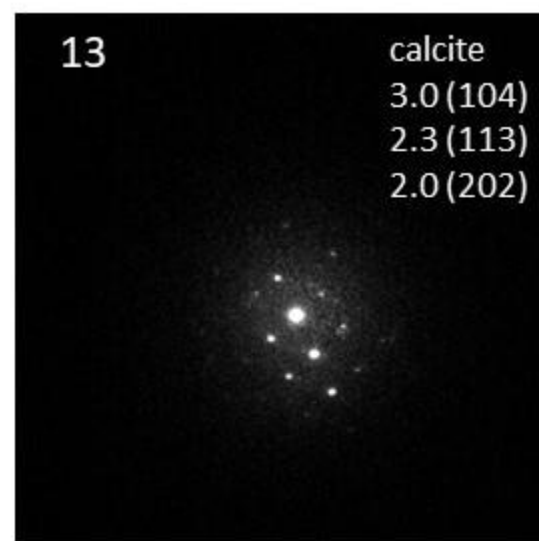
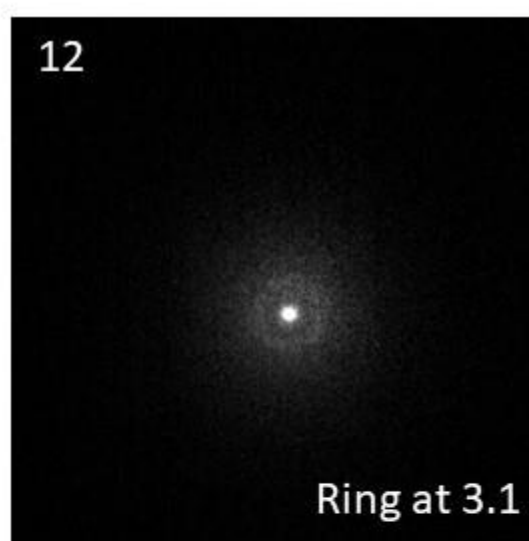
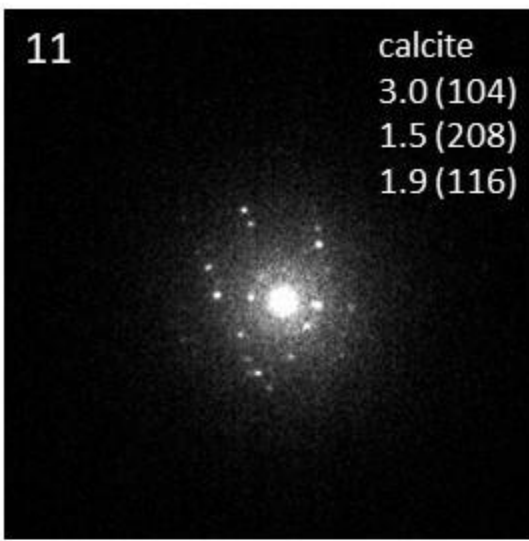


Figure S18. SAED pattern for the locations 11-16 indicated in S14; d-spacings and phases are listed in the corresponding pattern

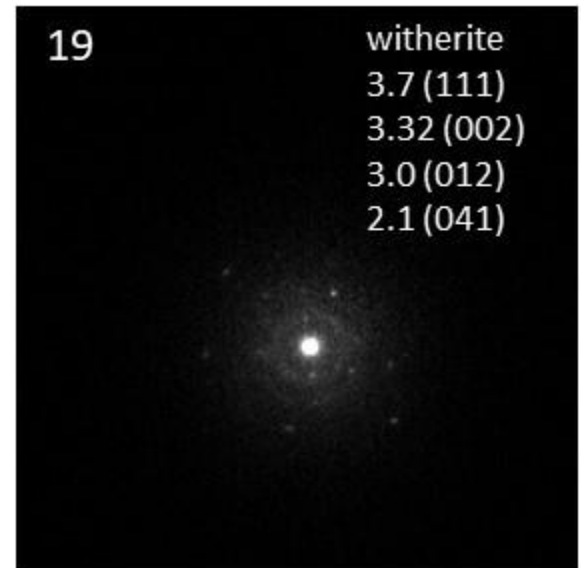
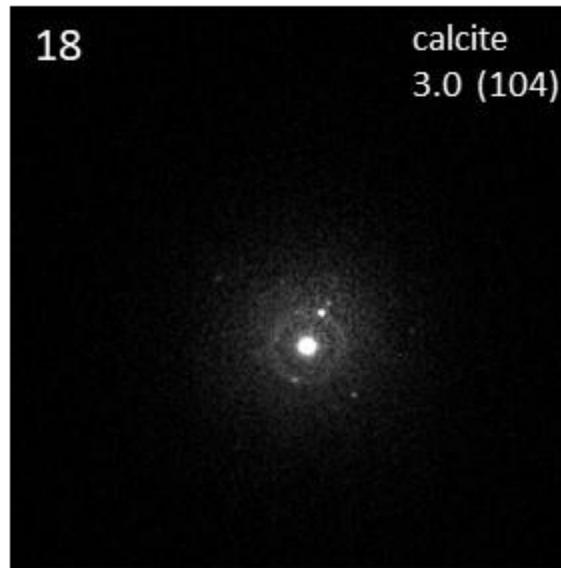
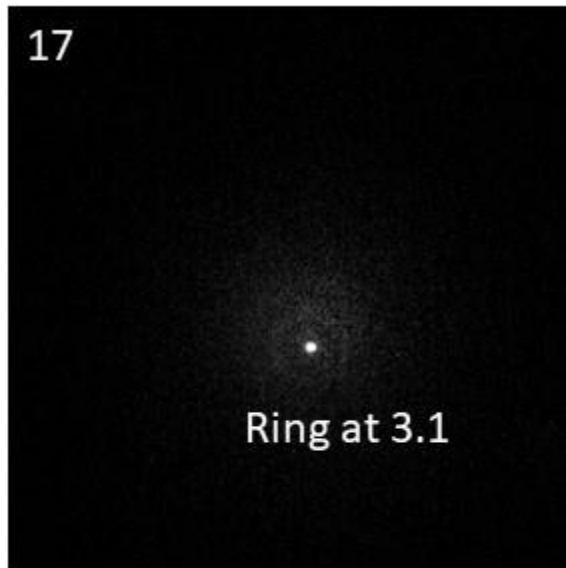


Figure S19. SAED pattern for the locations 17-19 indicated in S14; d-spacings and phases are listed in the corresponding pattern

Examples of High resolution TEM data
from areas between the particulates

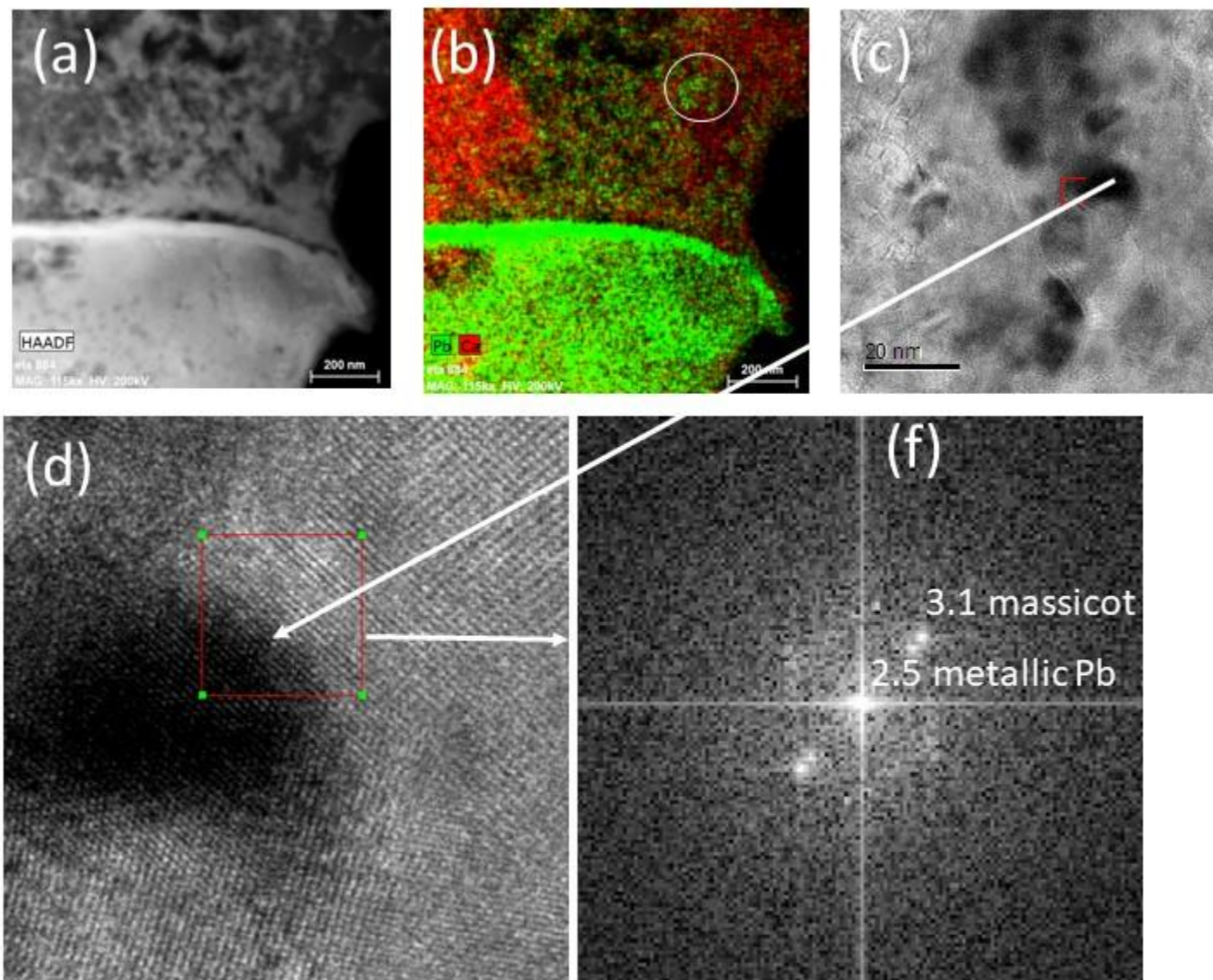


Figure S20. STEM, STEM-EDS chemical distribution for Pb (green) and Ca (red) of a selected area along the rim of the FIB section close to particulate 1; the area shown in (c) is indicated with a white rectangle in (b) TEM image of a chain of aggregated Pb-bearing nanoparticles; (d) rim of massicot on the surface of a metallic Pb nanoparticle; FFT pattern of rim and nanoparticle

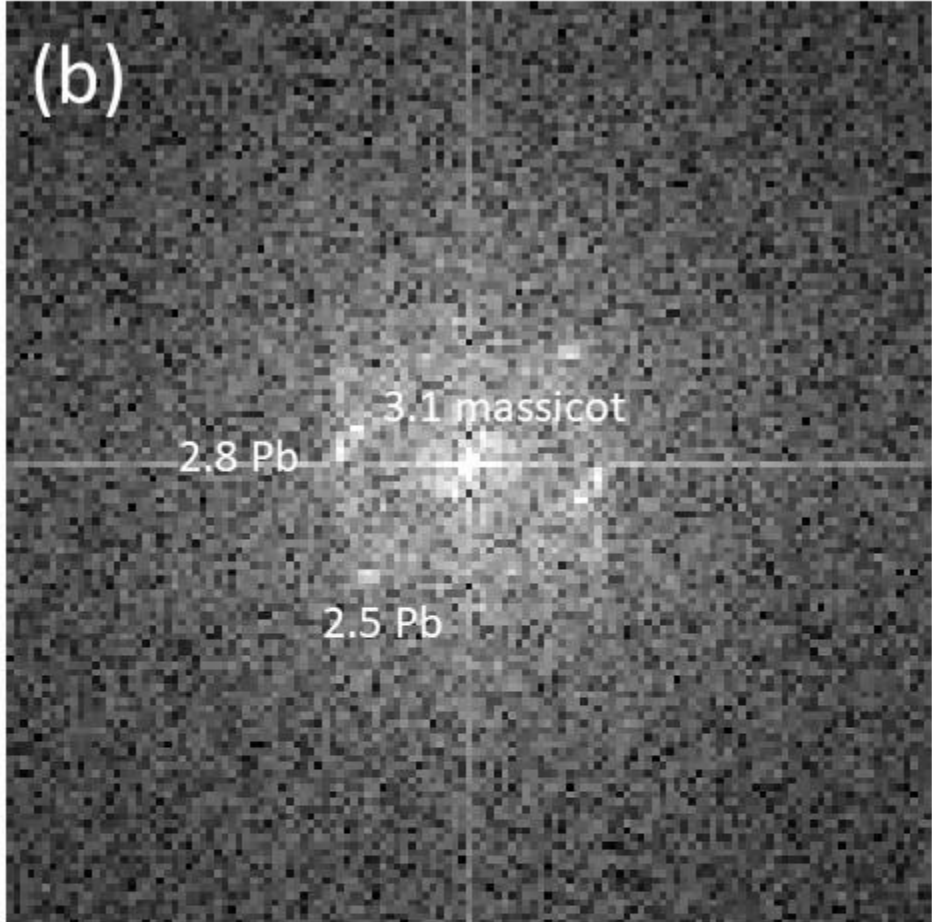
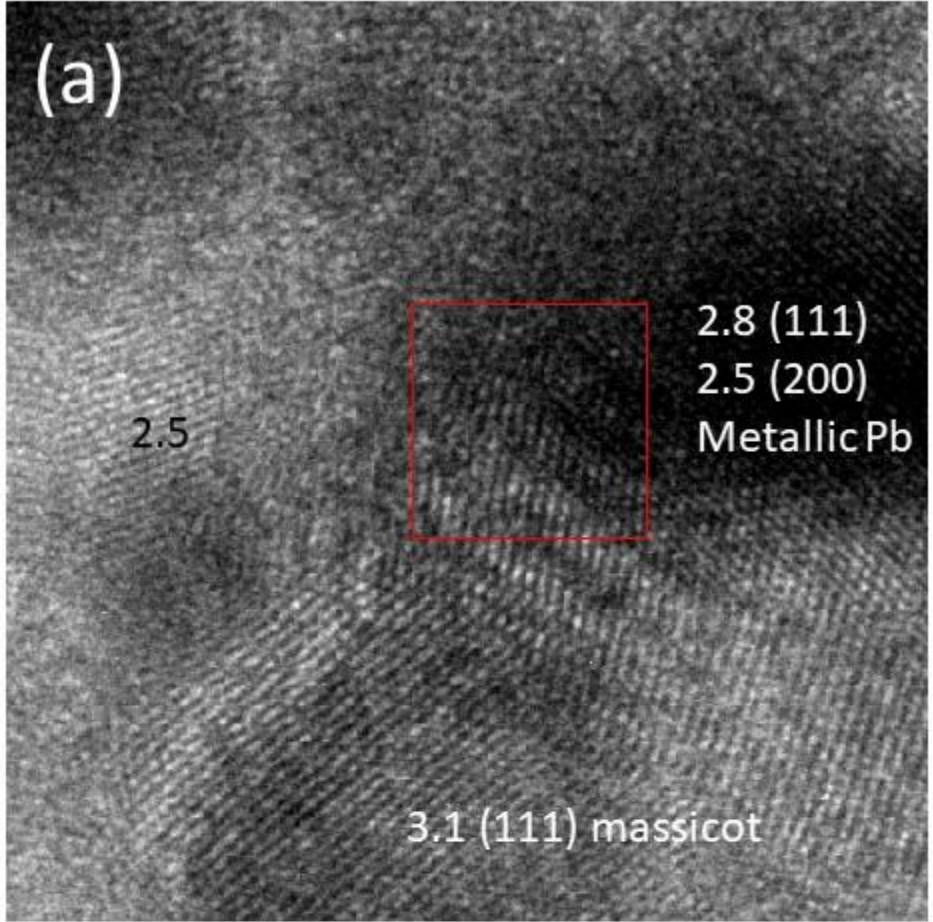
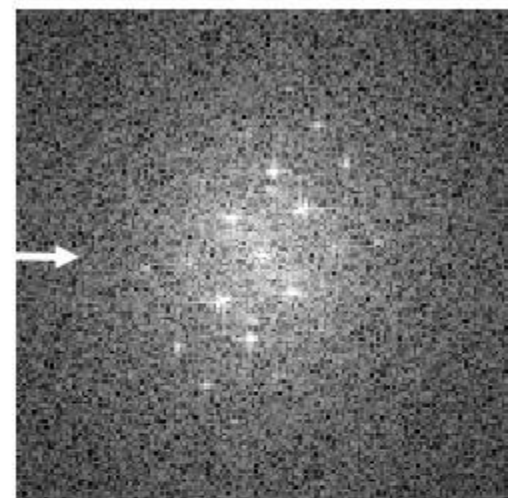


Figure S21. (a) TEM of the metallic Pb nanoparticle shown in S18 with a rim of massicot and a massicot nanoparticle below; (b) FFT pattern from the area indicated with a red rectangle in (a)

(a)

(b)



Aragonite
4.2 (110)
3.4 (111)
2.3 (112)

Figure S22. (a) TEM image of the chain Pb-bearing nanoparticles adjacent to a rim of aragonite (as indicated in S18); (b) FFT pattern taken from an area within the aragonite rim

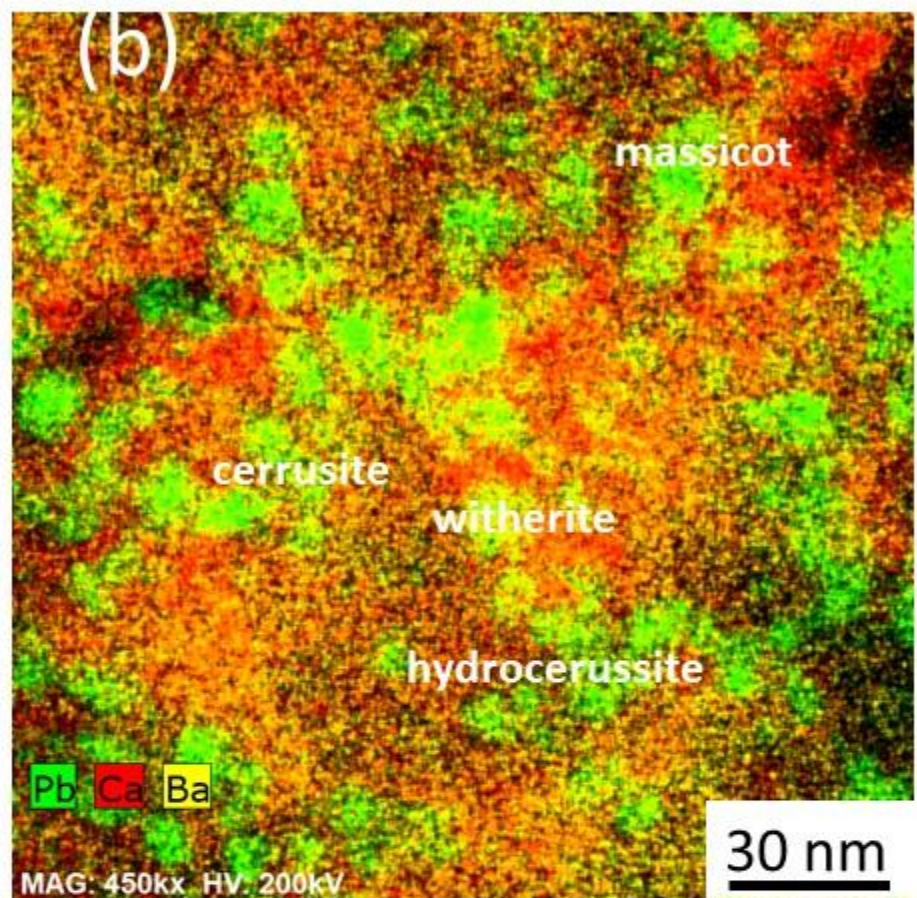
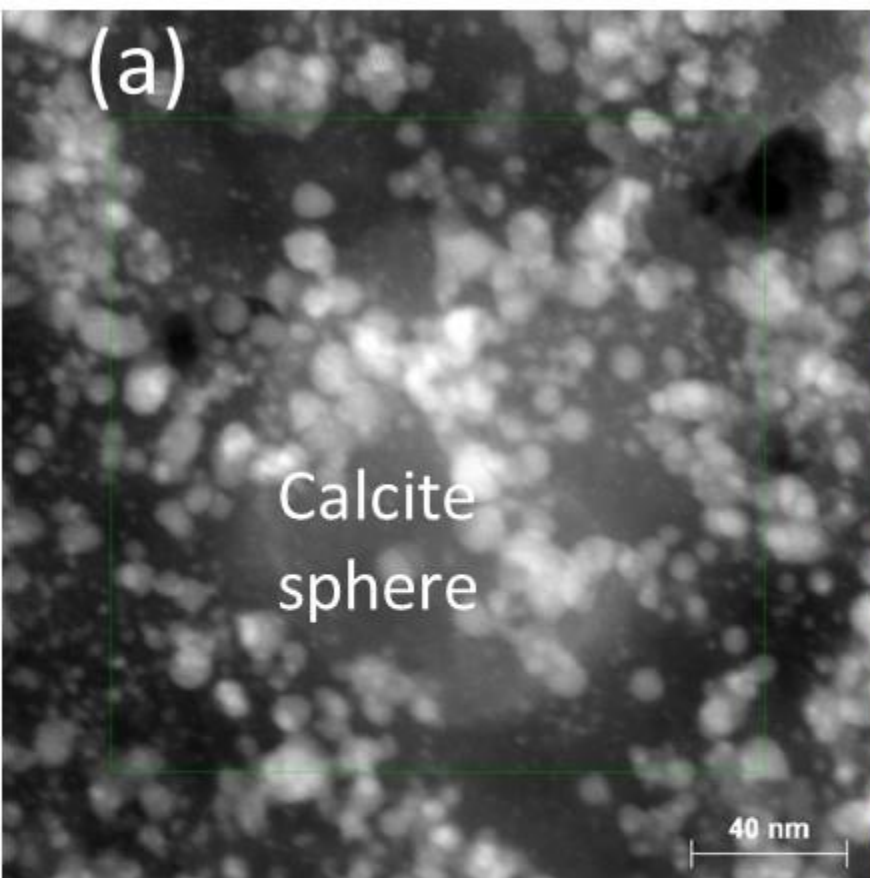
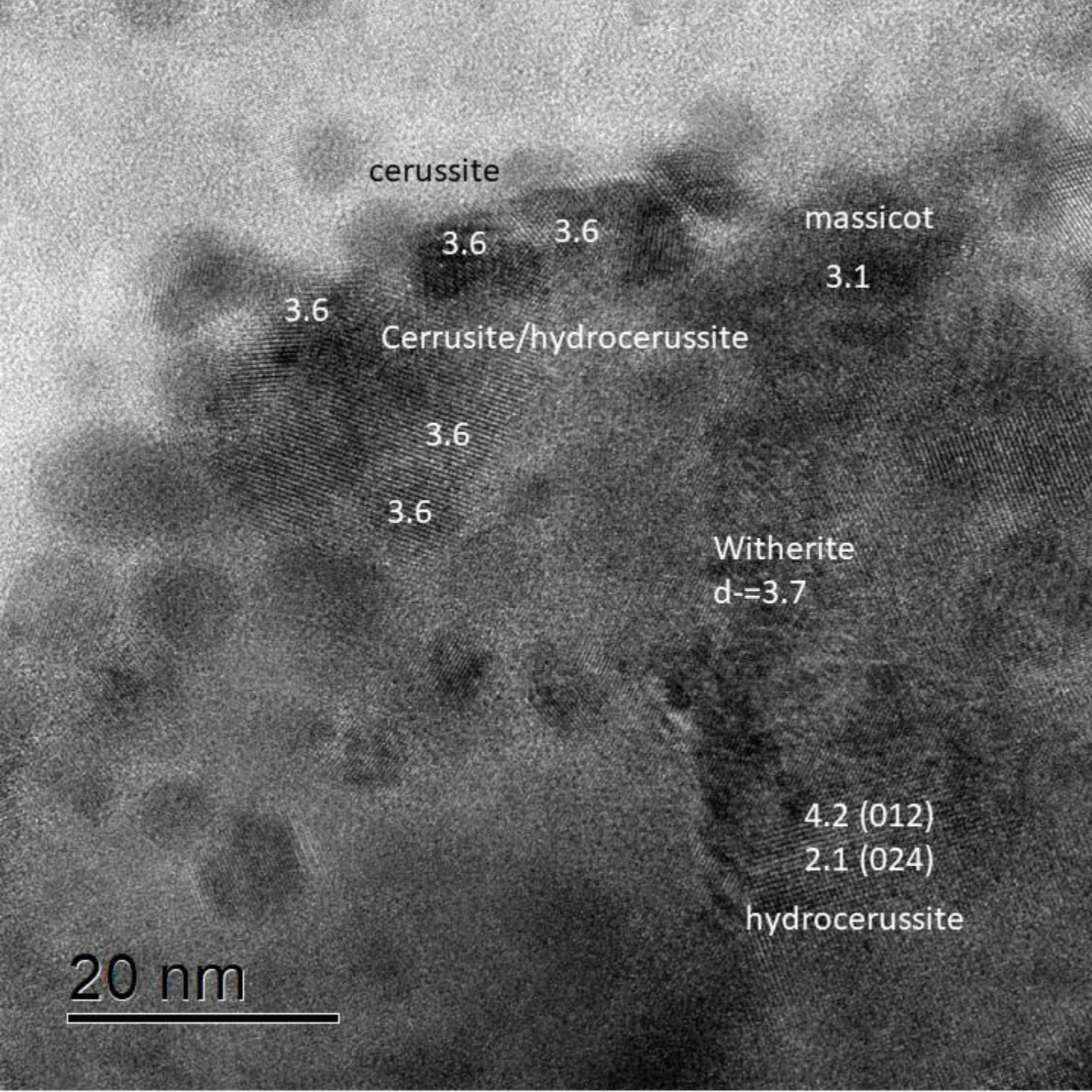


Figure S23. (a) STEM image and STEM-EDS chemical distribution map for Ca (red), Sb (blue), Pb (green) and Ba (yellow) for a calcite sphere encrusted by predominantly Ba-Pb-bearing phases. The corresponding lattice fringes are listed in Figure S22.



cerussite

massicot

3.6

3.6

3.1

3.6

Cerussite/hydrocerussite

3.6

3.6

Witherite

d=3.7

4.2 (012)

2.1 (024)

hydrocerussite

20 nm

Figure S24. TEM image for a calcite sphere encrusted by predominantly Ba-Pb-bearing phases. D-spacings and names of the phases are listed besides the lattice fringes

Selected Area Diffraction and Fast
Fourier Transformation pattern of
areas in selected colloids

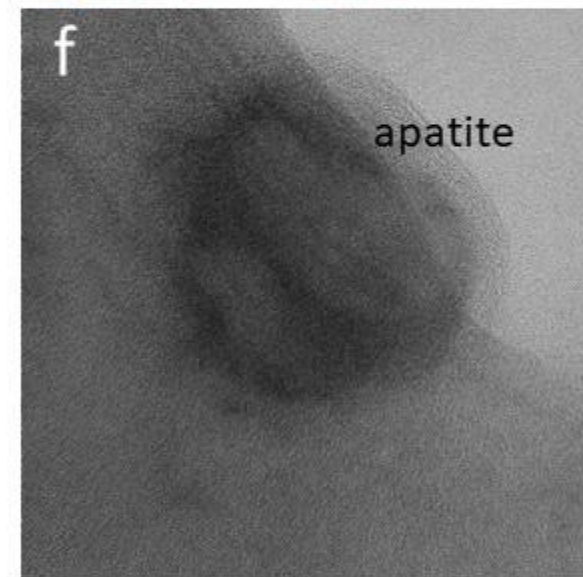
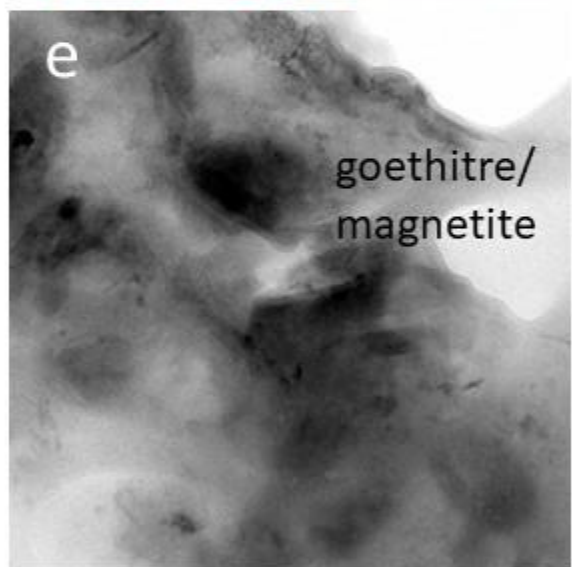
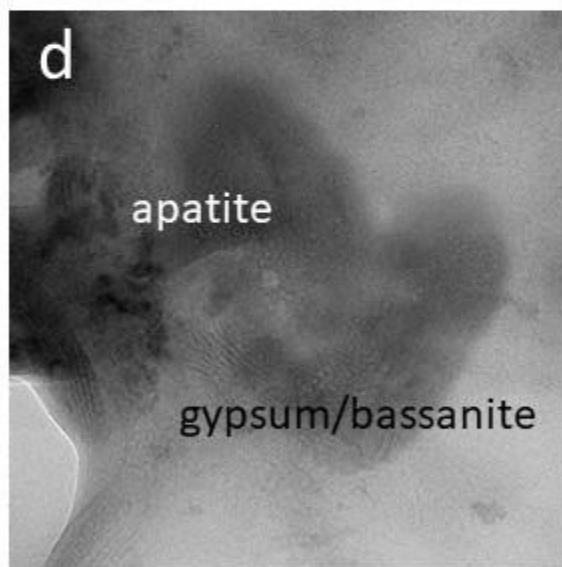
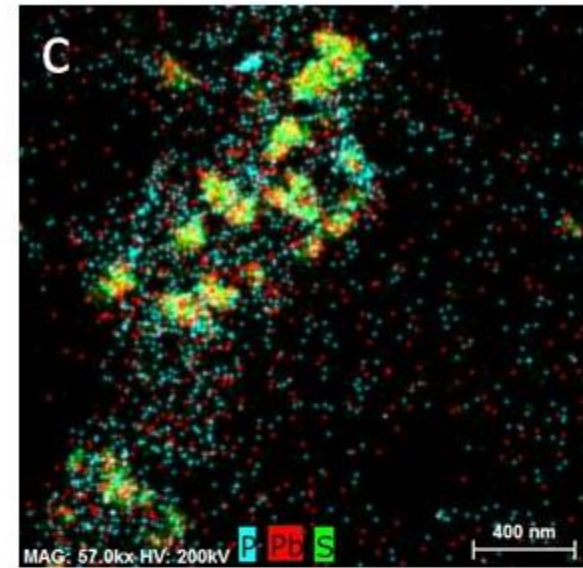
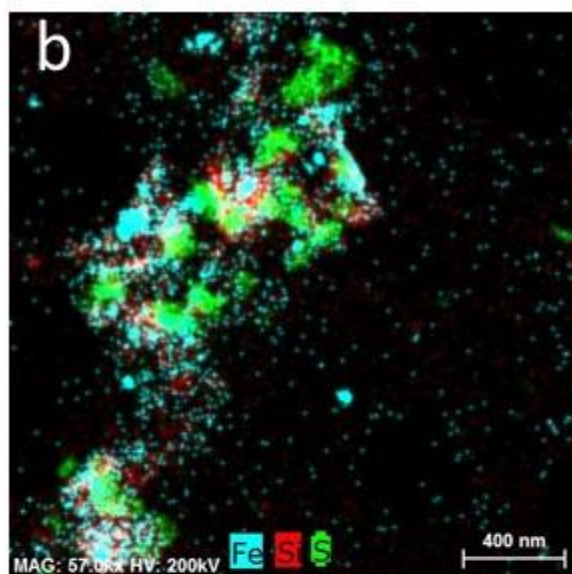
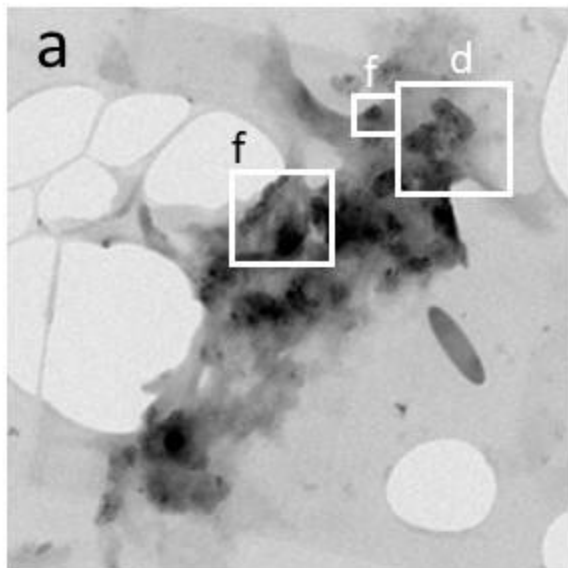


Figure S25. (a) STEM and (b)-(c) EDS-chemical distribution maps for (b) Fe (light blue), Si (red) and S (green) and (c) P (blue), Pb (red) and S (red) of a selected colloids; (d)-(f) TEM images of observed phases; Lattice fringes and corresponding d-spacings for the observed phases are listed in S23-28.

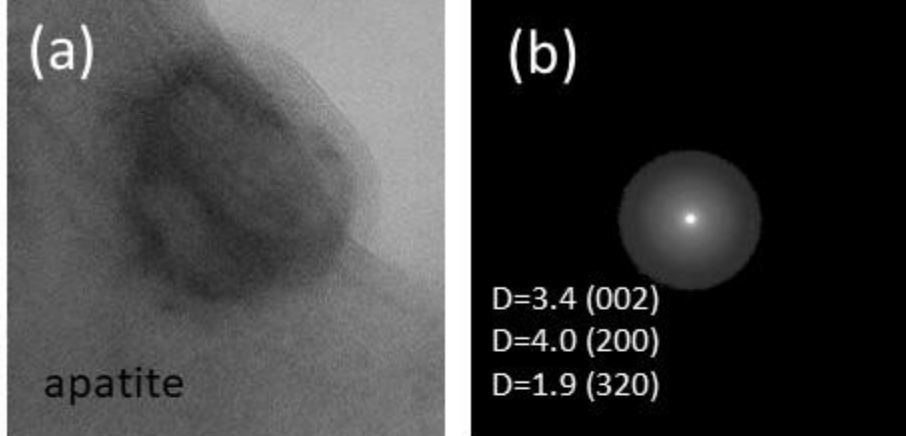
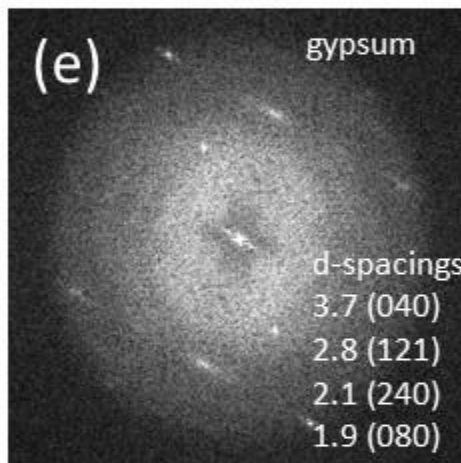
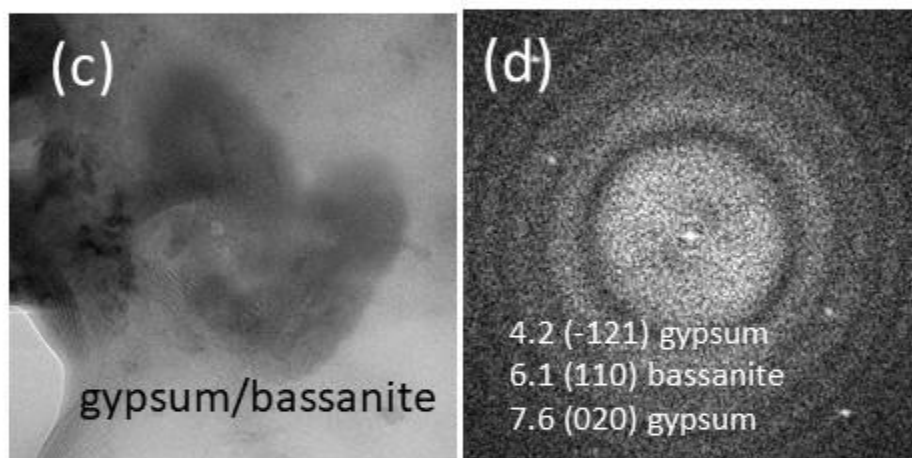


Figure S26.

(a) TEM images of a nano-size apatite crystal and (b) corresponding FFT pattern of lattice fringes visible in (a).



(c) TEM image of gypsum/bassanite crystals and (d)-(e) corresponding FFT patterns of lattice fringes visible in (c)

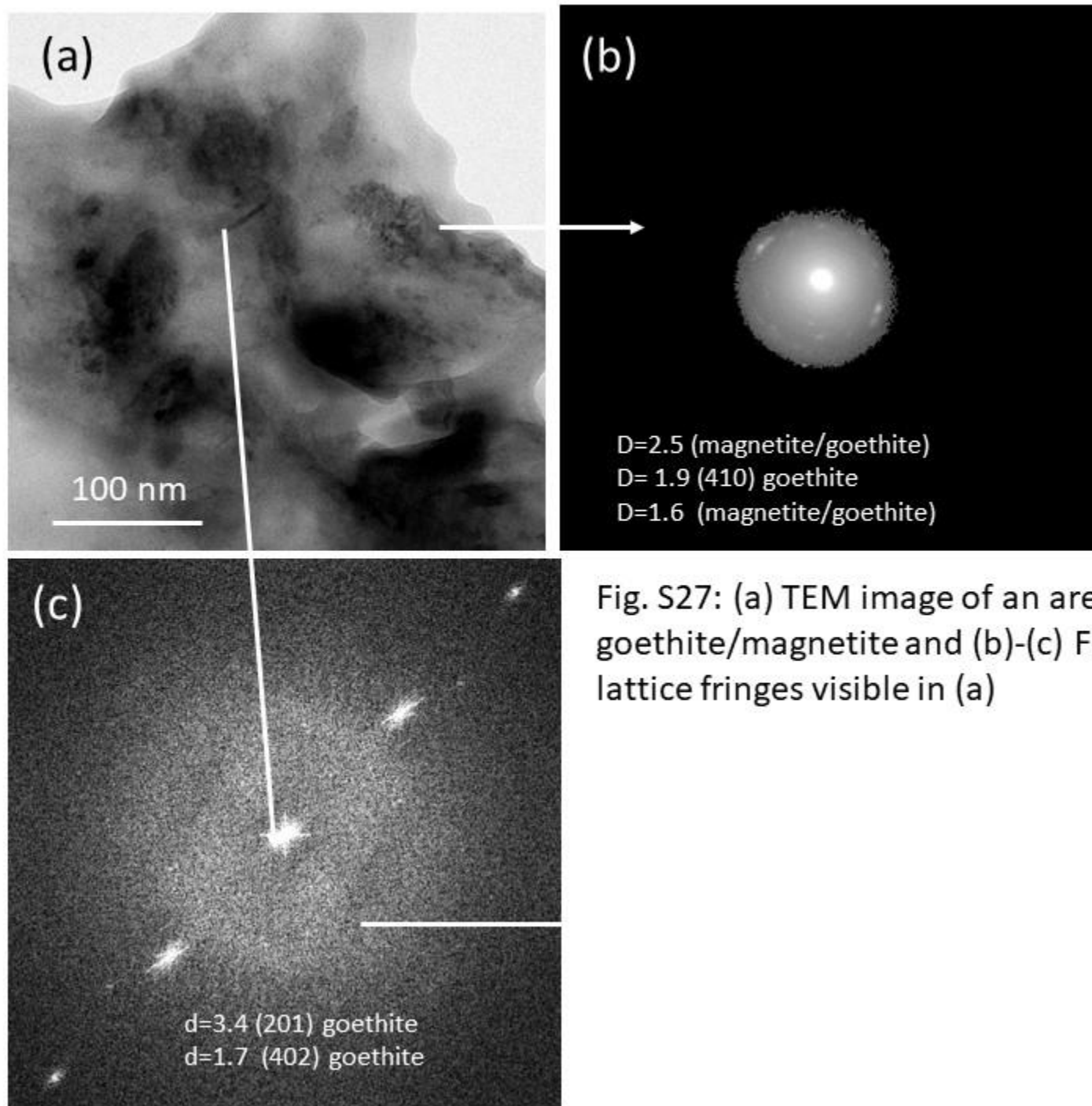


Fig. S27: (a) TEM image of an area composed of goethite/magnetite and (b)-(c) FFT patterns of lattice fringes visible in (a)

Fig. S28. XRD pattern of sample from site 2

