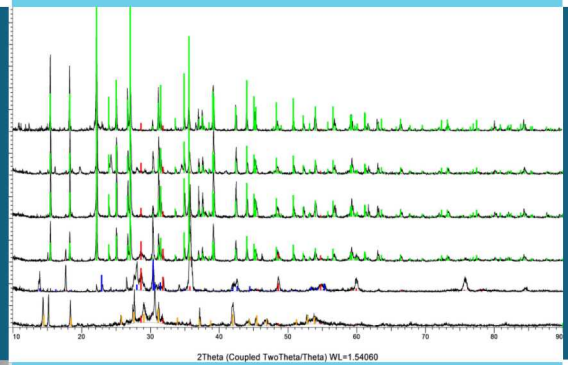
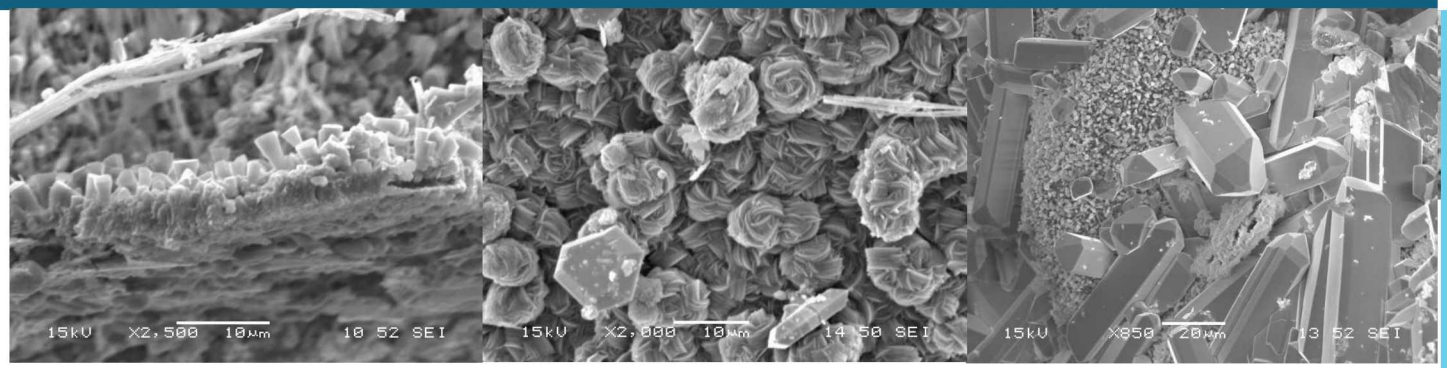
SAND2020-5302C

Solid transformation of litharge into laurionite and blixite



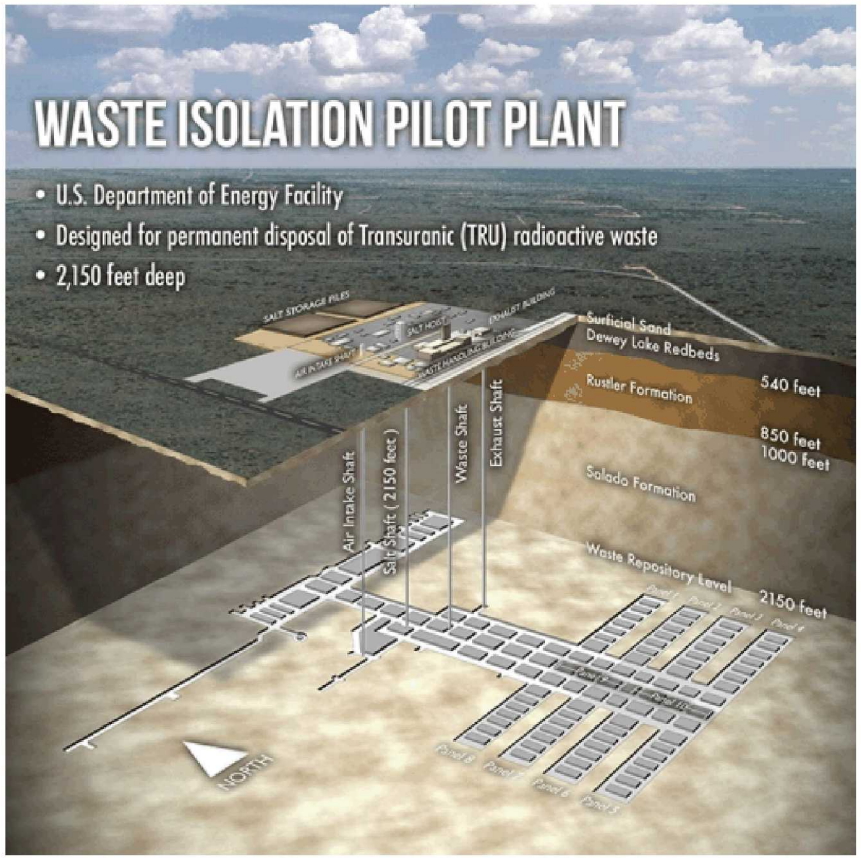


PRESENTED BY

LESLIE KIRKES

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This research is funded by WIPP programs administered by the Office of Environmental Management (EM) of the U.S. Department of Energy.

Waste Isolation Pilot Plant



https://www.energy.gov/em/articles/quick-facts-about-ems-waste-isolation-pilot-plant

Nelson, R.A. 2008

The Waste Isolation Pilot Plant (WIPP) is the nation's only deep geologic long-lived radioactive waste repository. Located 26 miles southeast of Carlsbad, New Mexico, WIPP permanently isolates defense-generated transuranic (TRU) waste 2,150 feet underground in an ancient salt formation.

TRU waste began accumulating in the 1940s with the beginning of the nation's nuclear defense program. As early as the 1950s, the National Academy of Sciences recommended deep disposal of long-lived TRU radioactive wastes in geologically stable formations, such as deep salt beds. Sound environmental practices and strict regulations require such wastes to be isolated to protect human health and the environment.

Bedded salt is free of fresh flowing water, easily mined, impermeable and geologically stable — an ideal medium for permanently isolating long-lived radioactive wastes from the environment. However, its most important quality in this application is the way salt rock seals all fractures and naturally closes all openings.

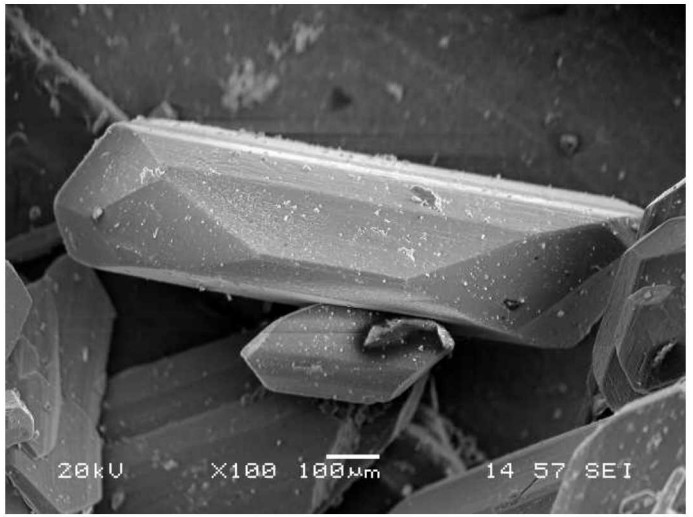
Lead is used as a shielding material in some of the waste drums and is also present in the waste inventory.

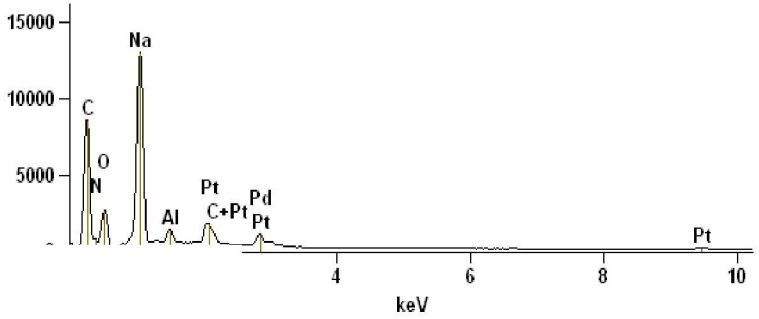
https://wipp.energy.gov/wipp-site.asp

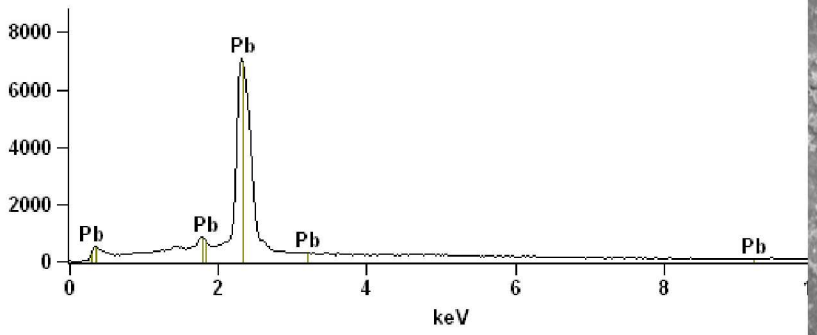
Experimental Set-up

Set-up ID	PbO(s) (g)	$MgCl_2$ (m)	Na_2H_2EDTA (m)	Reference	Density
PbO-0.01ED-1	2.0054	0.008	0.042	WIPP-Solubility-3, p. 35	1.0117
PbO-0.01ED-2	2.0004	0.008	0.042	WIPP-Solubility-3, p. 35	1.0117
PbO-0.1ED-1	2.0040	0.08	0.042	WIPP-Solubility-3, p. 35	1.0189
PbO-0.1ED-2	2.0043	0.08	0.042	WIPP-Solubility-3, p. 35	1.0189
PbO-1.0ED-1	2.0041	0.8	0.042	WIPP-Solubility-3, p. 35	1.0728
PbO-1.0ED-2	2.0056	0.8	0.042	WIPP-Solubility-3, p. 35	1.0728
PbO-1.5ED-1	2.0049	1.2	0.042	WIPP-Solubility-3, p. 35	1.0961
PbO-1.5ED-2	2.0005	1.2	0.042	WIPP-Solubility-3, p. 35	1.0961
PbO-2.0ED-1	2.0033	1.6	0.042	WIPP-Solubility-3, p. 35	1.1254
PbO-2.0ED-2	2.0069	1.6	0.042	WIPP-Solubility-3, p. 35	1.1254
PbO-2.5ED-1	2.0016	2	0.042	WIPP-Solubility-3, p. 35	1.1505
PbO-2.5ED-1	2.0036	2	0.042	WIPP-Solubility-3, p. 35	1.1505

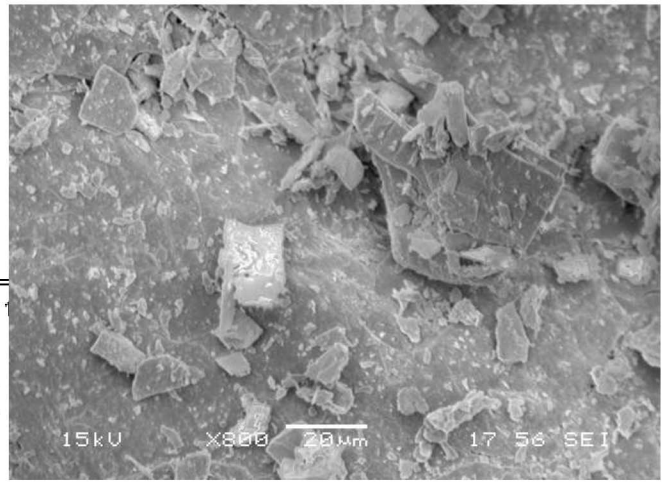
Na_2H_2EDTA starting material





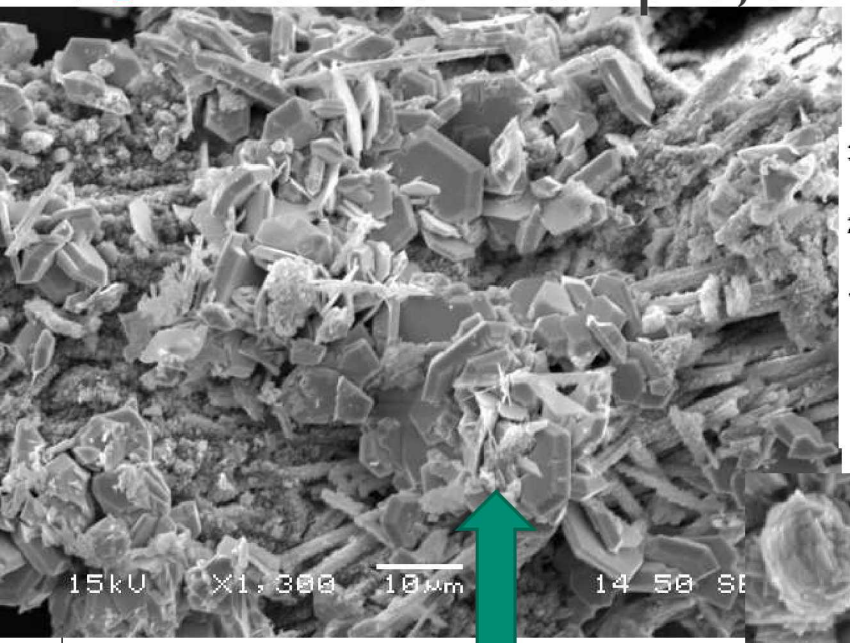


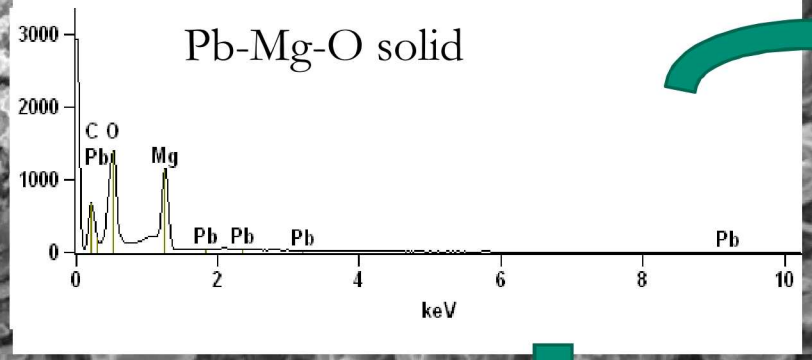
PbO (Litharge) starting material

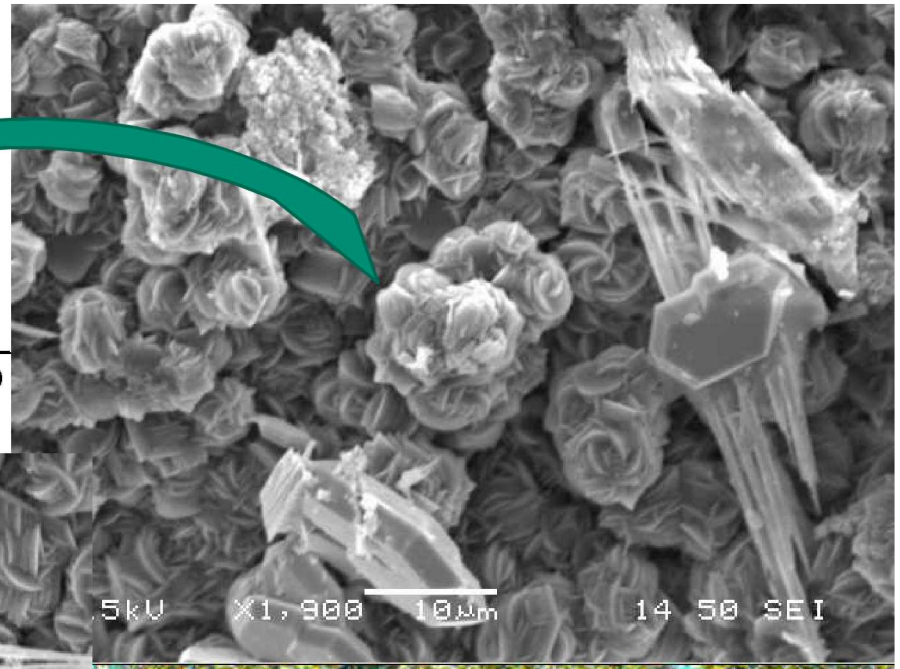


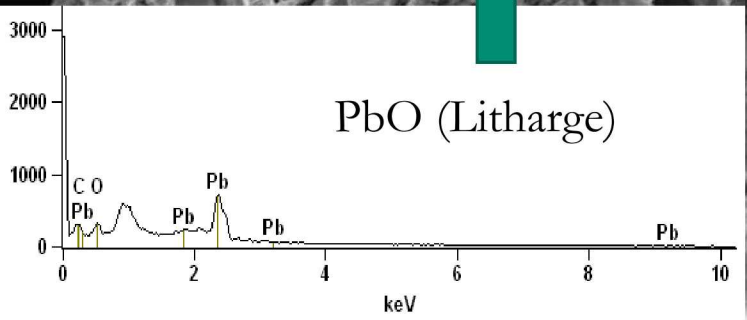
All solid characterization data in this presentation was collected at termination of the experiments: 3936-4074 days of experiment.

PbO-0.01 Sample,0.008m $MgCl_2$, 0.042m Na_2H_2EDTA



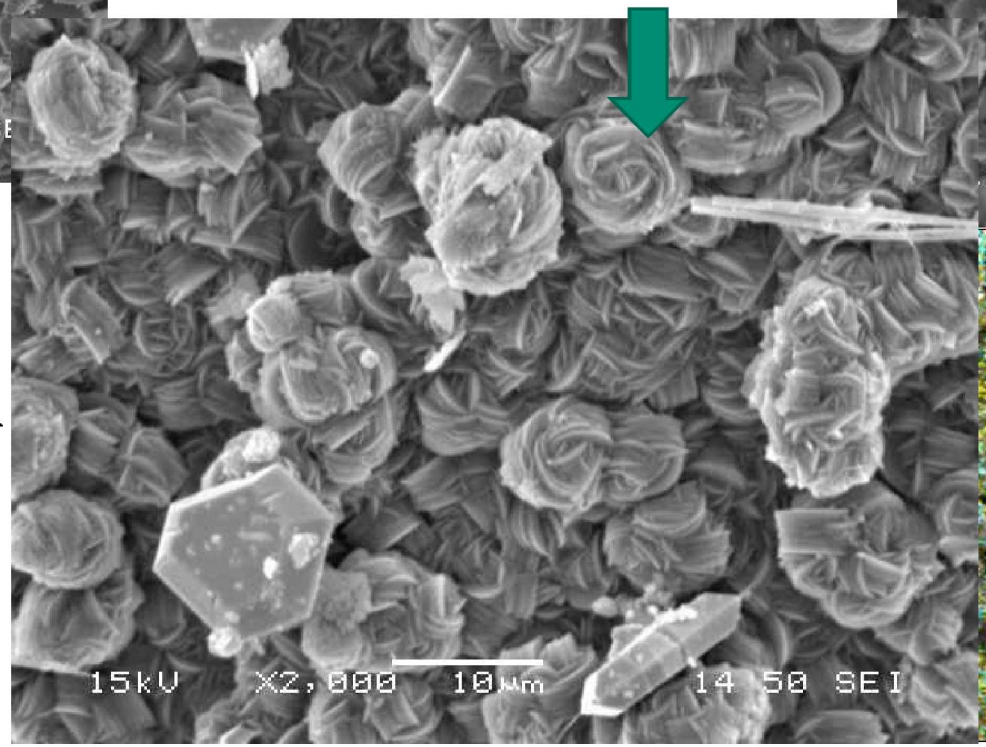




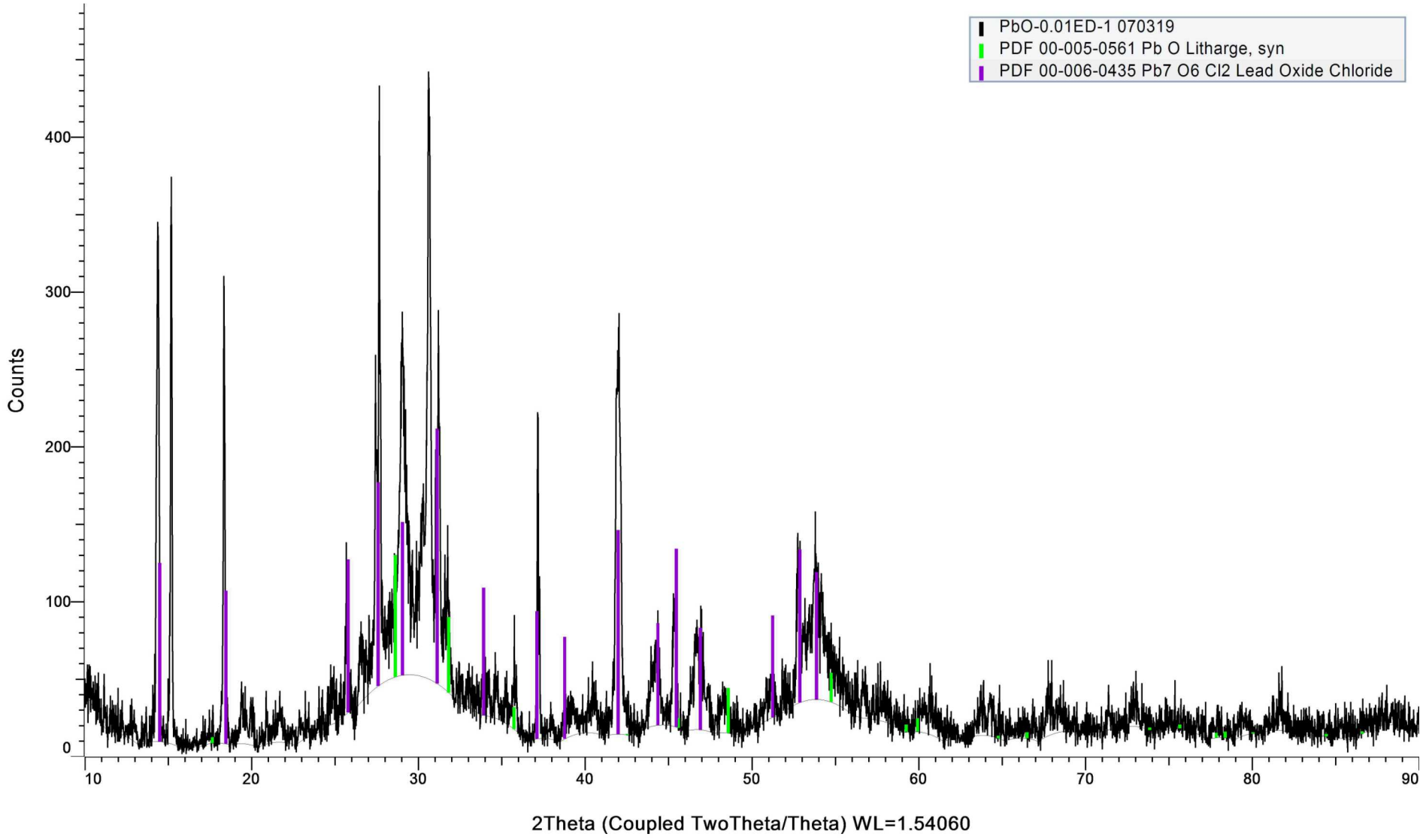


PbO (Litharge)

Tetragonal crystal habit



PbO-0.01 Sample,0.008m $MgCl_2$, 0.042m Na_2H_2EDTA

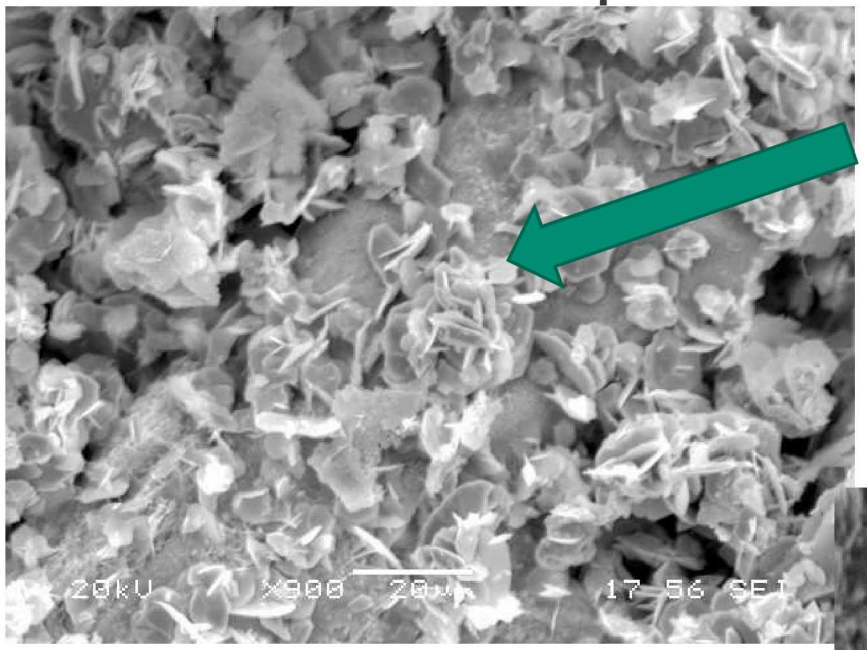


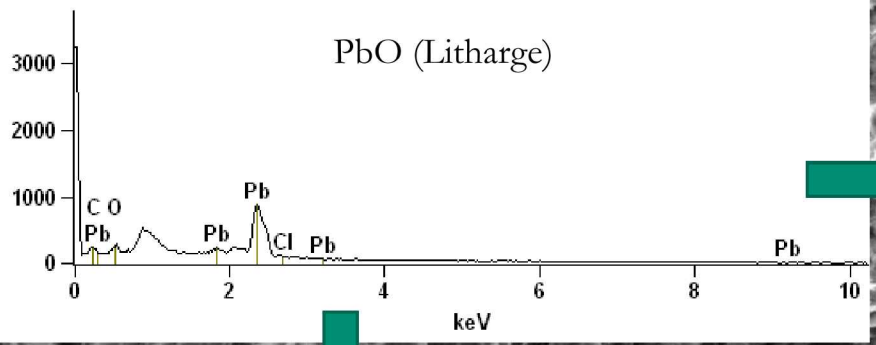
Kirkes, L. 2019

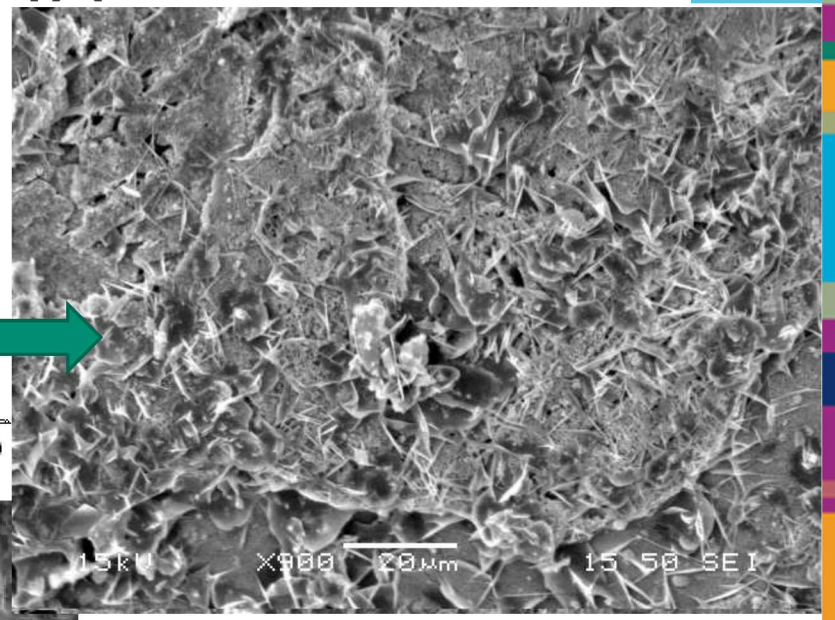
Litharge and Lead Oxide Chloride were identified in XRD analysis, however Lead Oxide Chloride was not seen in crystalline form in SEM/EDS analysis.

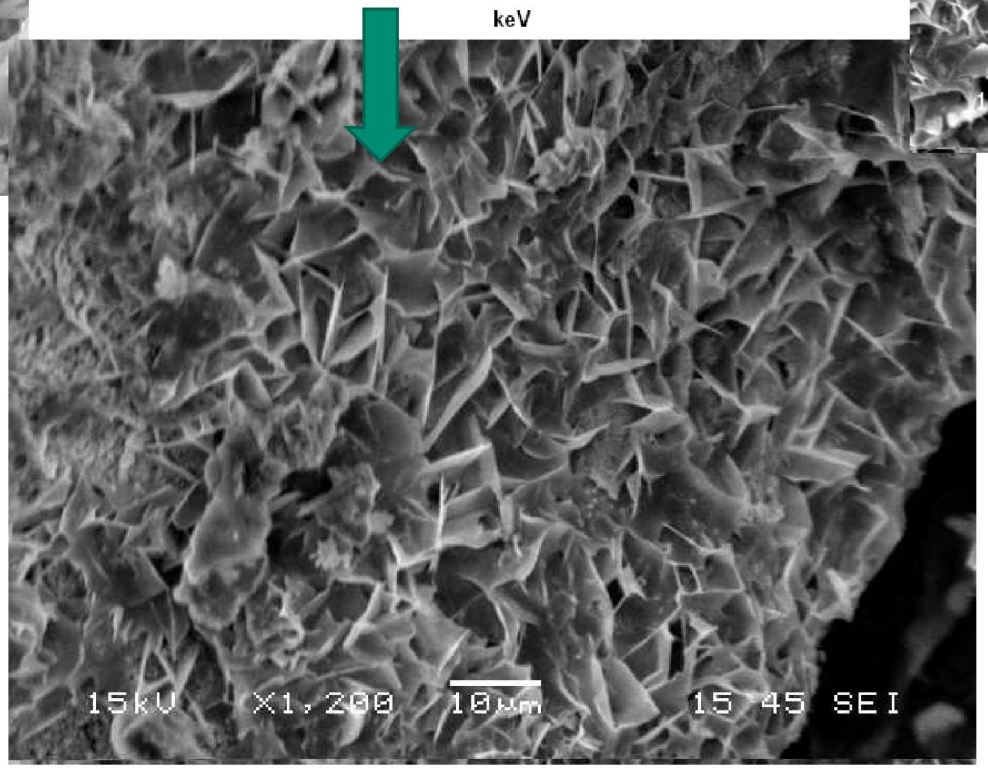
Pb-Mg-O solid was not identified by XRD. More research is needed and solid characterization is still underway.

PbO-0.1 Sample,0.08m $MgCl_2$, 0.042m Na_2H_2EDTA



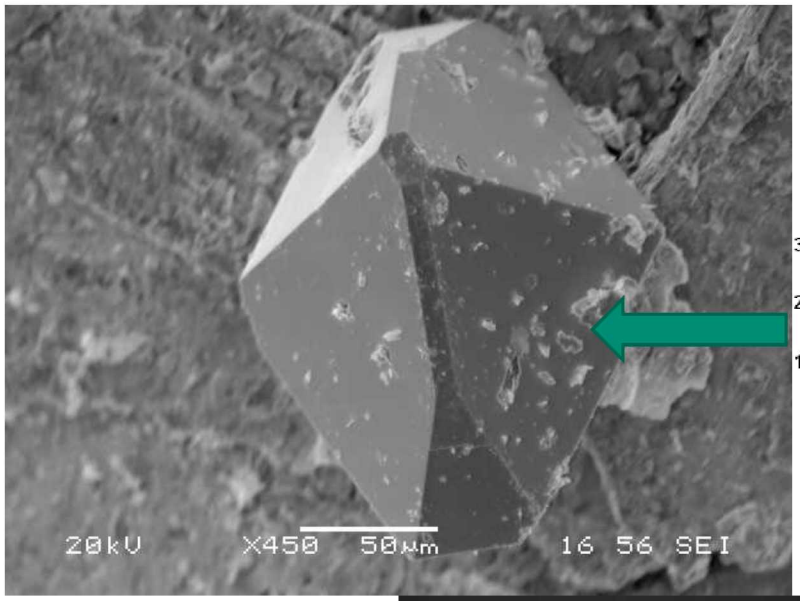


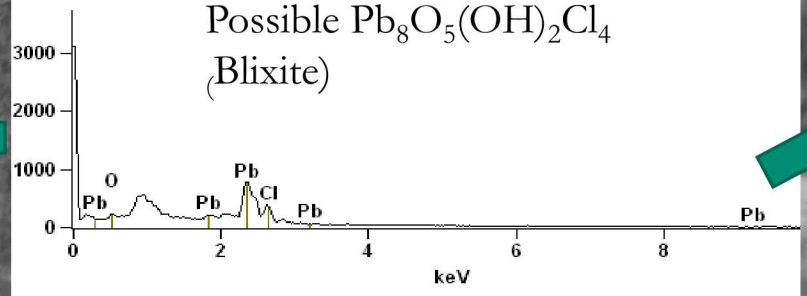


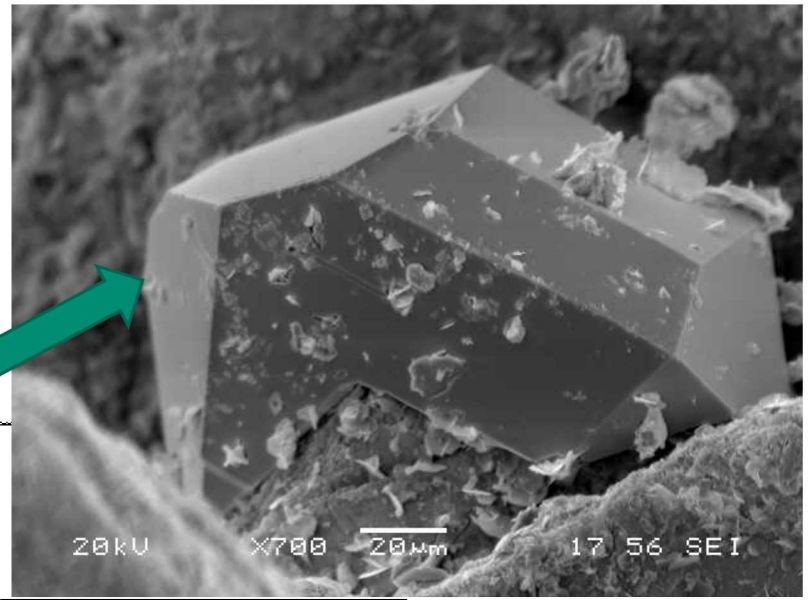


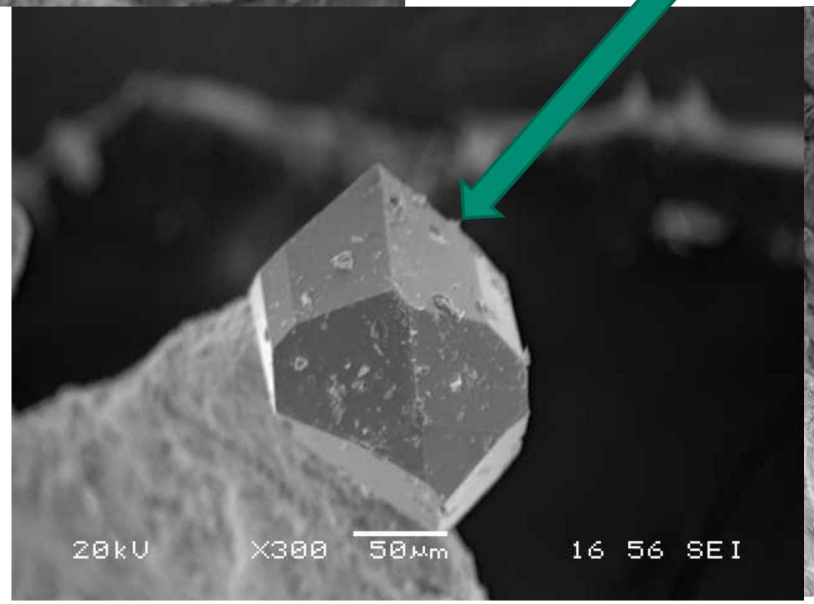
Similar lead oxide (litharge) film images were collected by Patel et al. 2014

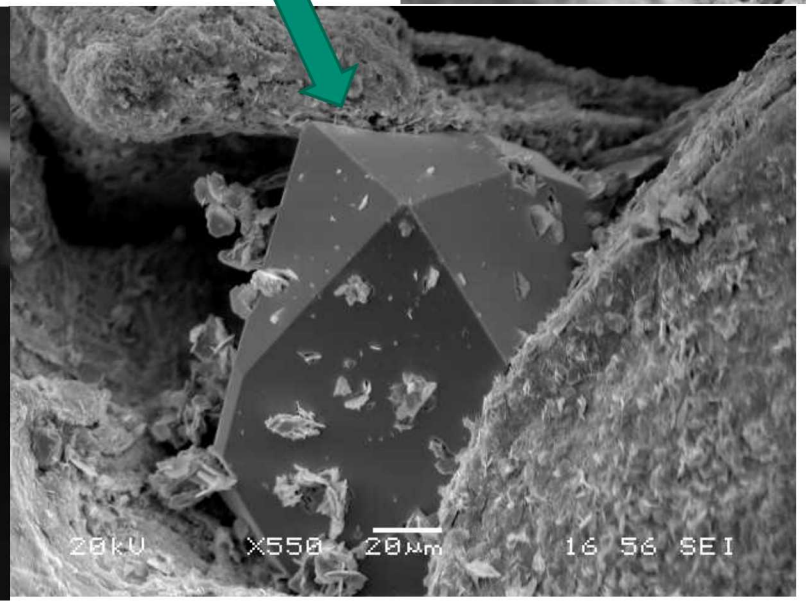
PbO-0.1 Sample,0.08m $MgCl_2$, 0.042m Na_2H_2EDTA





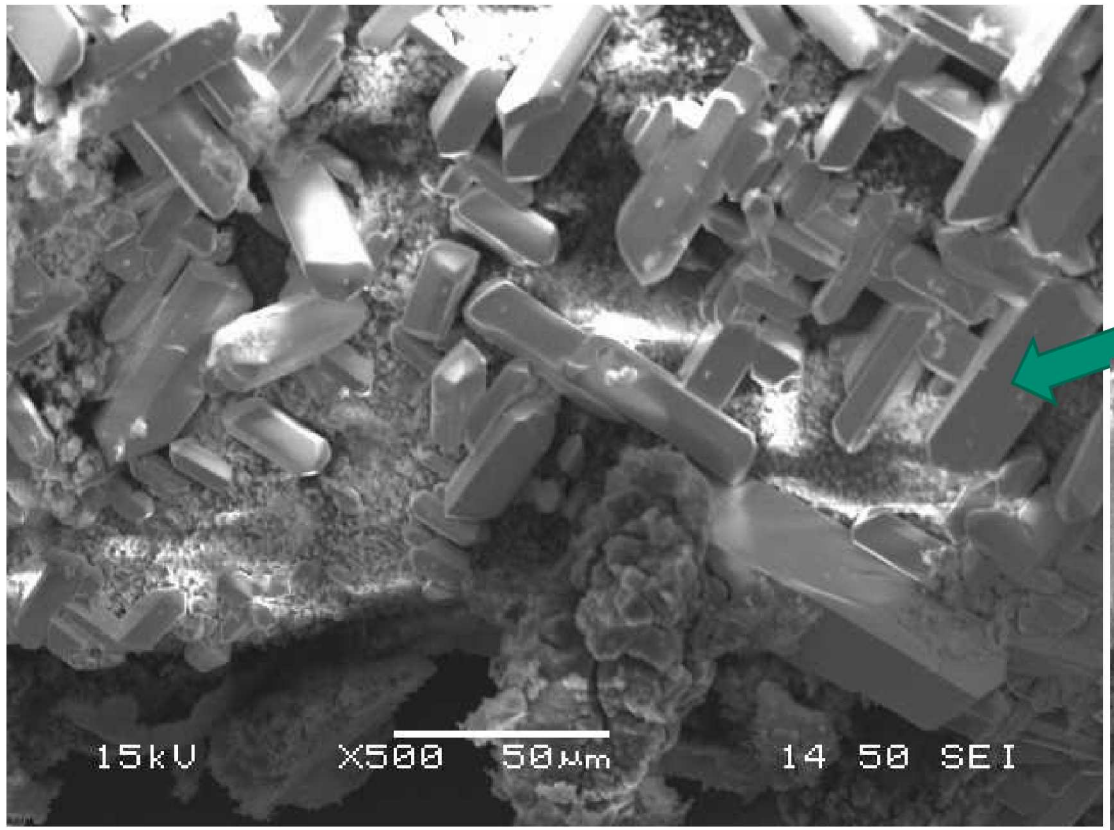


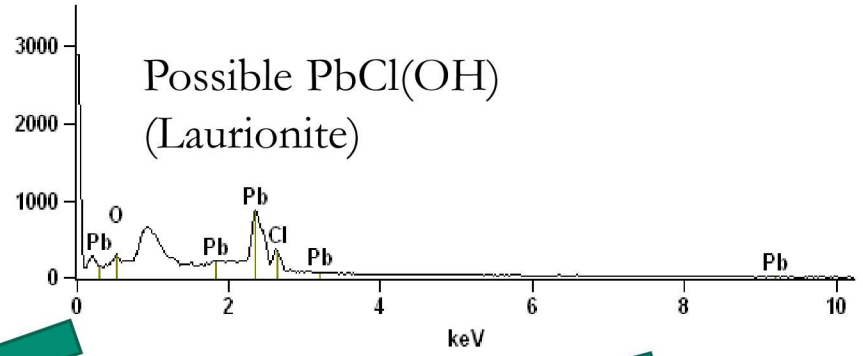


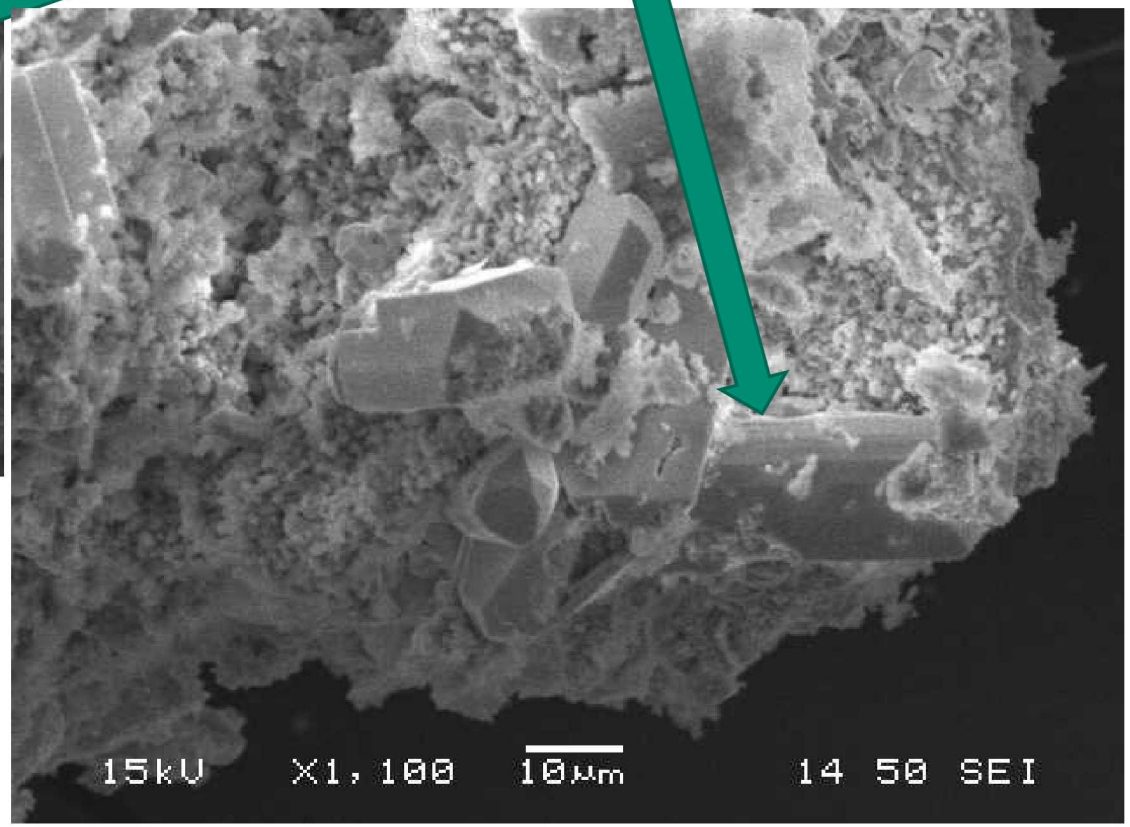


Monoclinic, prismatic habit
(Krivovichev and Burns 2006)

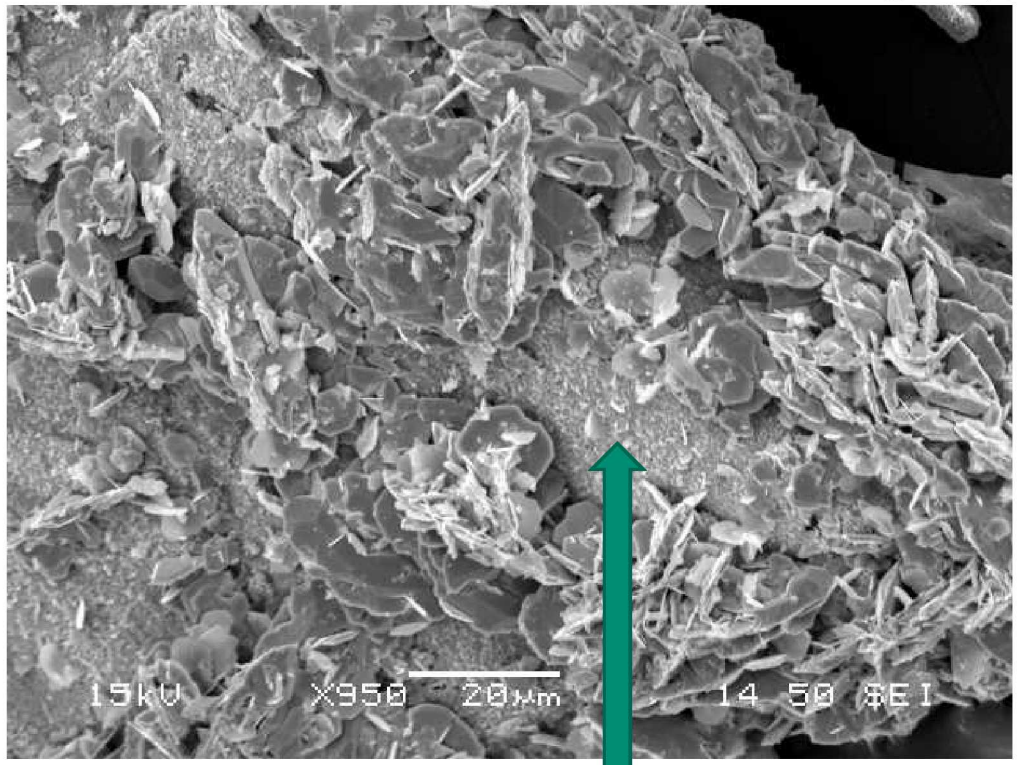
PbO-0.1 Sample,0.08m $MgCl_2$, 0.042m Na_2H_2EDTA

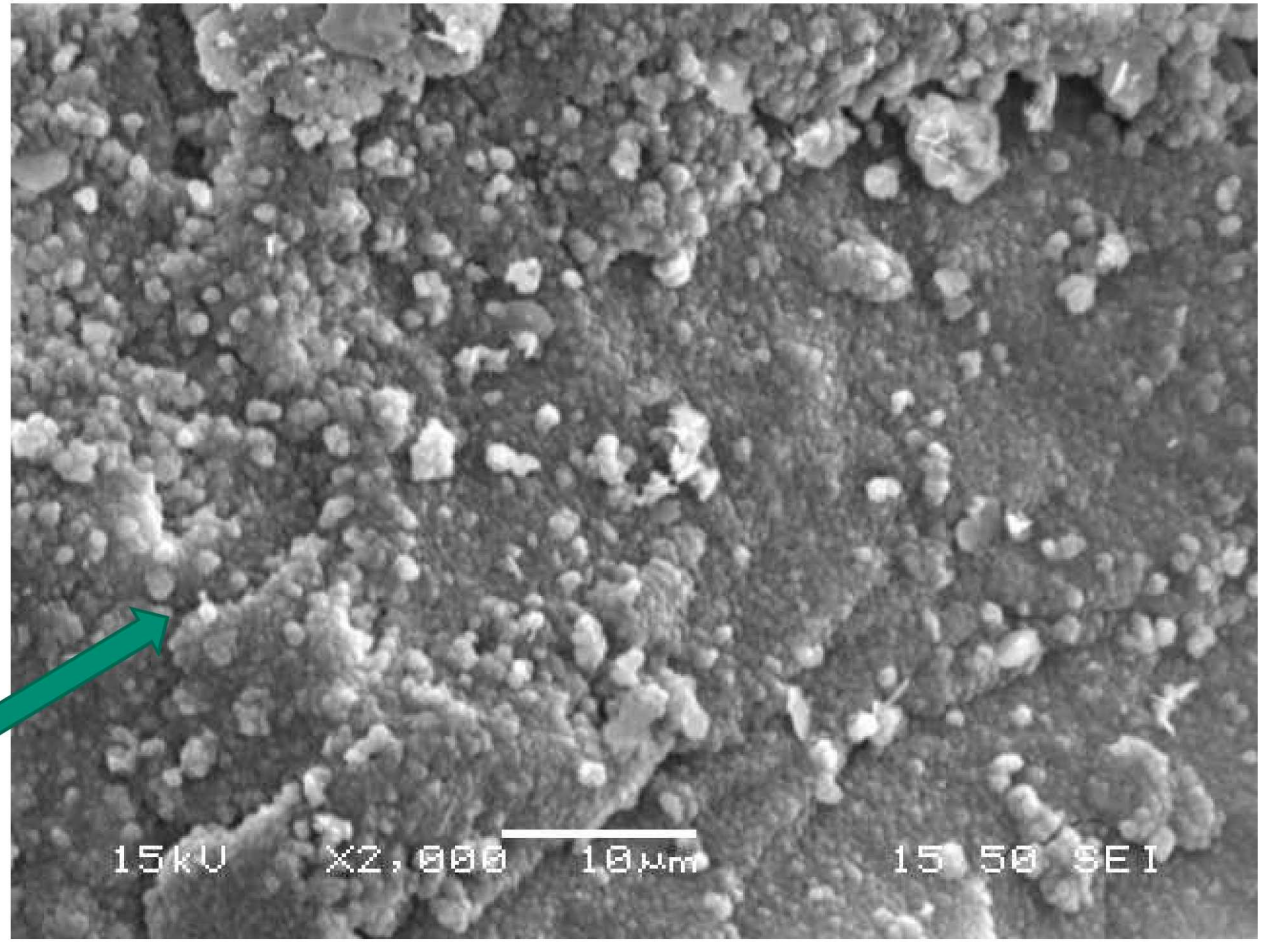




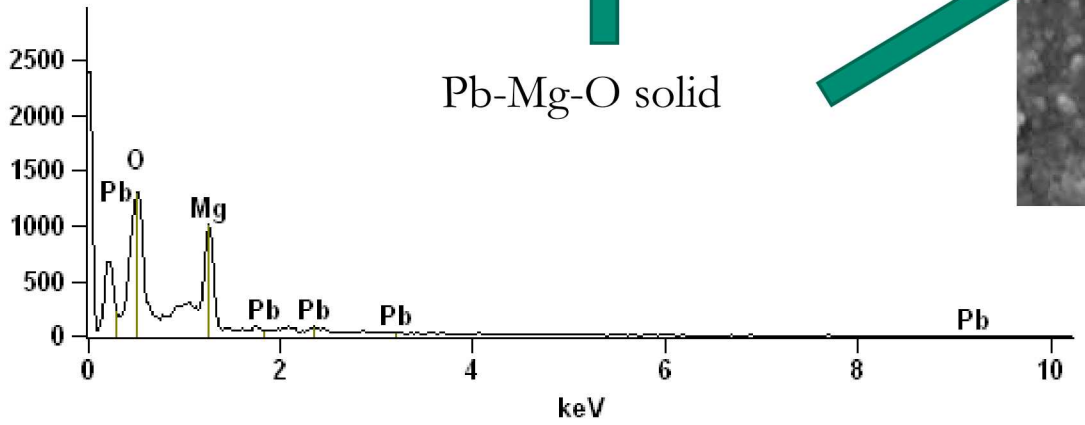


PbO-0.1 Sample,0.08m $MgCl_2$, 0.042m Na_2H_2EDTA

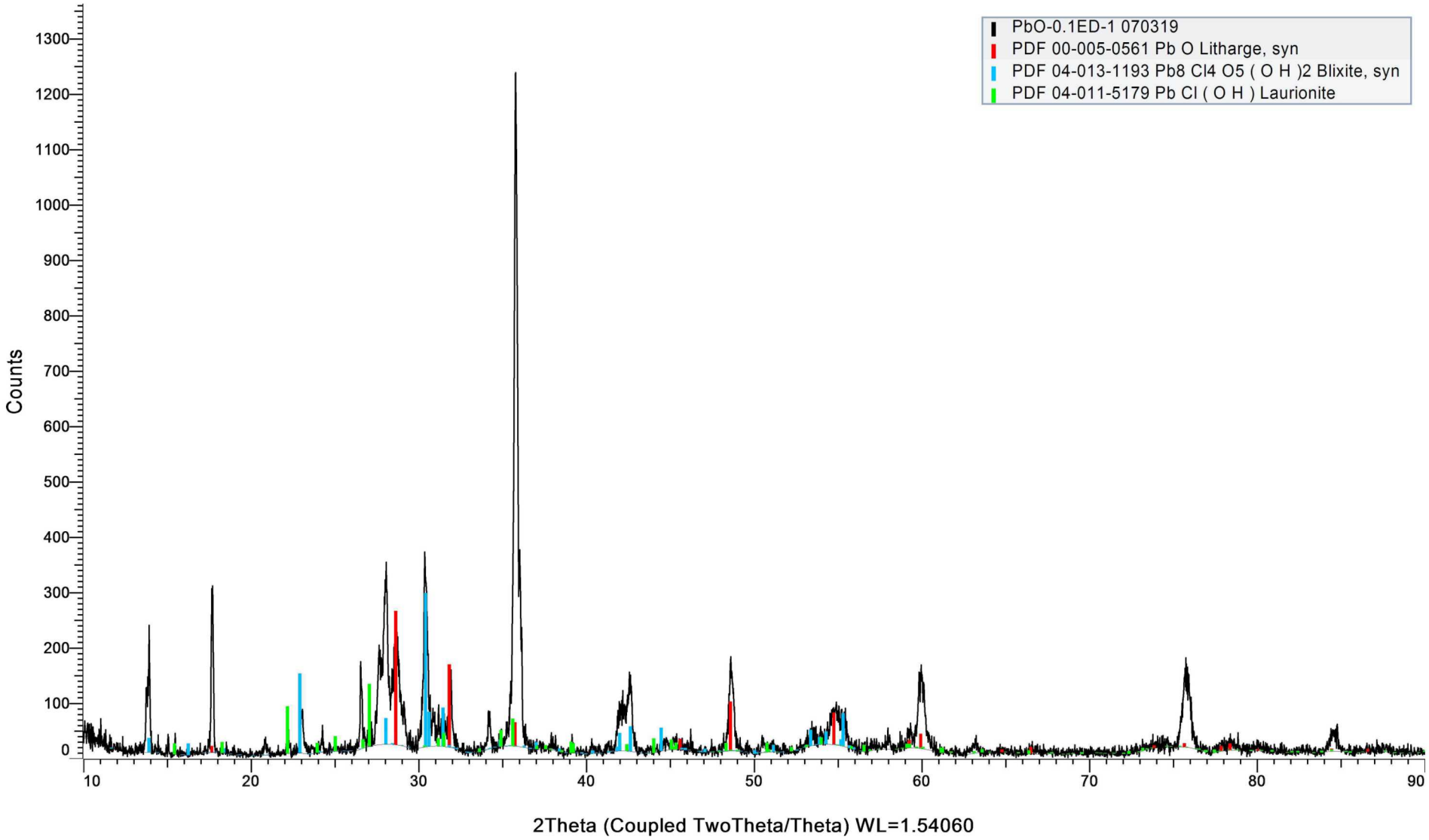




Pb-Mg-O solid



PbO-0.1 Sample,0.08m $MgCl_2$, 0.042m Na_2H_2EDTA

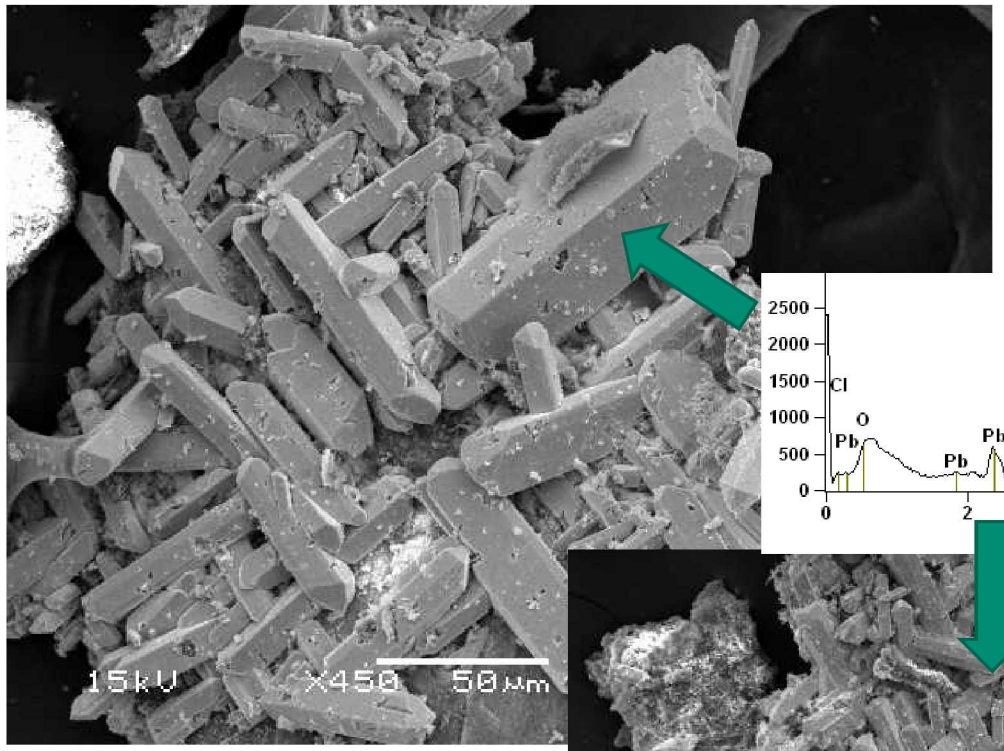


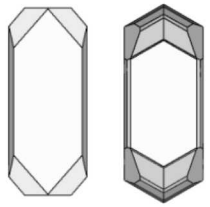
XRD confirms presence of Litharge, Blixite and Laurionite

Pb-Mg-O solid was not identified by XRD. More research is needed and solid characterization is still underway.

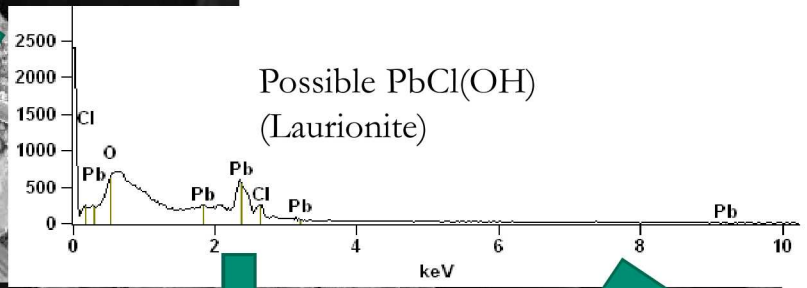
Kirkes, L. 2019

PbO-1.0 Sample,0.8m $MgCl_2$, 0.042m Na_2H_2EDTA

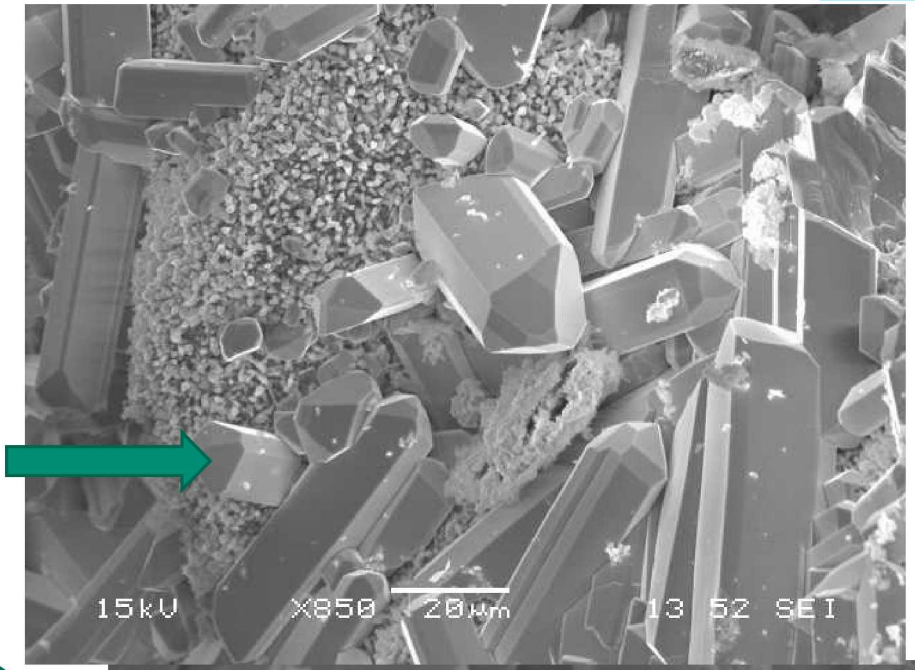


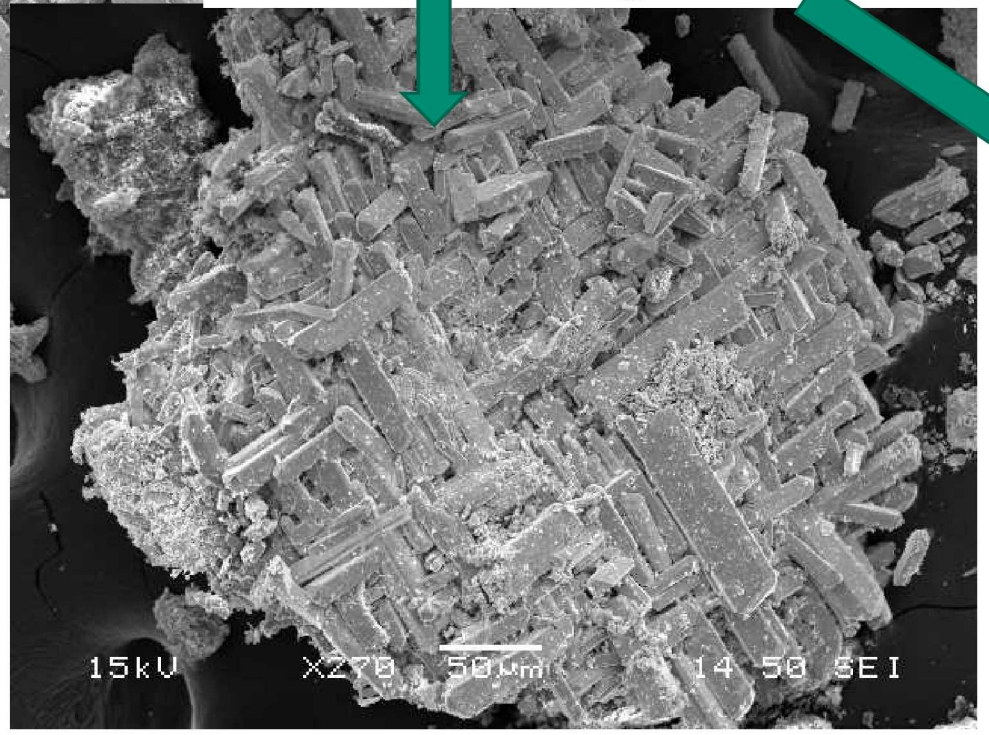


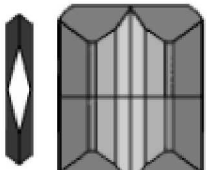
B-axis. Goldschmidt (1918)



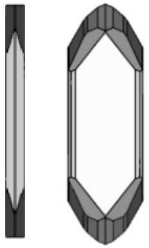
Possible PbCl(OH) (Laurionite)







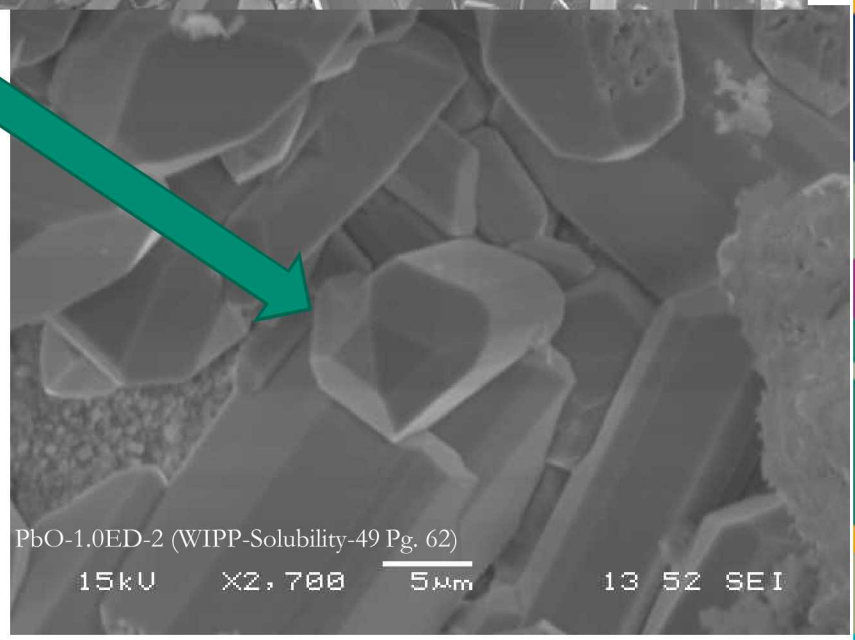
C-axis. Goldschmidt (1918)



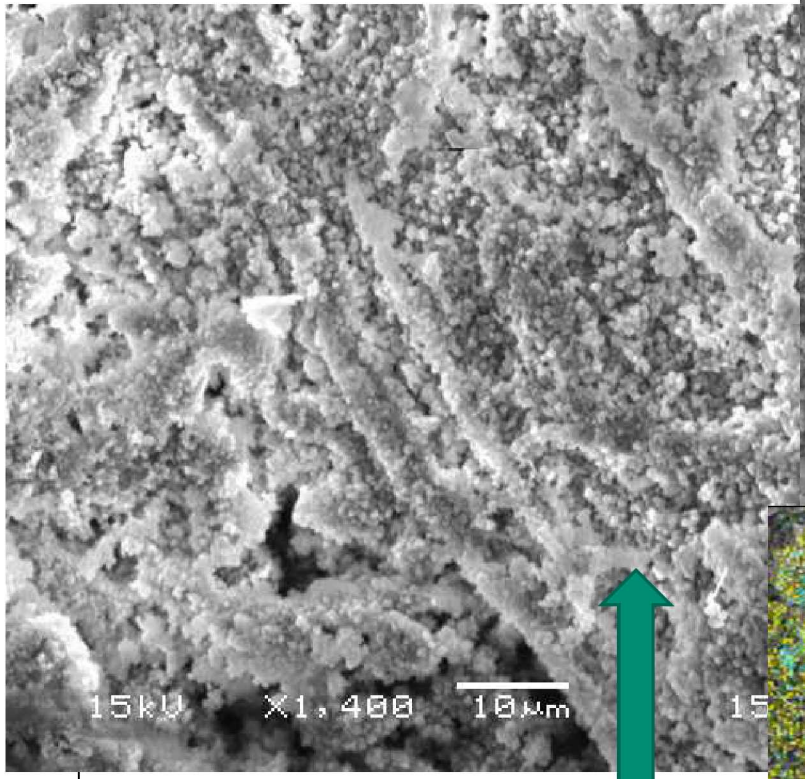
A-axis. Goldschmidt (1918)

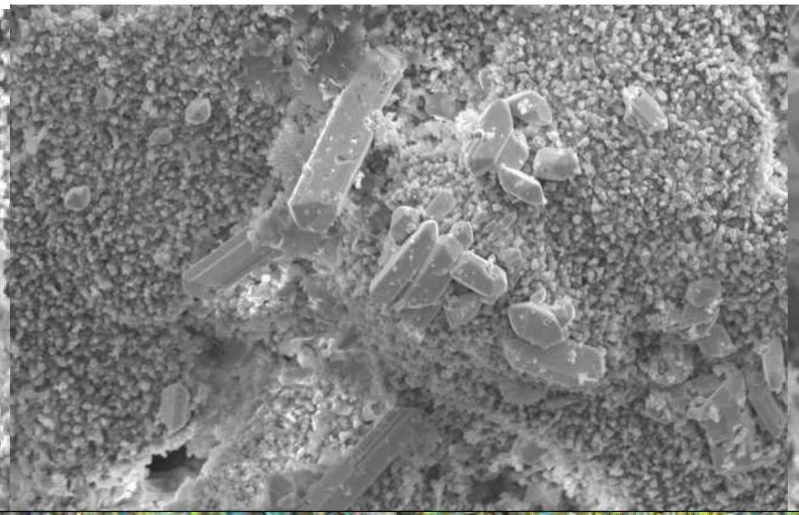
Orthorhombic crystal habit, Dipyramidal, thick to thin tabular.

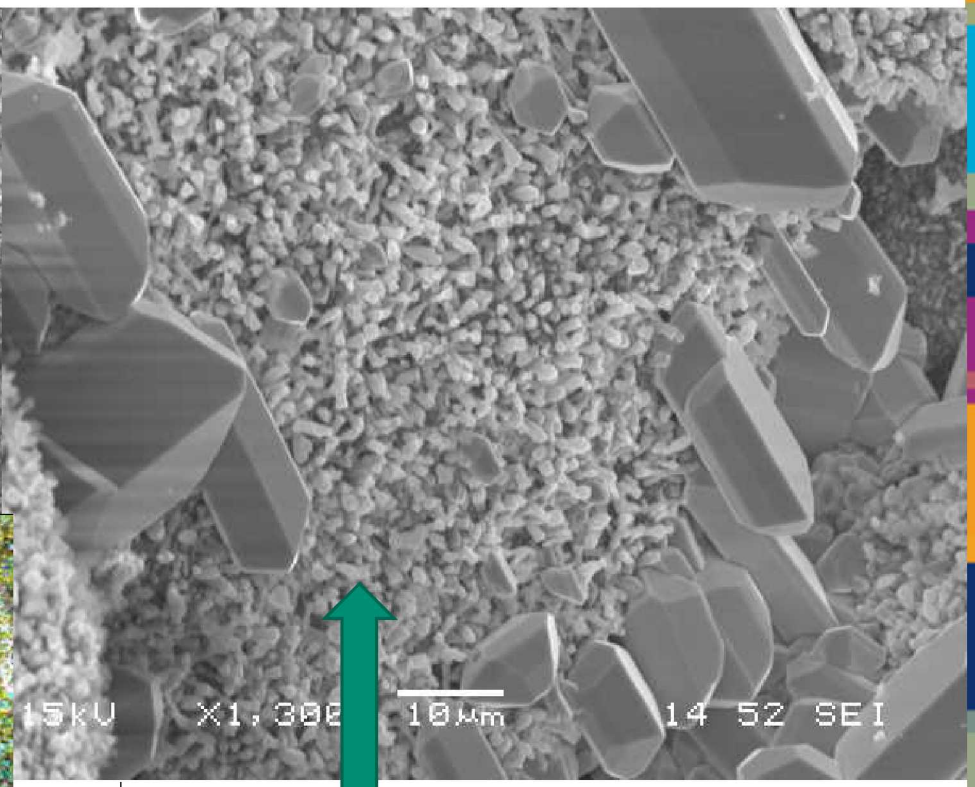
https://www.mindat.org/min-2343.html

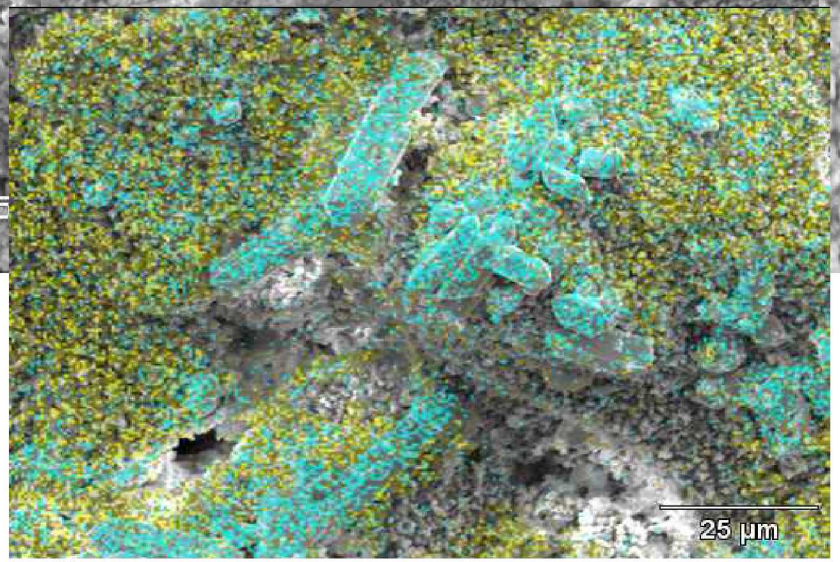


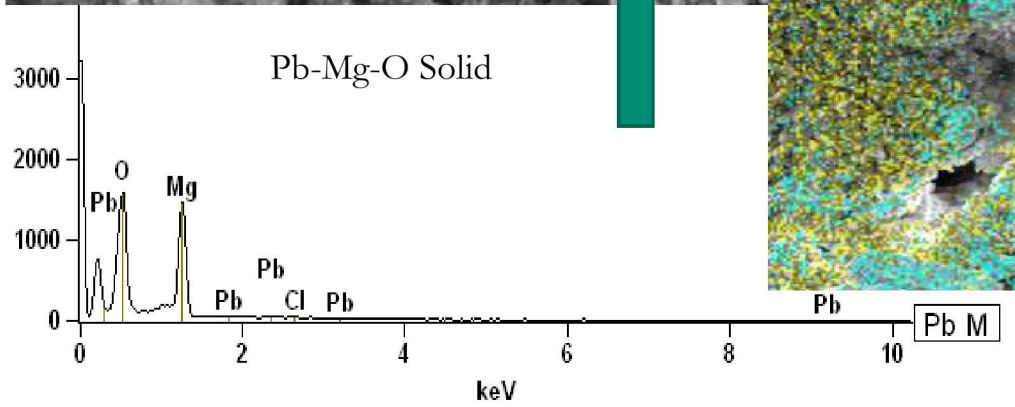
PbO-1.0 Sample,0.8m $MgCl_2$, 0.042m Na_2H_2EDTA

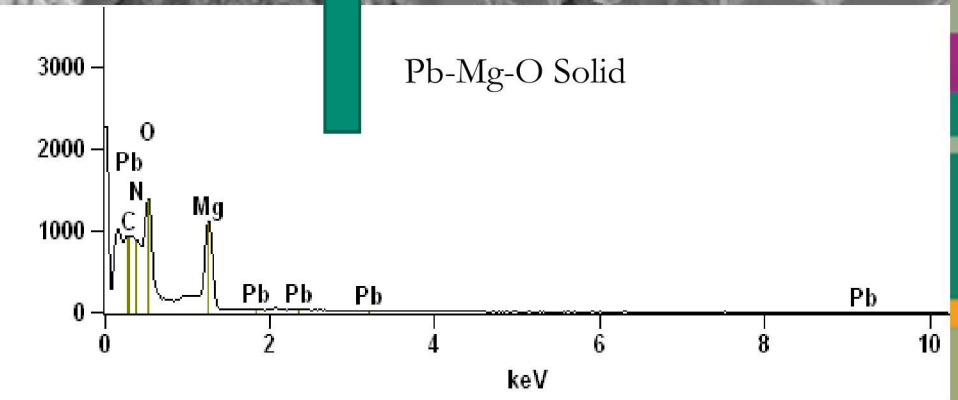




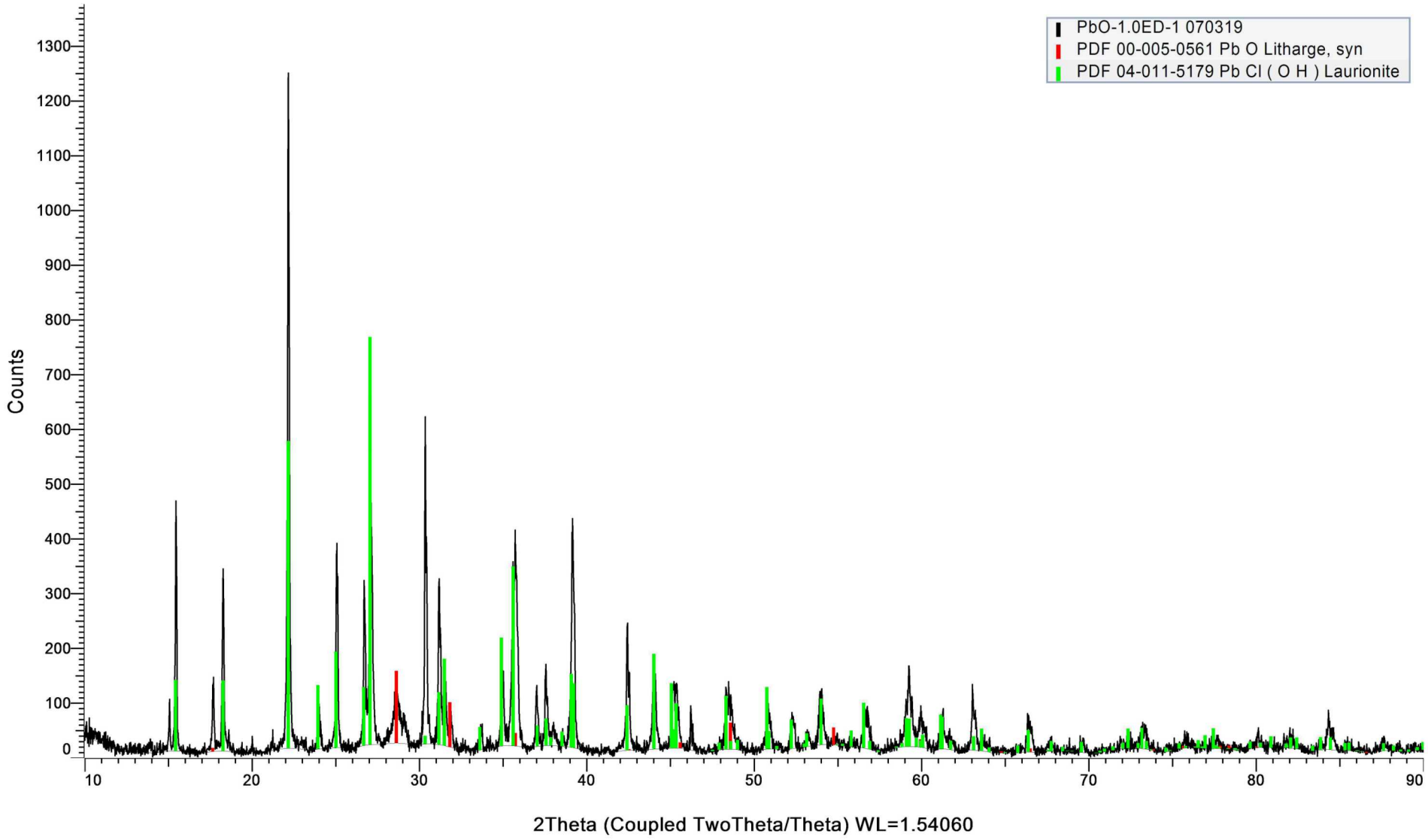








PbO-1.0 Sample,0.8m $MgCl_2$, 0.042m Na_2H_2EDTA

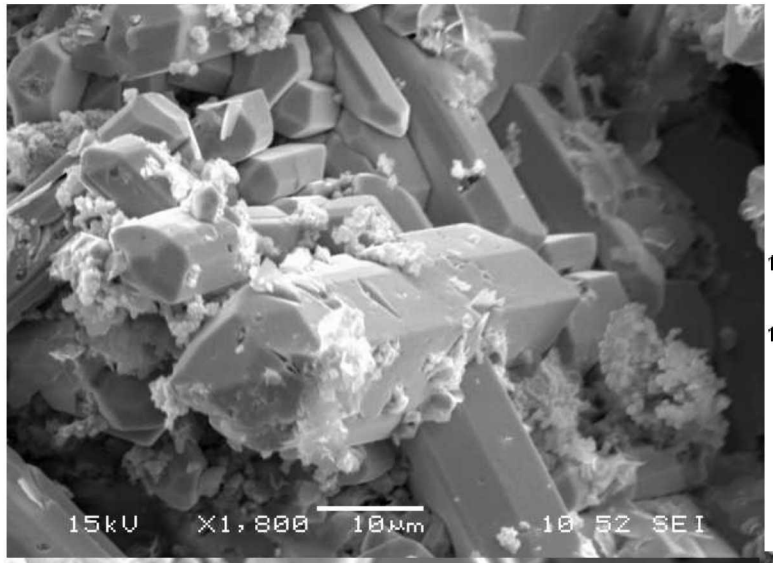


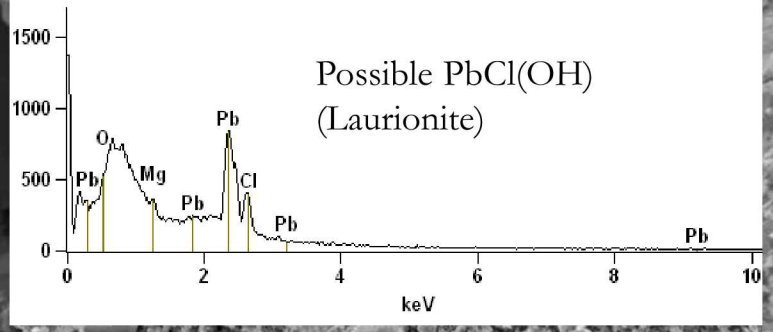
Litharge and Laurionite were identified in XRD analysis, however Litharge was not seen in crystalline form in SEM/EDS analysis

Pb-Mg-O solid was not identified by XRD. More research is needed and solid characterization is still underway.

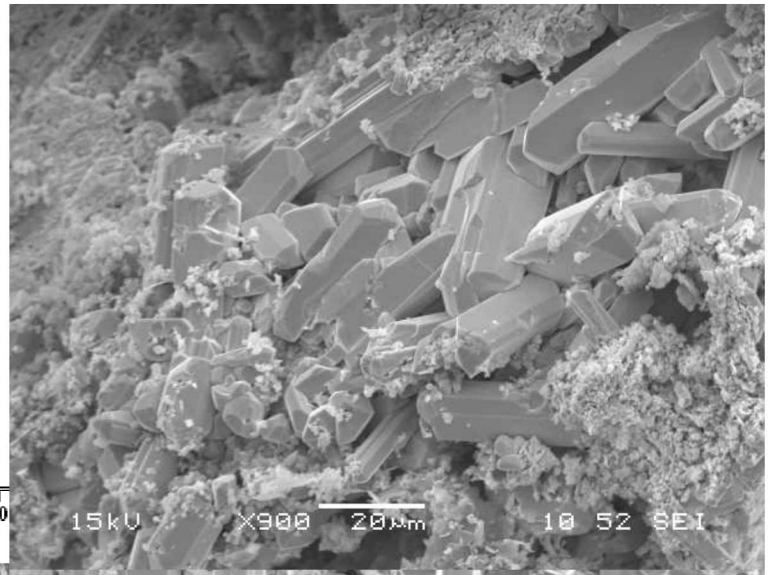
Kirkes, L. 2019

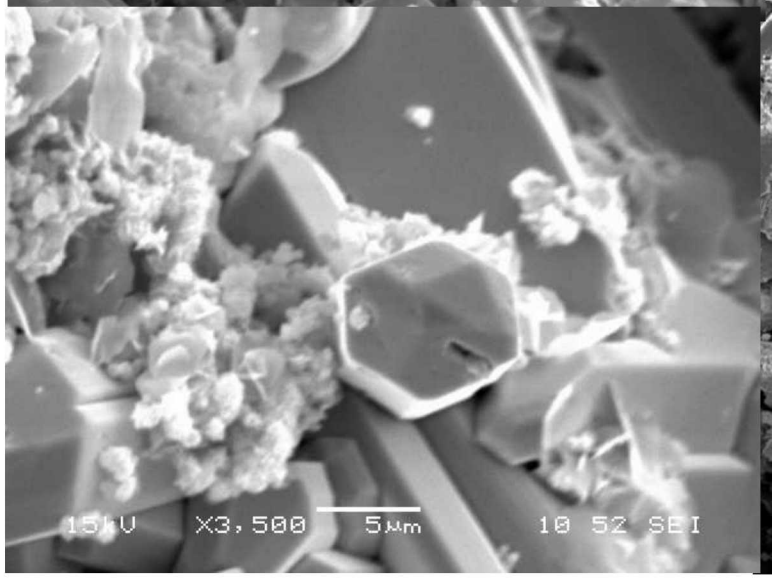
PbO-1.5 Sample, 1.2m $MgCl_2$, 0.042m Na_2H_2EDTA

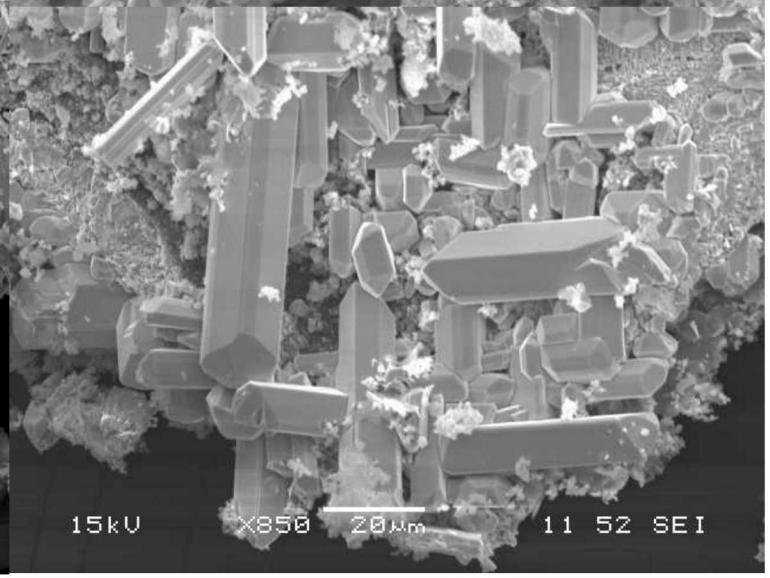




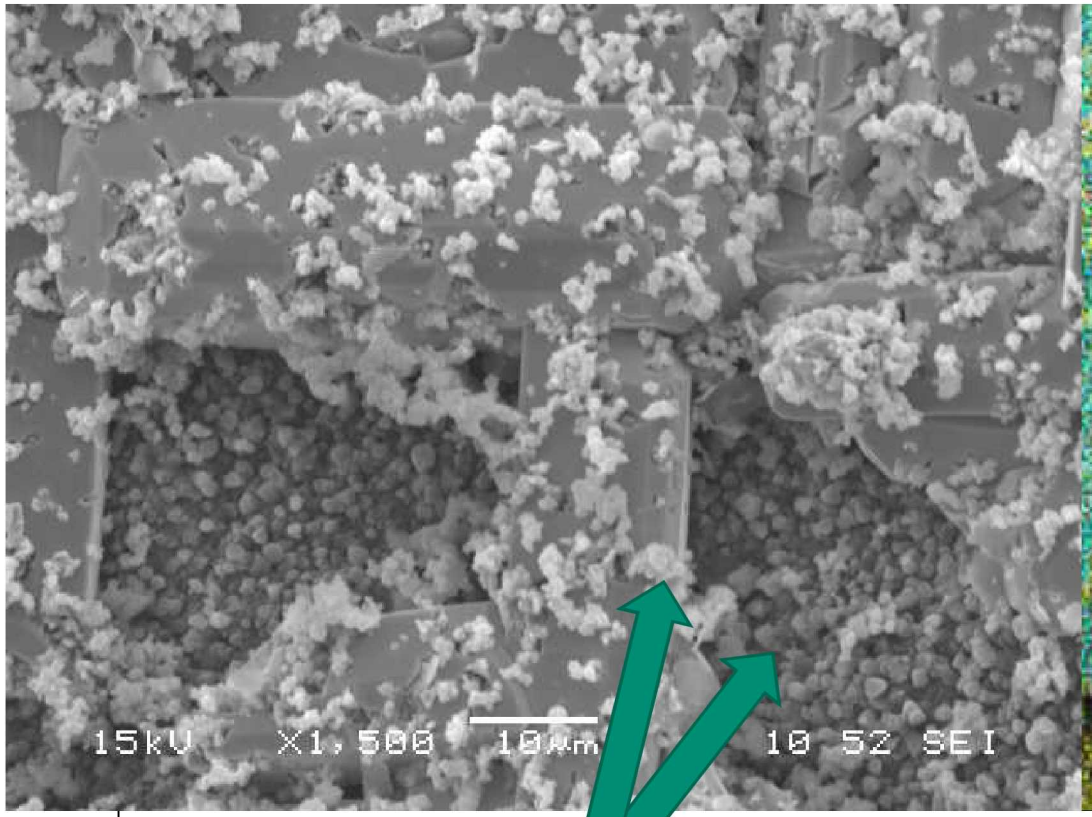
Possible PbCl(OH)
(Laurionite)

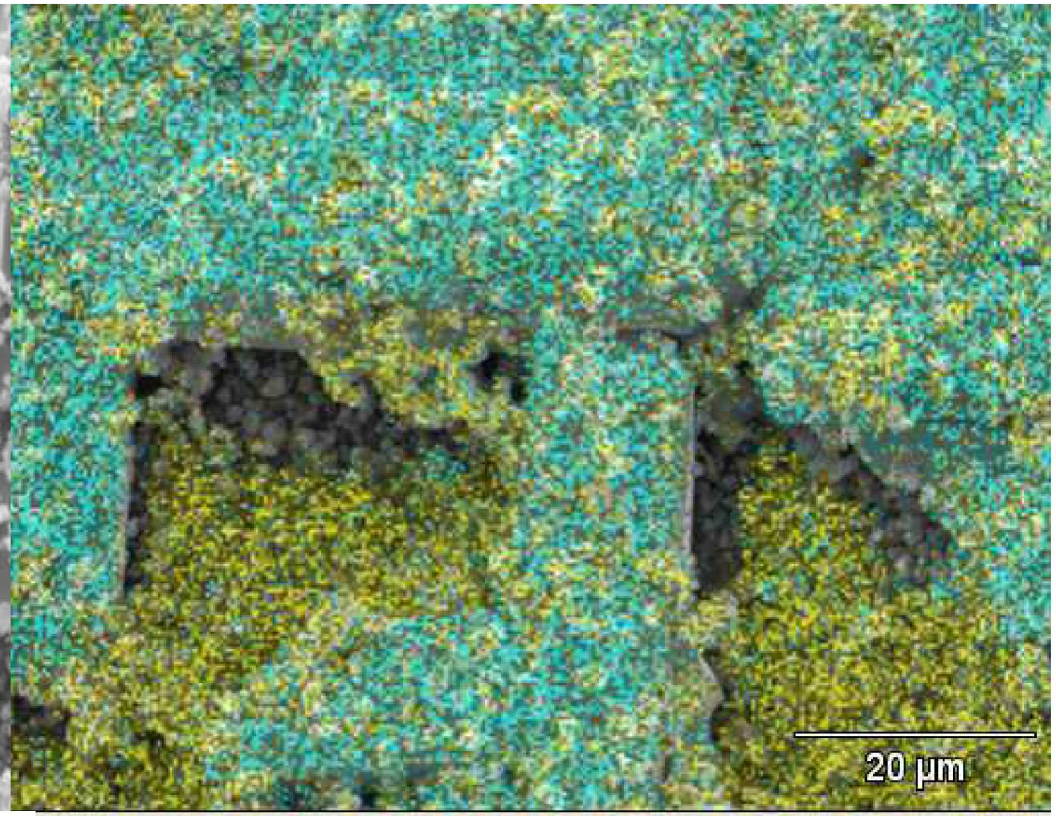




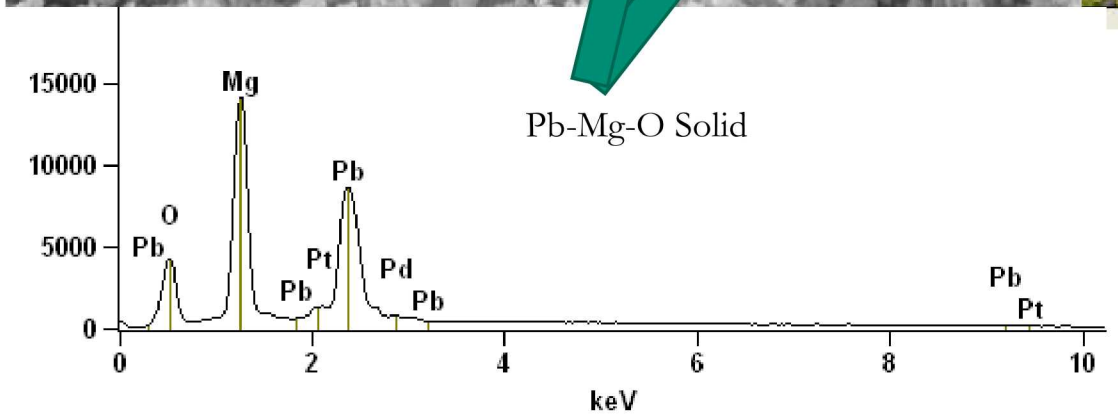


PbO-1.5 Sample, 1.2m $MgCl_2$, 0.042m Na_2H_2EDTA

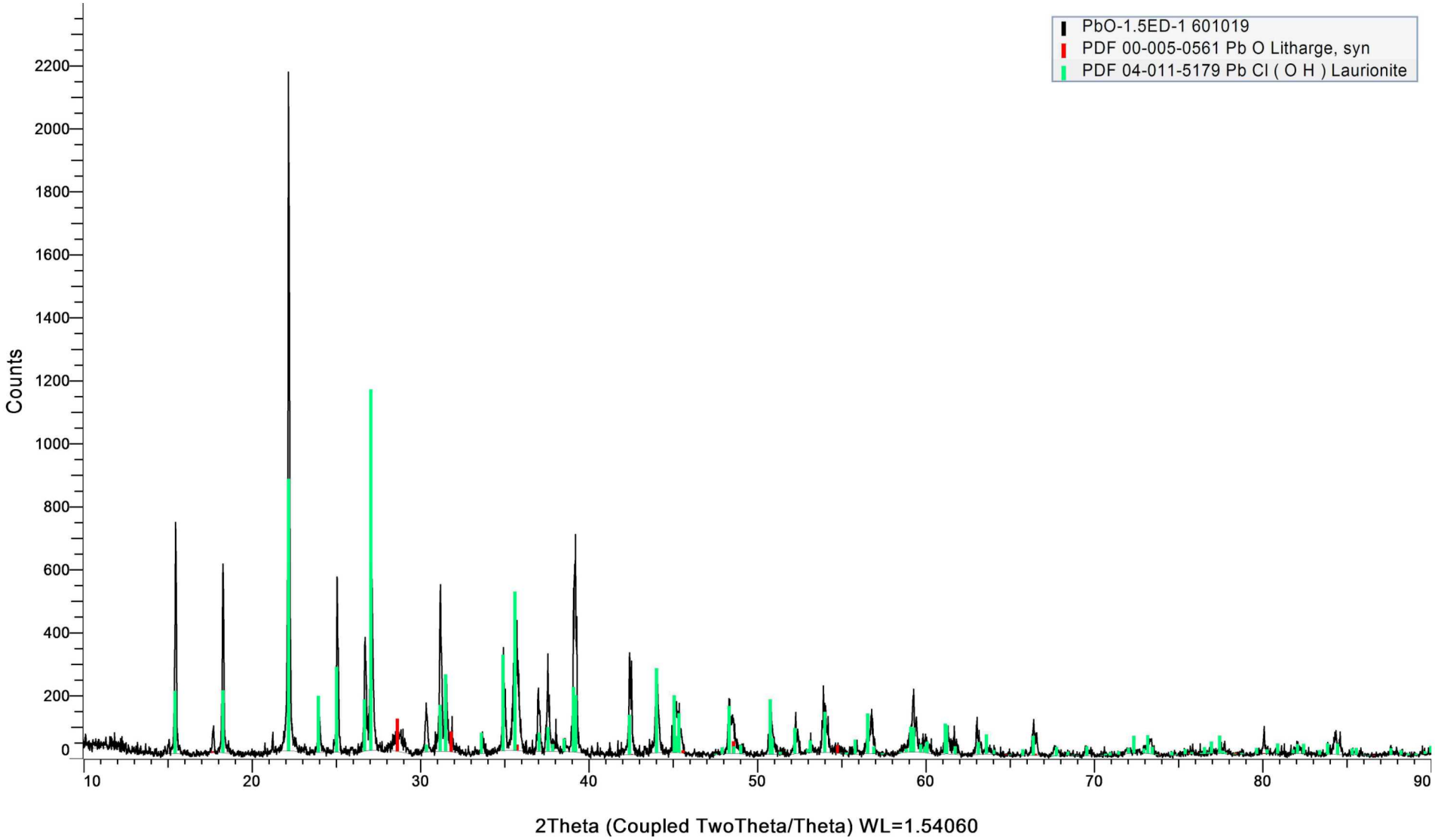




Pb-Mg-O Solid



PbO-1.5 Sample, 1.2m $MgCl_2$, 0.042m Na_2H_2EDTA

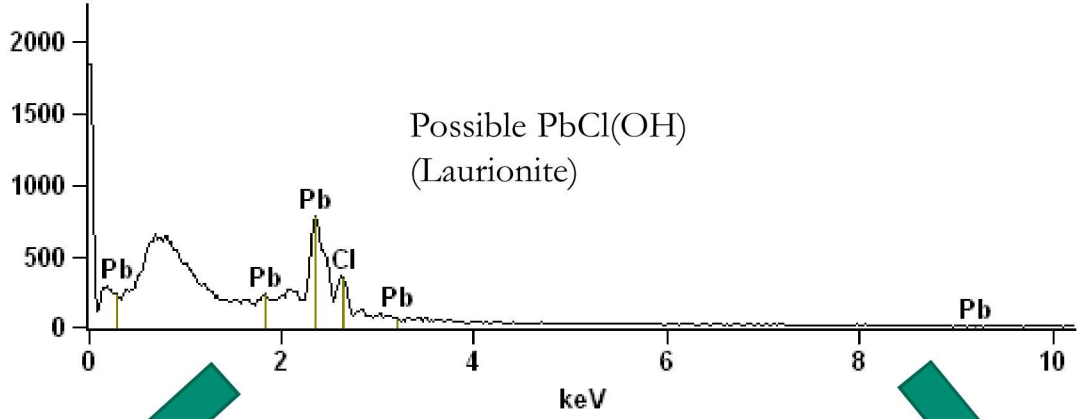


Litharge and Laurionite were identified in XRD analysis, however Litharge was not seen in crystalline form in SEM/EDS analysis

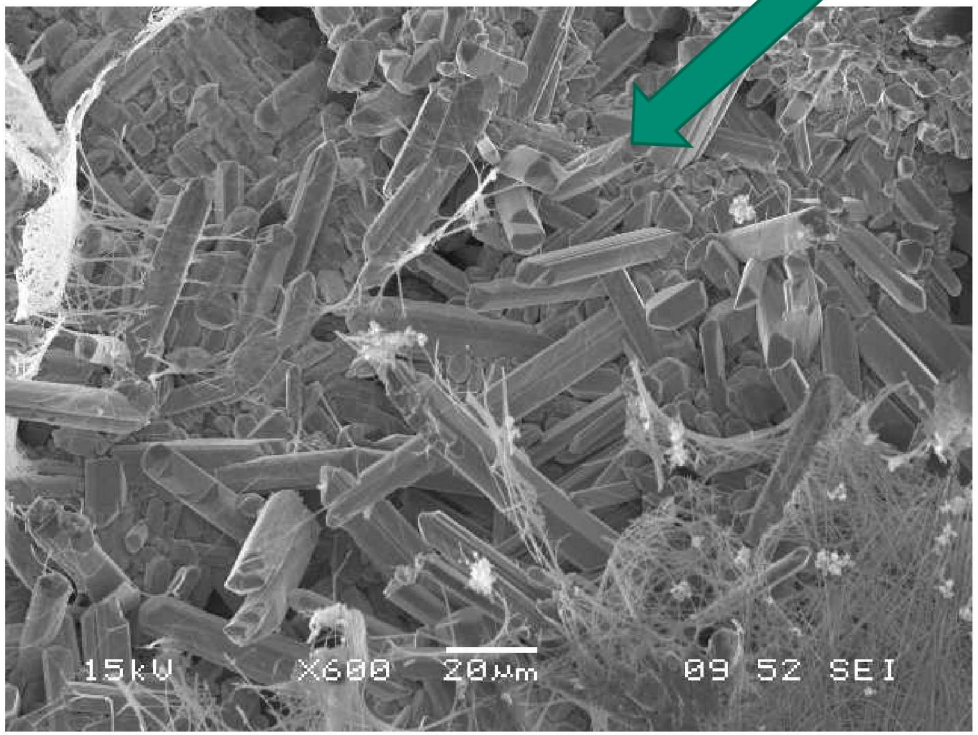
Pb-Mg-O solid was not identified by XRD. More research is needed and solid characterization is still underway.

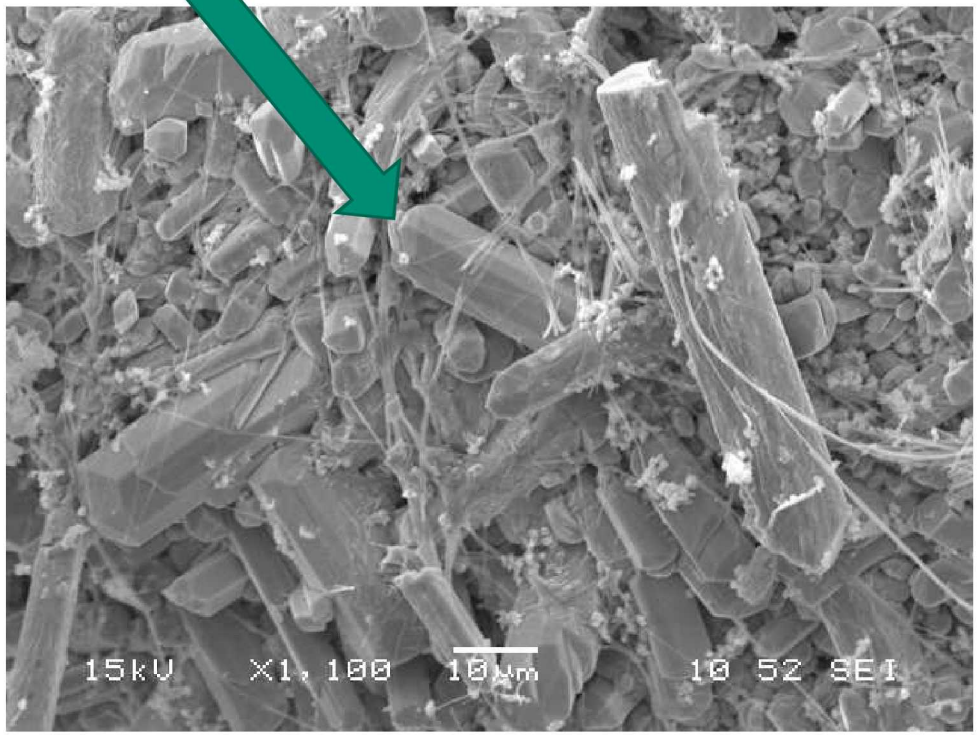
Kirkes, L. 2019

PbO-2.0 Sample, 1.6m $MgCl_2$, 0.042m Na_2H_2EDTA

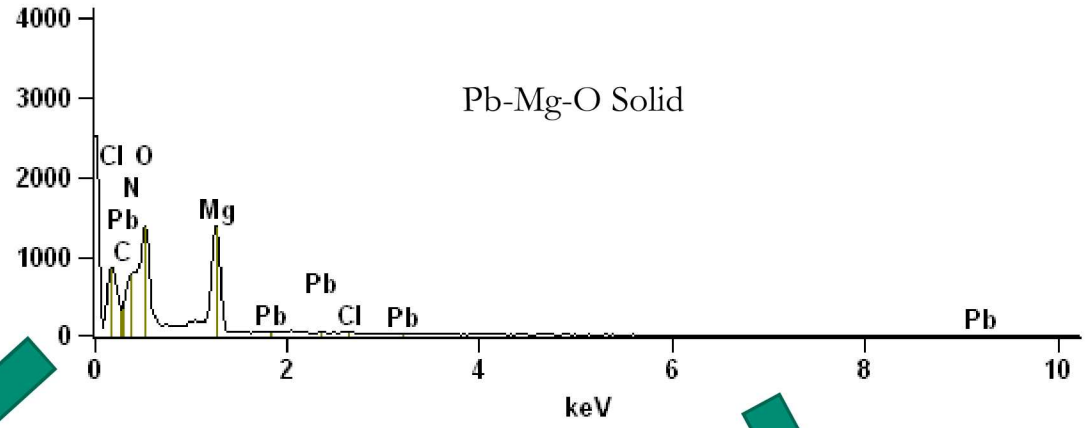


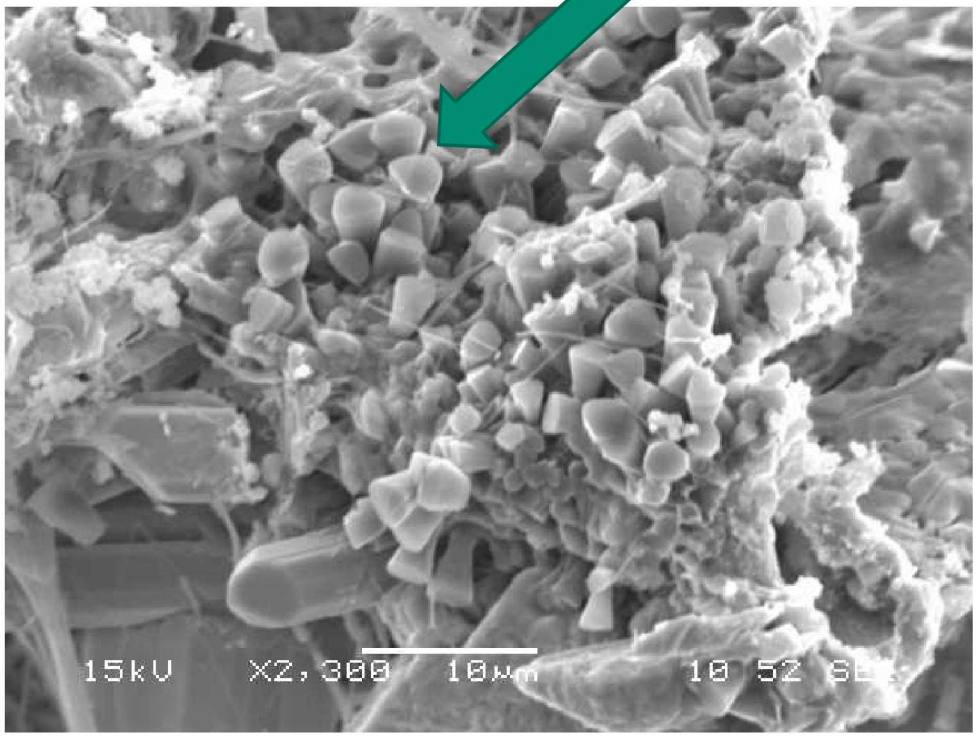
Possible PbCl(OH)
(Laurionite)

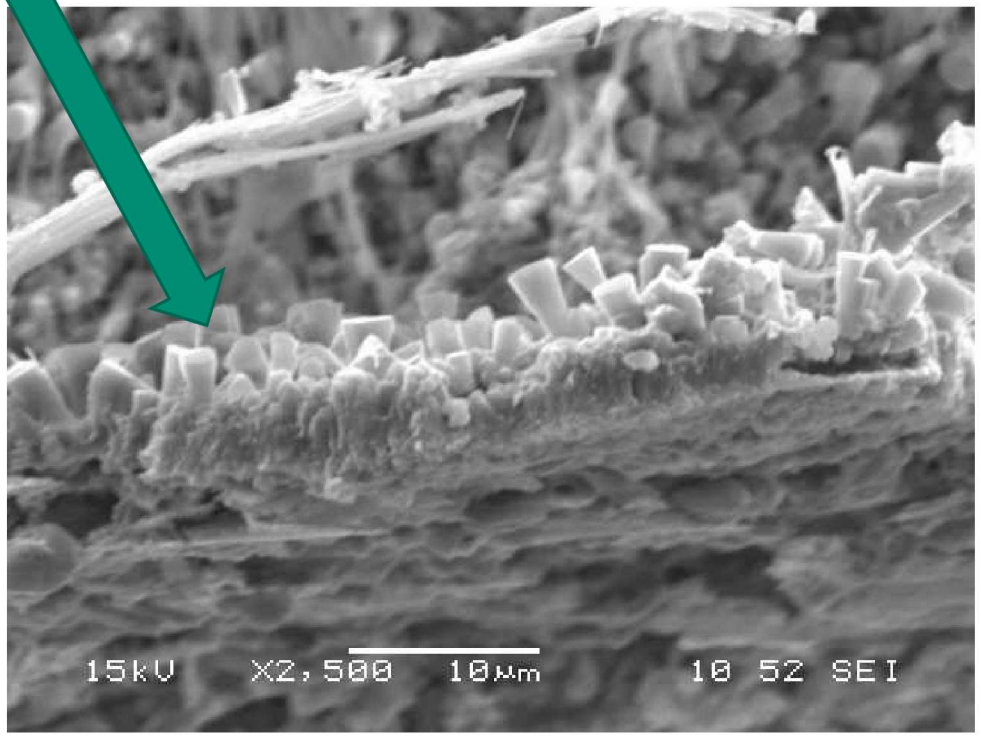




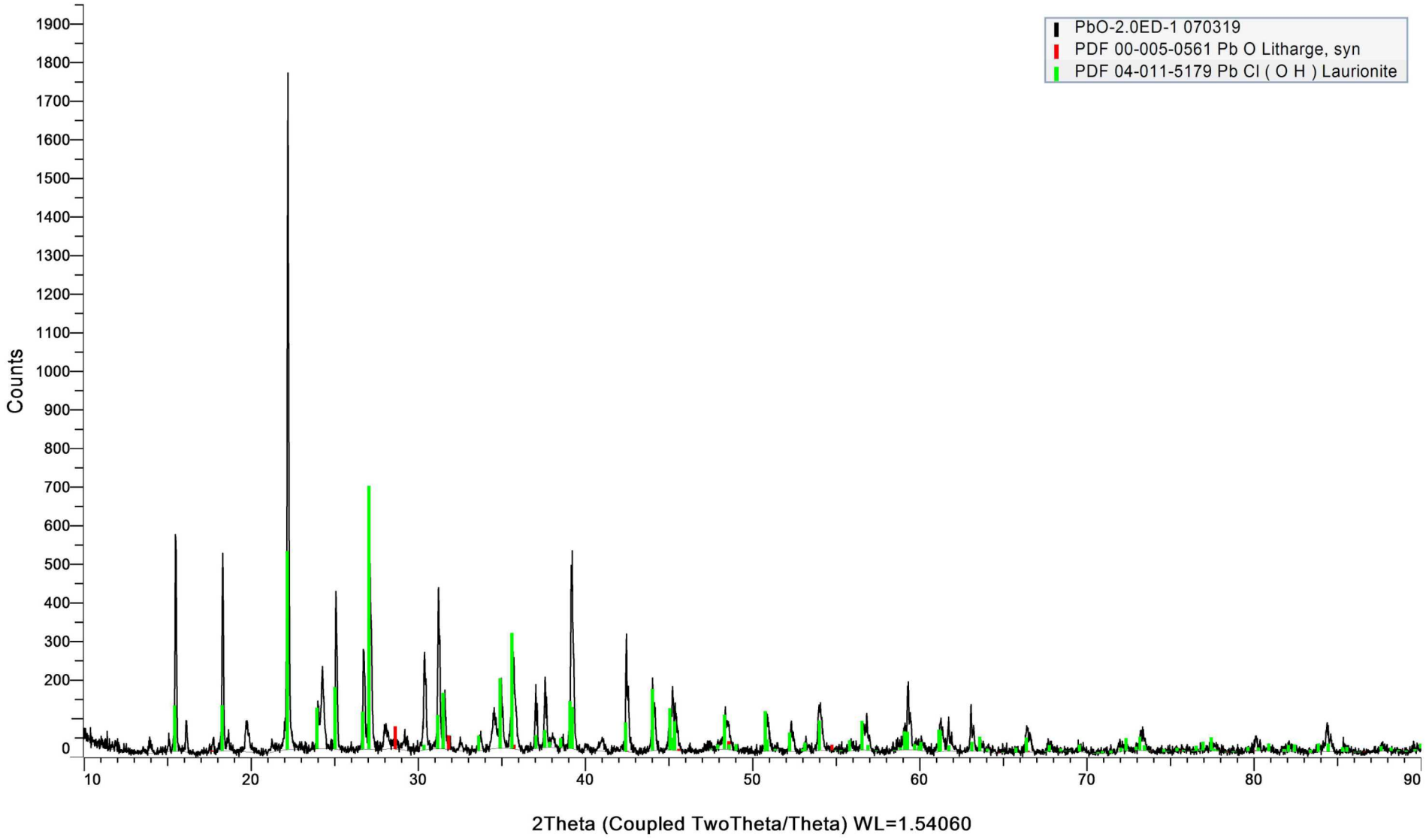
PbO-2.0 Sample, 1.6m $MgCl_2$, 0.042m Na_2H_2EDTA







PbO-2.0 Sample, 1.6m $MgCl_2$, 0.042m Na_2H_2EDTA



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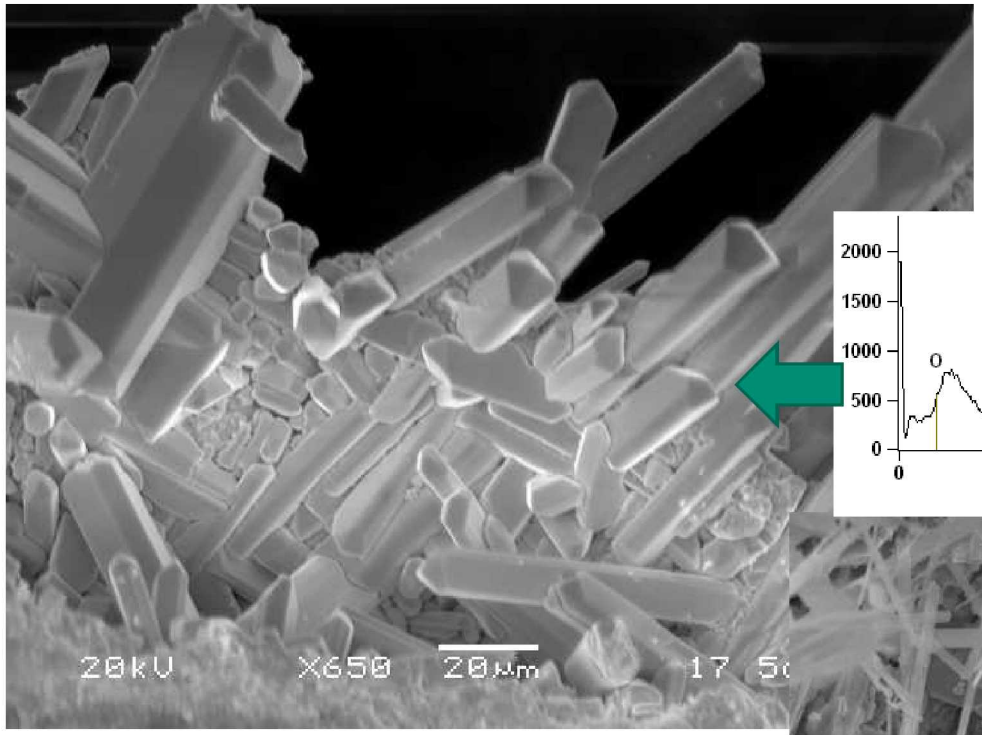
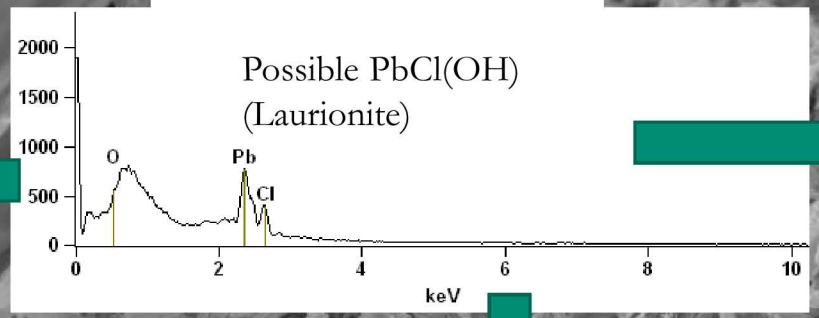
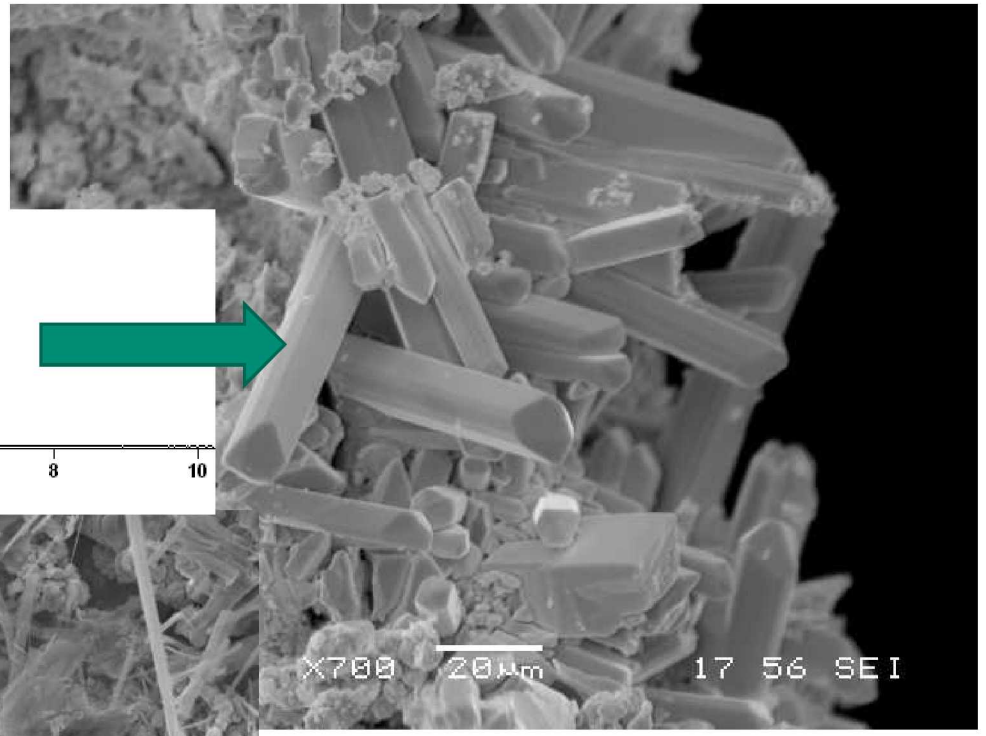
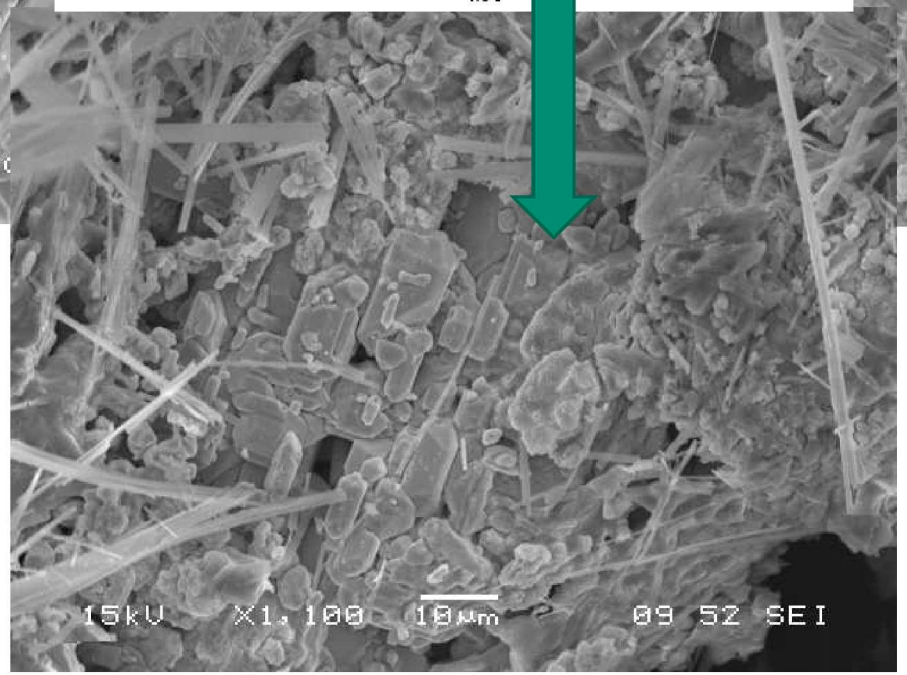
PbO-2.5 Sample,2.0 m $MgCl_2$, 0.042m Na_2H_2EDTA

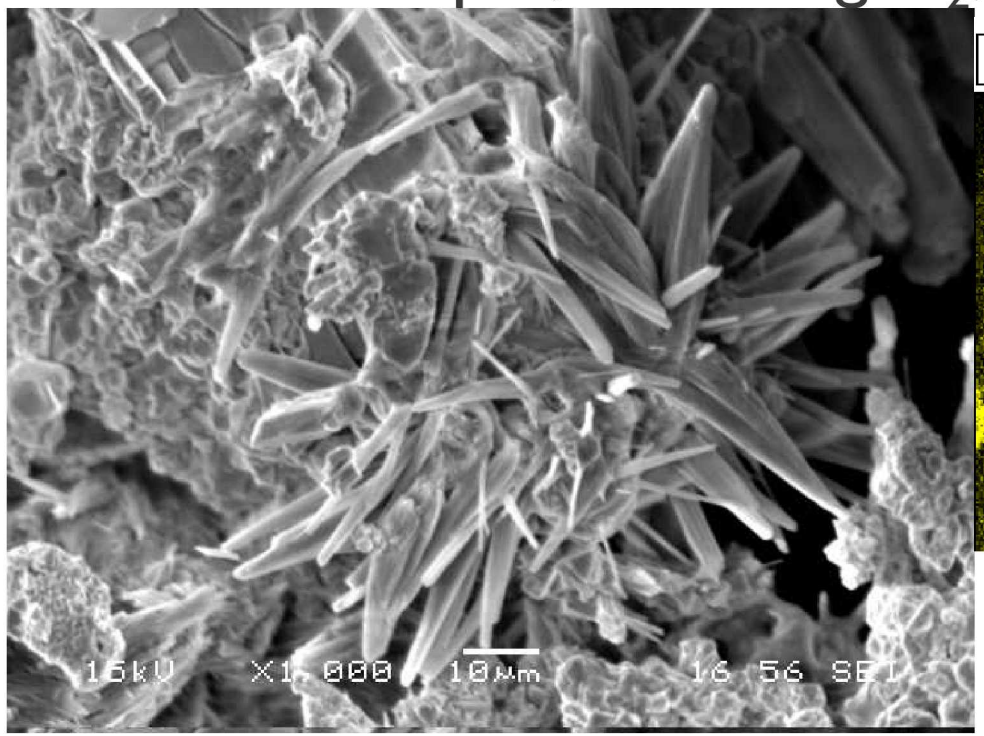


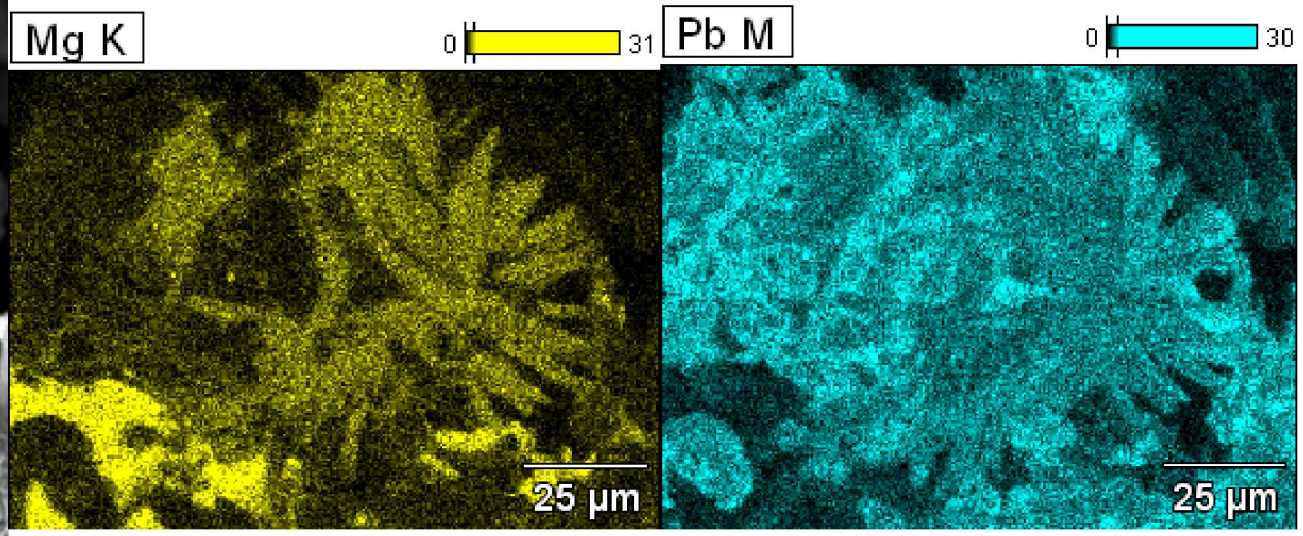


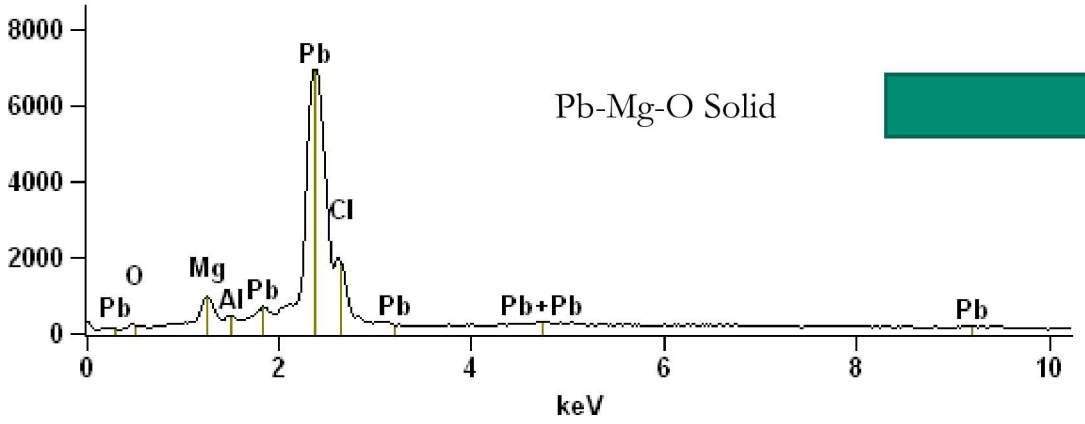




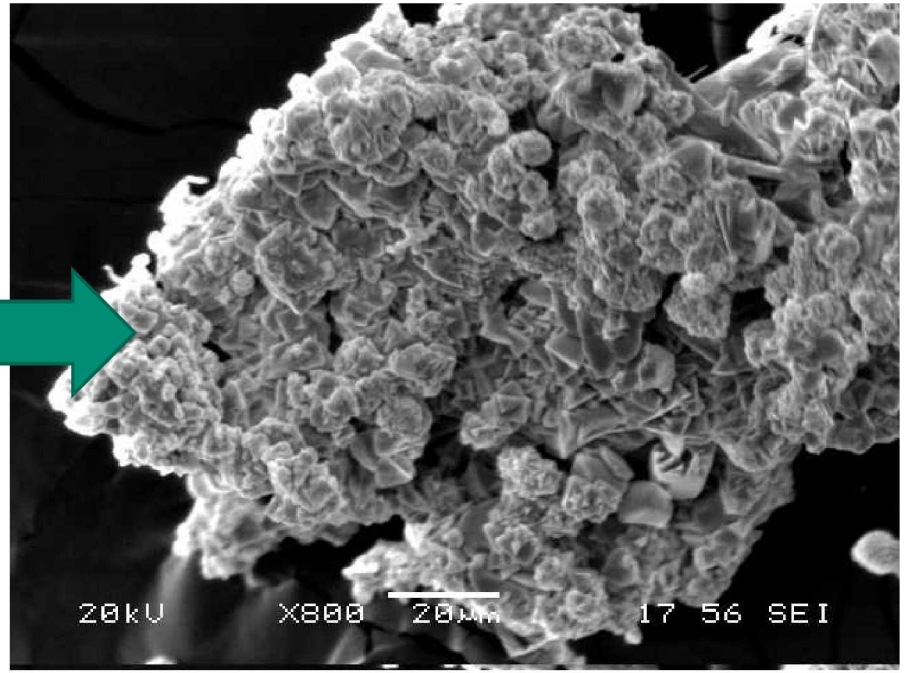
PbO-2.5 Sample,2.0 m $MgCl_2$, 0.042m Na_2H_2EDTA



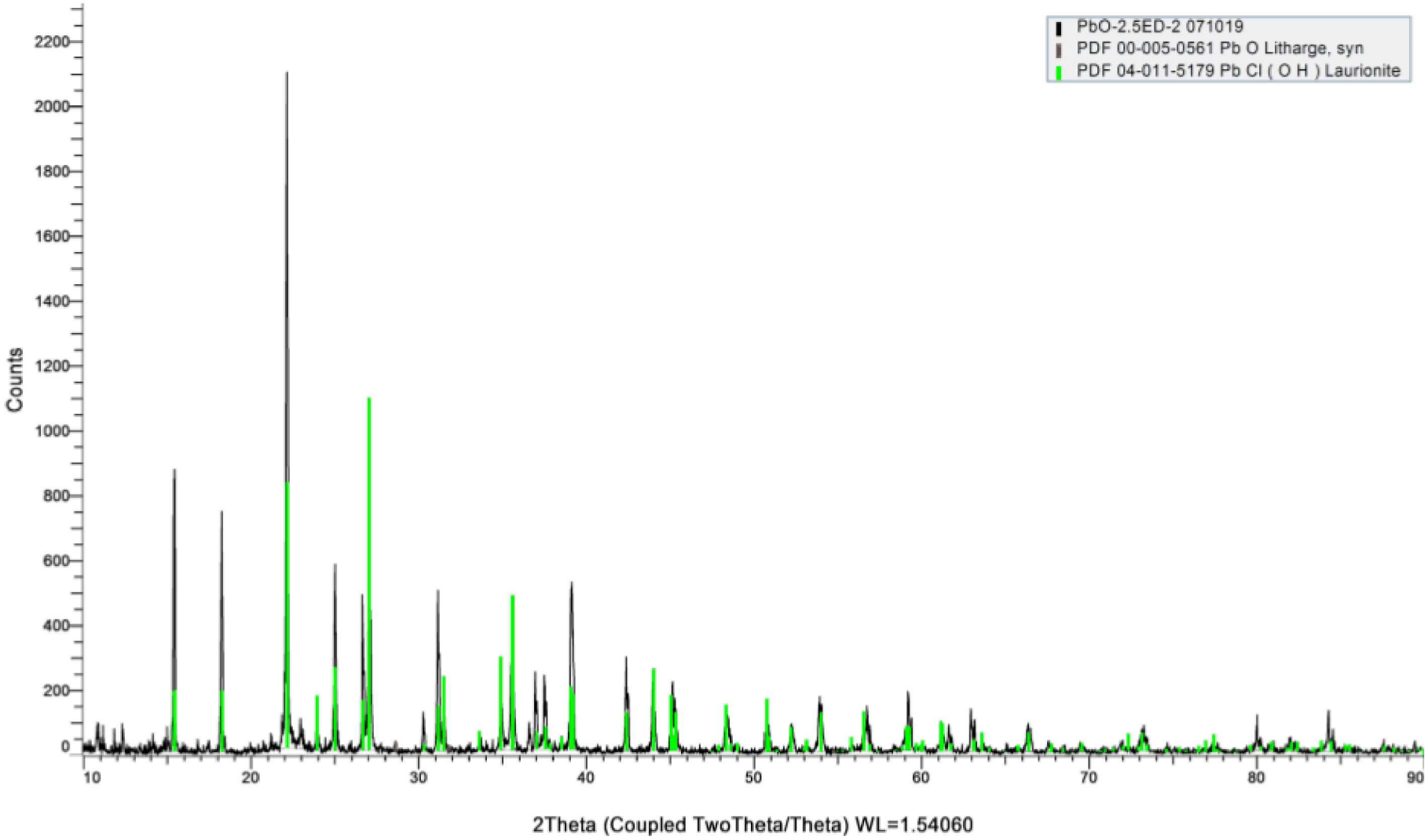




Pb-Mg-O Solid



PbO-2.5 Sample,2.0 m $MgCl_2$, 0.042m Na_2H_2EDTA



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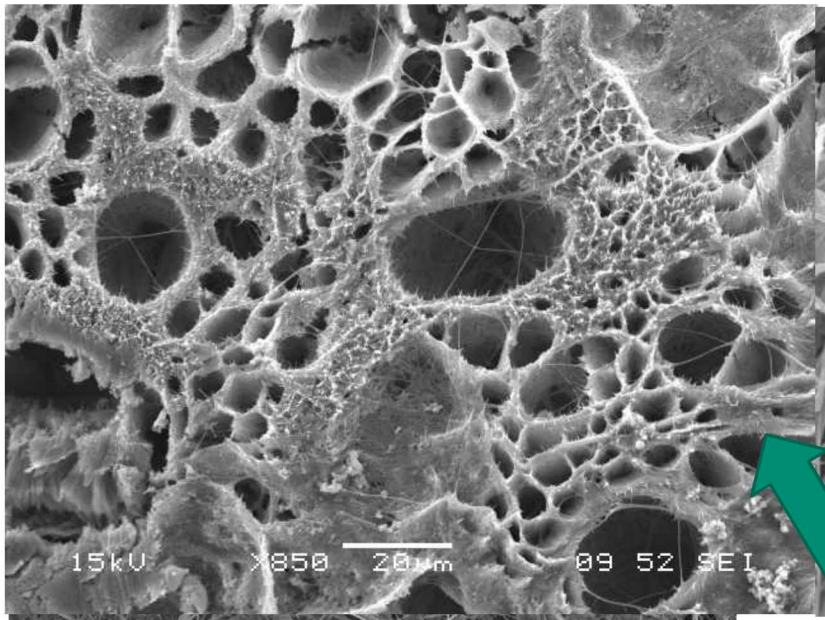
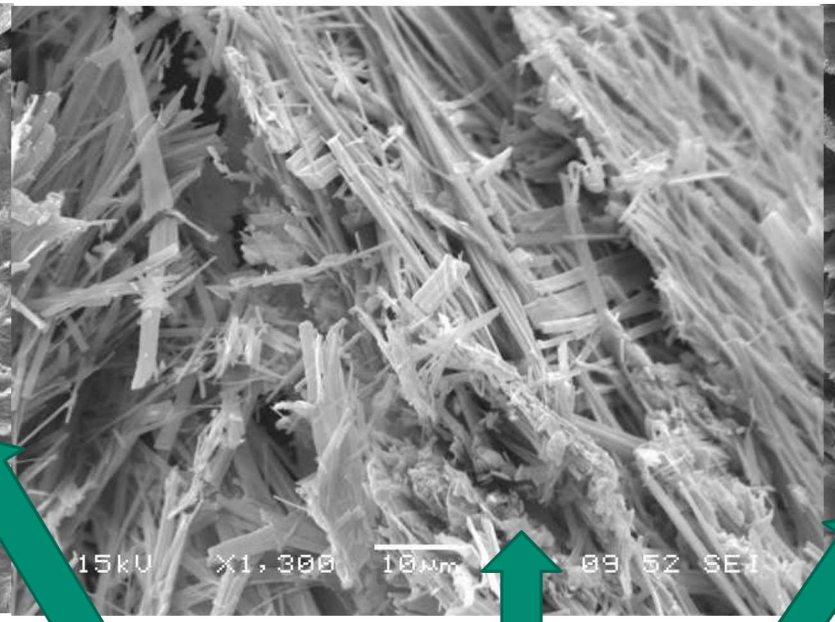
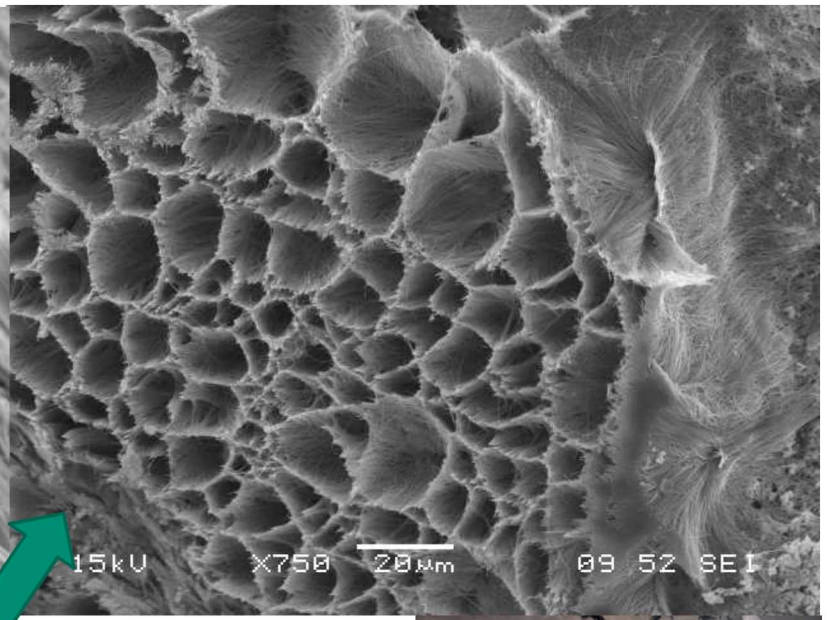
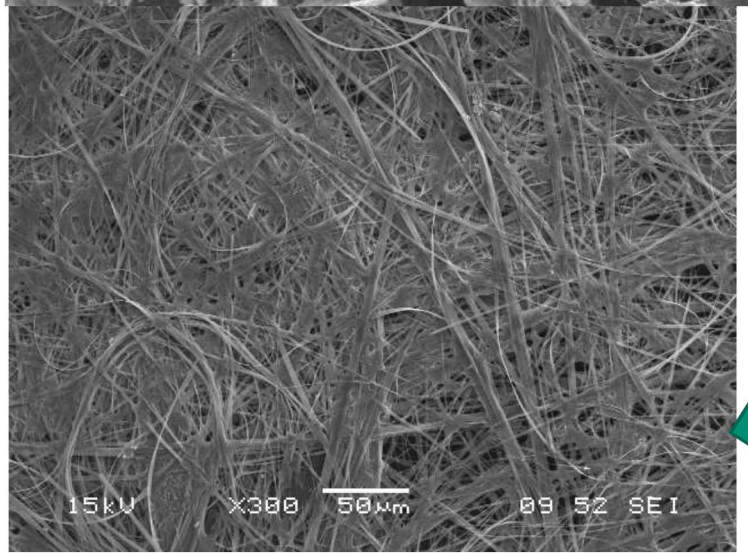
PbO-2.0 & 2.5 Sample 1.6 to 2 m $MgCl_2$

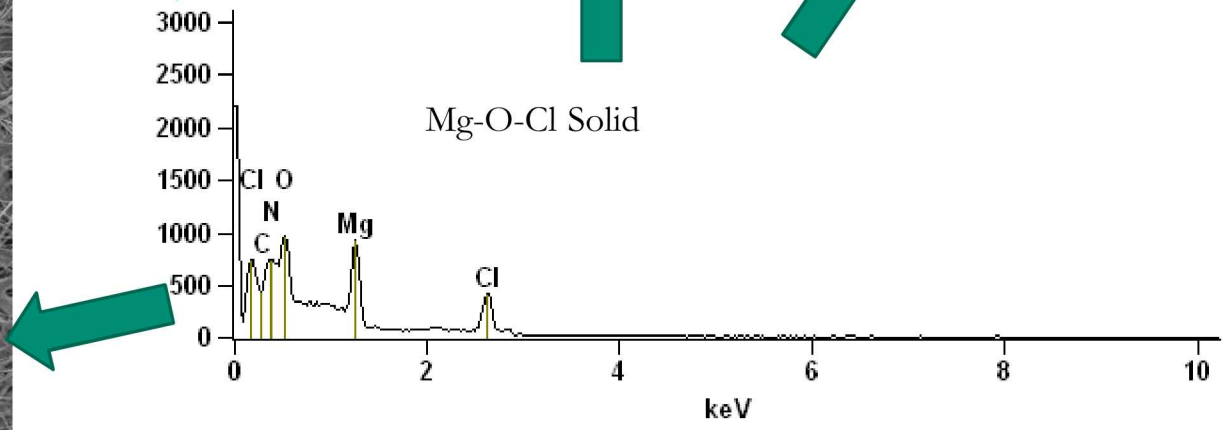
Samples PbO-2.0 and 2.5 had a SUSPENDED solid in the solution. (Magnesium Oxychloride, phase 3?)

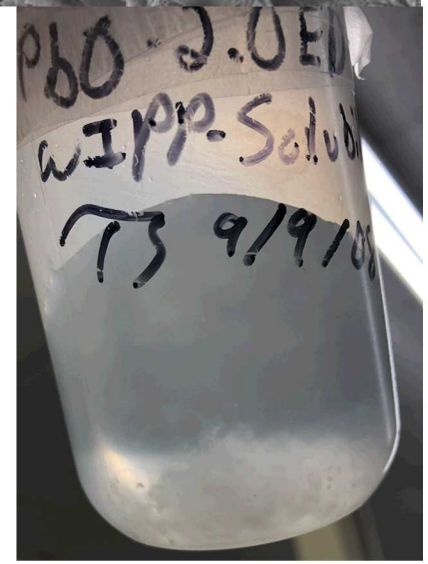






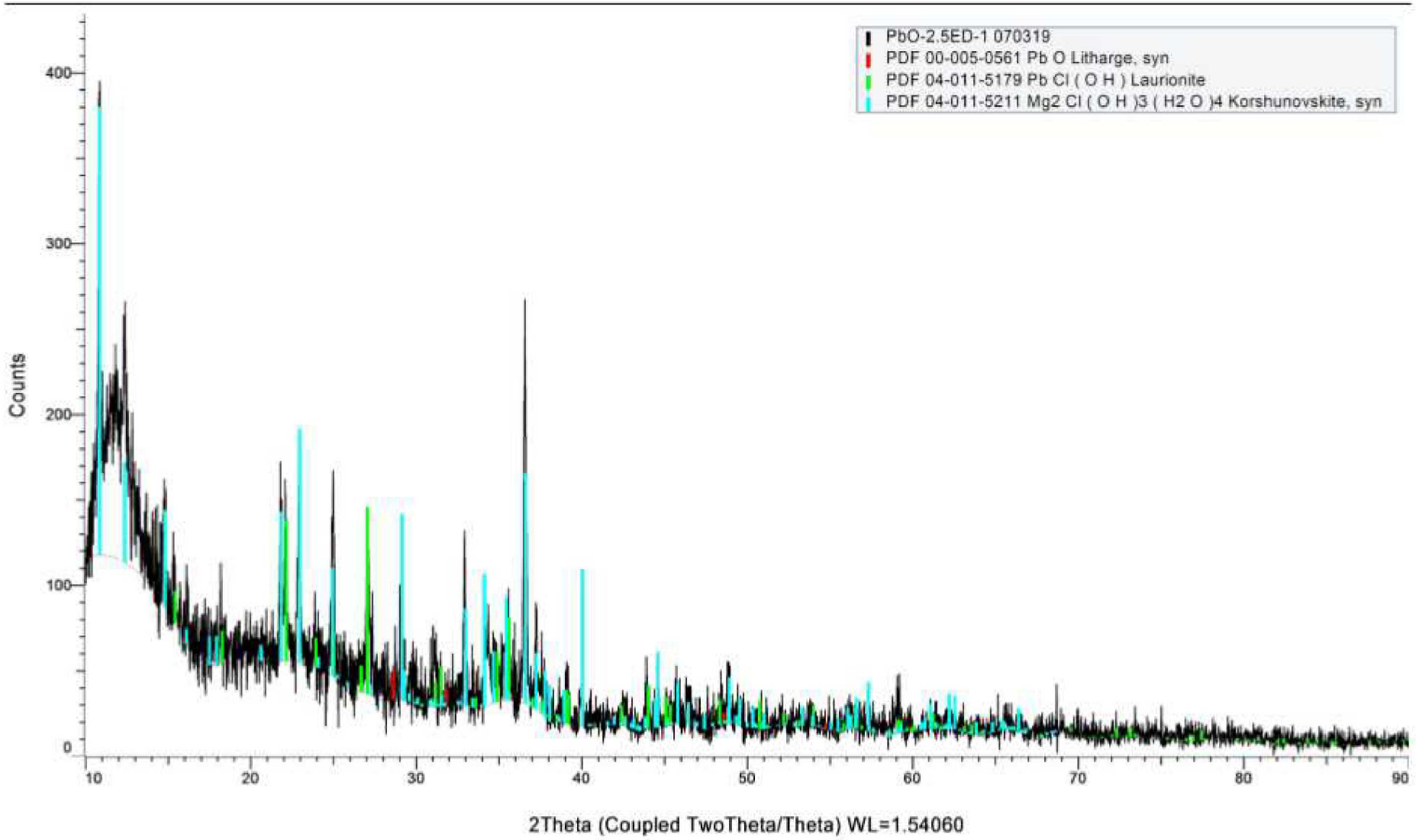




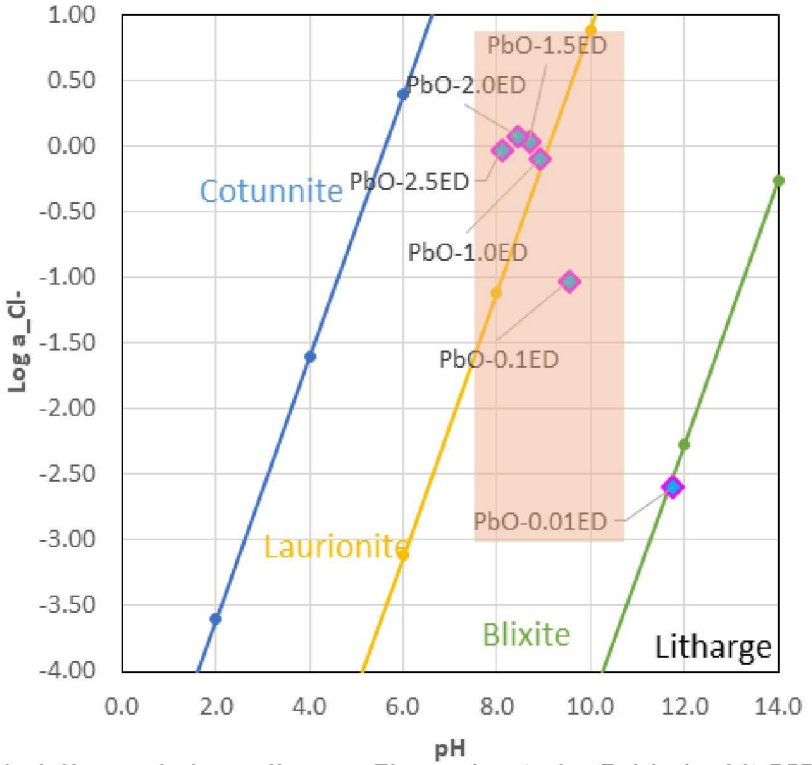


PbO-2.0 & 2.5 Sample 1.6 to 2 m $MgCl_2$

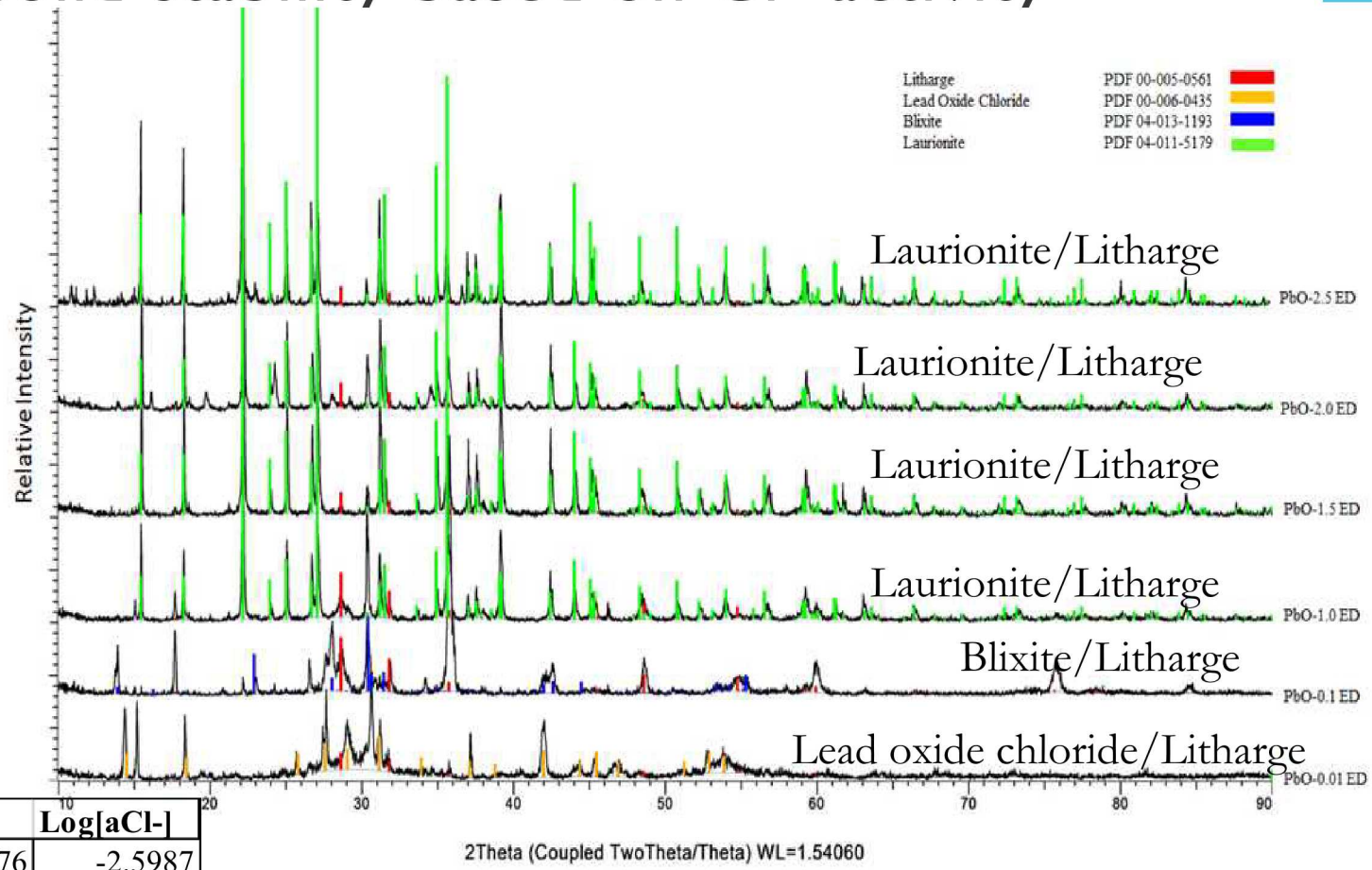
XRD of SUSPENDED solid in the solution identified as Korshunovskite. (Magnesium OxyChloride, Phase3)



Stability diagram of Lead solid stability based on Cl- activity



Modeling and phase diagram Zhang, L. et al., Goldschmidt 2020



Set-up ID	Lead (M)	Chloride (M)	Magnesium (M)	pH*	Log[aCl-]
PbO-0.01 ED	4.07E-02	3.76E-03	3.49E-06	11.76	-2.5987
PbO-0.1 ED	4.04E-02	1.54E-01	7.07E-02	9.53	-1.0246
PbO-1.0 ED	3.92E-02	1.56E+00	7.19E-01	8.91	-0.0987
PbO-1.5 ED	3.90E-02	2.24E+00	1.08E+00	8.70	0.0342
PbO-2.0 ED	3.88E-02	2.98E+00	1.44E+00	8.44	0.0776
PbO-2.5 ED	3.82E-02	3.68E+00	1.79E+00	8.10	-0.0273

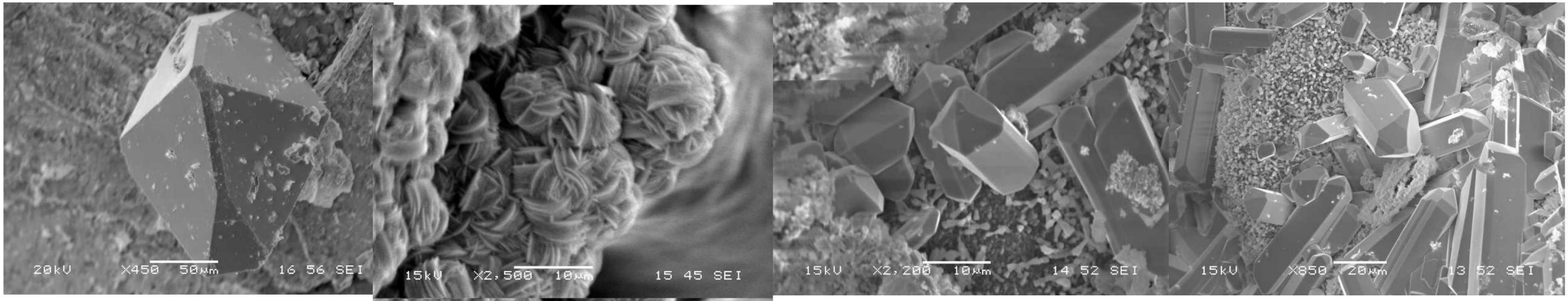
All solution chemistry is an average of Days 1035 to 4074. Kirkes, et al., 2014

*pH values are representative of insitu, non-corrected measurements, and were self-buffered by the experimental components

Stability Diagram of lead solids in $MgCl_2$ matrix shows experimental data (pink diamonds) matching with good agreement to the predicted solid. XRD analysis and solution chemistry data support the phase diagram modeling. More research is continuing on this work to identify and further characterize the secondary solids seen in the system.

Conclusions

- At [$MgCl_2$]=0.008m, and pH=11.76, the stable solid was litharge
- At [$MgCl_2$]=0.08m, and pH=9.53, the stable solids were blixite and laurionite
- At [$MgCl_2$]=0.8m to 2m, and pH=8.91 to 8.10, the stable solid was laurionite
- Suspended solid of Magnesium oxychloride forms at [$MgCl_2$]=1.6 to 2 m (likely phase 3 or korshunovskite)
- Experimental data and EQ3/6 modeling are consistent with each other
- Pb-O-Mg secondary solid may exist



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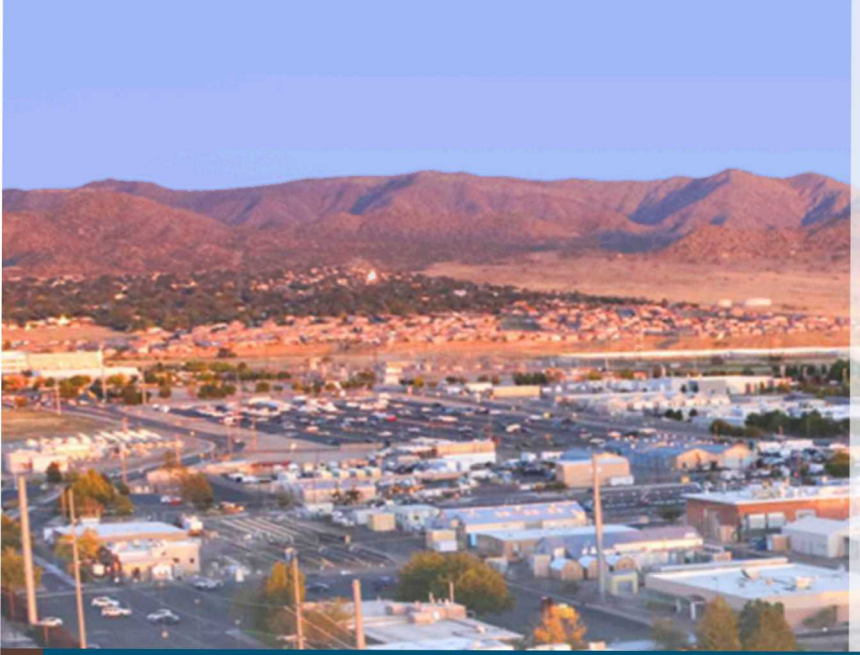

Questions?

lkirkes@sandia.gov