William & Mary Summary: 1018 Mild Steel and Characterization of Proposed Black Oxide Coatings

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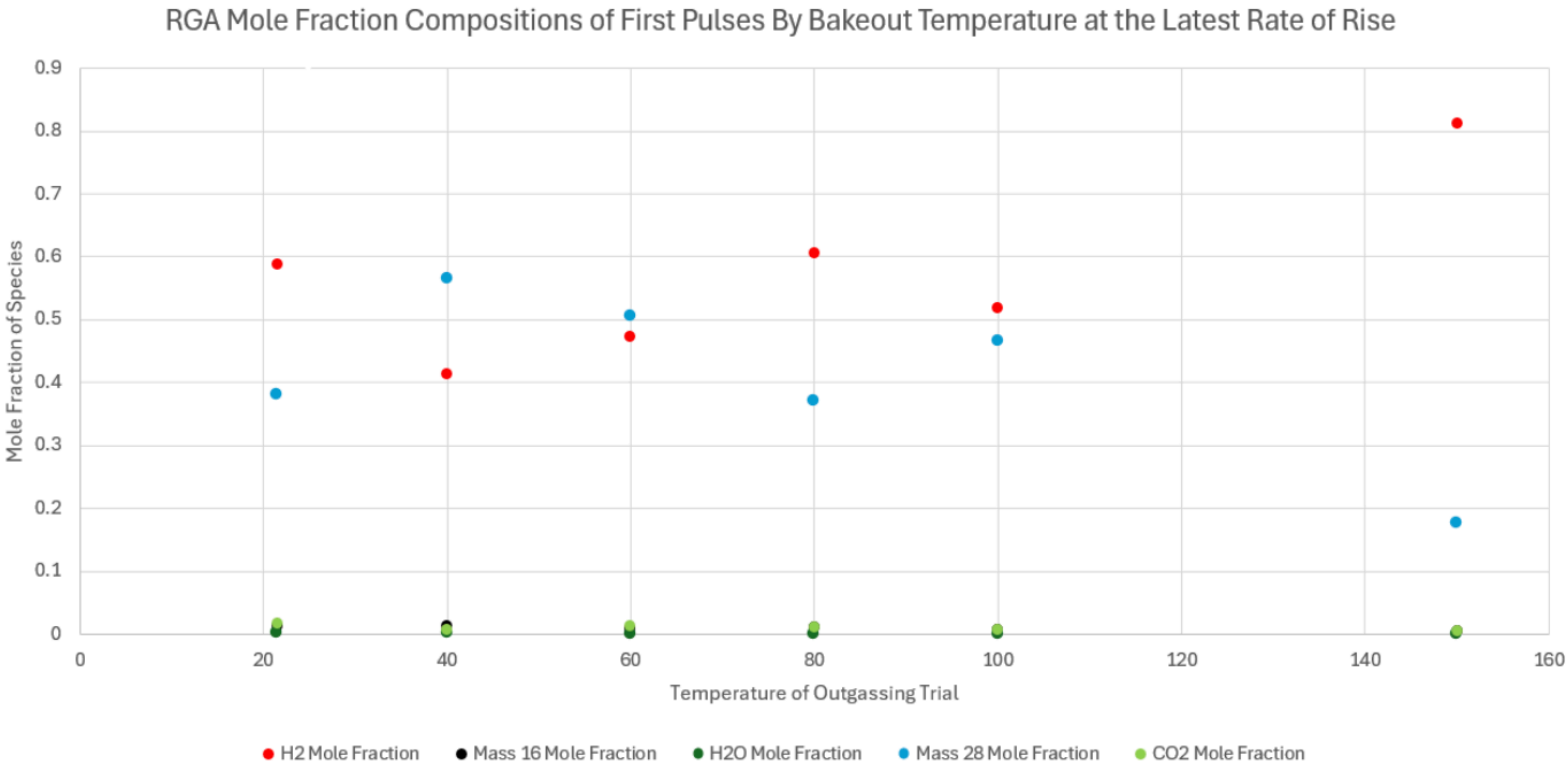
W&M Efforts Since Workshop II

- W&M 1018 low-carbon steel campaign 2023-2024
  - replicate outgassing studies on 1018 mild steel to verify the work of Park, CERN, JLab and prior W&M studies on air baked 1020.
  - Specific outgassing rates acquired by RoR/accumulation method. Outgassing composition by RGA analysis of pulsed contents after accumulation in 1018 chamber.
  - Sequential low temperature bakes —> (RT, 40, 60, 80, 100 and 150 C).

- Structural characterization of candidate black oxide conversion coatings for reduced outgassing
  - Commercial processes: Sun Steel magnetite, CERN Magnetil
  - W&M coatings: heat treatments of mild steel by steam, HT annealing + quench (by immersion and cold water spray)
  - Structural Characterization by X-ray diffraction and Raman spectroscopy
  - Morphology with SEM micrographs and stoichiometric estimates by EDXS

Outgassing rates after 100 hours of pumping for each bake-out temperature

Bakeout Temp (48hr)	Total Outgassing Rate Torr L / s cm^2 (~100 hours into pumpdown)	Outgassing Rate Uncertainty Torr L / s cm^2	Dominant Species at the end of the pump down (RGA)
RT	1.36 E -12	5 E -14	H_2
40 C	1.08 E -12	4 E -14	CO
60 C	9.64 E -13	4.2 E -14	CO
80 C	8.39 E -13	4.0 E -14	H_2
100 C	1.15 E -13	4.3 E -14	H_2
150 C	3.99 E -12	1.5 E -13	H_2
RT Replicate	9.78 E -13	3.7 E -14	H_2


RGA Mole Fraction Compositions of First Pulses By Bakeout Temperature at the Latest Rate of Rise
Mole Fraction of Species
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
100
120
140
160
Temperature of Outgassing Trial
H2 Mole Fraction
Mass 16 Mole Fraction
H2O Mole Fraction
Mass 28 Mole Fraction
CO2 Mole Fraction

W&M 1018 Outgassing Takeaways

- 1018 mild steel achieves overall pressures at various times during the pump down that are comparable to or better than stainless steel vacuum vessels.
- Low temperature bakes (~80 C) show significant reduction in water content; however this approach would require a longer pumping period to achieve base pressures and outgassing rates observed with higher temperature bakes.
- We reproduced the work of Park and others that indicates mild steel is a “good” vacuum material even after minimal conditioning of the vacuum surface (see photos below).
- Mild steels outgassing rates are sensitive are sensitive to the history of surface treatment and pump down/bakeout history.
- Lingering questions regarding the presence of CO_x, particularly in bakes less than 100 C in our data set.

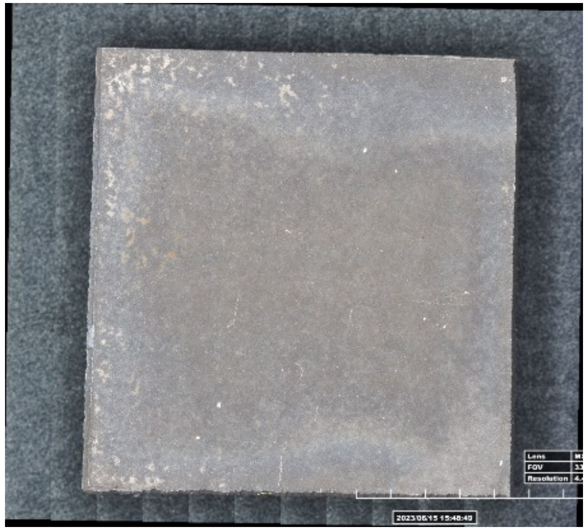
Characterization Methods used to interrogate black oxide surfaces on mild steel

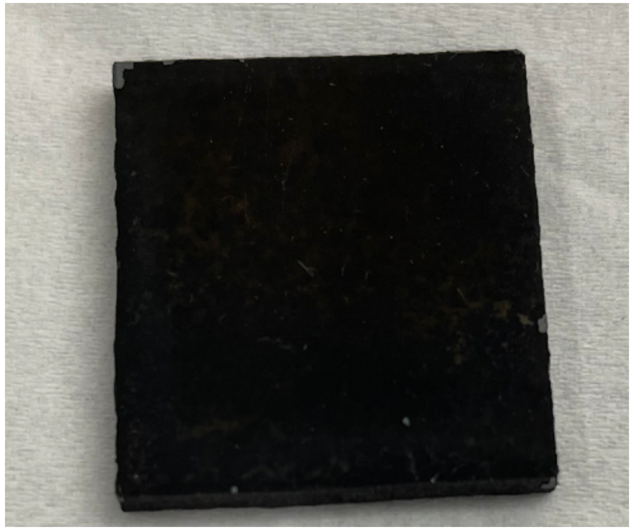
- Scanning Electron Microscope (SEM) with energy dispersive x-ray spectroscopy (EDXS)
    - Surface morphology and stoichiometric information pertaining to the oxide surface.
- Structural Characterization by X-ray Diffraction
    - Phase identification
    - Access to grazing incidence techniques suitable surface characterization for smooth films as well as film metrology
- Structural Characterization by Raman Spectroscopy
    - In conjunction with XRD, allows for differentiation and identification of iron oxides and hydroxides at stainless steel surfaces.

Optical images of black oxides

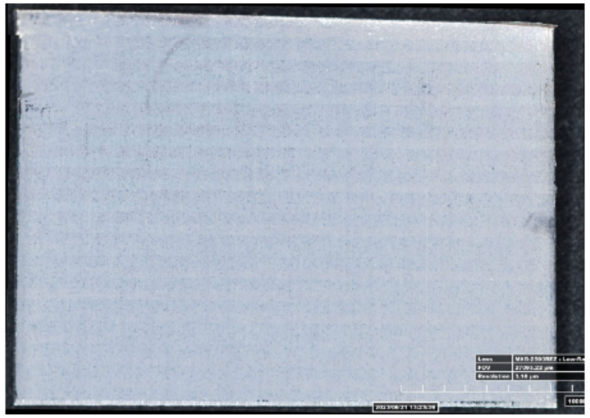
Hirox Optical Microscope Image
High Illumination Indirect Lighting

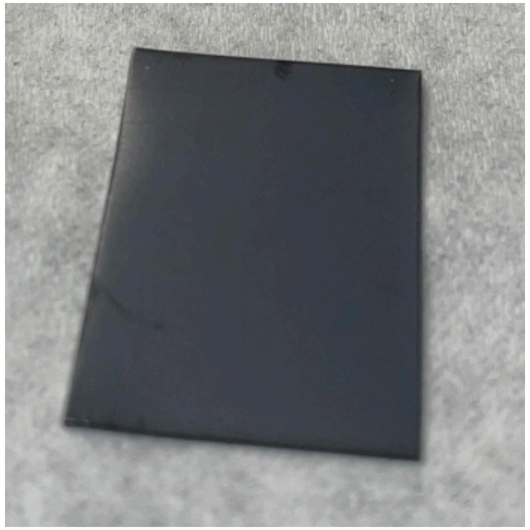
Photo in Fluorescent light





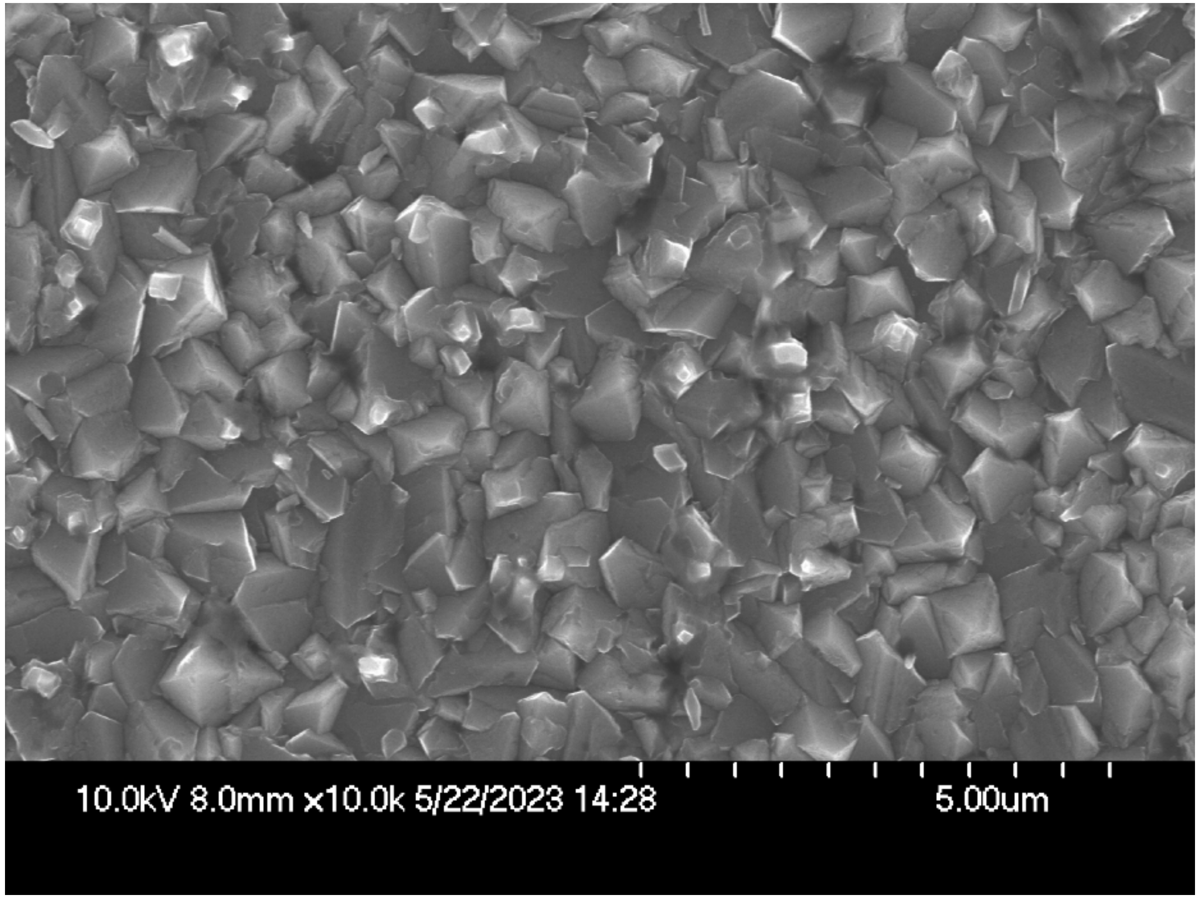
W&M Black Oxide

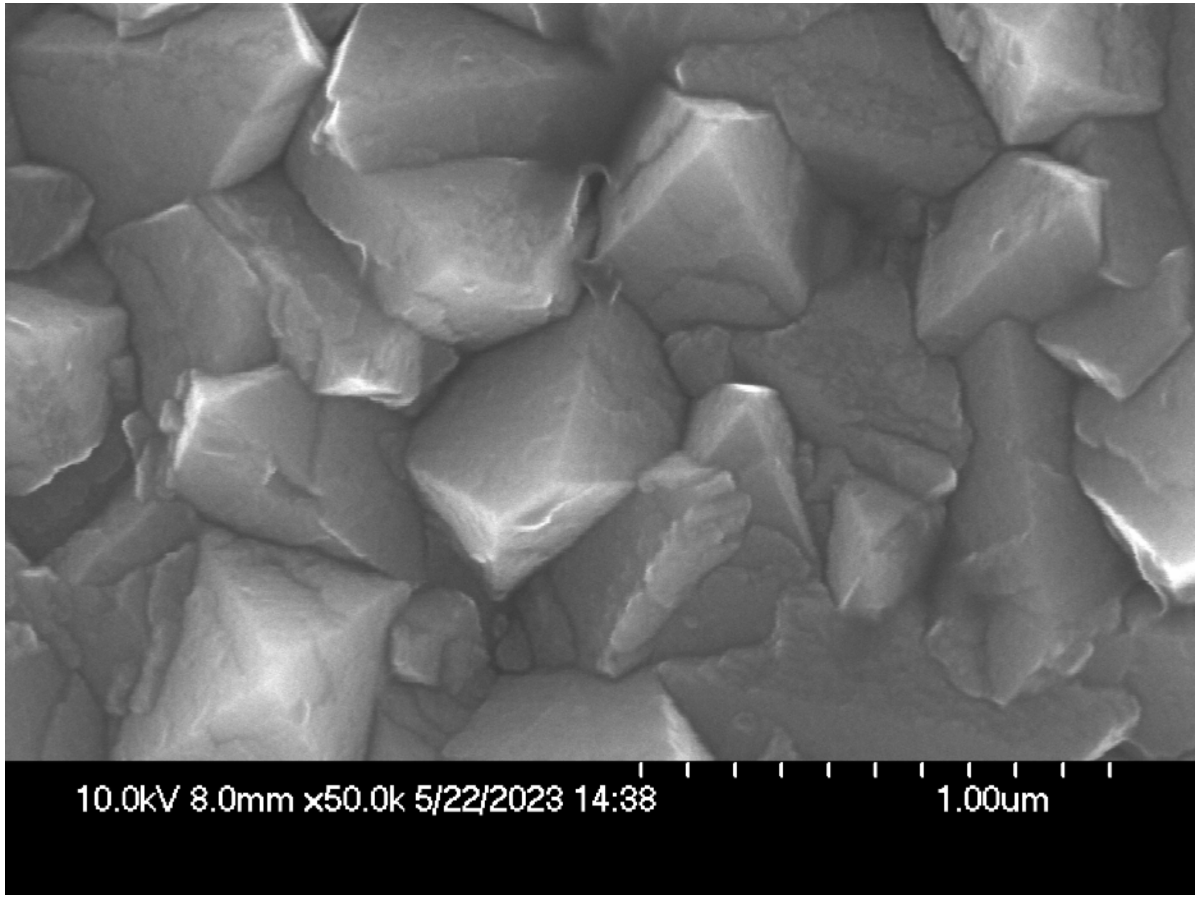




Sun Steel Sample

FESEM — Sun Steel Sample





Octahedral crystal habits consistent with magnetite formation

Sun Steel Oxide Sample —XRD Phase Identification

- Agreement of sample peak positions with respect to XRD reference data for BCC Iron and Magnetite.
- no other Fe oxide phases appear to be present
- Presence of magnetite peaks over the High Angle scan suggests a polycrystalline magnetite film

BCC Iron
(COD reference code : 96-110-0109)

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	0	1	1	2.02798	44.647	100.0
2	0	0	2	1.43400	64.982	14.5
3	1	1	2	1.17086	82.279	27.5

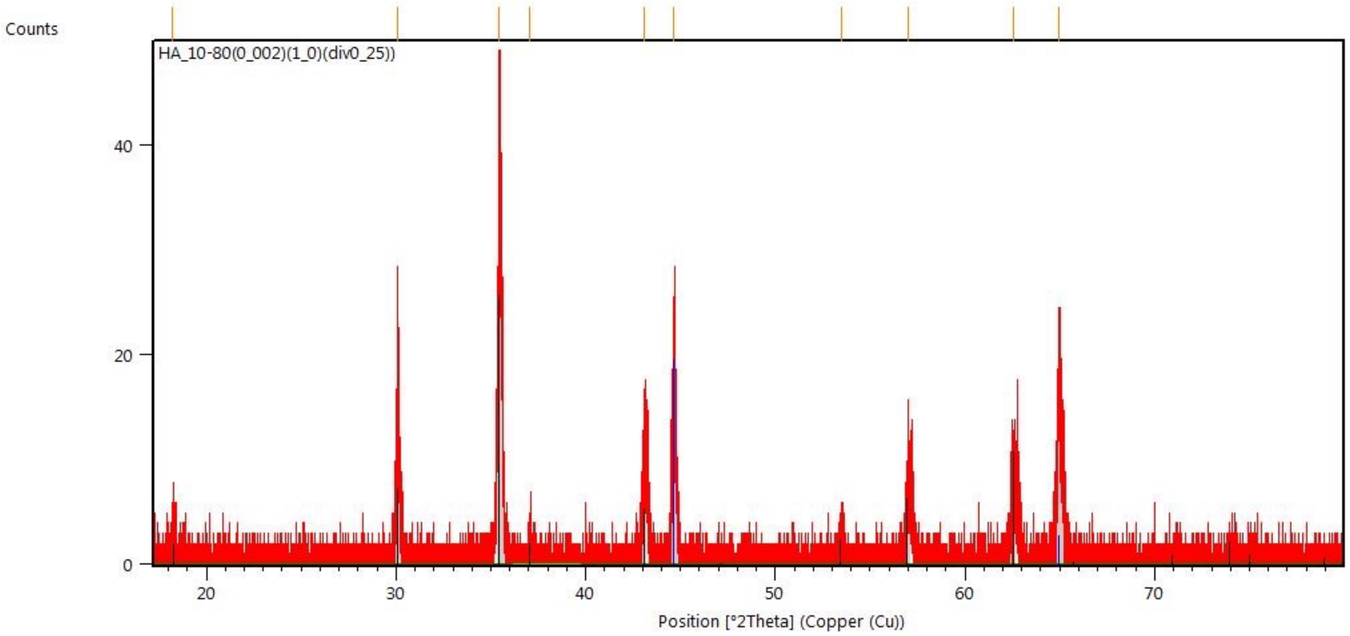
Magnetite

References

Structure: Wechsler, B. A., Lindsley, D. H., Prewitt, C. T., American Mineralogist, **69**, 754 - 770, (1984)

Peak list

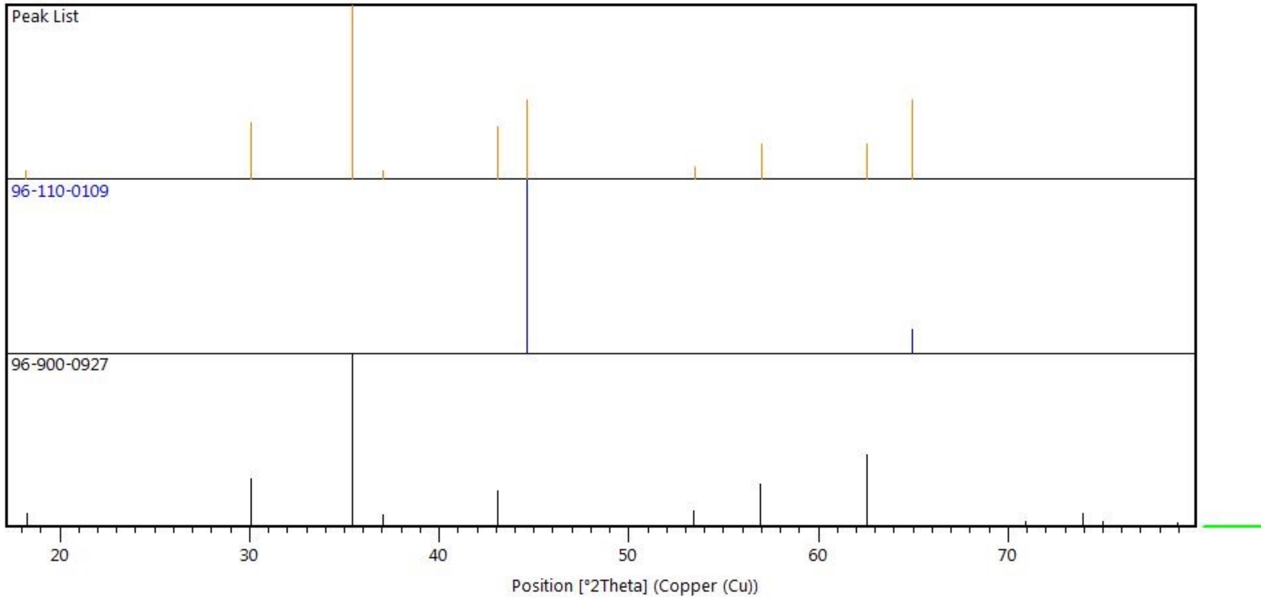
No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	1	1	4.84743	18.287	8.1
2	0	2	2	2.96843	30.080	28.2
3	1	1	3	2.53149	35.431	100.0
4	2	2	2	2.42372	37.062	7.8
5	0	0	4	2.09900	43.059	21.1
6	1	3	3	1.92617	47.145	0.6
7	2	2	4	1.71383	53.418	9.5
8	1	1	5	1.61581	56.944	24.8
9	0	4	4	1.48422	62.530	42.2
10	1	3	5	1.41918	65.746	1.0
11	2	4	4	1.39933	66.799	0.0
12	0	2	6	1.32752	70.937	3.5
13	3	3	5	1.28038	73.972	8.6
14	2	2	6	1.26574	74.973	3.7
15	4	4	4	1.21186	78.934	2.7
16	1	5	5	1.17568	81.869	0.4
17	2	4	6	1.12196	86.718	3.8
18	1	3	7	1.09307	89.613	8.6



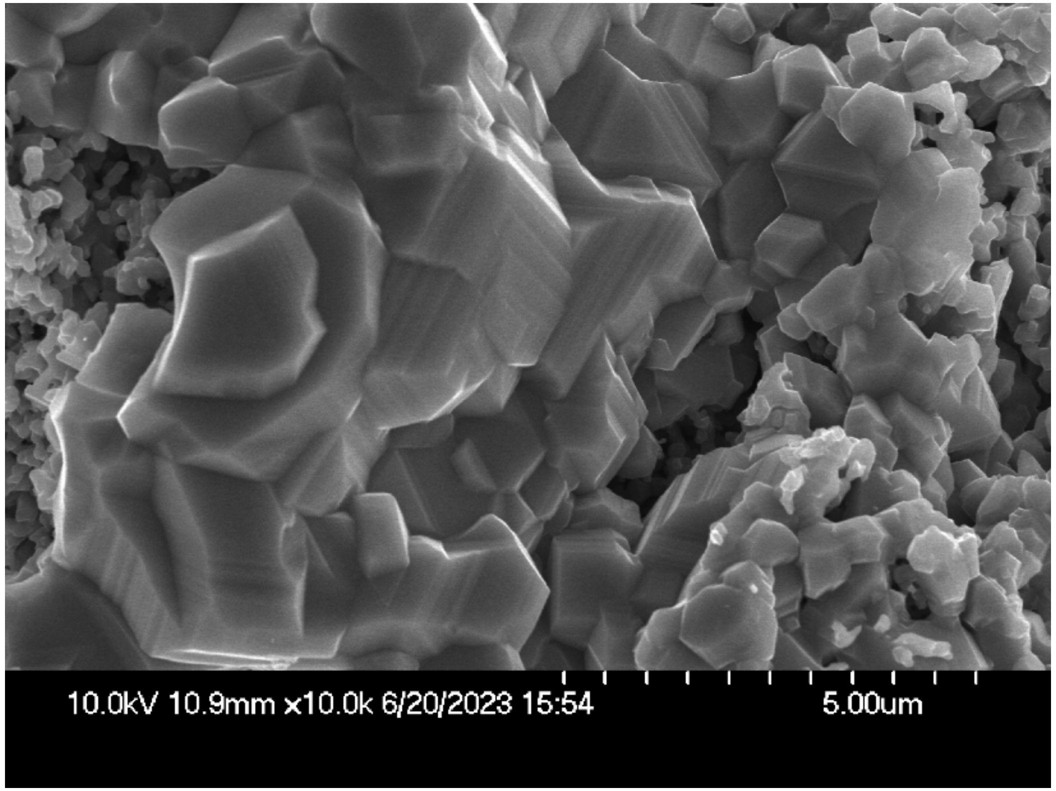
Sample Peaks

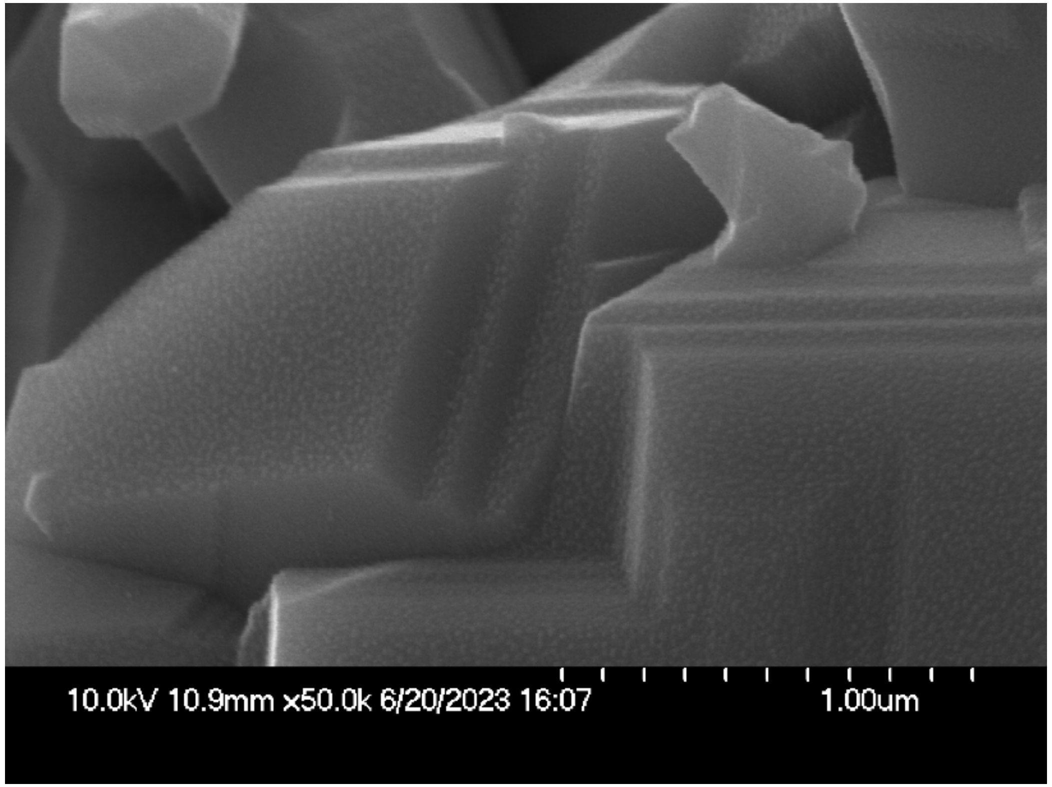
BCC Iron

Magnetite



FESEM W&M Black Oxide (800º C Quenched)

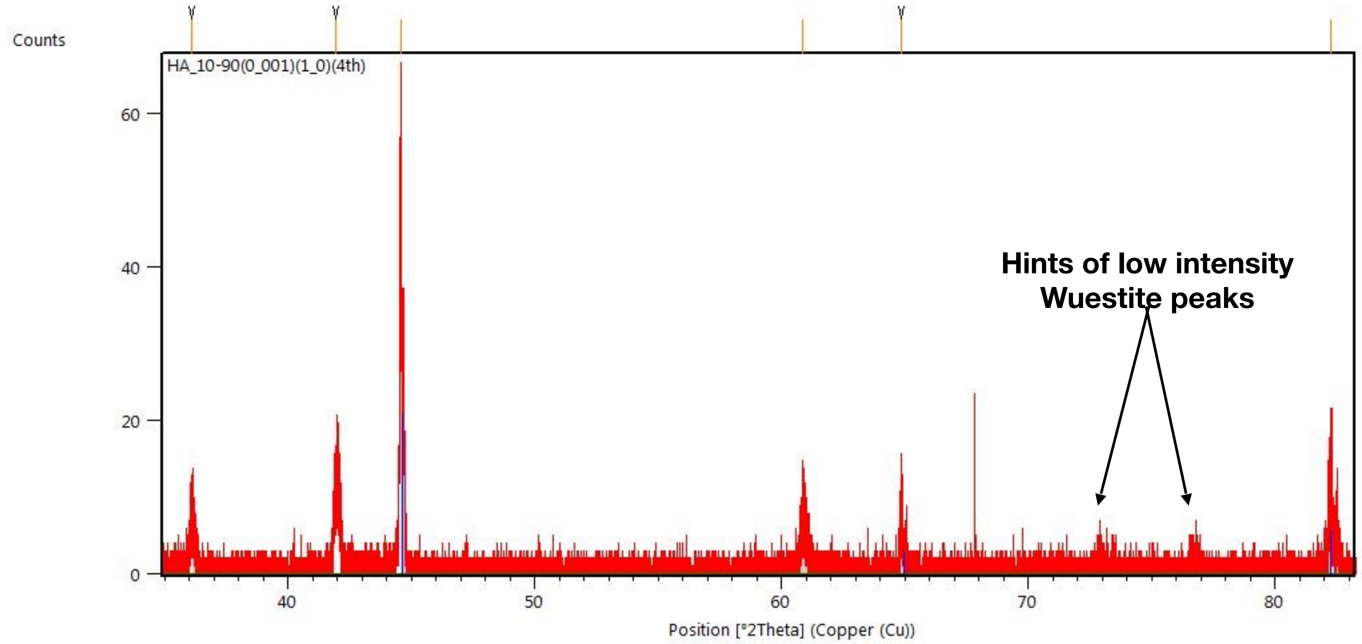


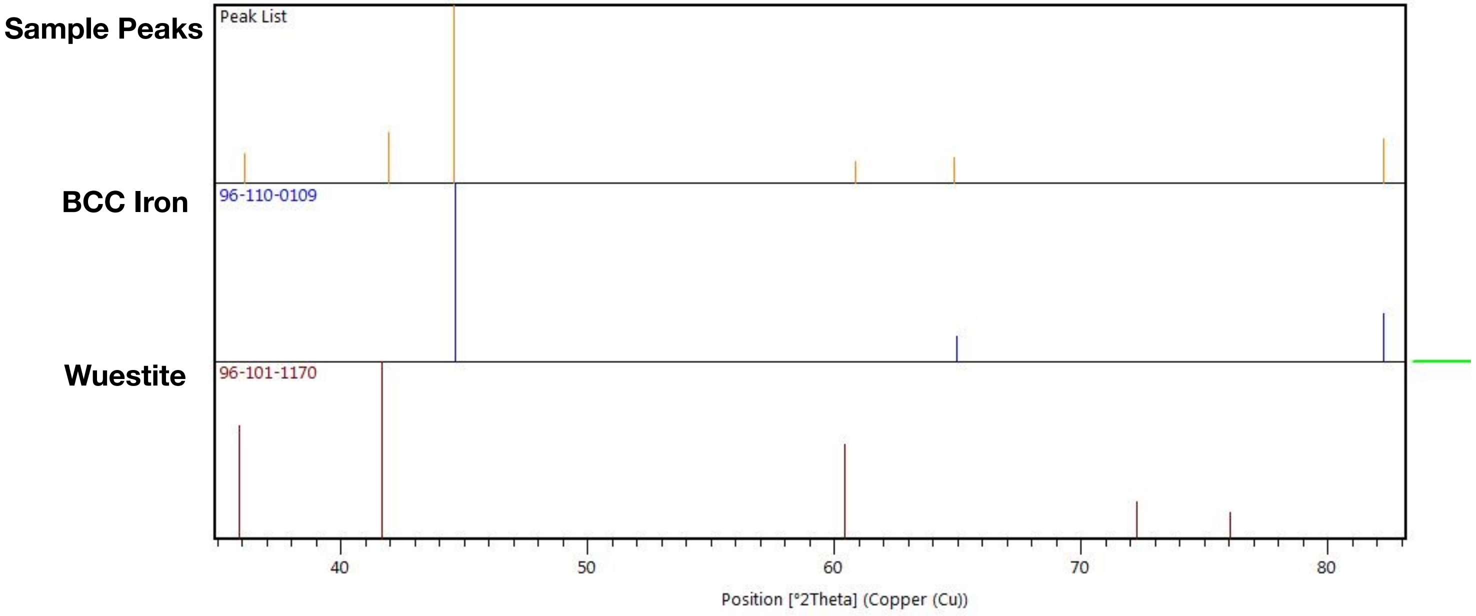


Pyramidal crystal habits consistent with Wuestite formation

W&M Black Oxide Sample —XRD Phase Identification

- Agreement of sample peak positions with respect to XRD reference data for BCC Iron and Wuestite.
- no obvious signatures to suggest the presence of other Fe Oxide phases.
- Oxide coating is likely polycrystalline Wuestite.





BCC Iron
(COD reference code : 96-110-0109)

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	0	1	1	2.02798	44.647	100.0
2	0	0	2	1.43400	64.982	14.5
3	1	1	2	1.17086	82.279	27.5

Wuestite

References

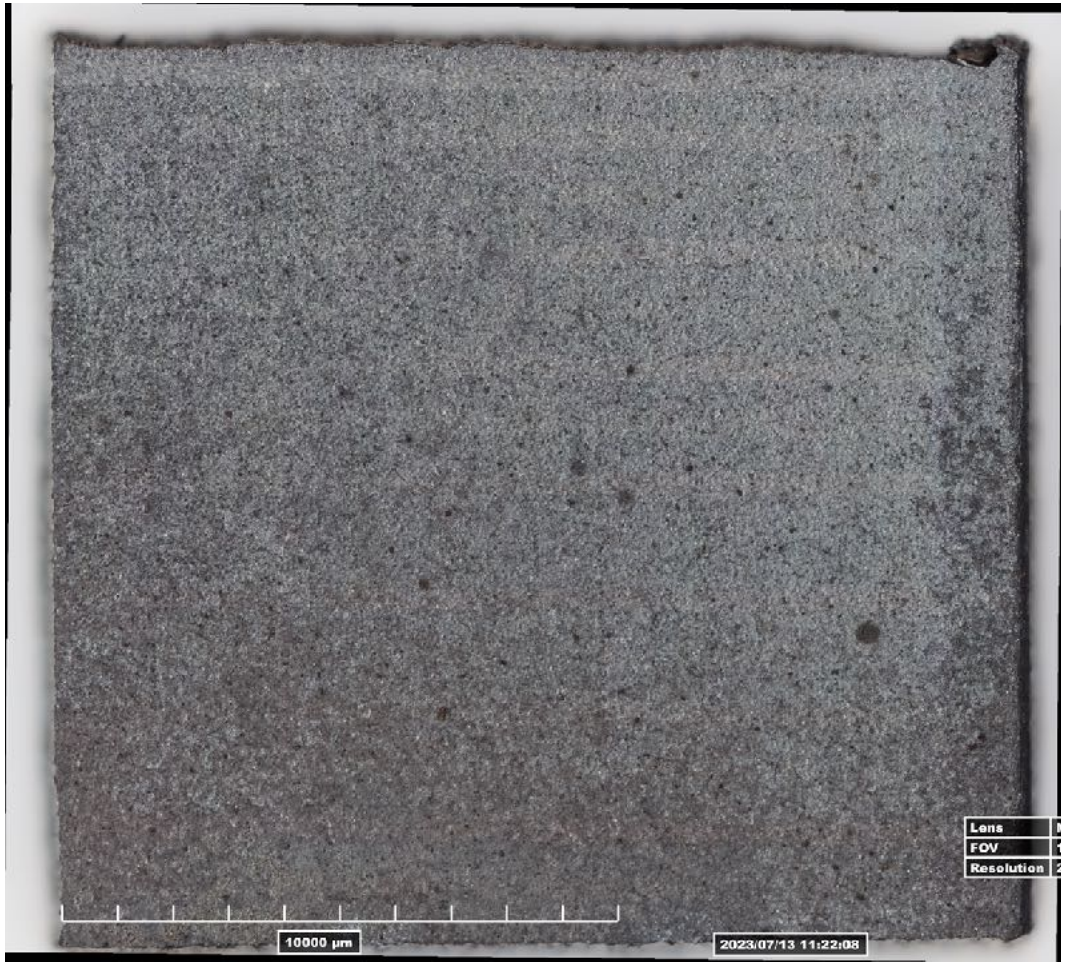
Structure: Jette, E R, Foote, F, Journal of Chemical Physics, **1**, 29 - 36, (1933)

Peak list

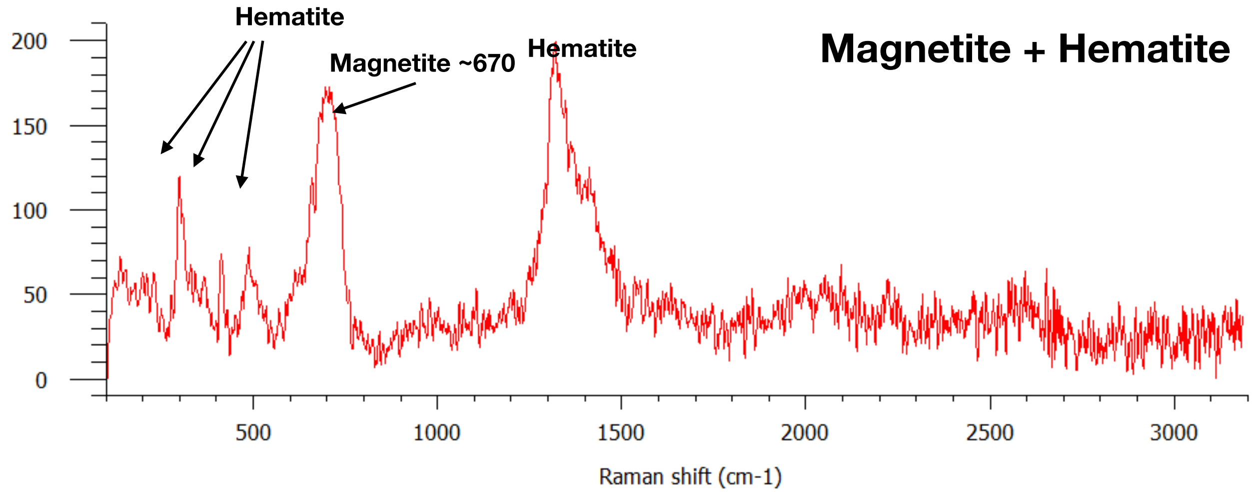
No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	1	1	2.50108	35.876	64.4
2	0	0	2	2.16600	41.664	100.0
3	0	2	2	1.53159	60.389	53.9
4	1	1	3	1.30615	72.279	21.6
5	2	2	2	1.25054	76.045	15.4

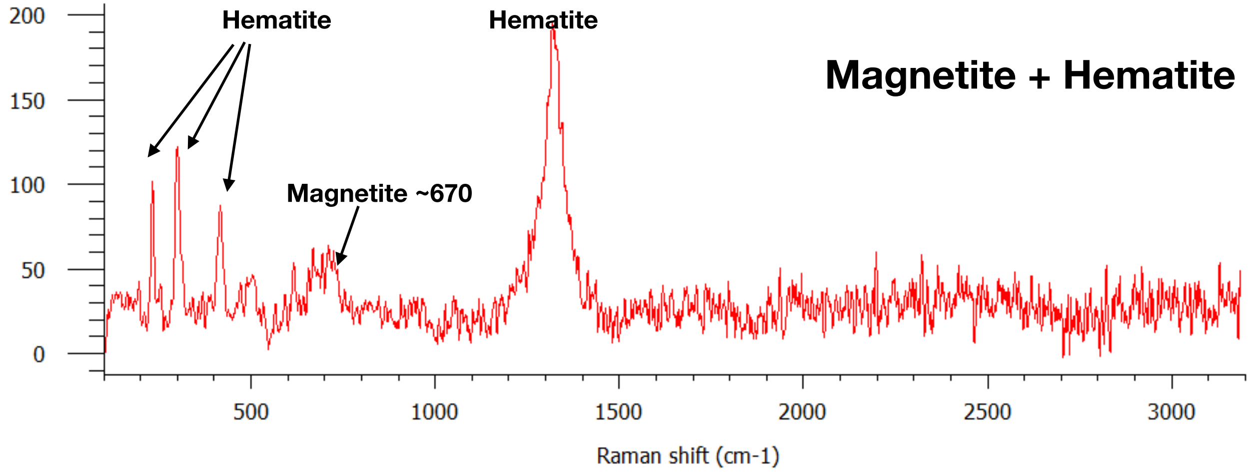
W&M Steam Processed Sample

Hirox Optical Image — 071223A_HR



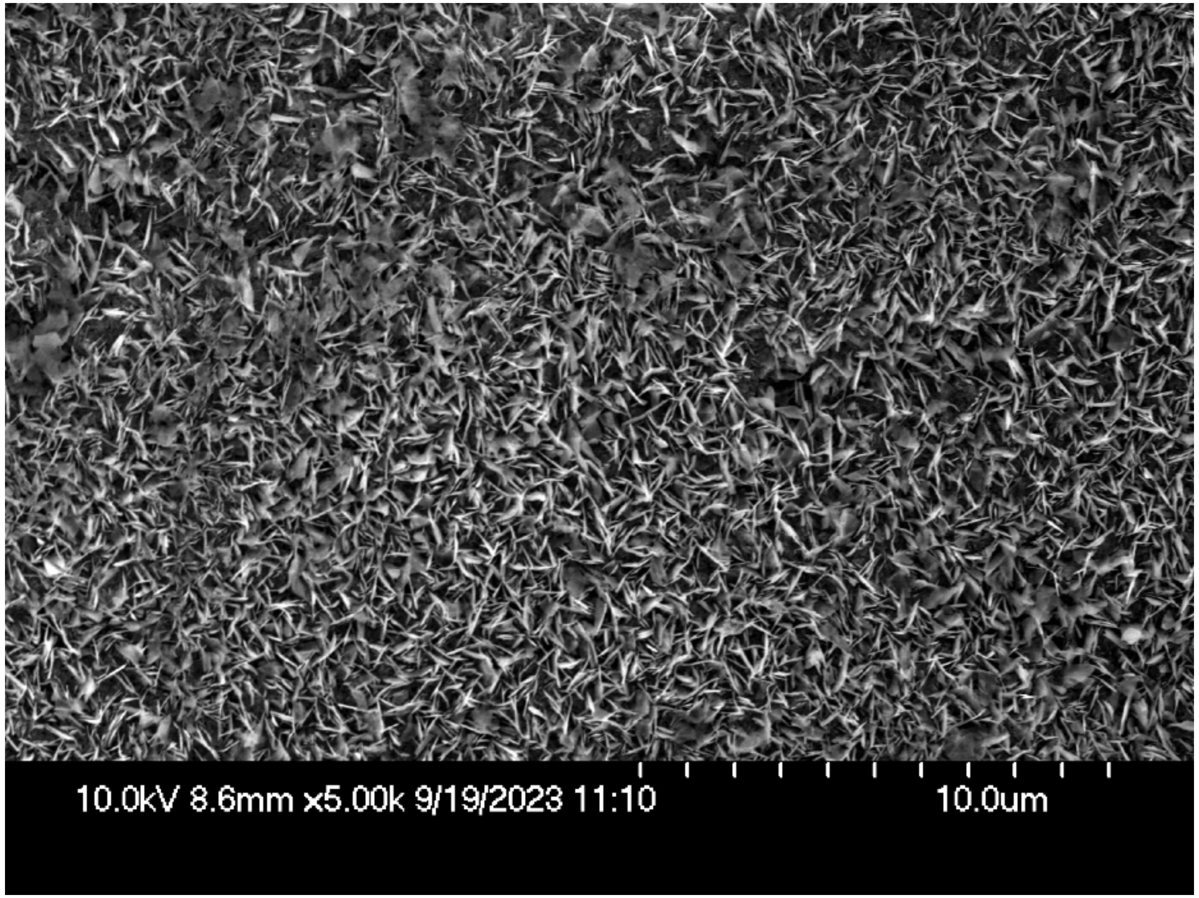
Raman Spectra - 514 nm probe wavelength

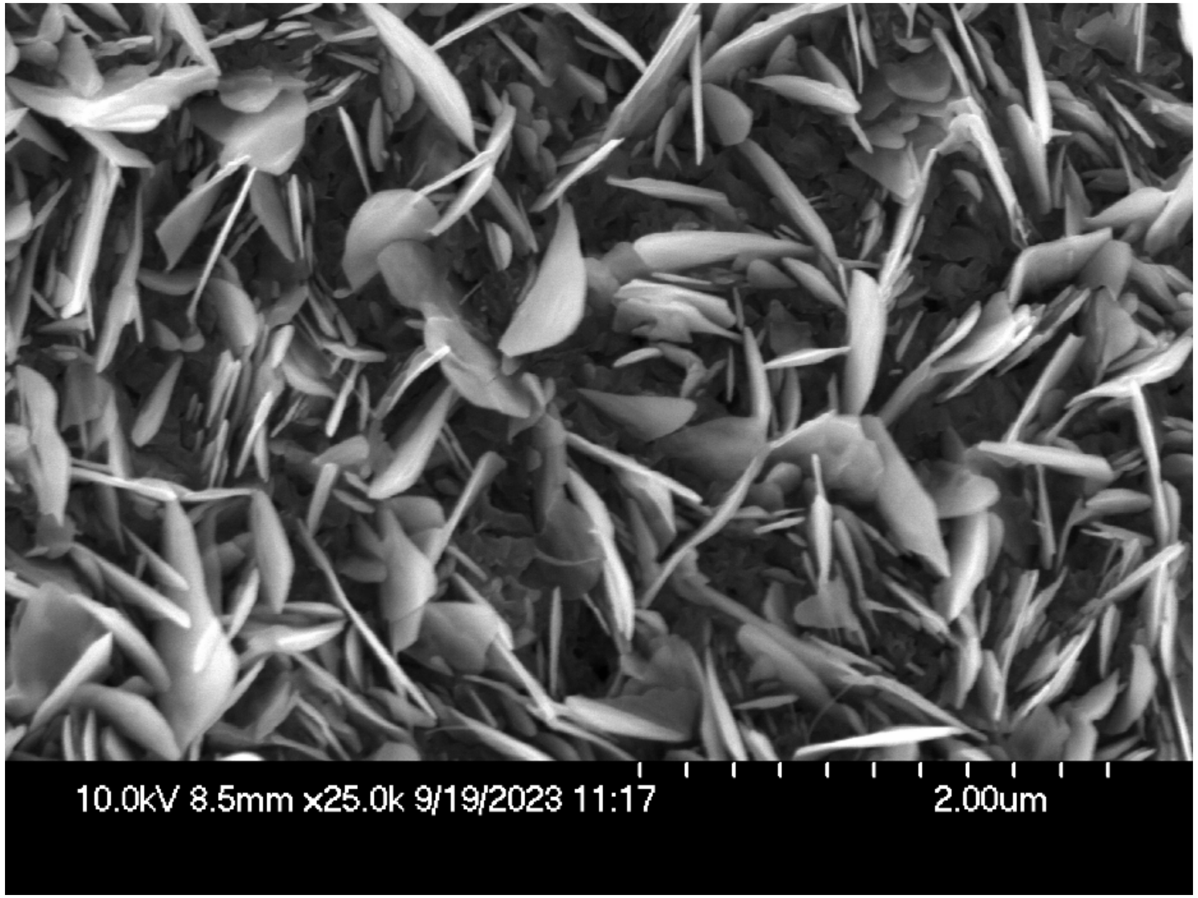




Reference Study:
M. K. Nieuwoudt, J. D. Comins and I. Cukrowski, J. Raman Spectrosc. 2011, 42, 1335-1339

FESEM W&M Steam processed sample (500 C exposure ~ 1 hour)





W&M Materials Characterization Review

- Commercial and lab-grown Fe-oxide coatings were characterized by SEM, XRD and Raman spectroscopy.
- Stabilization of specific iron oxide phases is possible, but questions remain as to which processes will enable optimization of a well-controlled oxide thickness, surface morphology and how well adhered these coatings are over the lifetime of GW experiments.
- Head to head study of bare and magnetite coated chambers at JLab (available in pre-print, A. Al-Allaq, M. A. Mamun, M. Poelker and A. Elmustafa) suggest no improvements in water outgassing rates of the coated chambers at 80 C and 150 C bakeout temperatures relative to the bare mild steel.
- Coarse W&M survey studies of low angle reflectivity of nominally "Black" oxide surfaces does not correspond to strong IR absorption at 940 nm, suggesting that optical baffles remain necessary for any black Fe-oxide coating scheme.
- We concluded that the overall risks of implementing a conversion coating on mild steels require careful consideration and that the native oxide of mild steels may be sufficient for vacuum performance requirements. (If CO is a problem in larger scale mild steel studies, perhaps more NEG pumping will be required for low temperature bakes?)
- At what stage of the process will the proposed black oxide coating be introduced? Will it survive forming, welding etc.?
- Please contact dbberinger@wm.edu if you would like access to W&M's 1018 outgassing repository.