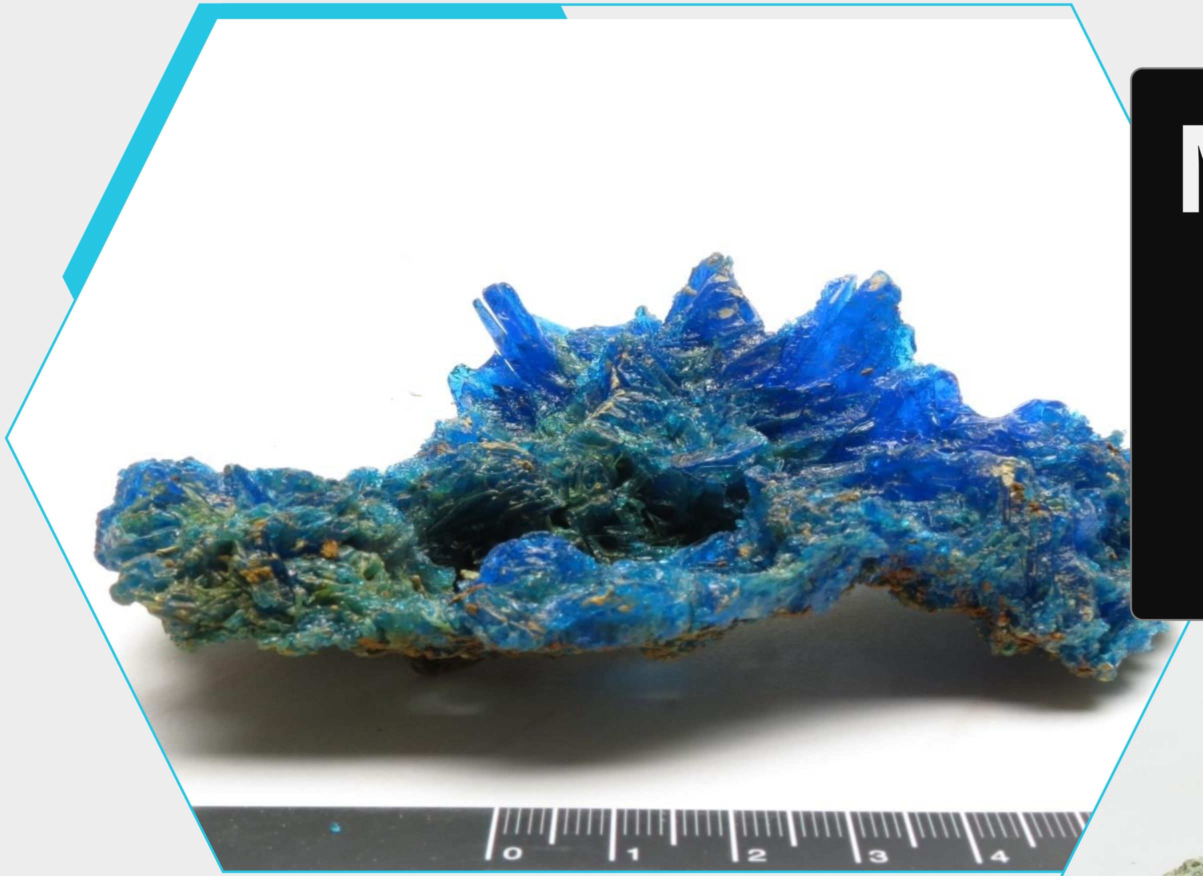
An Investigation of Analytical Methods Applied to Mineralogical Collection Assessments

Kathryn Royce Schronk

Minerals ≠ Stable Objects



1992 – 350 of 3,500 known minerals

Nov. 2018 – ? of 5,400 identified minerals

How many more are vulnerable?

Melanterite & Chalcanthite

Melanterite

$FeSO_4 \cdot 7\ H_2O$

Chalcanthite

$CuSO_4 \cdot 5H_2O$

Ferrohexahydrate – $FeSO_4 \cdot 6H_2O$
Siderotil – $FeSO_4 \cdot 5H_2O$
Rozenite – $FeSO_4 \cdot 4H_2O$
Szomolnokite – $FeSO_4 \cdot H_2O$

Dehydrate

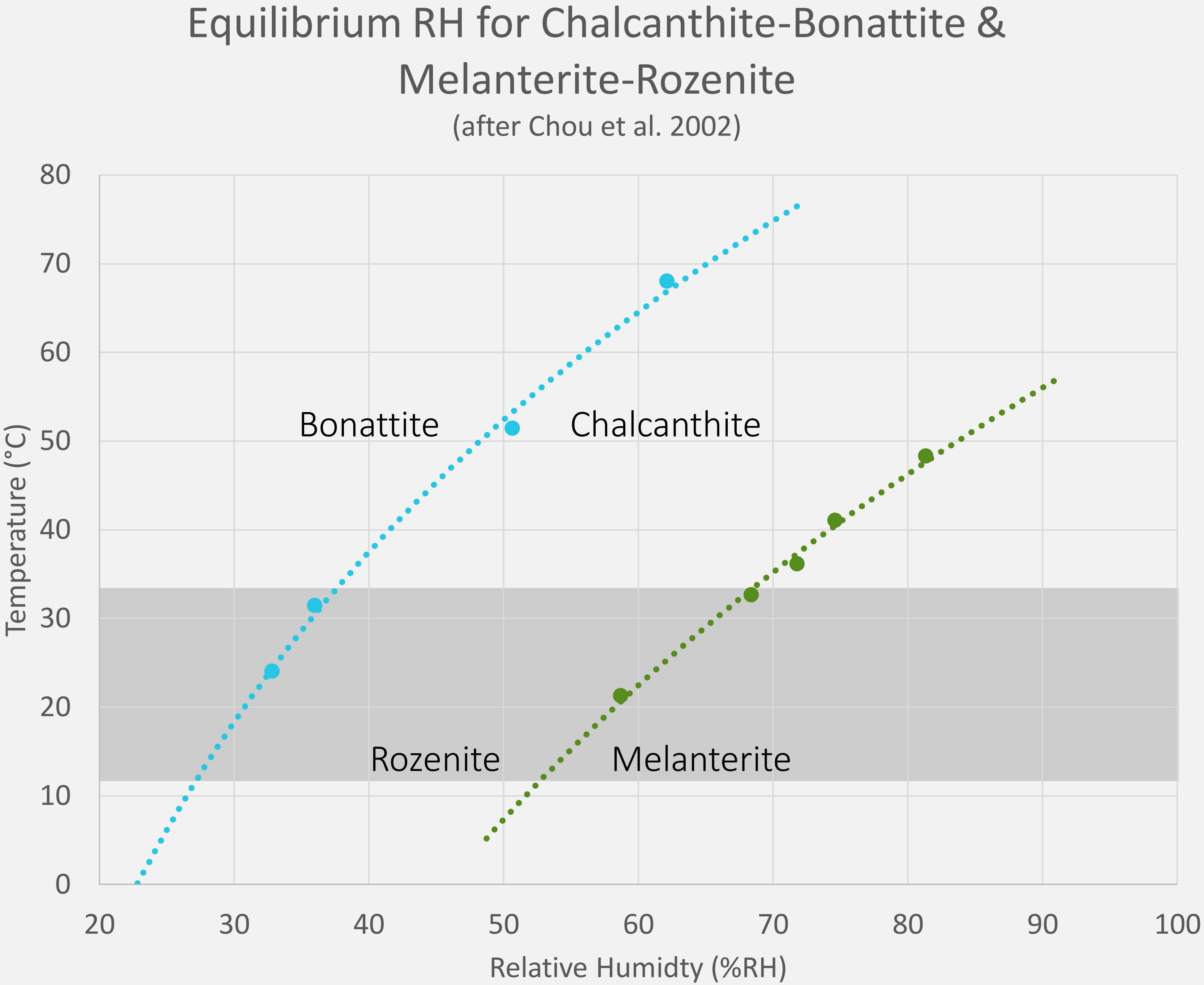
Fe

Cu

Bonattite – $CuSO_4 \cdot 3H_2O$
Poitevinite – $CuSO_4 \cdot H_2O$
Chalcocyanite – $CuSO_4$

Dehydration

Experiment:
30°C & 35% RH



Research Questions

Does the short-term dehydration of melanterite and chalcanthite produce chemically or visually detectable change?

Do synthetic crystals present changes similar to those observed in museum specimens?

What analytical methods are optimal for determining physical and chemical changes to mineral specimens? Which would be most applicable to the average museum, in terms of efficacy and cost benefit?

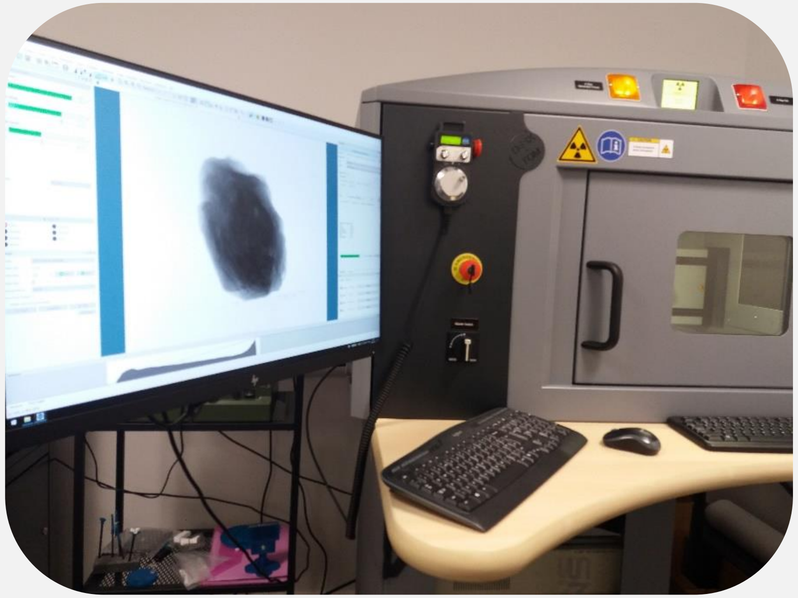
Analysis

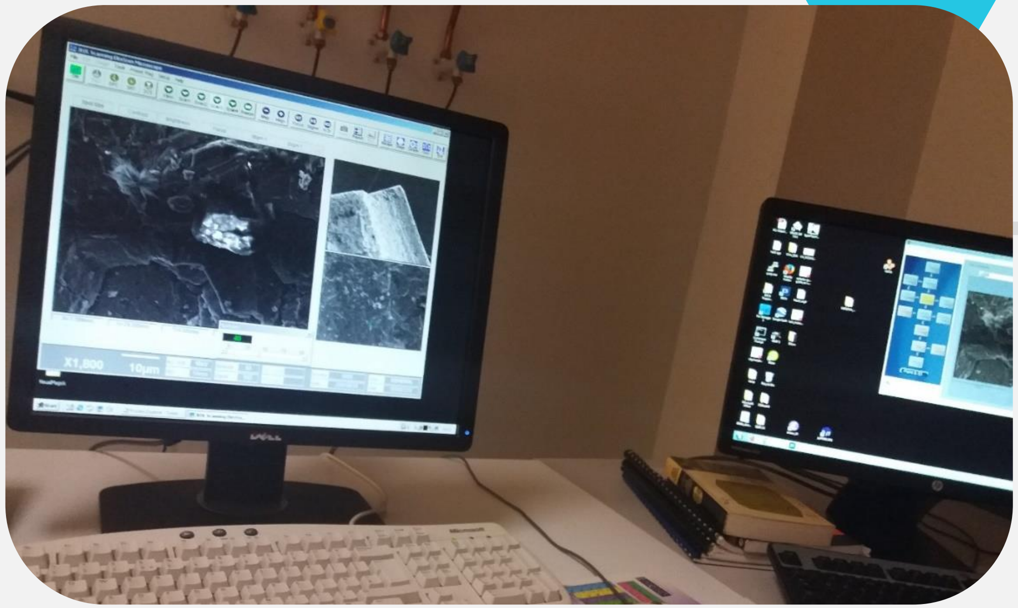
Determine methods for identifying & monitoring change

- Weight measurements
- Colorimetry

- Photography
- X-radiography
- CT scans
- SEM

- EDX
- XRD
- FT-IR
- Raman





Weight Measurements

Average of 3 readings | accuracy = ±0.01mg

Melanterite

- Samples = significant change (>10%)
- Controls = minimal change (<0.25%)

Chalcanthite: minimal change compared to melanterite

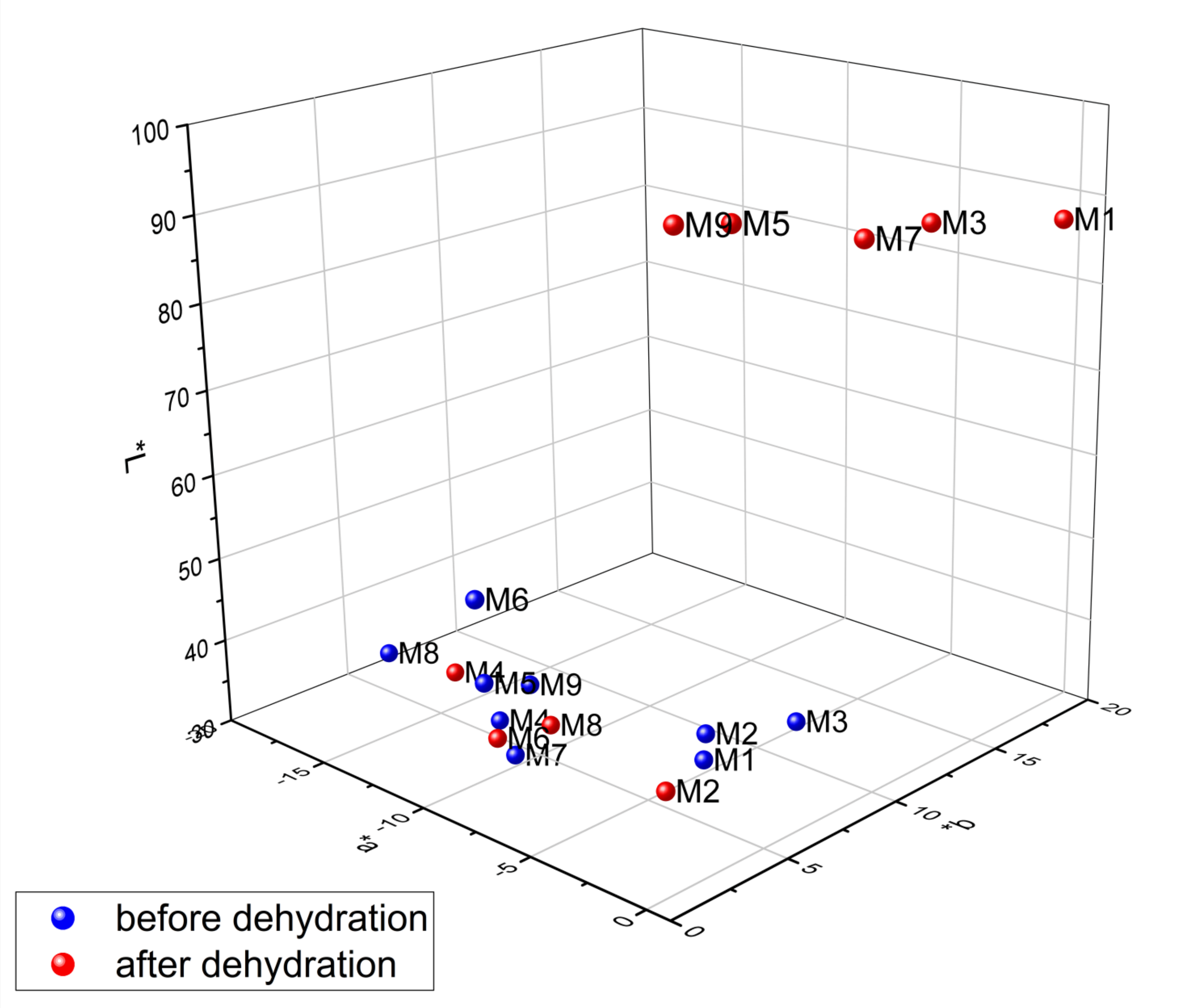
Melanterite

	Sample #	Δ Weight (g)	Δ Weight (%)
Sample	M1	-2.3287	61.84%
	M3	-0.3533	10.57%
	M5	-0.6635	27.49%
	M7	-0.8511	25.19%
	M9	+0.3356	13.50%
Control	M2	-0.0045	0.11%
	M4	-0.0056	0.19%
	M6	-0.0051	0.24%
	M8	-0.0037	0.17%

Chalcanthite

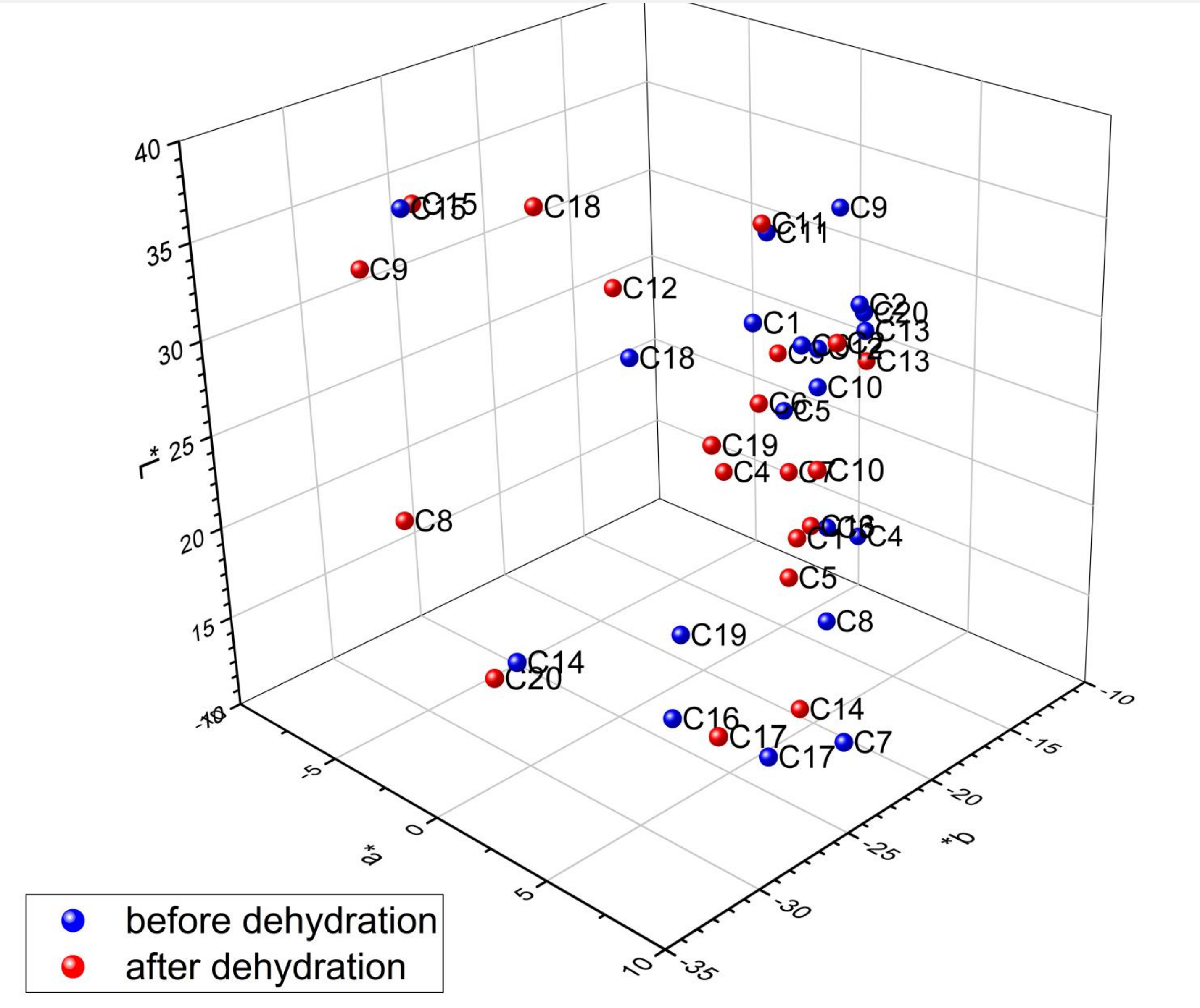
	Sample #	Δ Weight (g)	Δ Weight (%)
Sample	C1	-0.0208	0.26%
	C2	-0.0574	0.81%
	C3	-0.0490	0.60%
	C4	-0.2965	1.87%
	C5	-0.1230	1.01%
	C6	-0.0893	0.93%
	C7	-0.0578	0.58%
	C8	-0.0891	0.45%
	C9	-0.0805	0.70%
	C10	-0.1502	1.20%
Control	C11	-0.1654	0.96%
	C12	-0.0077	0.15%
	C13	-0.0221	0.29%
	C14	-0.0140	0.19%
	C15	-0.0346	0.71%
	C16	-0.0201	0.30%
	C17	-0.0034	0.05%
	C18	-0.0144	0.20%
	C19	-0.0164	0.35%
	C20	-0.0586	0.78%

Colorimetry: Melanterite



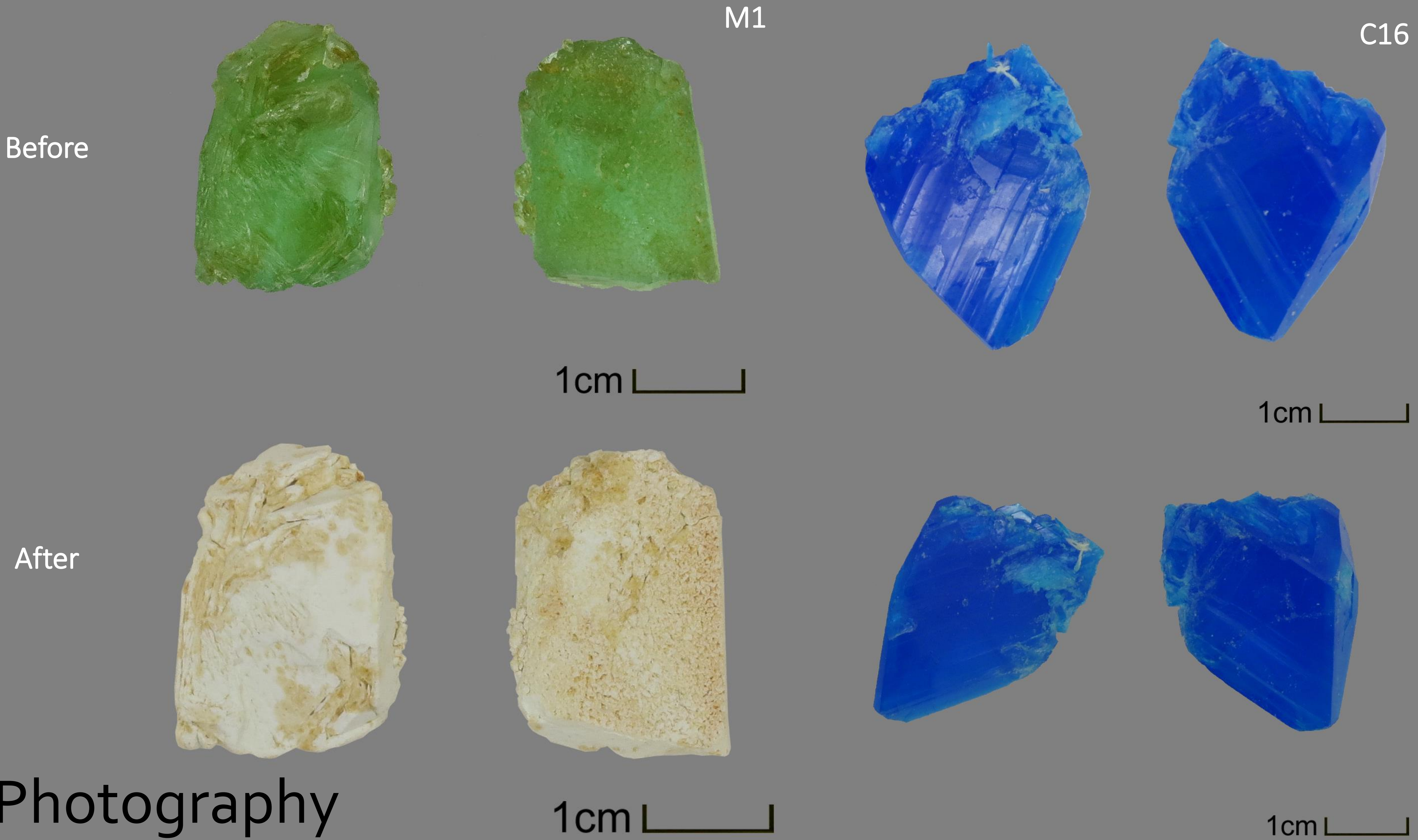
	Melanterite	ΔE^*_{ab}(D65)
Samples	M1	58.43
	M3	57.85
	M5	56.96
	M7	63.51
	M9	58.40
	Mean	59.03
	Standard Deviation	2.30
Controls	M2	3.78
	M4	4.50
	M6	18.38
	M8	7.90
	Mean	8.64
	Standard Deviation	5.83

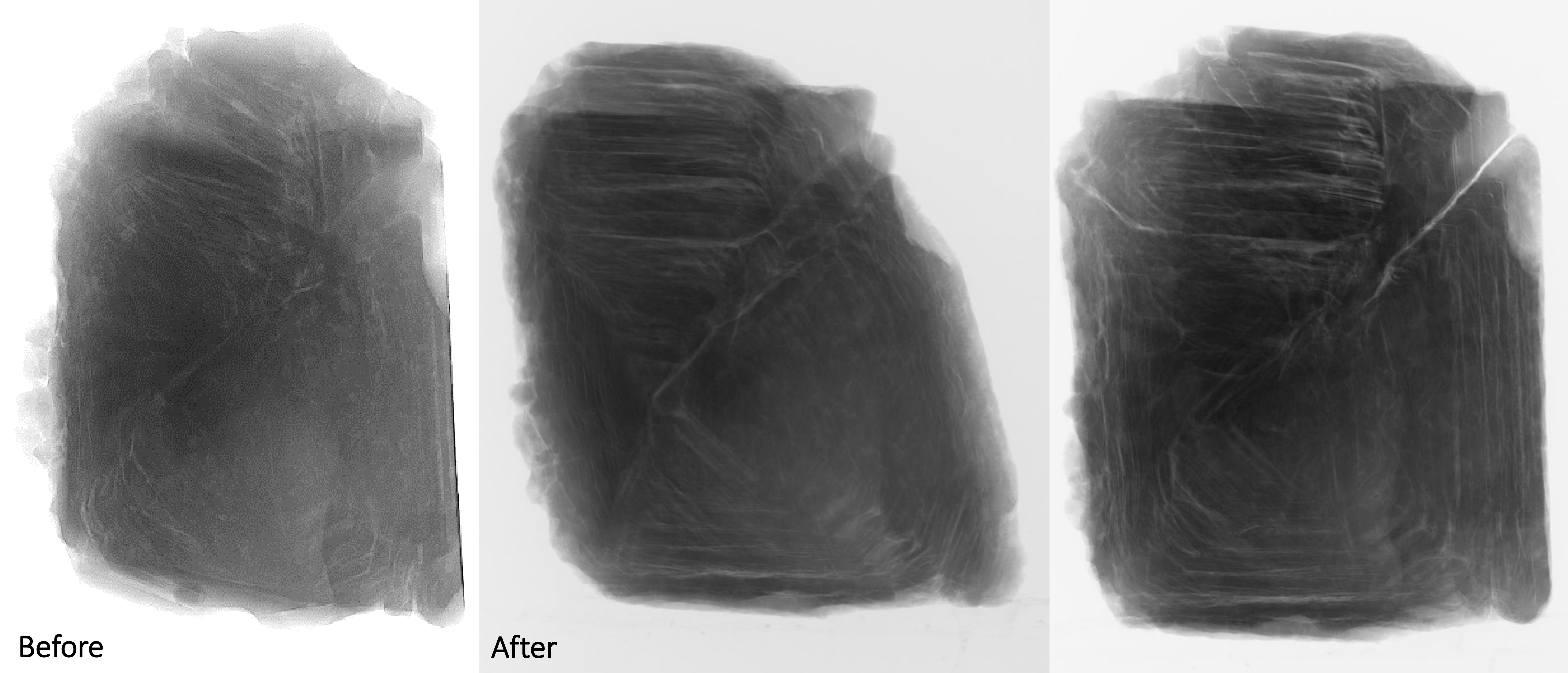
Colorimetry: Chalcanthite



	Chalcanthite	ΔE^*_{ab}(D65)
Samples	C1	10.27
	C2	2.38
	C3	8.28
	C4	7.35
	C5	7.99
	C6	3.18
	C7	11.92
	C8	16.99
	C9	18.64
	C10	4.85
	Mean	9.19
	Standard Deviation	5.16
Controls	C11	1.51
	C12	7.75
	C13	3.01
	C14	12.57
	C15	0.85
	C16	10.68
	C17	3.96
	C18	8.58
	C19	8.99
	C20	22.31
	Mean	8.02
	Standard Deviation	6.07

Photography



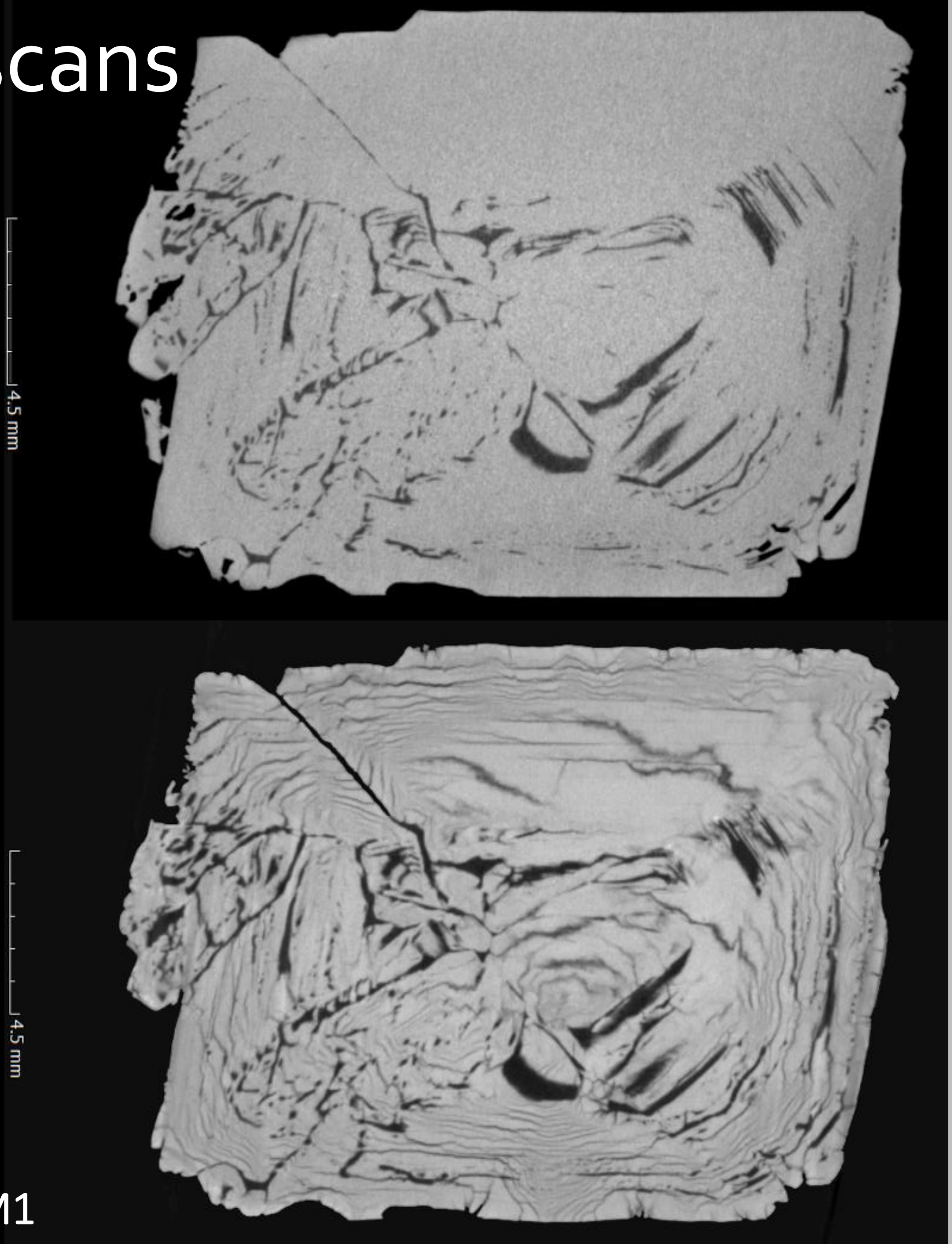


X-radiography: M1 before & after

CT scans

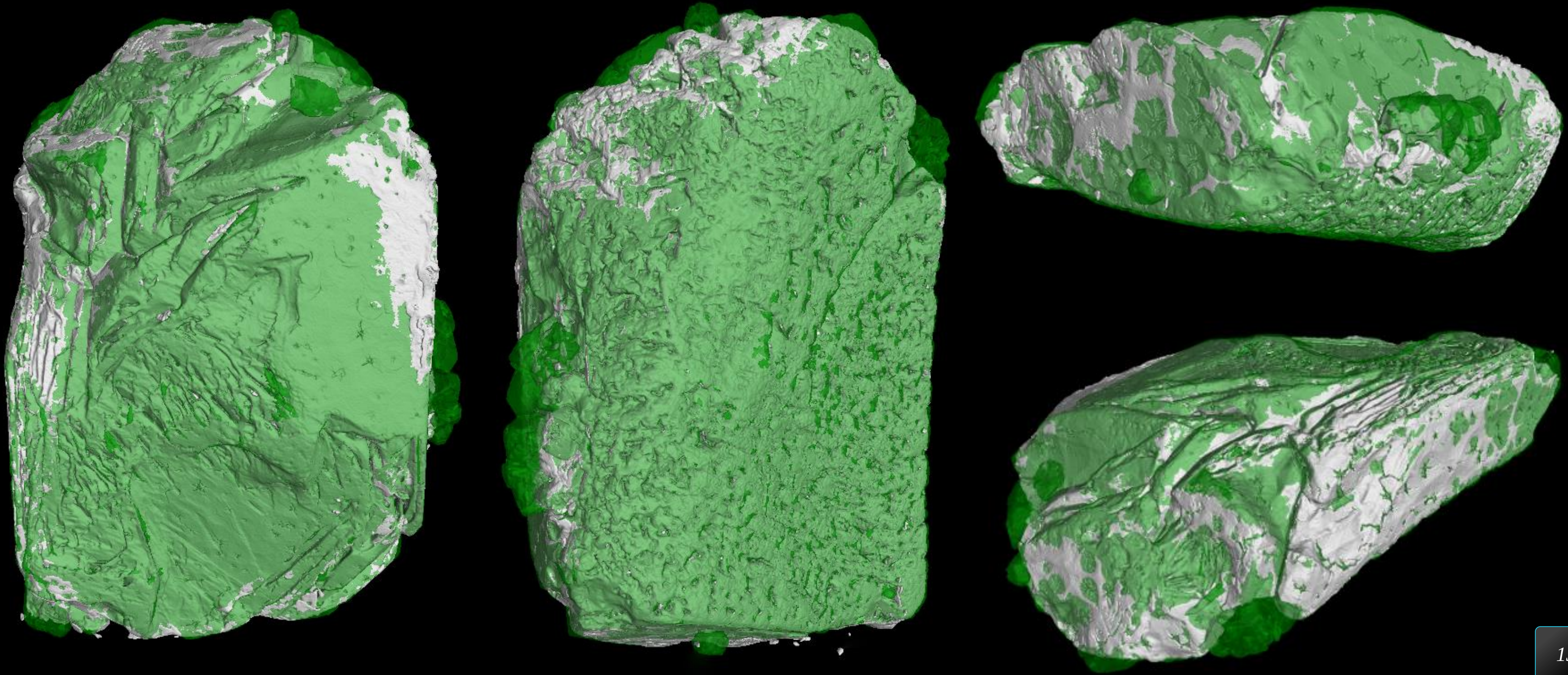
Before

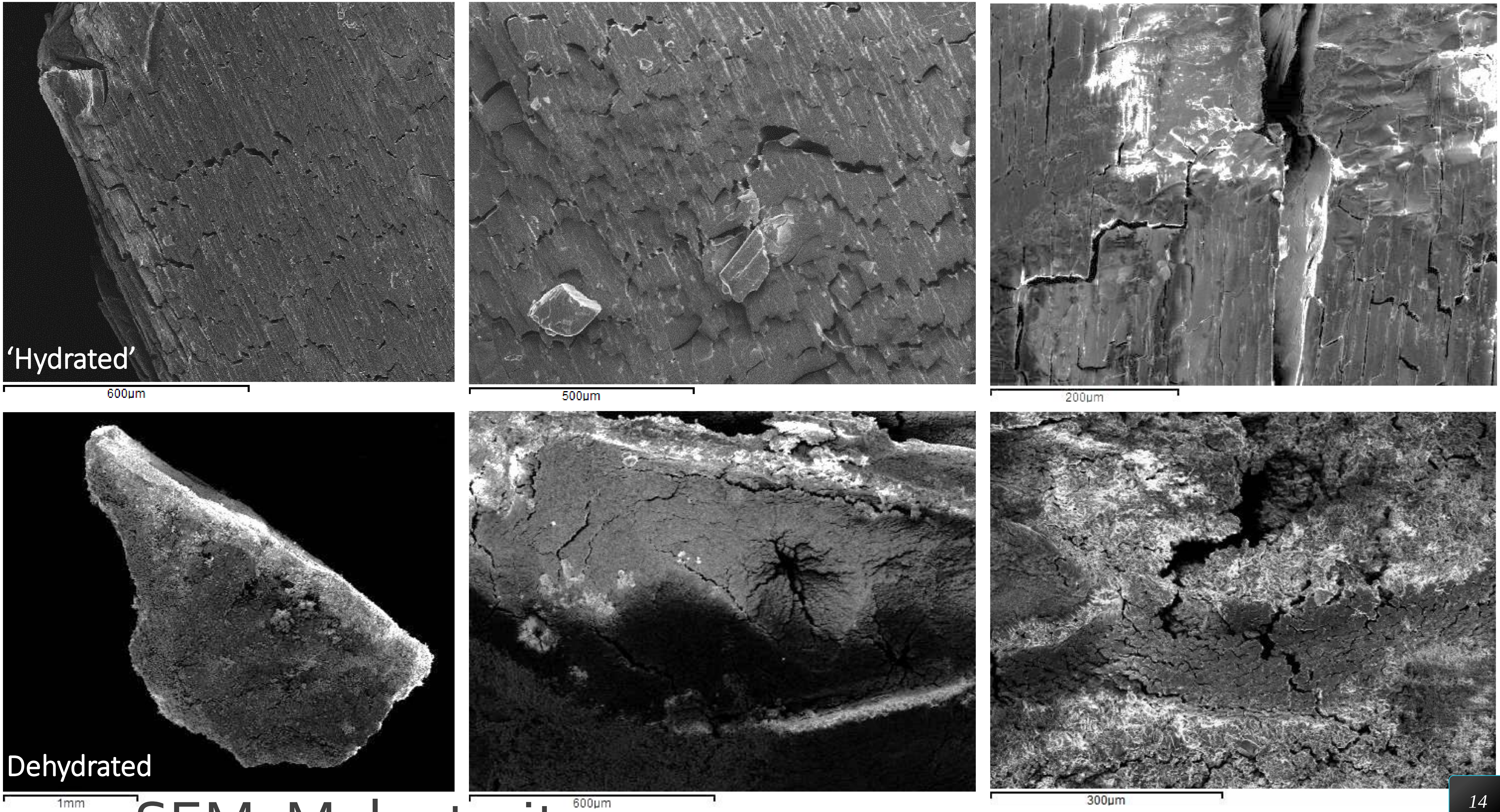
After



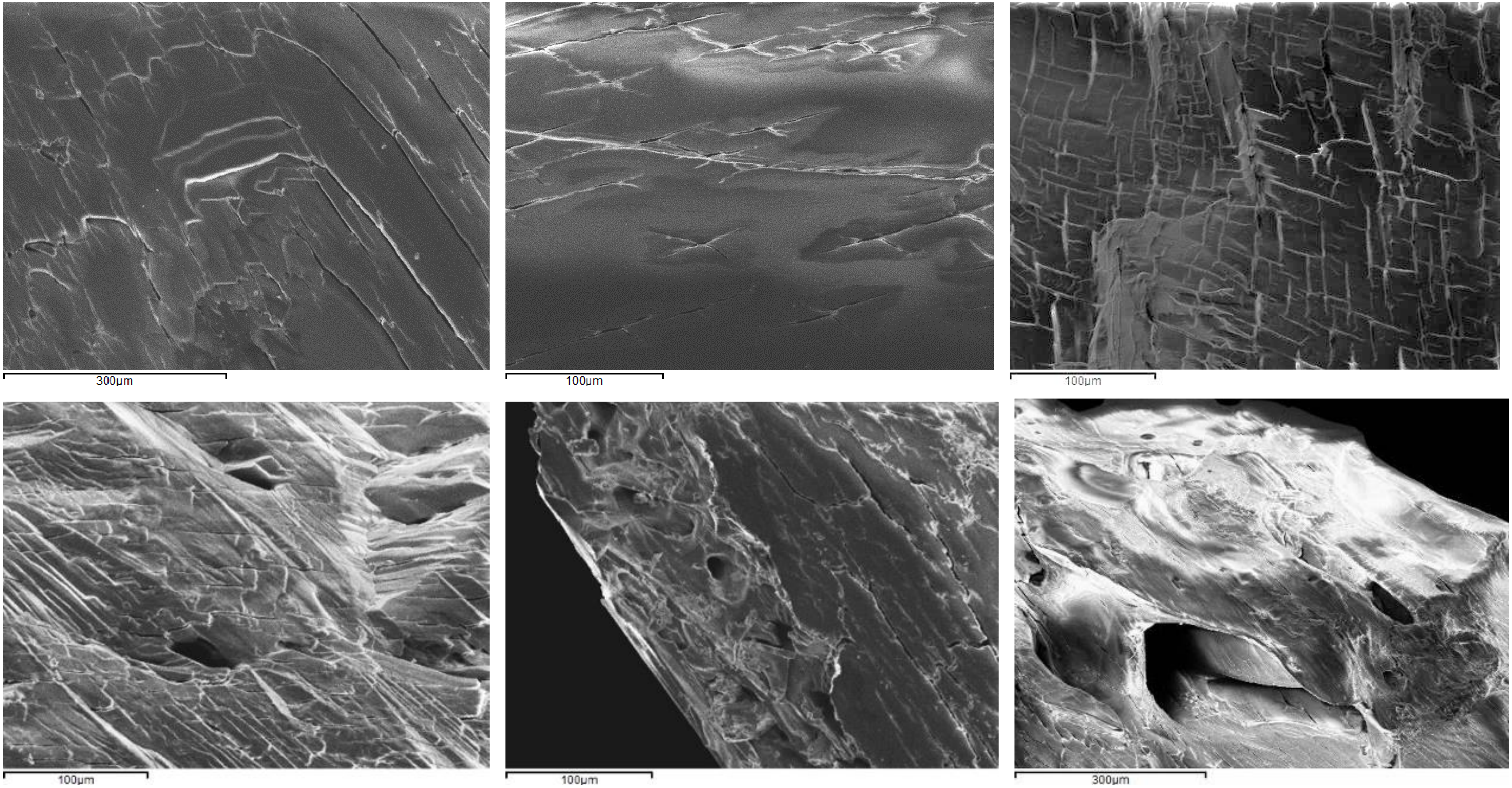
2D slices

CT scans: M1 3D overlay



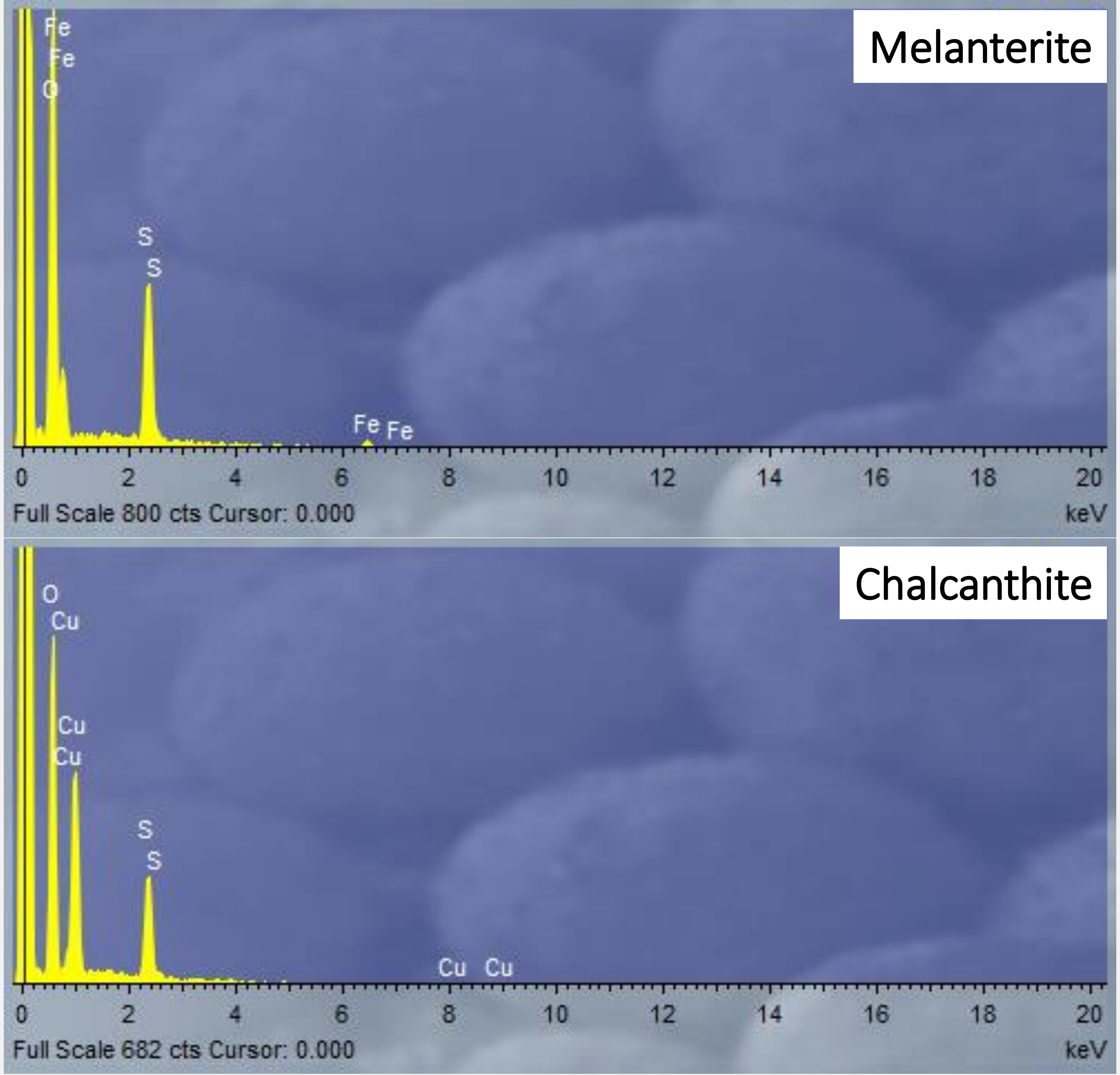


SEM: Melanterite



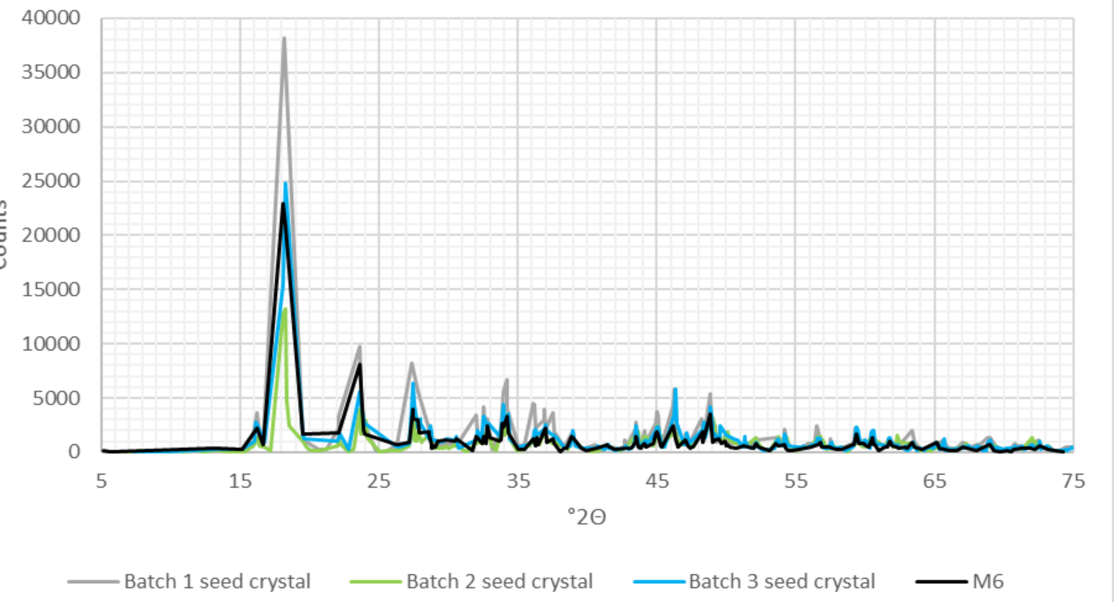
SEM: Chalcanthite

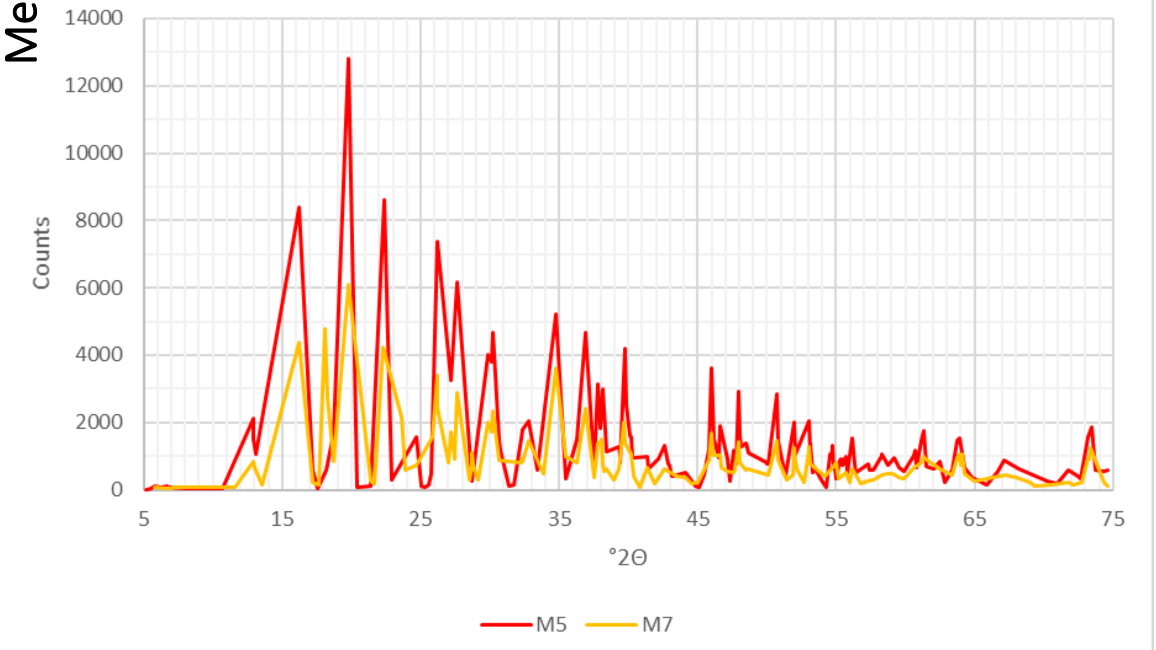
EDX


Melanterite
Fe
Fe
O
S
S
Fe Fe
0 2 4 6 8 10 12 14 16 18 20
Full Scale 800 cts Cursor: 0.000
keV
Chalcanthite
O
Cu
Cu
Cu
S
S
Cu Cu
0 2 4 6 8 10 12 14 16 18 20
Full Scale 682 cts Cursor: 0.000
keV

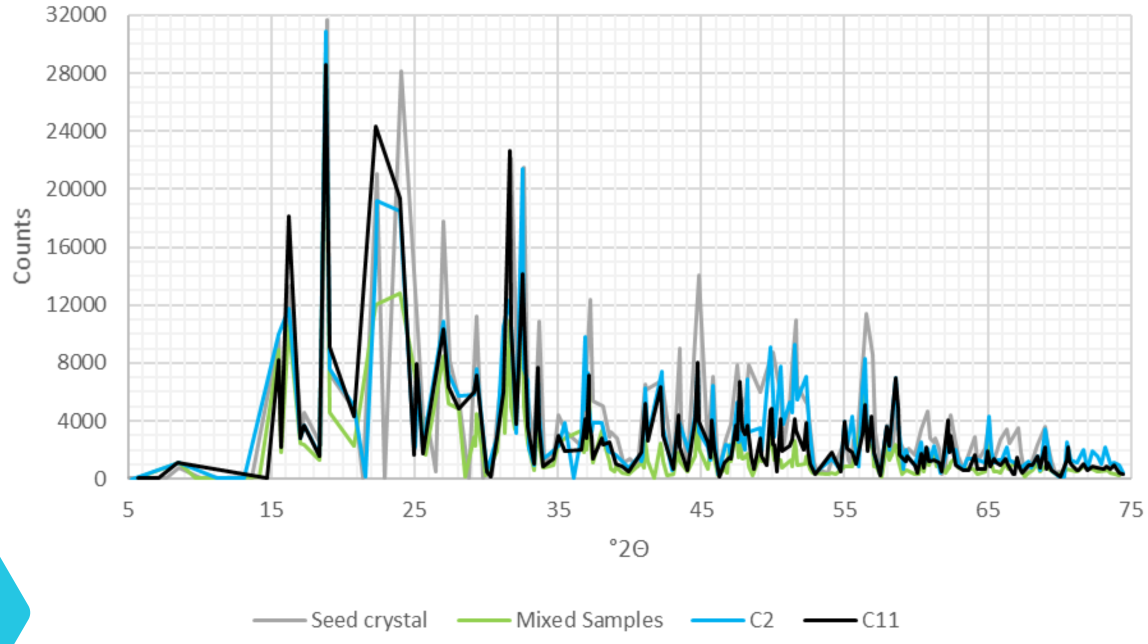
	Sample	XRD Results
Chalcanthite	seed crystal	chalcanthite
	loose flakes from mixed samples	chalcanthite
	C2	chalcanthite
	C11	chalcanthite
Melanterite	batch 1 seed crystal	melanterite
	batch 2 seed crystal	melanterite
	batch 3 seed crystal	melanterite
	M5	rozenite
	M7 surface product	rozenite, melanterite, szomolnokite
	M6	melanterite

Melanterite





Chalcanthite



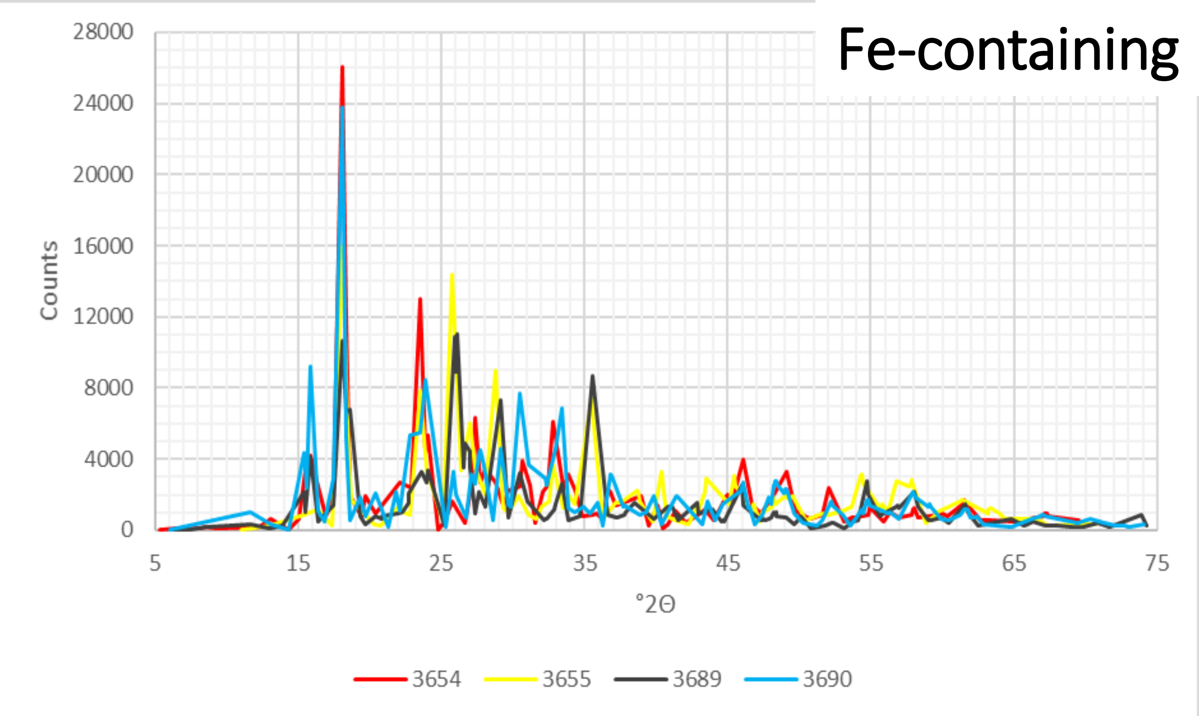
XRD: Synthetic Minerals

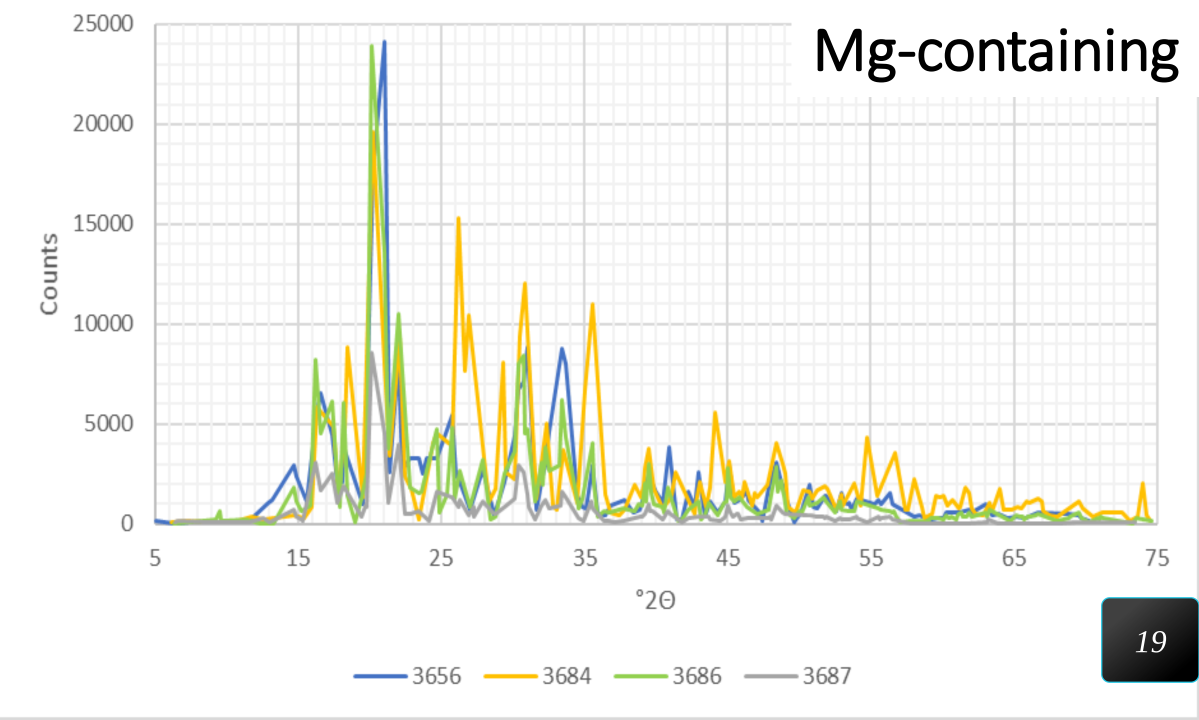
XRD: Museum Specimens

XRD: Museum Specimens

Minerals misidentified at accession

Sample #	Accession #	Listed Mineral	XRD Results
3654	83.41G.M8476	chalcanthite	siderotil & melanterite
3655	83.41G.M8504	pisanite	szomolnokite, siderotil, melanterite
3656	26.157.GR1	melanterite	hexahydrite, epsomite, jurbanite
3684	26.151.GR_	melanterite	kieserite, hexahydrite
3685	83.41G.M8482	chalcanthite	szomolnokite
3686	26.157.GR1	melanterite	hexahydrite, epsomite
3687	26.157.GR1	melanterite	hexahydrite, epsomite
3688	83.41G.M8481	chalcanthite	siderotil
3689	83.41G.M8479	chalcanthite	kieserite, siderotil, melanterite
3690	83.41G.M8479	chalcanthite	siderotil, melanterite





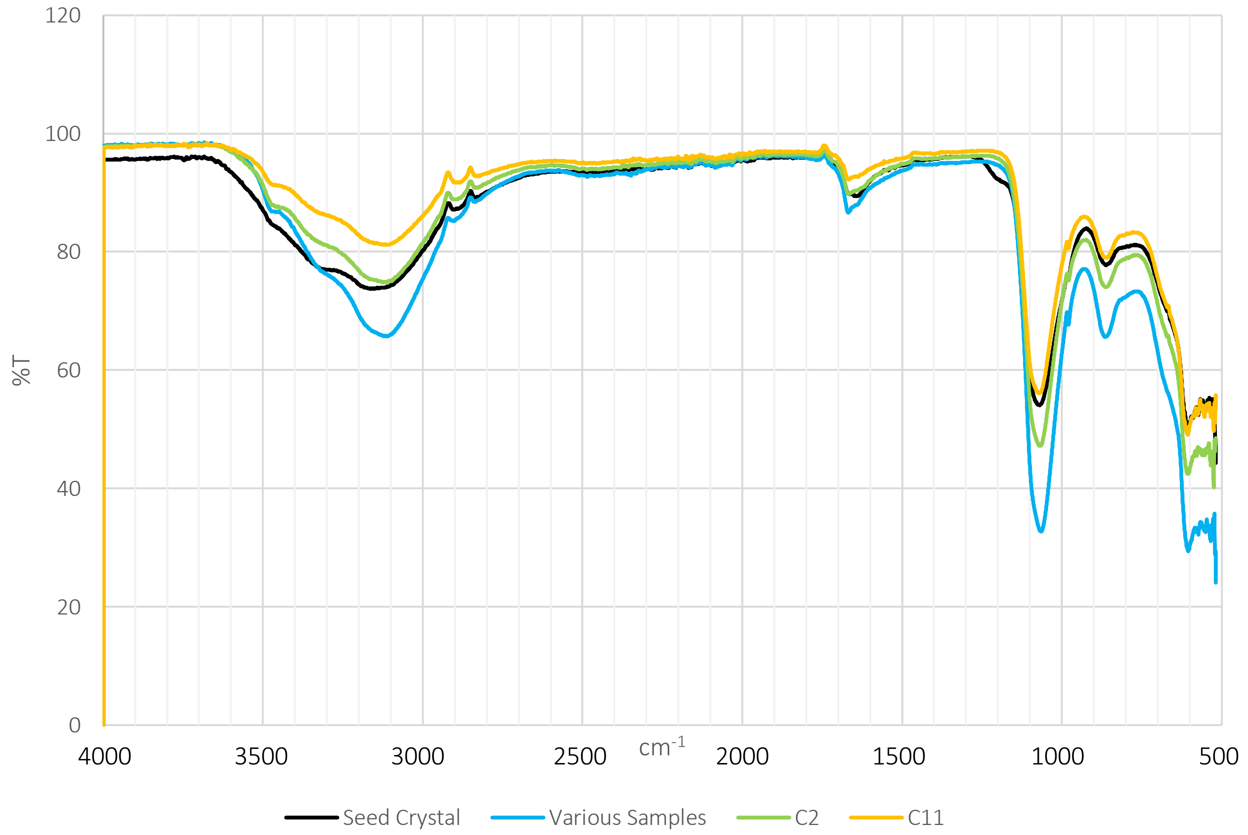
FT-IR

Melanterite v. Chalcanthite

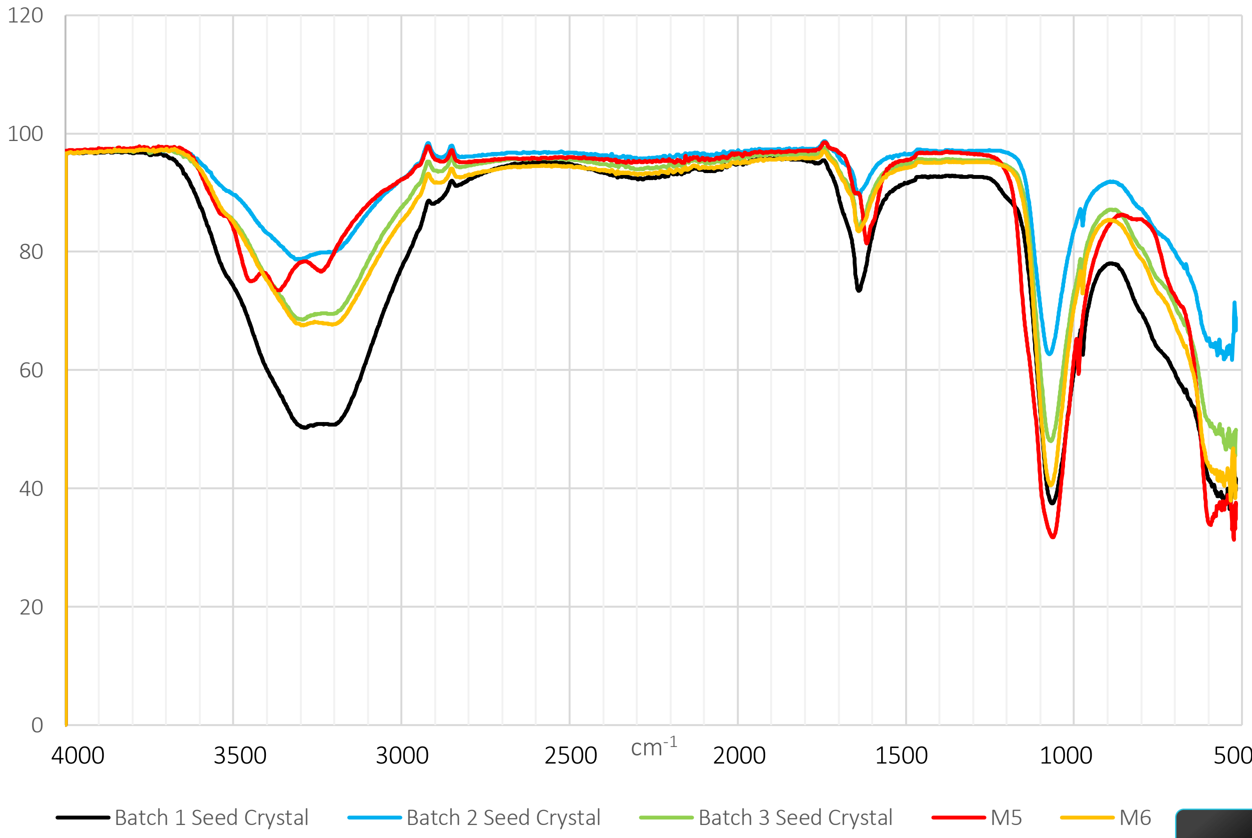
- Larger, broader H_2O stretching band
- Larger H_2O bending peak
- Doesn't have H_2O liberation peak
- Different pattern in 'fingerprint' region

M5

- Resolution & shift in H_2O stretching peaks
- Shoulder resolved in H_2O bending peak
- Different pattern in 'fingerprint' region



Chalcanthite

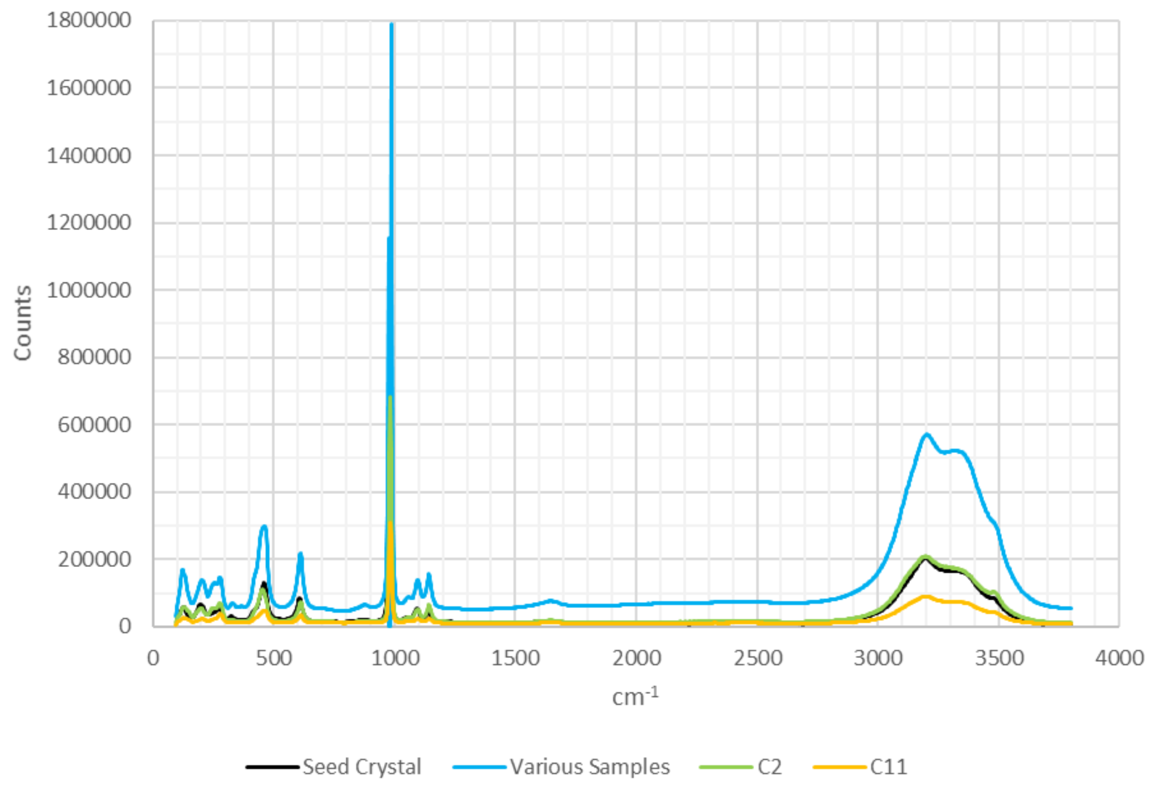


Melanterite

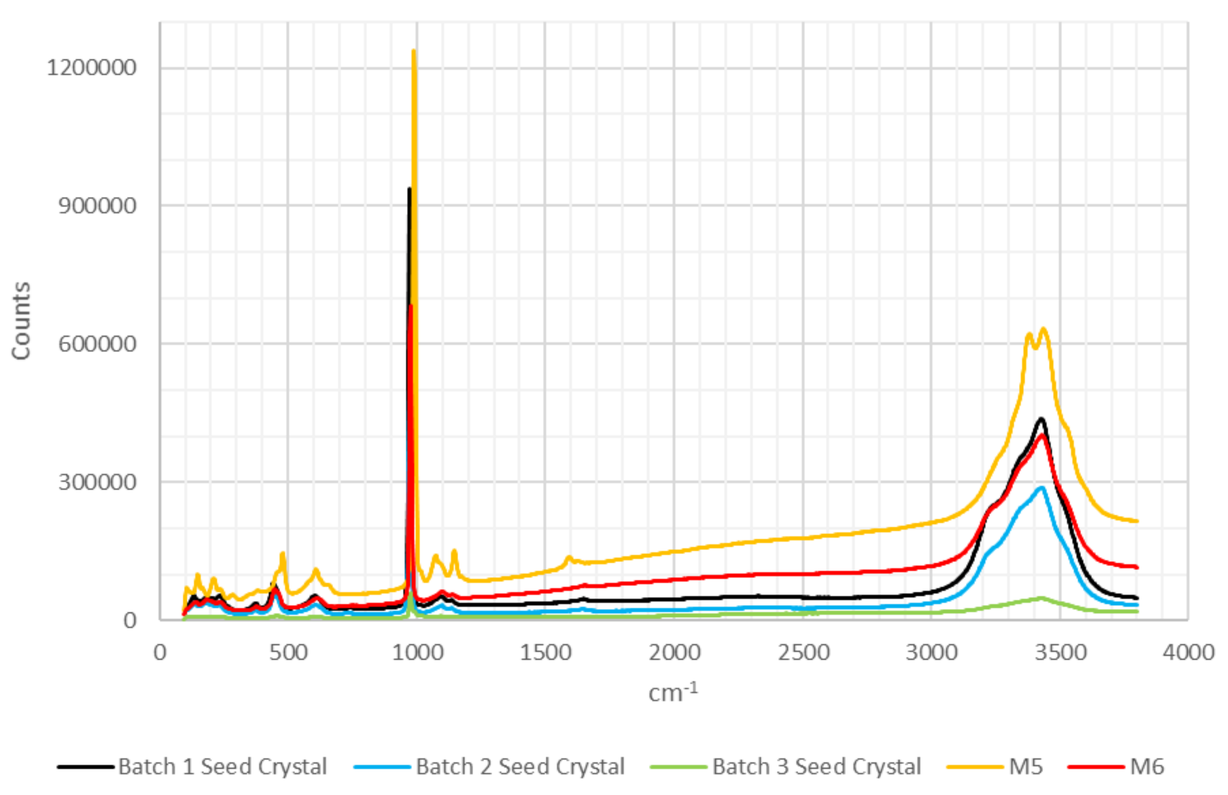
Raman Spectroscopy

$SO_4^{-2}(v_1)$ versus H_2O stretch

- Heights: chalcanthite = 30%; melanterite & rozenite = 50%
- Shift: chalcanthite = 2900-3600 cm-1; melanterite = 3100-3650; rozenite = 3200-3650
- Distance: further apart => easier to break H-bonds => more readily dehydrates



Chalcanthite



Melanterite

Assessment of Methods for Museum Use

- Most pragmatic at present = colorimetry*, photography*, XRD, FT-IR, Raman
- CT has potential

*requires refinement

	Identification	Monitoring	Access	Time/ Sample	Cost Effective	Sampling Required	Knowledge Required	Standalone Method	Practicality
Weight Measurements	0	2	3	1	3	0	1	0	1
Colorimetry	0	2	2	1	3	0	2	3	2
Photography	0	3	3	1-3	1-3	0	1-2	3	3
CT	0	2	1	3	1	0-2	2	2	1
X-radiography	0	2	1	2	1	0-2	2	1	1
SEM	2	0	2	3	1	0-2	2	1	1
EDX	3	3	1	1	1	0-2	2	0	1
XRD	3	3	2	2	2	1	2-3	2	2
FT-IR	3	3	2-3	1	3	1	1-2	2	3
Raman	3	3	1-2	2	2	1	1-2	2	2

Conclusions

Dehydrating melanterite and chalcanthite produced detectable change

Inconclusive whether synthetic crystals present changes similar to those of natural specimens

All methods can be used to determine changes to minerals

Colorimetry, photography, XRD, FT-IR, & Raman spectroscopy presently most pragmatic for average museum

Areas of Further Research

October-December 2019

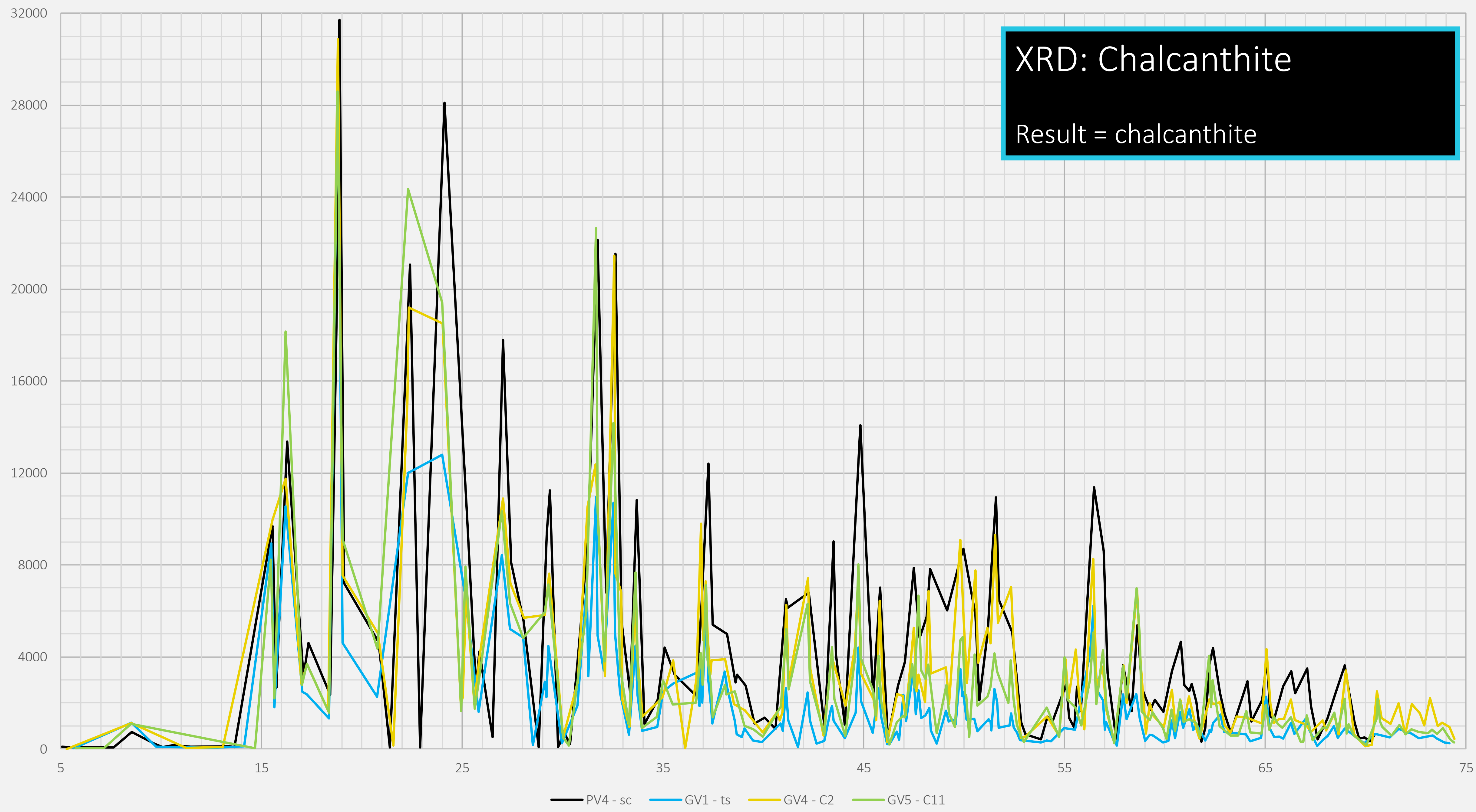
- Defining & quantifying damage
  - Species-specific?
- Detailed review of NMC mineral store
  - Visual identification of sensitive minerals
  - Narrow focus
- Assessment of sample acquisition

2020-2022

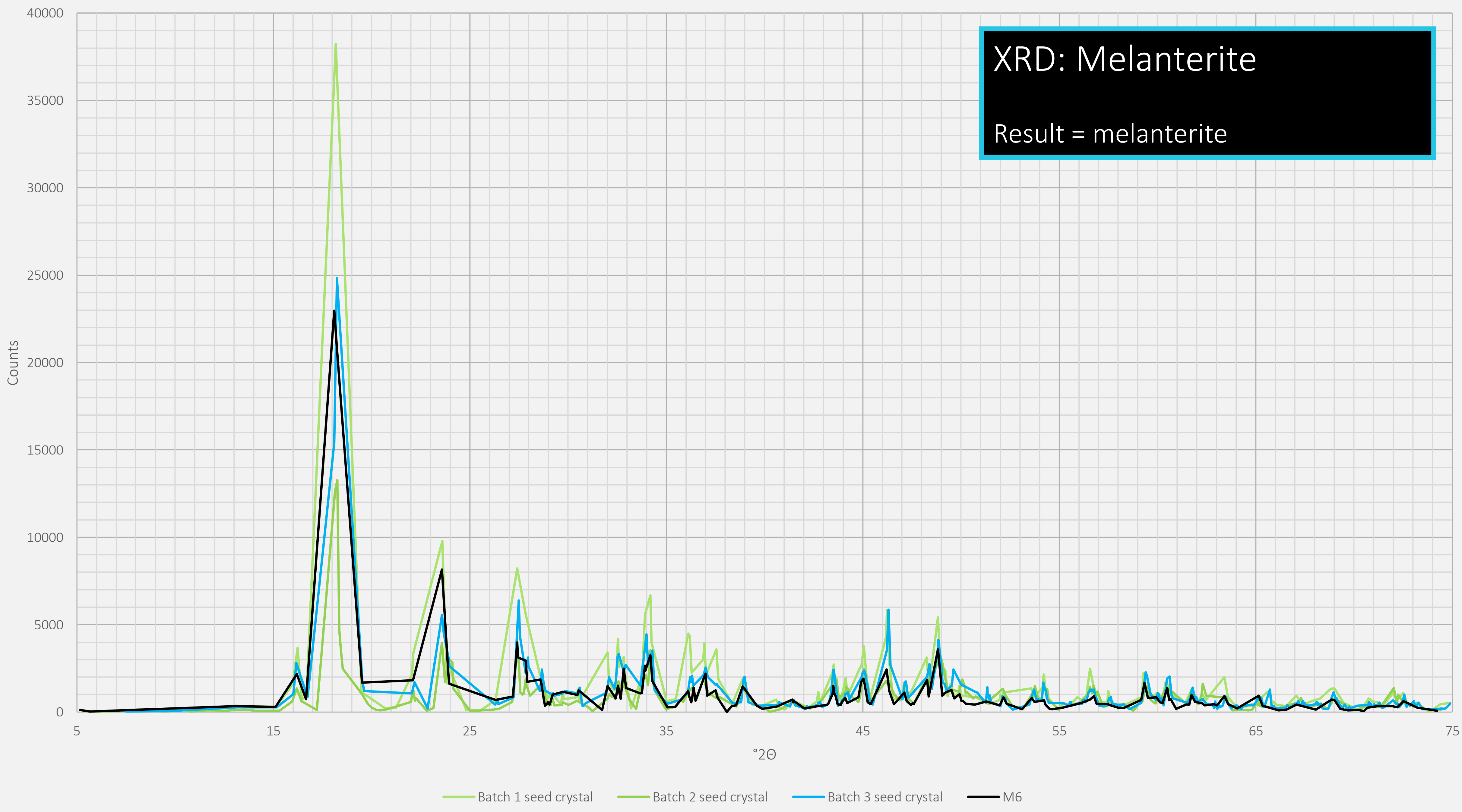
- Rehydration study of melanterite & chalcanthite
- Long-term study on use of Parafilm as moisture barrier
- Additional analytical techniques
  - ESEM
  - XRF
- Utilizing digital technologies
  - 3D scanning / photogrammetry
  - AI

Thank You

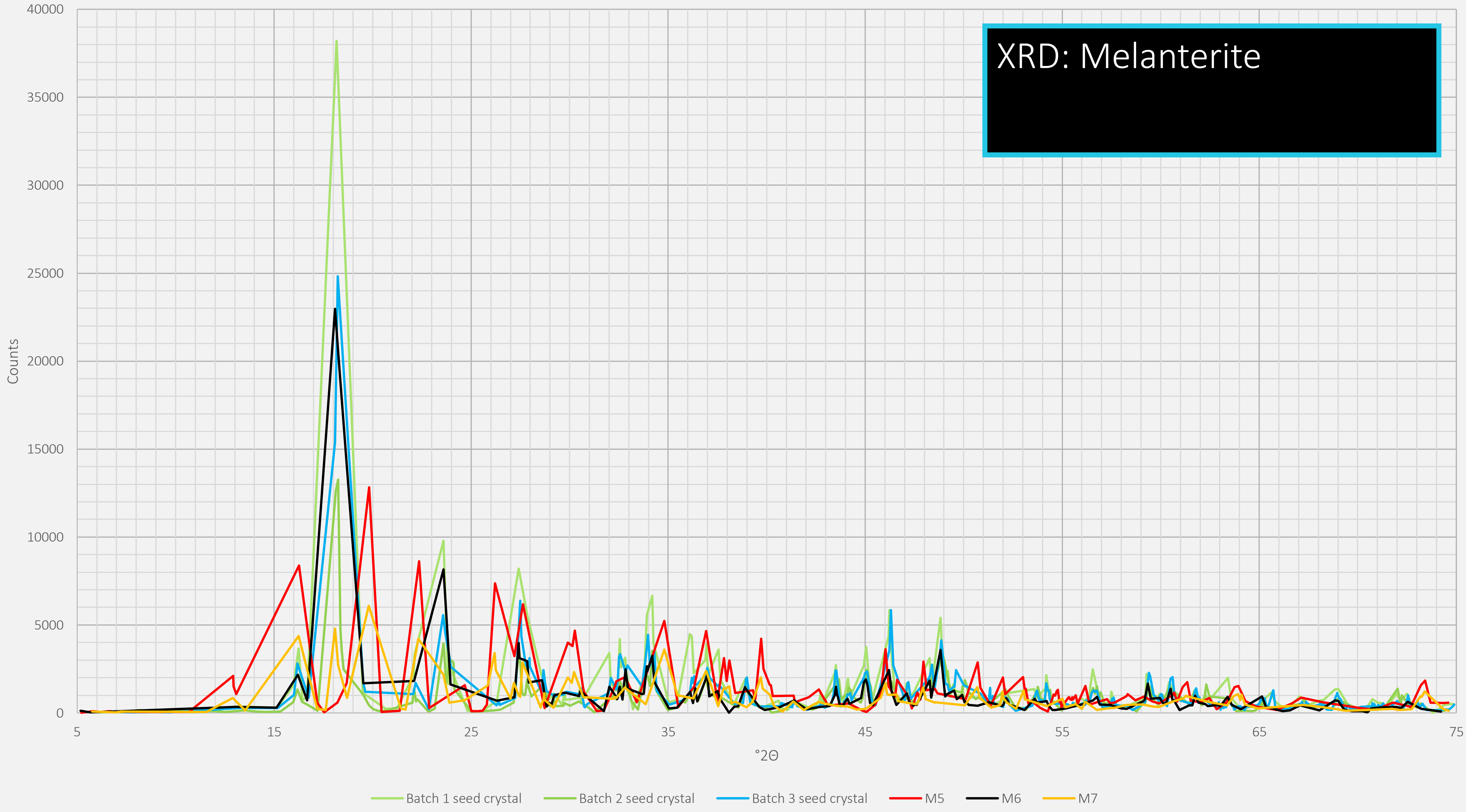
- **Dr. Heather Viles**, University of Oxford
- **Dr. Christian Baars, Dr. Jana Horak, Tom Cotterell, Amanda Valentine-Baars**, National Museum Wales Cardiff
- **James Earl, James Appleby, Robert Wells**, OR3D
- **David Howell**, Weston Library, University of Oxford
- **Prof. Tony Parker**, Rutherford-Appleton Laboratories
- **Chris Doherty**, University of Oxford



XRD: Chalcanthite
Result = chalcanthite
32000
28000
24000
20000
16000
12000
8000
4000
0
5
15
25
35
45
55
65
75
PV4 - sc
GV1 - ts
GV4 - C2
GV5 - C11

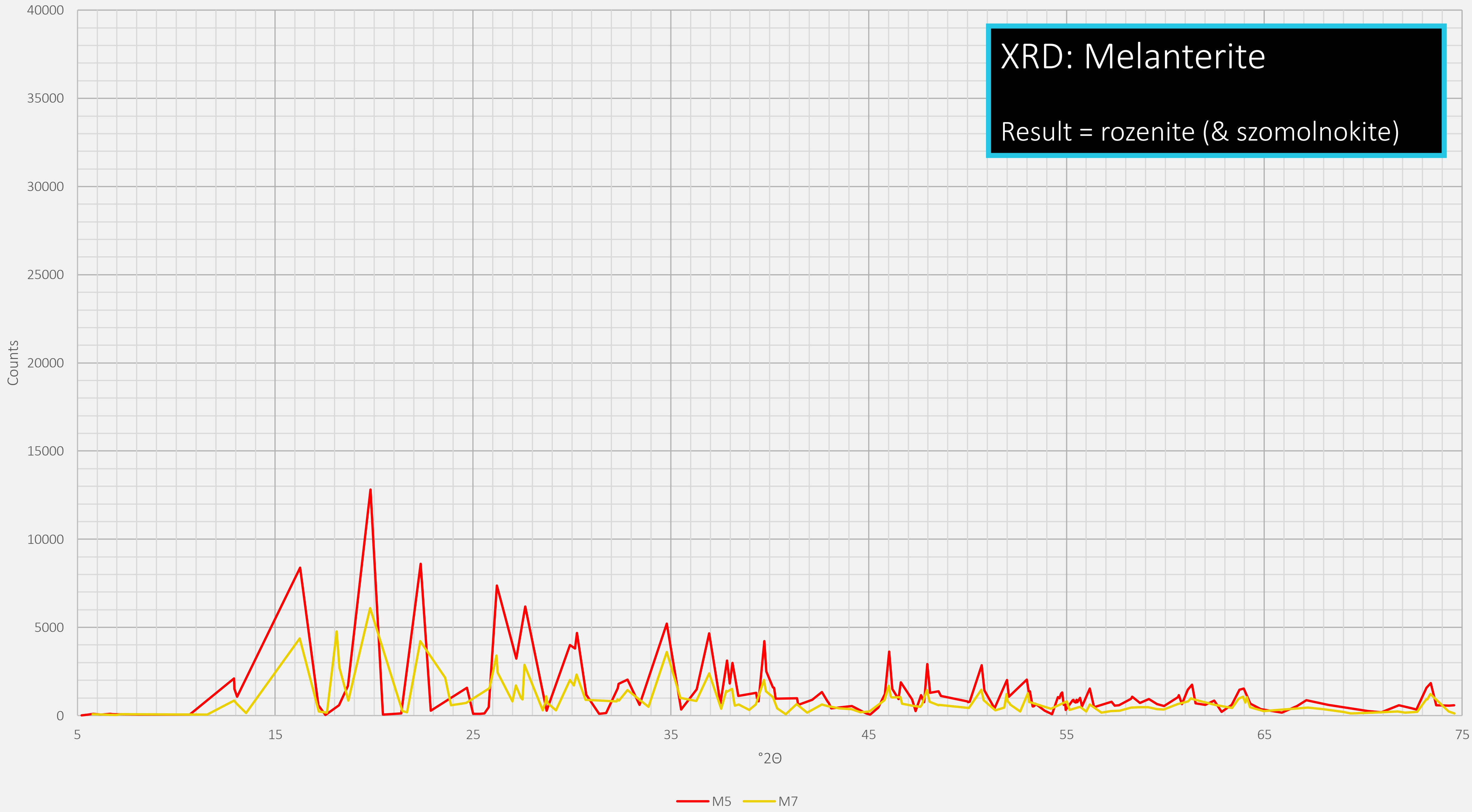

XRD: Melanterite
Result = melanterite
Counts
°2Θ
40000
35000
30000
25000
20000
15000
10000
5000
0
5
15
25
35
45
55
65
75
Batch 1 seed crystal
Batch 2 seed crystal
Batch 3 seed crystal
M6

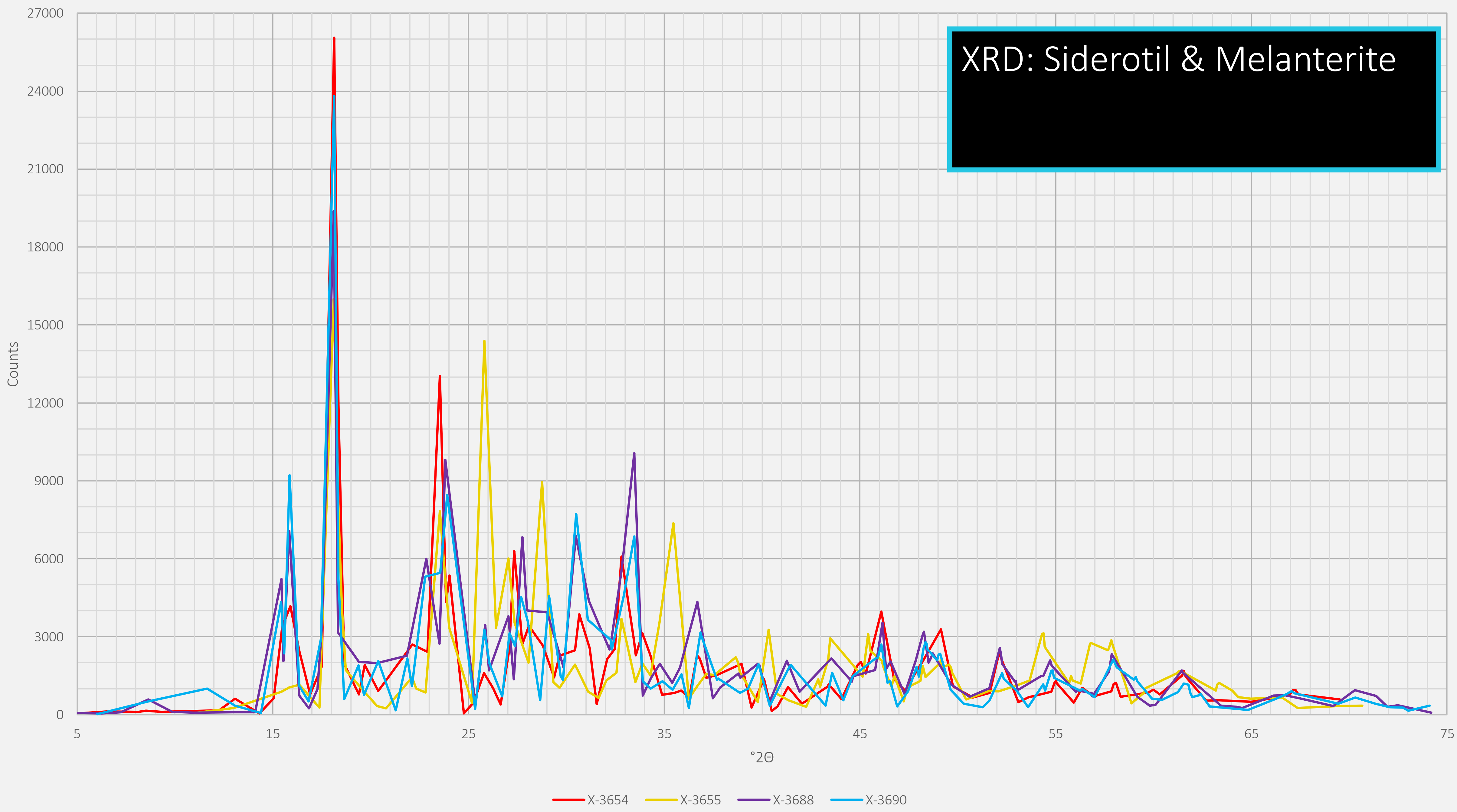
XRD: Melanterite

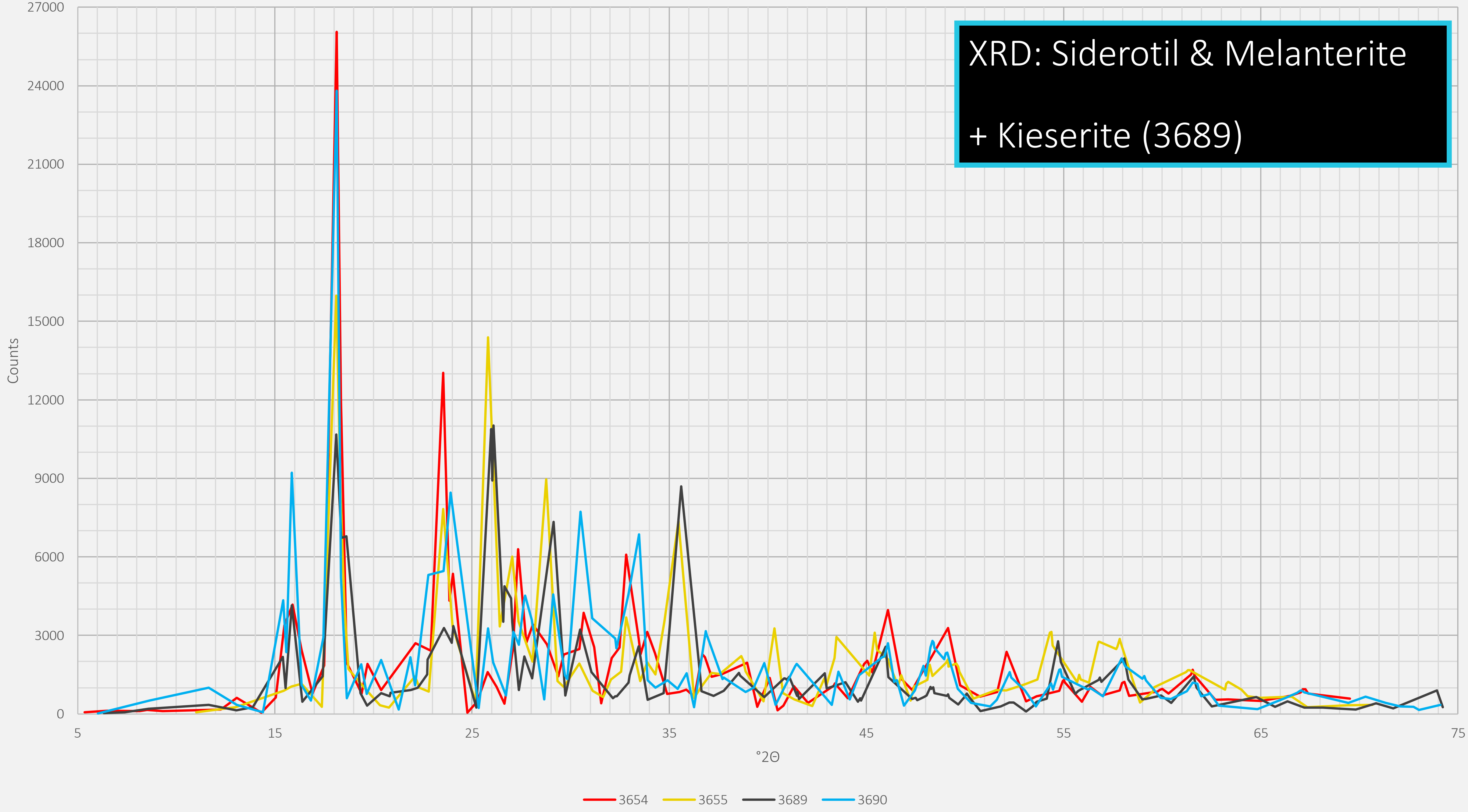


XRD: Melanterite

Result = rozenite (& szomolnokite)

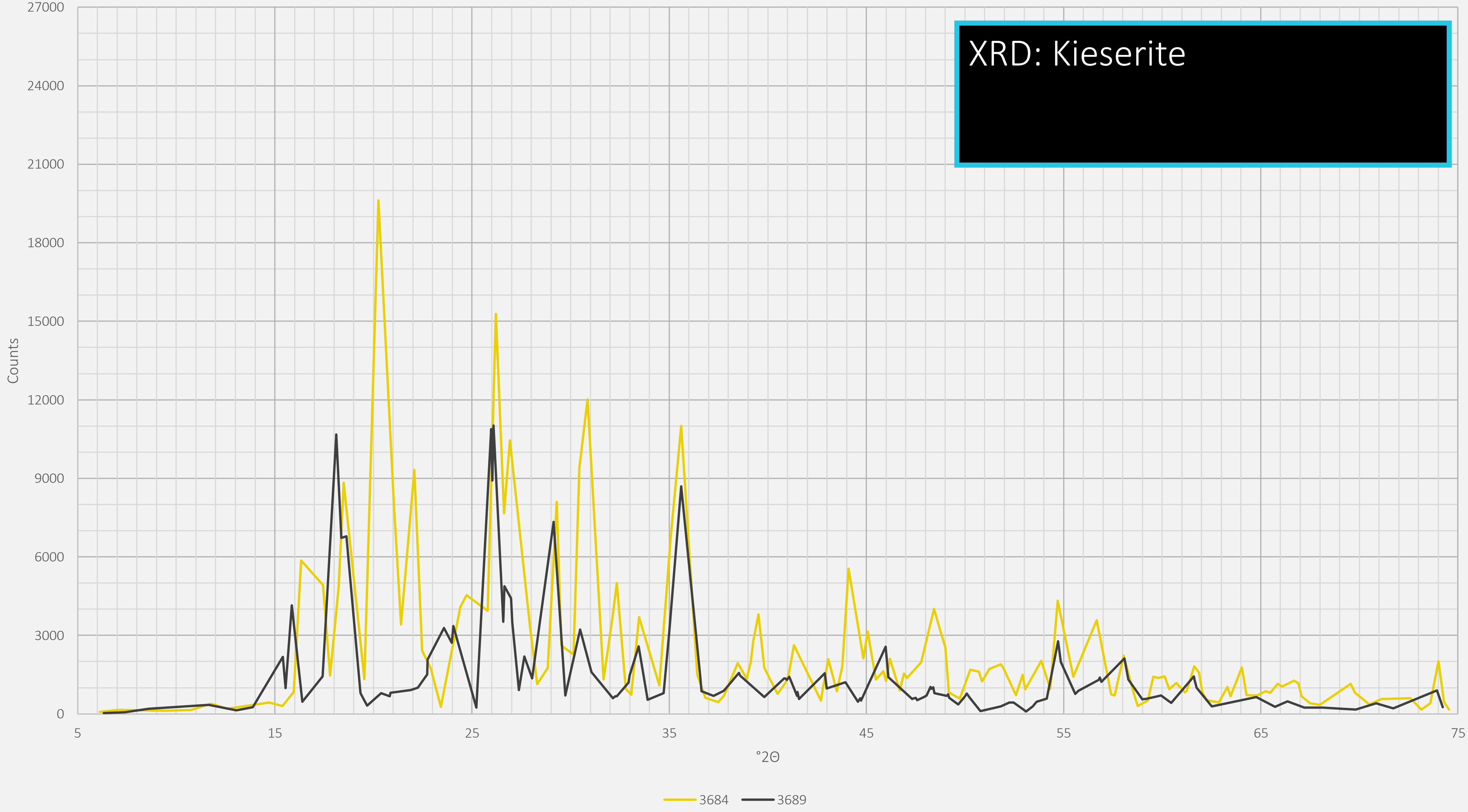


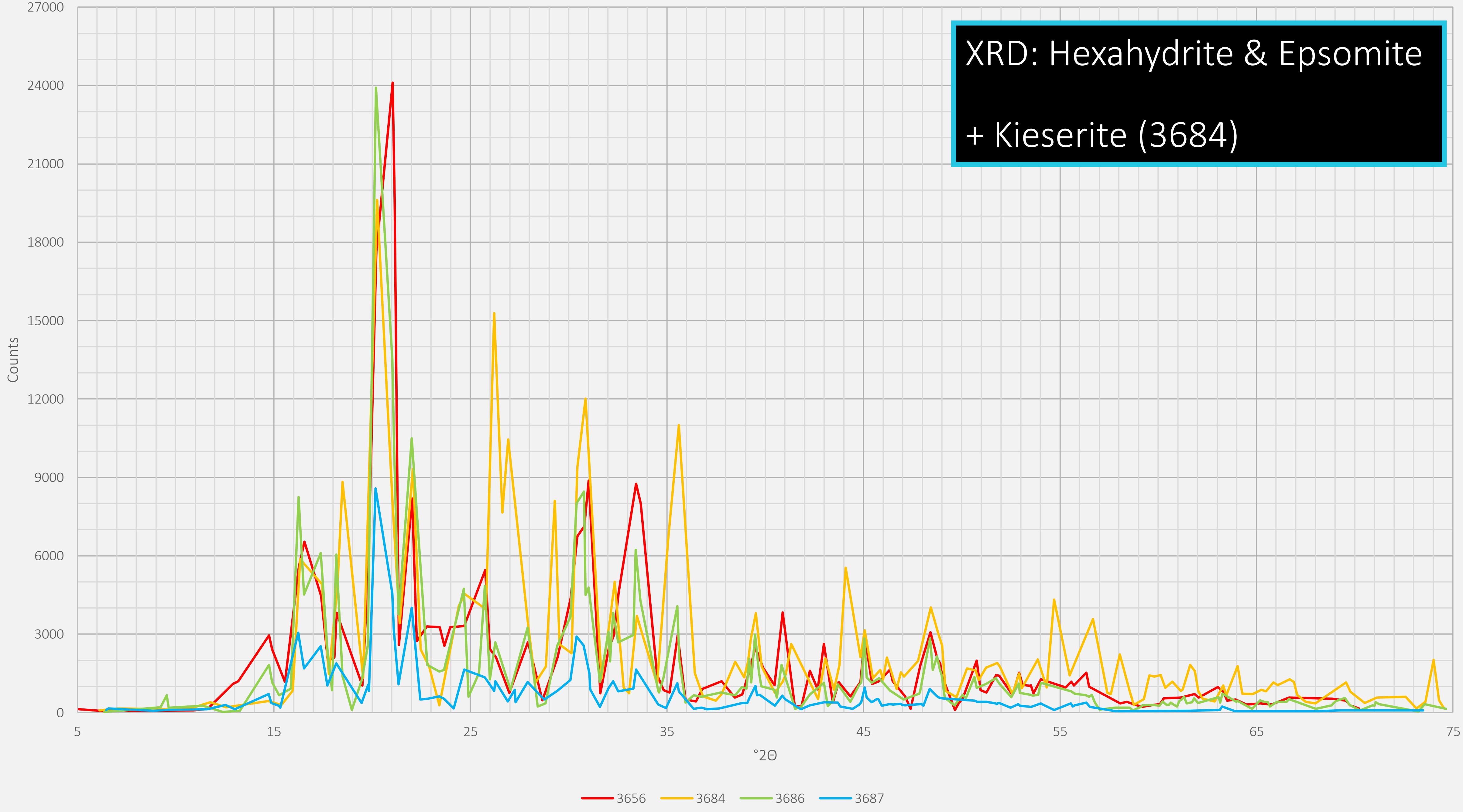

XRD: Siderotil & Melanterite
Counts
27000
24000
21000
18000
15000
12000
9000
6000
3000
0
5
15
25
35
45
55
65
75
°2Θ
X-3654
X-3655
X-3688
X-3690



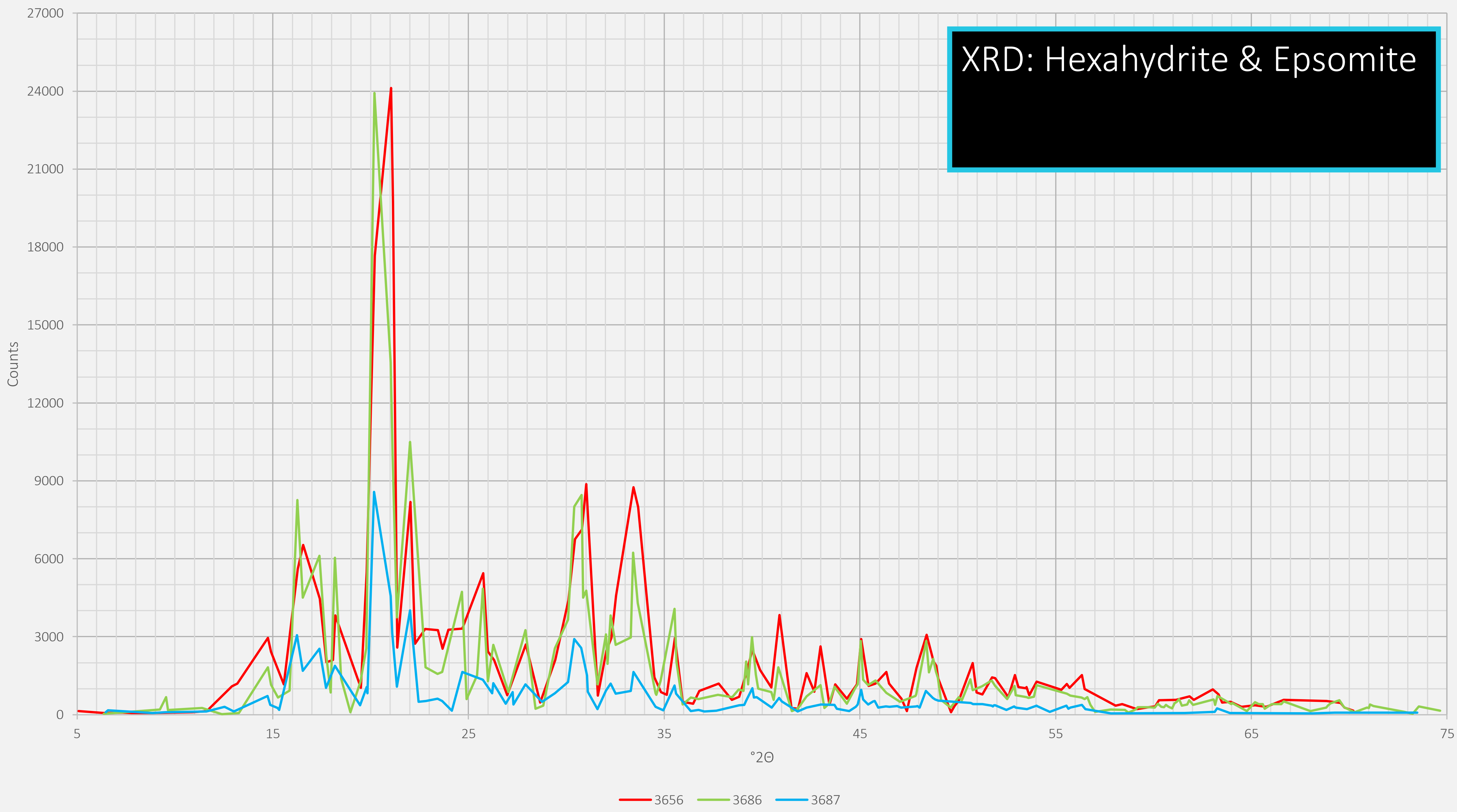
XRD: Siderotil & Melanterite
+ Kieserite (3689)
Counts
27000
24000
21000
18000
15000
12000
9000
6000
3000
0
5
15
25
35
45
55
65
75
°2Θ
3654
3655
3689
3690

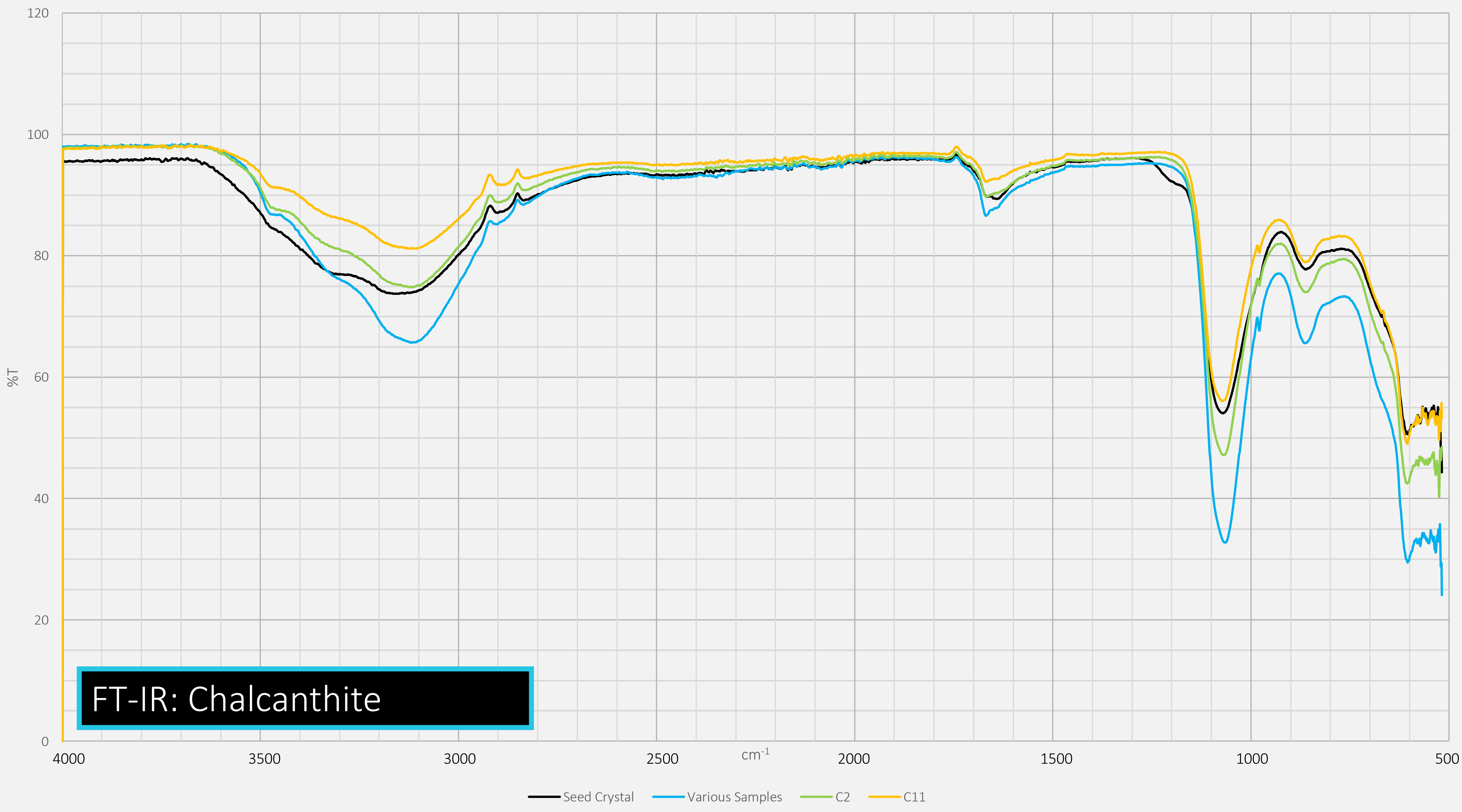
XRD: Kieserite



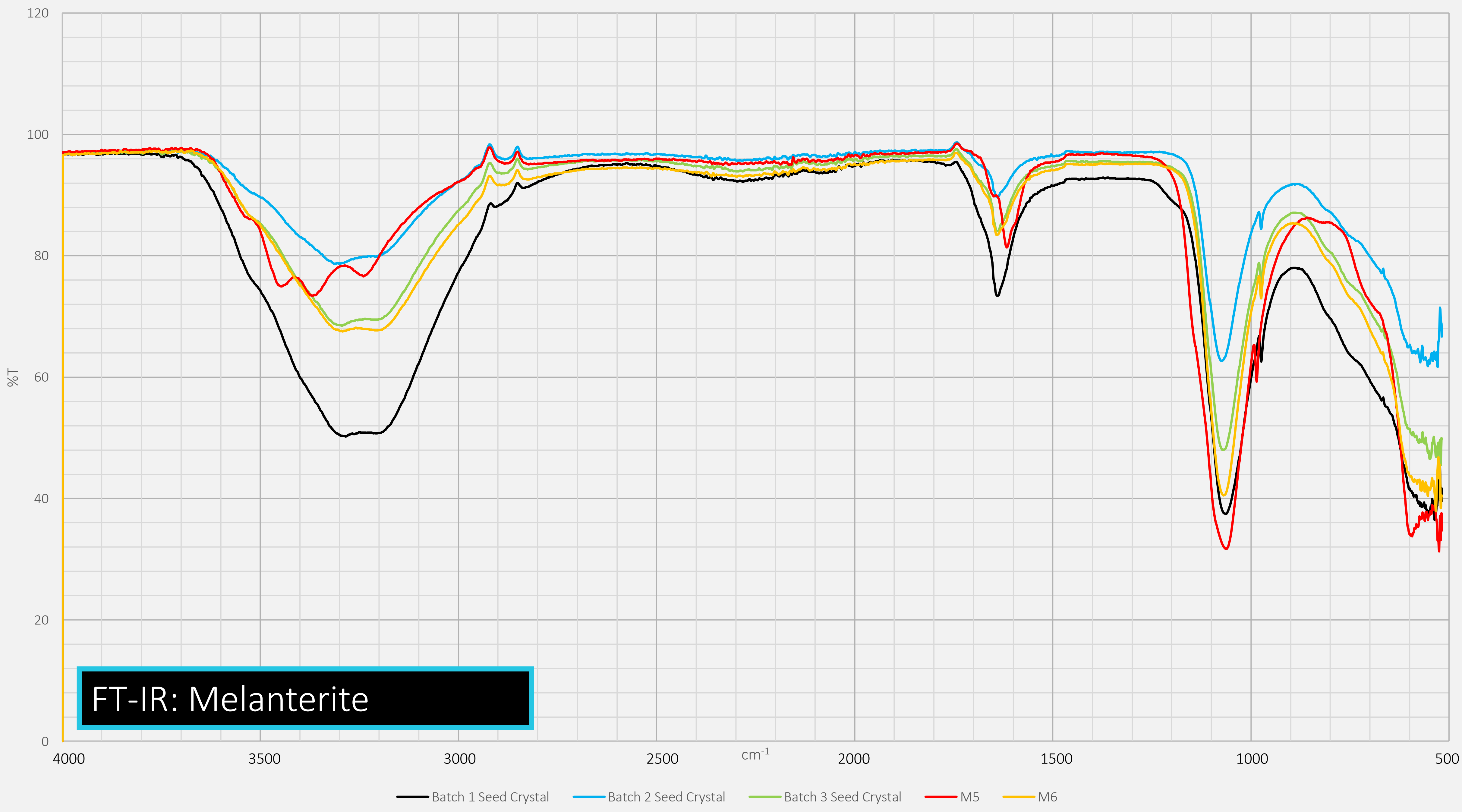


XRD: Hexahydrite & Epsomite
+ Kieserite (3684)
Counts
27000
24000
21000
18000
15000
12000
9000
6000
3000
0
5
15
25
35
45
55
65
75
°2Θ
3656
3684
3686
3687


XRD: Hexahydrite & Epsomite
Counts
27000
24000
21000
18000
15000
12000
9000
6000
3000
0
5
15
25
35
45
55
65
75
°2Θ
3656
3686
3687



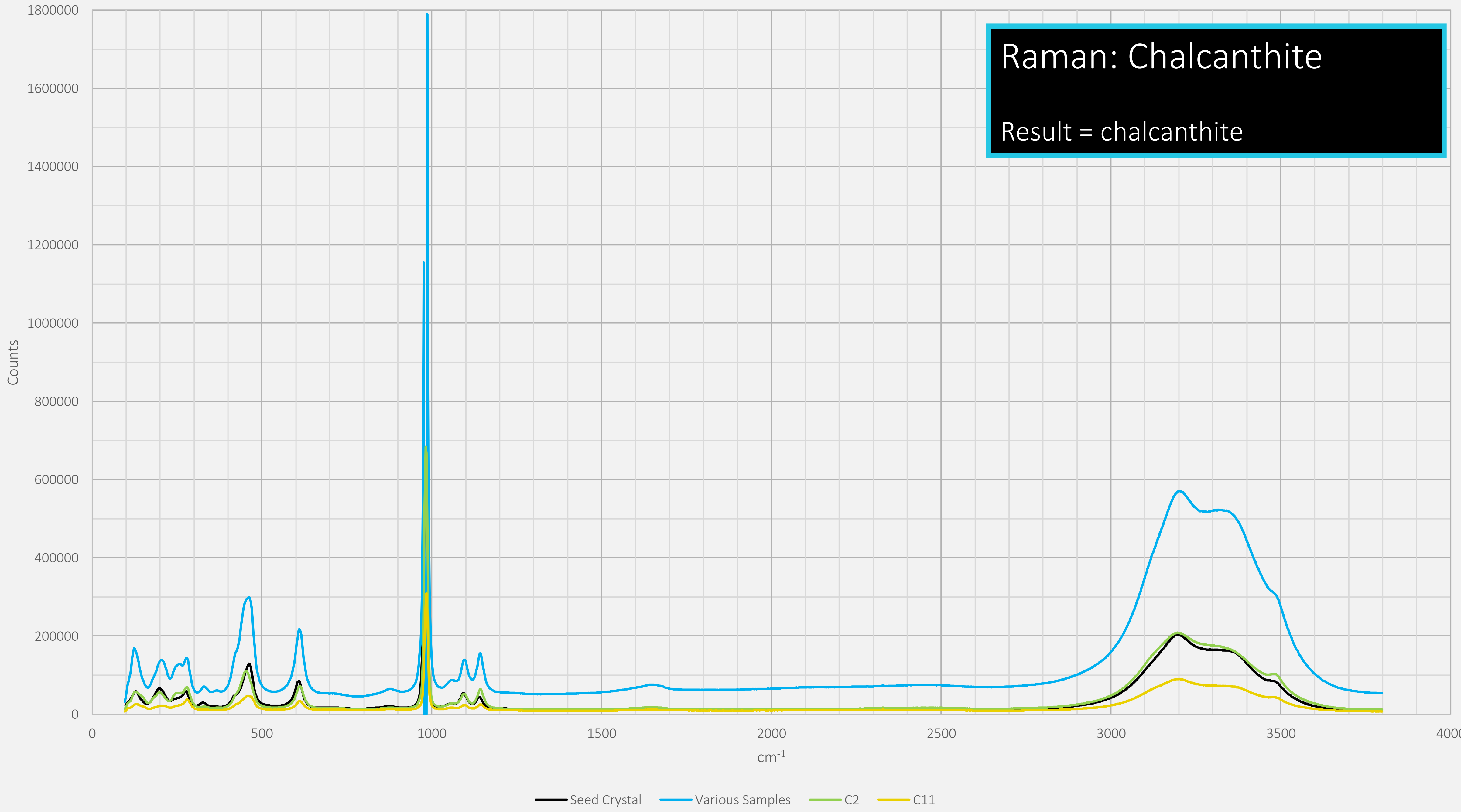
FT-IR: Chalcanthite
%T
cm-1
120
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
Seed Crystal
Various Samples
C2
C11



FT-IR: Melanterite
%T
120
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
cm-1
Batch 1 Seed Crystal
Batch 2 Seed Crystal
Batch 3 Seed Crystal
M5
M6

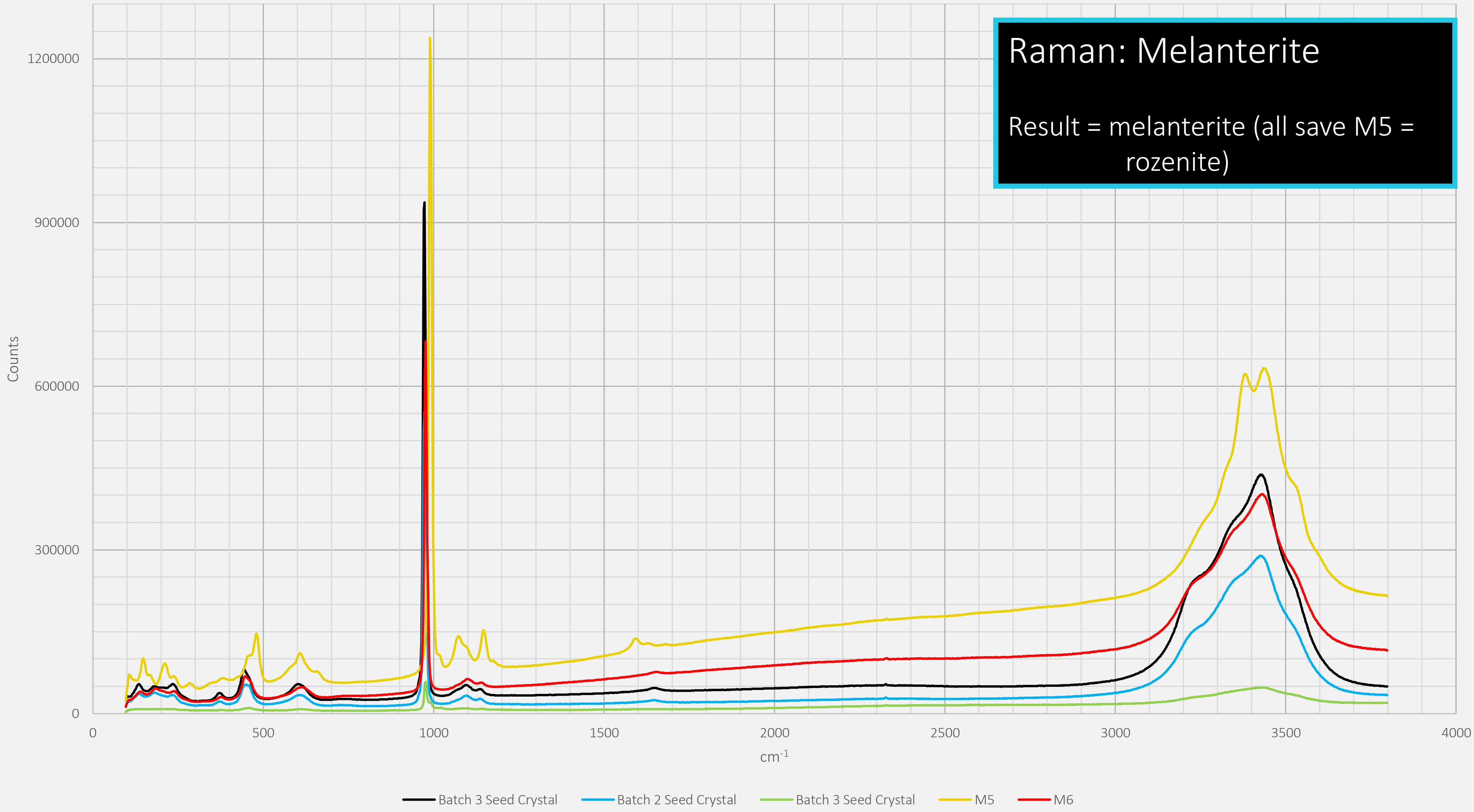
Raman: Chalcanthite

Result = chalcanthite



Raman: Melanterite

Result = melanterite (all save M5 = rozenite)



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