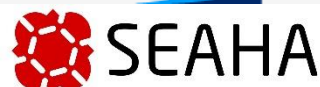


Cracking it Open:

Addressing Mineral Instability within Museum Environments

Kathryn Royce & Dr. Christian Baars



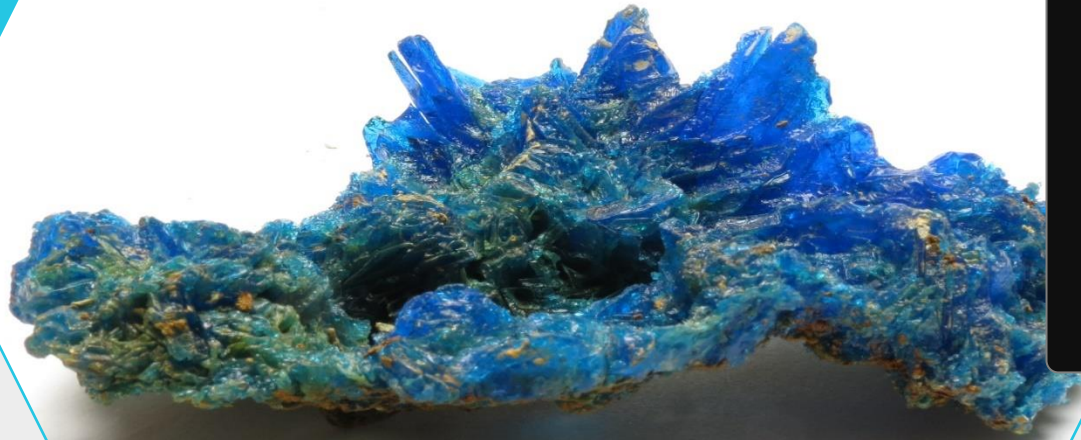
EPSRC CENTRE FOR DOCTORAL TRAINING
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ARTS HERITAGE AND ARCHAEOLOGY

Minerals ≠ Stable Objects

1992 – 350 of 3,500 known minerals

Nov. 2018 – ? of 5,400 identified minerals

How many more are vulnerable?



Why are some minerals less stable than others?

Diversity



Metastability

Variable
Conditions



Consequences of Inappropriate Conditions

Temperature

- Decrepitation
- Dissociation
- Fracture
- Increased reaction rate
- Polymorphism
- Pseudomorphism
- Sublimation
- Volatization



Relative Humidity (RH)

- Corrosion / oxidation
- Cracking
- Dehydration
- Deliquescence
- Efflorescence
- Hydration
- Swelling
- Water film formation

Pollutants

- Corrosion
- Efflorescence
- Moisture retention
- Surface reactions

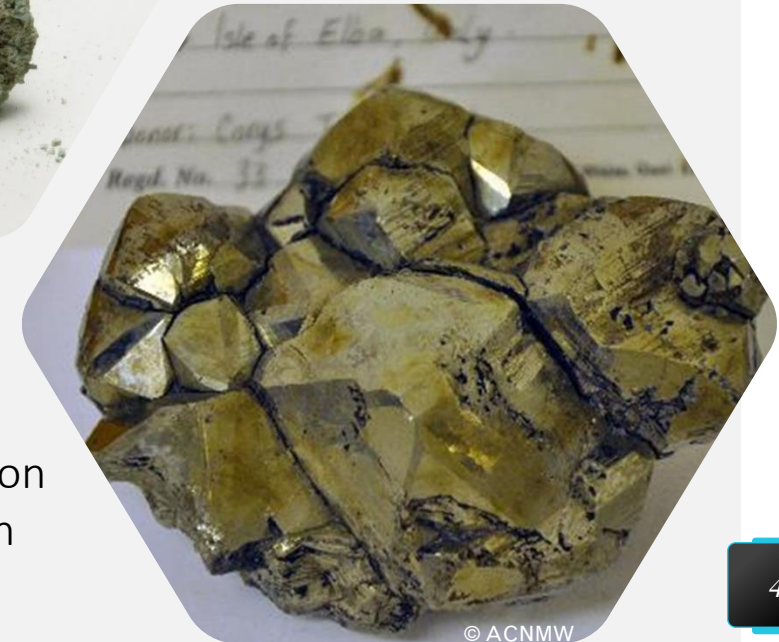
Light

- Chemical & physical alterations
- Fading / darkening
- Loss of colour / fluorescence
- Surface reactions
- Other heat-related effects



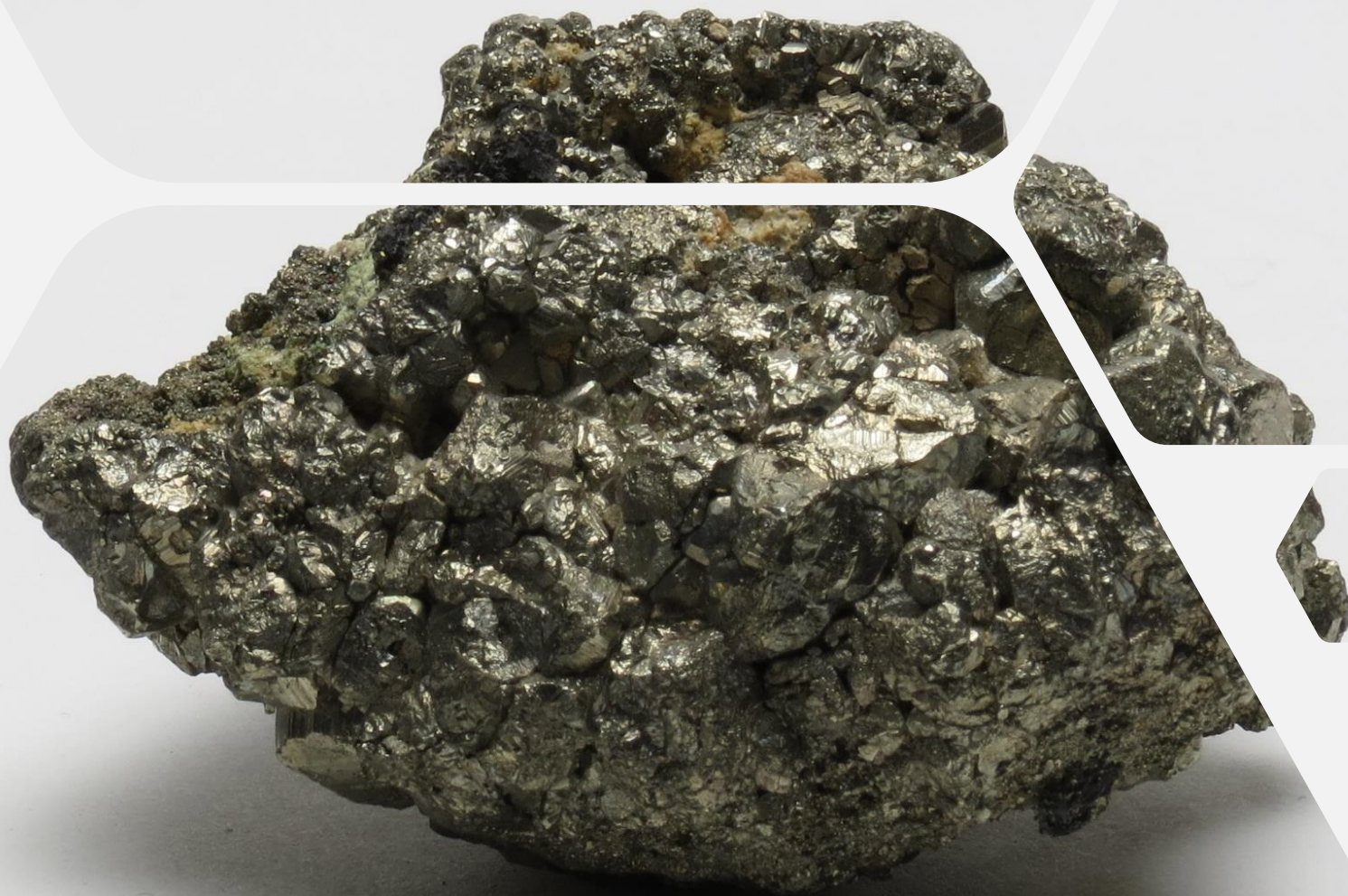
Stresses

- Cracking
- Crumbling
- Decrepitation
- Dissociation
- Fracture



© ACNMW

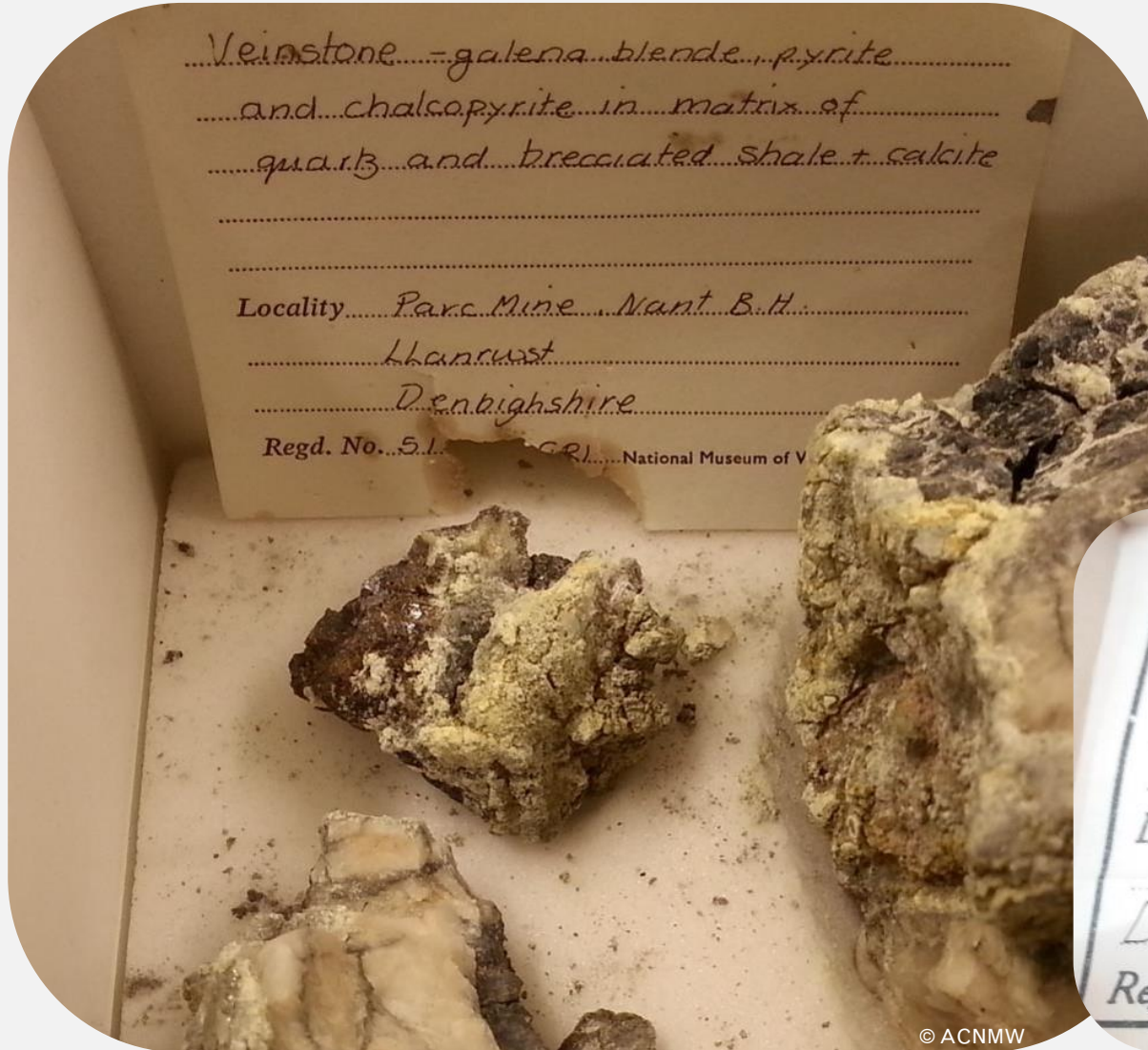
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Pyrite & Marcasite

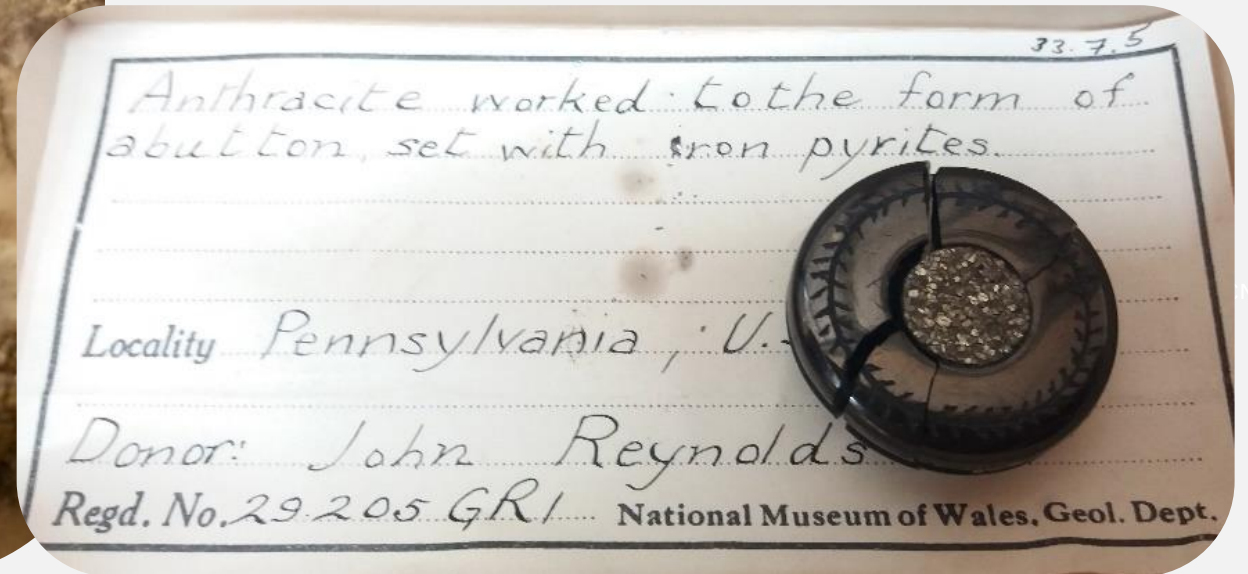
An infamous example

Pyrite & marcasite deterioration has long been a recorded issue

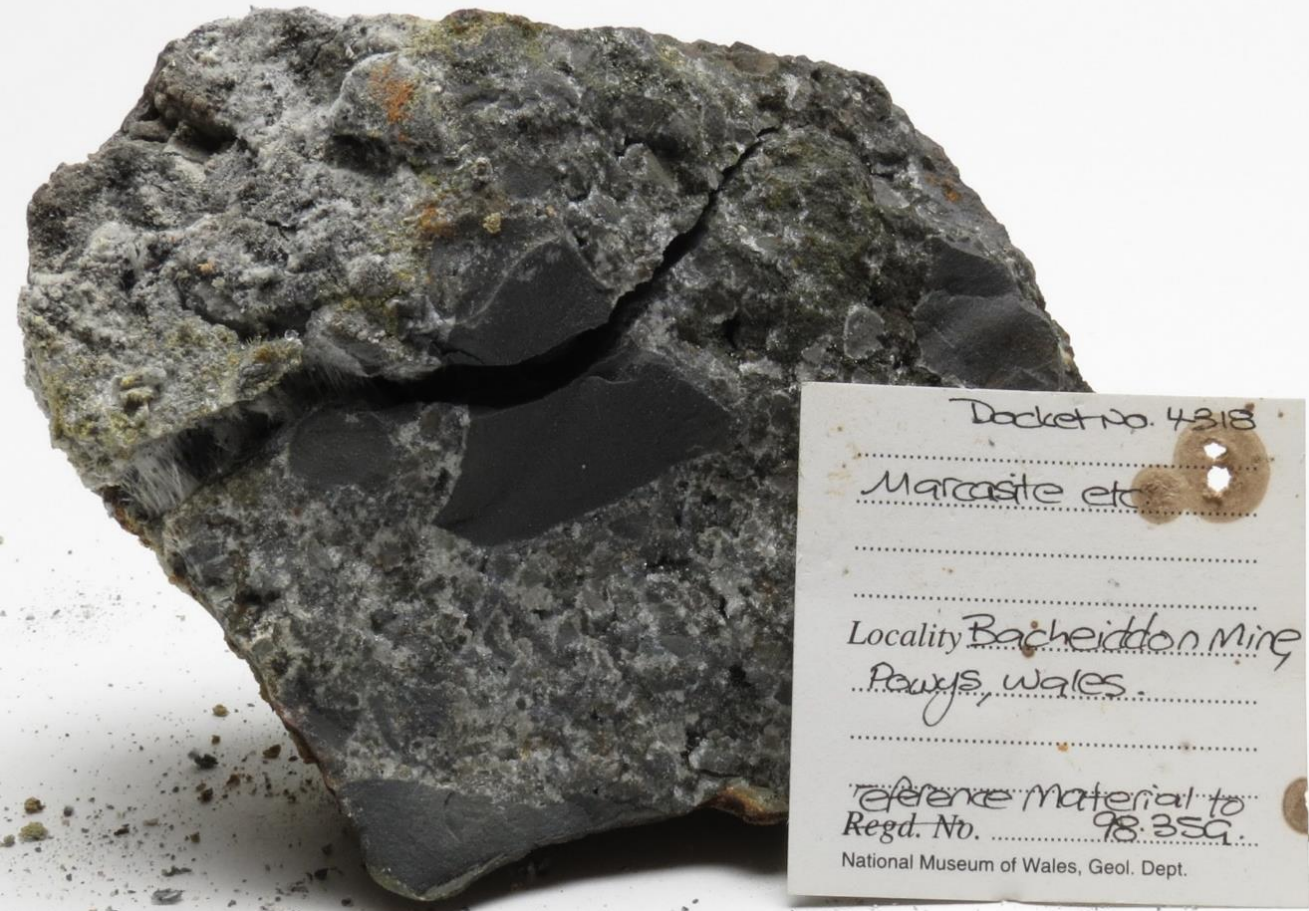


Why is it so problematic?

- Common in many rock-types
- Oxidizes $\geq 30\%$ RH
- Releases sulphuric acid
- Alteration creates volumetric expansion



Its deterioration is actively being researched



- Aqueous
 - Marine
 - Mine
- Near aqueous
- Extra-terrestrial
- Museums
- Roles of agents of deterioration
 - pH
 - Surface moisture & oxygen
 - Bacteria
- Conservation methods
 - Microenvironments
 - Anoxic environments

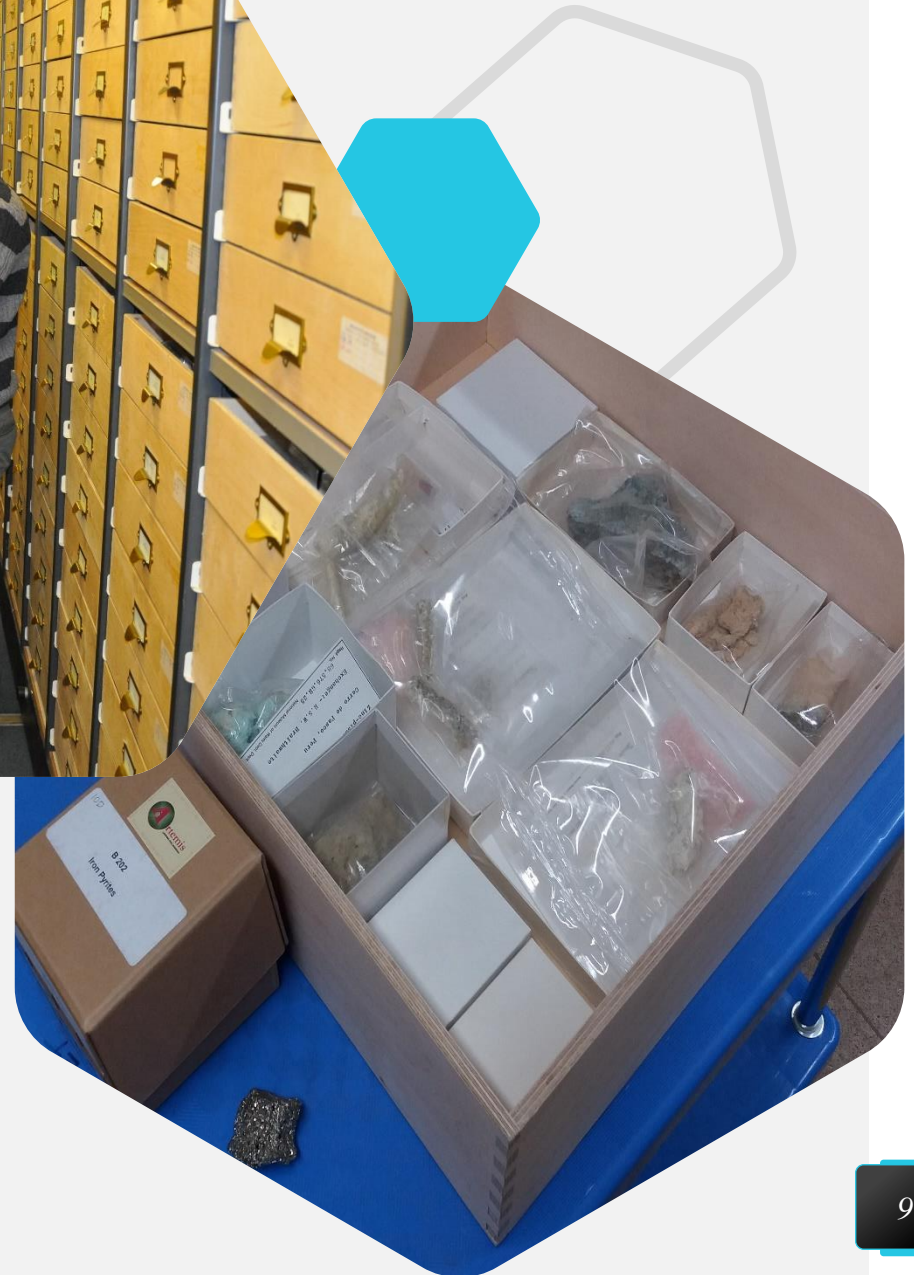
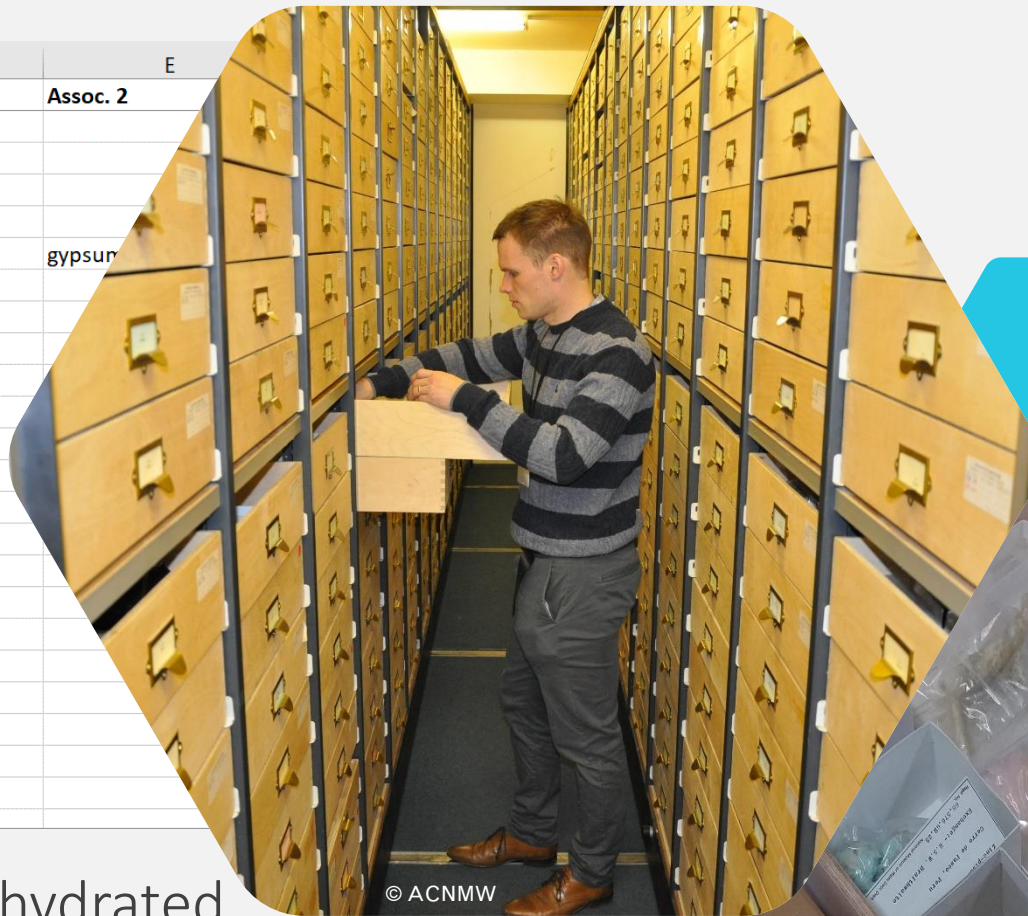
But the same cannot be said for other minerals



The Research Project

Beginning to fill in the gaps

	A	B	C	D	E
1	Acc Number	Specimen	Hey	Assoc. 1	Assoc. 2
170	64.370.GR.7	gaylussite	11.1.14		
171	64.370.GR.8	gaylussite	11.1.14		
172	64.370.GR.9	gaylussite	11.1.14		
173	83.41G.M.4698	gaylussite	11.1.14		
174	84.19G.M.760	gibbsite	7.6.4	aluminite	gypsum
175	20.348.GR.133	goslarite	25.5.2		
176	28.5.GR.3 a	goslarite	25.5.2		
177	48.264.GR.446	goslarite	25.5.2		
178	83.41G.M.8995	goslarite	25.5.2		
179	2002.9G.M.5	gypsum	25.4.3	fibroferrite	
180	2003.1G.M.548	gypsum var. selenite	25.4.3	chalcantite	
181	84.19G.M.772	ha ³ yne	17.10.4	chalcantite	
182	80.213	halite	8.1.3		
183	90.314	halite	8.1.3		
184	13.140.GR.24	halite	8.1.3		
185	14.311.GR.28	halite	8.1.3		
186	15.132.GR.2	halite	8.1.3		
187	15.133.GR.7	halite	8.1.3		
188	15.156.GR.112	halite	8.1.3	lapilli	
189	15.156.GR.42	halite	8.1.3		
190	15.156.GR.45	halite	8.1.3		
191	15.156.GR.46	halite	8.1.3		
192	20.338.GR.20	halite	8.1.3		



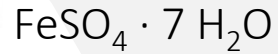
- Melanterite & Chalcantite = dehydrated
- Gaylussite = efflorescence
- Some sulphides = tarnished & cracking
- Halotrichite = friable & breaking

A Review of a Museum's Stores

Melanterite & Chalcanthite

Rare Welsh specimens – great concern for their stability

Melanterite



Cuprian Melanterite



Fe

Form a
solid
solution
series

Cu



Chalcanthite



Ferrohexahydrate – $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

Siderotil – $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$

Rozenite – $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$

Szomolnokite – $\text{FeSO}_4 \cdot \text{H}_2\text{O}$

Dehydrate

Fe

Cu

Bonattite – $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$

Poitevinite – $\text{CuSO}_4 \cdot \text{H}_2\text{O}$

Chalcocyanite – CuSO_4



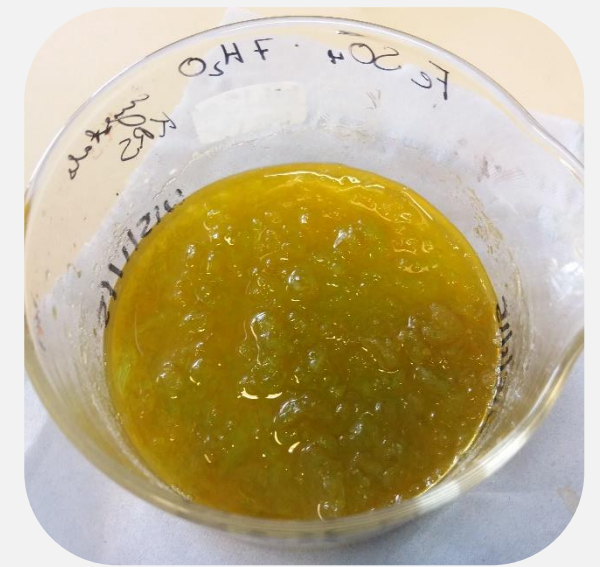
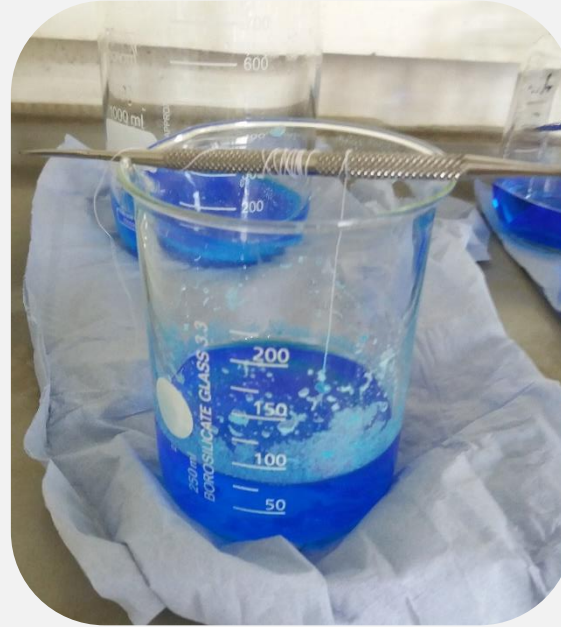


Master's Experiment: *Dehydration of Melanterite & Chalcantite*

1. Crystal Growth

Chalcanthite: quick & easy

1. Create supersaturated solution with deionized water
2. Decant into container
3. Produce seed crystals
4. Add seed crystals to containers of supersaturated solution
5. Et voilà!



Melanterite: more difficult & longer, but not impossible

- Filter supersaturated solution upon creation & throughout crystal growth
- Add sulphuric acid to lower pH & reduce $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ conversion
- Cover to avoid oxidation
- Produce much smaller and finer seed crystals



2. Dehydration

from Waller 1992 & Blount 1993

- Chalcantite: $\geq 33\%$
- Bonattite: $22 \leq x \leq 30\%RH$
- Poitevinite: $\leq 22\%RH$

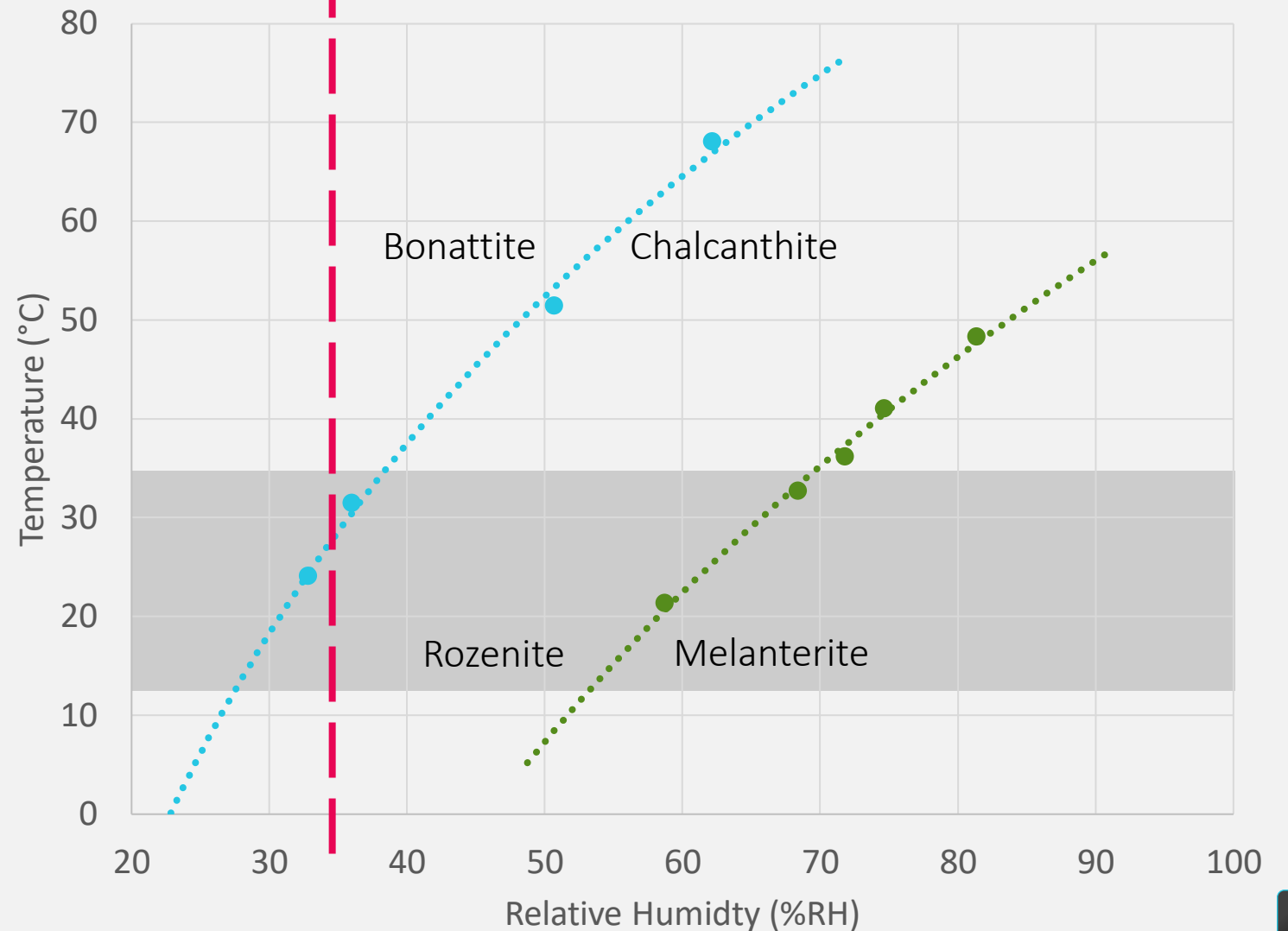
- Melanterite: $\geq 57\%RH$
- Rozenite: $30 \leq x \leq 57\%RH$
- Szomolnokite: $11 \leq x \leq 30\%RH$



Experiment:
30°C & 35% RH
for 6 weeks

Equilibrium RH for Chalcantite-Bonattite & Melanterite-Rozenite

(after Chou et al. 2002)



XRD of Dehydration Products

Determine alteration products & anticipate experimental results



1. Chalcantite => siderotil & szomolnokite
2. Pisanite => siderotil & szomolnokite
3. Melanterite => epsomite & hexahydrate

Specimens were misidentified when accessioned

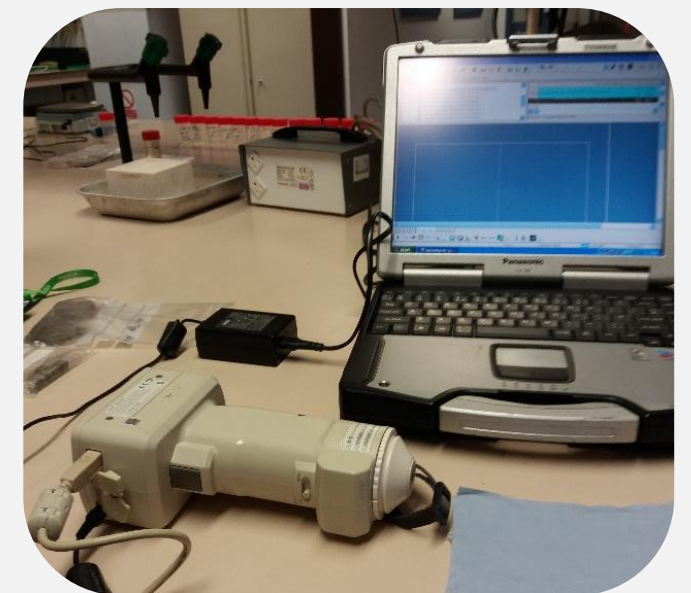
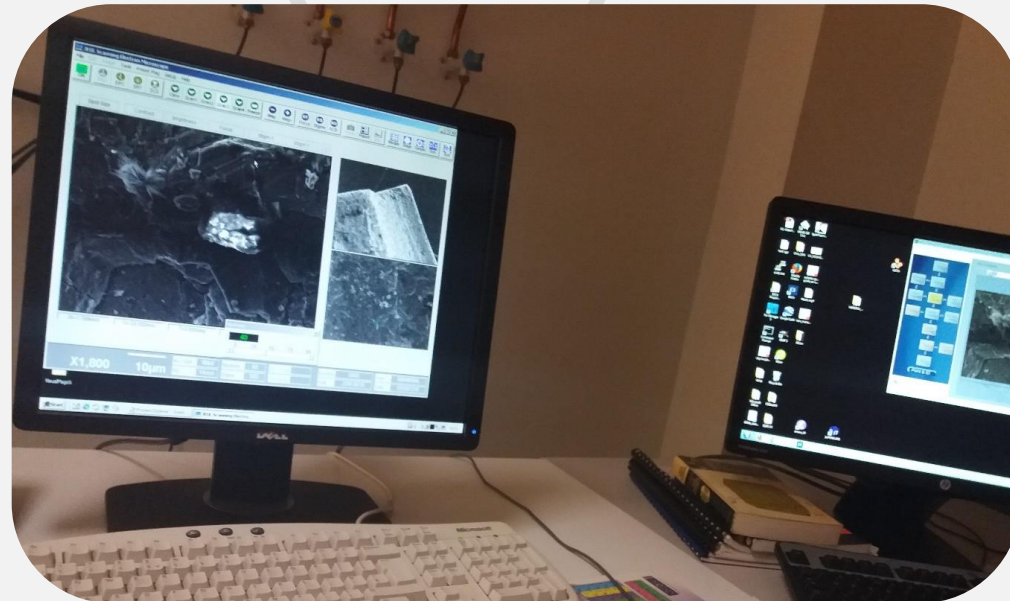
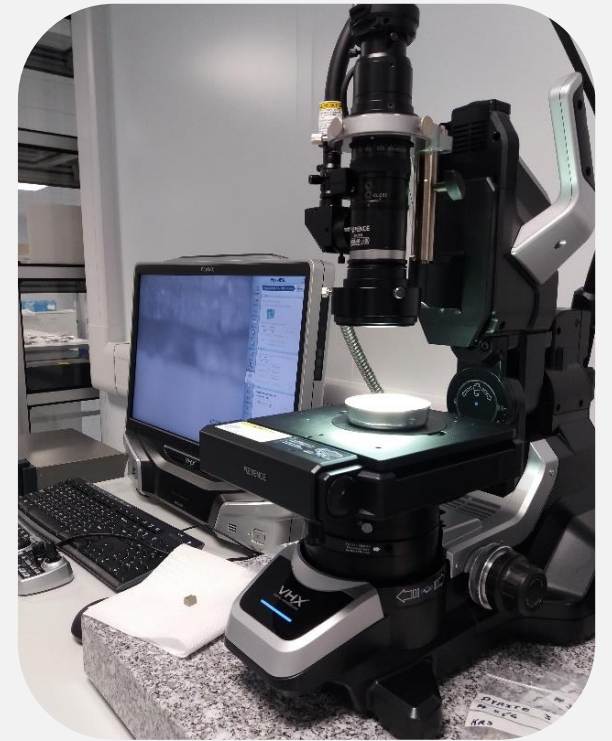
1. Cuprian melanterite
3. Epsomite



3. Analysis

Determine quantitative methods of identifying & monitoring change

- Weight gain
- Photography
- SEM – EDX
- XRD
- FT-IR
- Raman
- CT scans
- 3D microscopy
- Colorimetry



Areas of Further Research

Next few months

- More detailed review of mineral store
 - Visual identification of sensitive minerals
 - Narrow focus
- Rehydration study of melanterite & chalcantite
- Additional analytical techniques
 - Specific gravity
 - Hardness
 - Polarized microscopy

Longer-term

- Defining & quantifying damage
 - Species specific?
- Utilizing digital technologies
 - 3D scanning / photogrammetry
 - AI
- Assessment of sample acquisition
- Further development of experimental design(s)
 - Allow for incorporation of pollutants & light






Thank You

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- Pilgrim Trust



Thank You

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References & Reading

- Blount, A.M. 1993. Nature of the alterations which form on pyrite and marcasite during collection storage. *Collection Forum*, 9 (1), 1-16.
- Chou, I.M., Seal, I.R., and Hemingway, B.S., 2002. Determination of melanterite-rozenite and chalcantite-bonattite equilibria by humidity measurements at 0.1 MPa. *American Mineralogist*, 87 (1), 108–114.
- Chou, I.M., Seal, R.R., and Wang, A., 2013. The stability of sulfate and hydrated sulfate minerals near ambient conditions and their significance in environmental and planetary sciences. *Journal of Asian Earth Sciences*, 62, 734–758.
- Eggleston, C.M., Ehrhardt, J.J., and Stumm, W., 1996. Surface structural controls on pyrite oxidation kinetics: An XPS-UPS, STM, and modeling study. *American Mineralogist*, 81 (9–10), 1036–1056.
- Howie, F.M.P., 1992. *The Care and Conservation of Geological Material: minerals, rocks, meteorites, and lunar finds*. Butterworth-Heinemann.
- Jambor, J.L., Nordstrom, D.K., and Alpers, C.N., 2000. Metal-sulfate Salts from Sulfide Mineral Oxidation. *Reviews in Mineralogy and Geochemistry*, 40 (1), 303–350.
 - Jerz, J.K. and Rimstidt, J.D., 2004. Pyrite oxidation in moist air. *Geochimica et Cosmochimica Acta*, 68 (4), 701–714.
 - Móricz, F., Máдай, F., and Walder, I.F., 2012. Pyrite oxidation under circumneutral pH conditions, 1 (2), 1–6.



References & Reading

- Odin, G.P., Rouchon, V., Béthoux, O., and Ren, D., 2018. Gypsum growth induced by pyrite oxidation jeopardises the conservation of fossil specimens: an example from the Xiaheyan entomofauna (Late Carboniferous, China). *Palaeogeography, Palaeoclimatology, Palaeoecology*, 507 (May), 15–29.
- Odin, G.P., Vanmeert, F., Farges, F., Gand, G., Janssens, K., Romero-Sarmiento, M.F., Steyer, J.S., Vantelon, D., and Rouchon, V., 2015. Alteration of fossil-bearing shale (Autun, France; Permian), part II: Monitoring artificial and natural ageing by combined use of S and Ca K-edge XANES analysis, Rock-Eval pyrolysis and FTIR analysis. *Annales de Paleontologie*, 101 (3), 225–239.
- Riaza, A., García-Meléndez, E., and Mueller, A., 2011. Spectral identification of pyrite mud weathering products: A field and laboratory evaluation. *International Journal of Remote Sensing*, 32 (1), 185–208.
- Rimstidt, D.D. and Vaughan, D.J., 2003. Pyrite oxidation: A state-of-the-art assessment of the reaction mechanism. *Geochimica et Cosmochimica Acta*, 67 (5), 873–880.
- Soliman, M.F. and El Goresy, A., 2012. Framboidal and idiomorphic pyrite in the upper Maastrichtian sedimentary rocks at Gabal Oweina, Nile Valley, Egypt: Formation processes, oxidation products and genetic implications to the origin of framboidal pyrite. *Geochimica et Cosmochimica Acta*, 90, 195–220.
- Wiese, R.G., Powell, M.A., and Fyfe, W.S., 1987. Spontaneous formation of hydrated iron sulfates on laboratory samples of pyrite- and marcasite-bearing coals. *Chemical Geology*, 63 (1–2), 29–38.

