THE INSTITUTE OF CONSERVATION

Conditions for the safe storage of early glass

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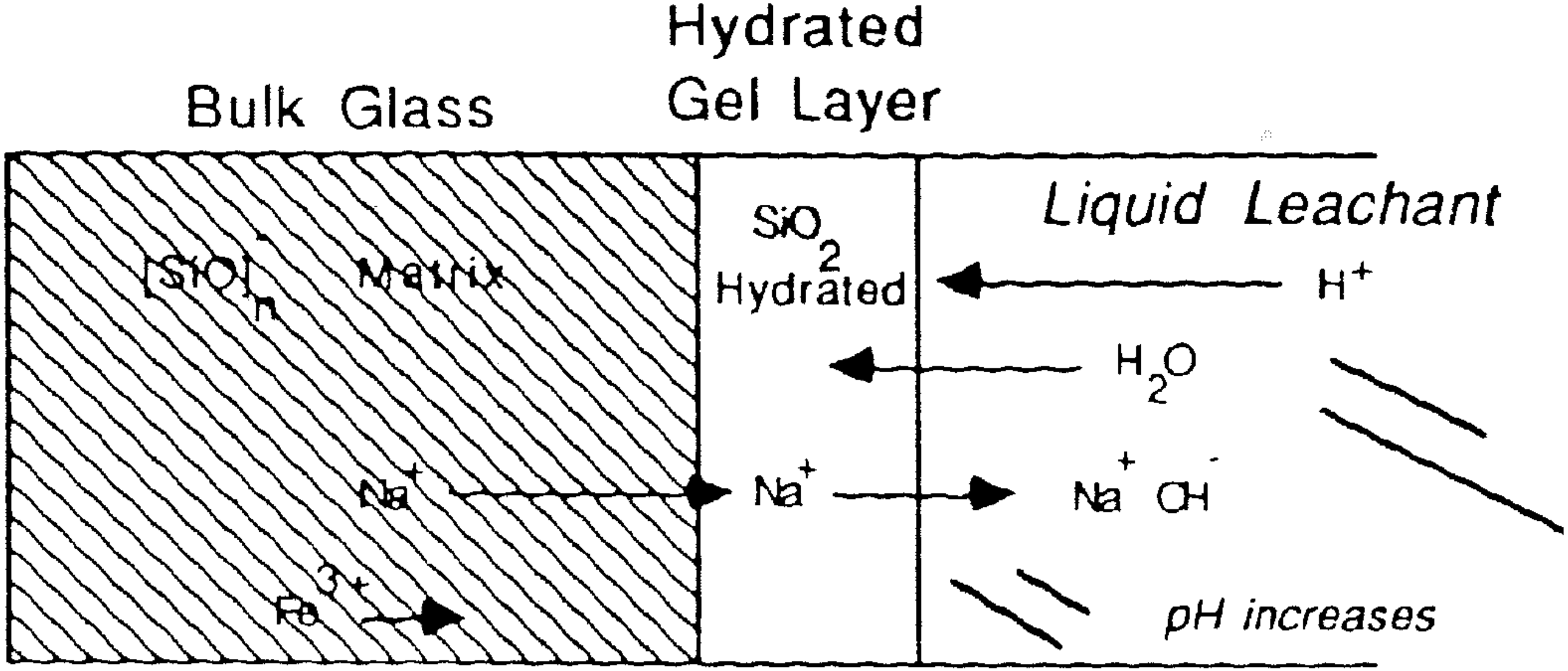
Glass degradation in collections

- Numerous glass objects in museum and archaeological storage are unstable
- Of the estimated 250,000 archaeological and historical specimens stored by partner English Heritage (EH), many are in advanced stages of deterioration

Satu Mare County Museum, Romania

Pharmacy Museum, Lisbon

The nature of the leached layer



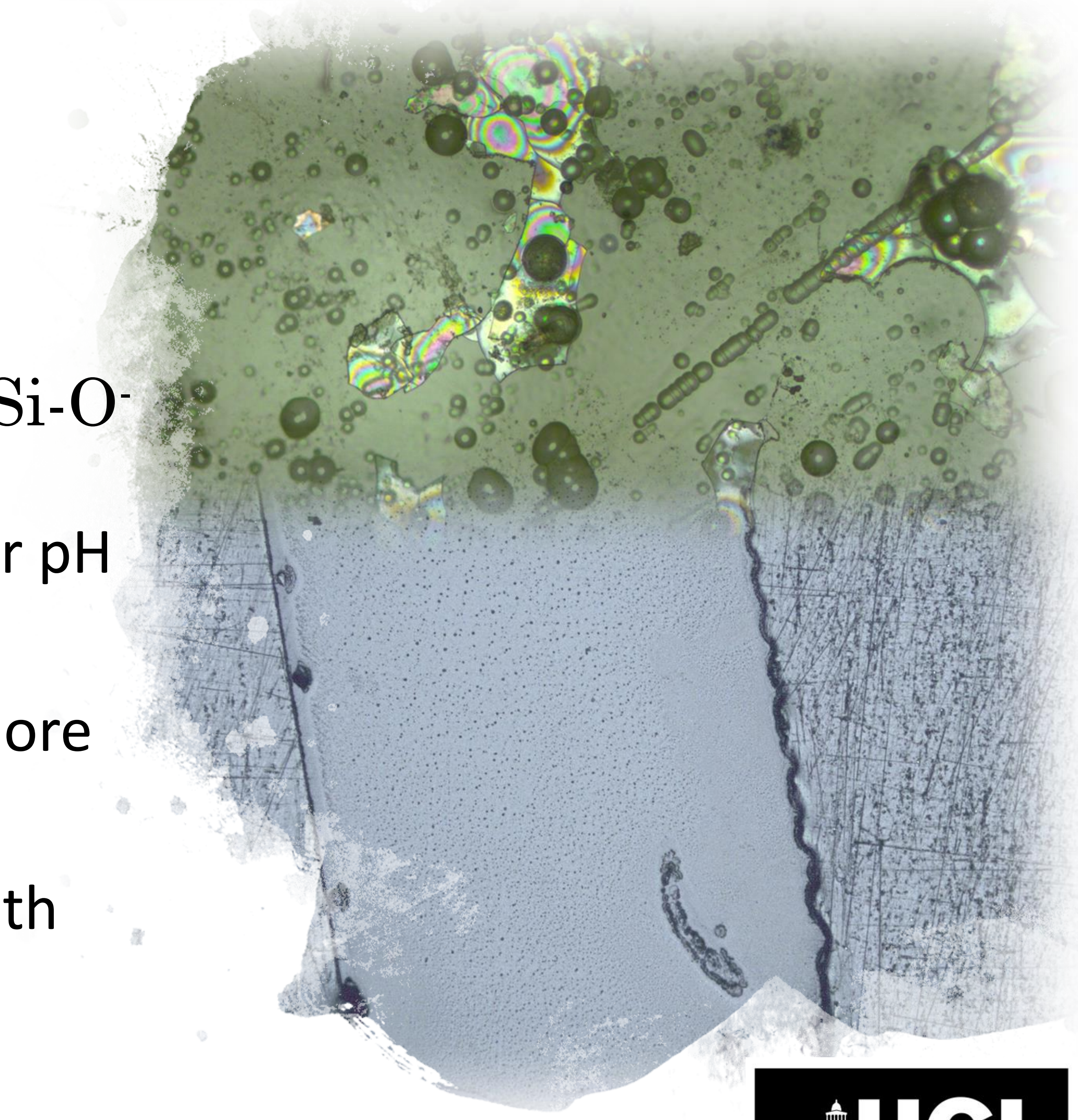
$$H_3O^+ + {=}Si{-}O^{-}{-}Na^{+} \rightarrow {=}Si{-}OH + H_2O + Na$$

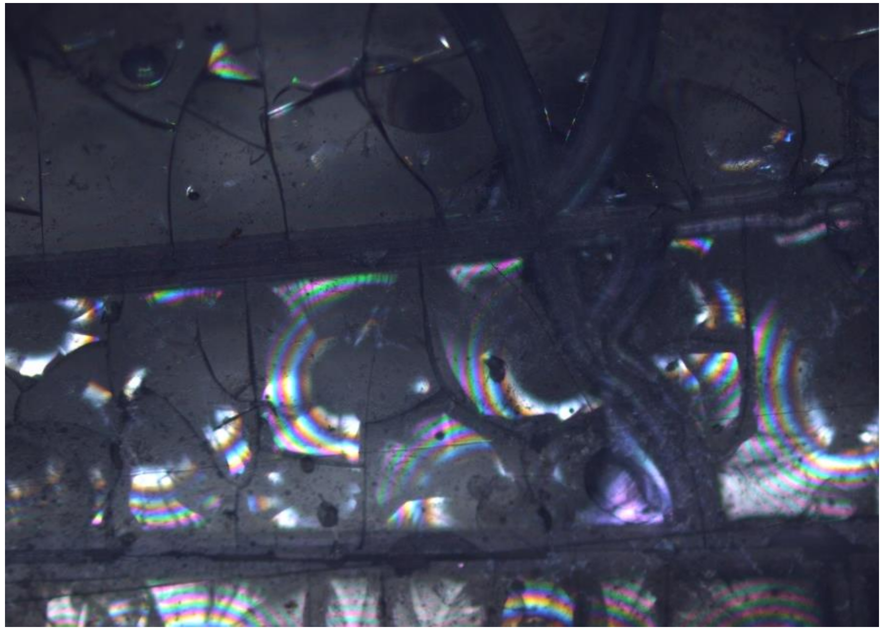
Classic model: selective leaching of alkali in exchange for hydrogen compounds from the environment. Pristine glass mostly retains its silica framework.

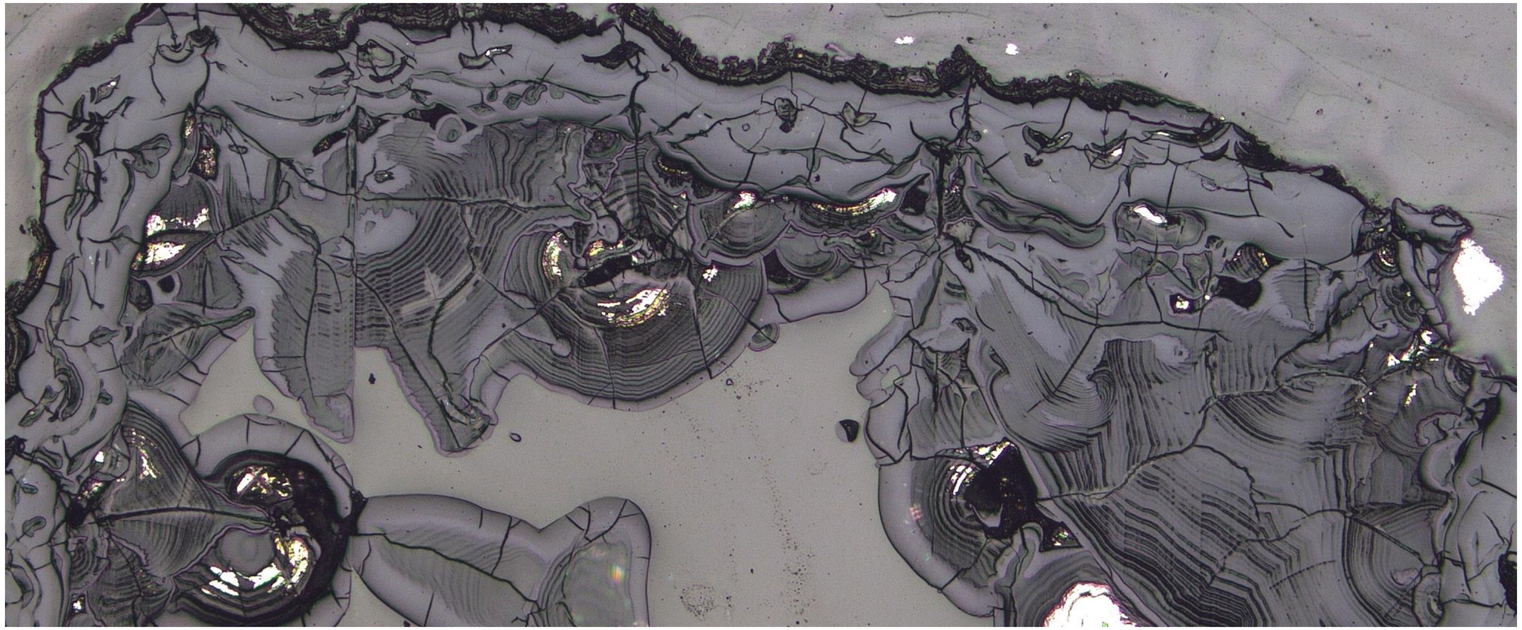
Hydrolysis

$\equiv$Si-O-Si$\equiv$ +OH^- $\Leftrightarrow$ $\equiv$Si-OH + $\equiv$Si-O^-

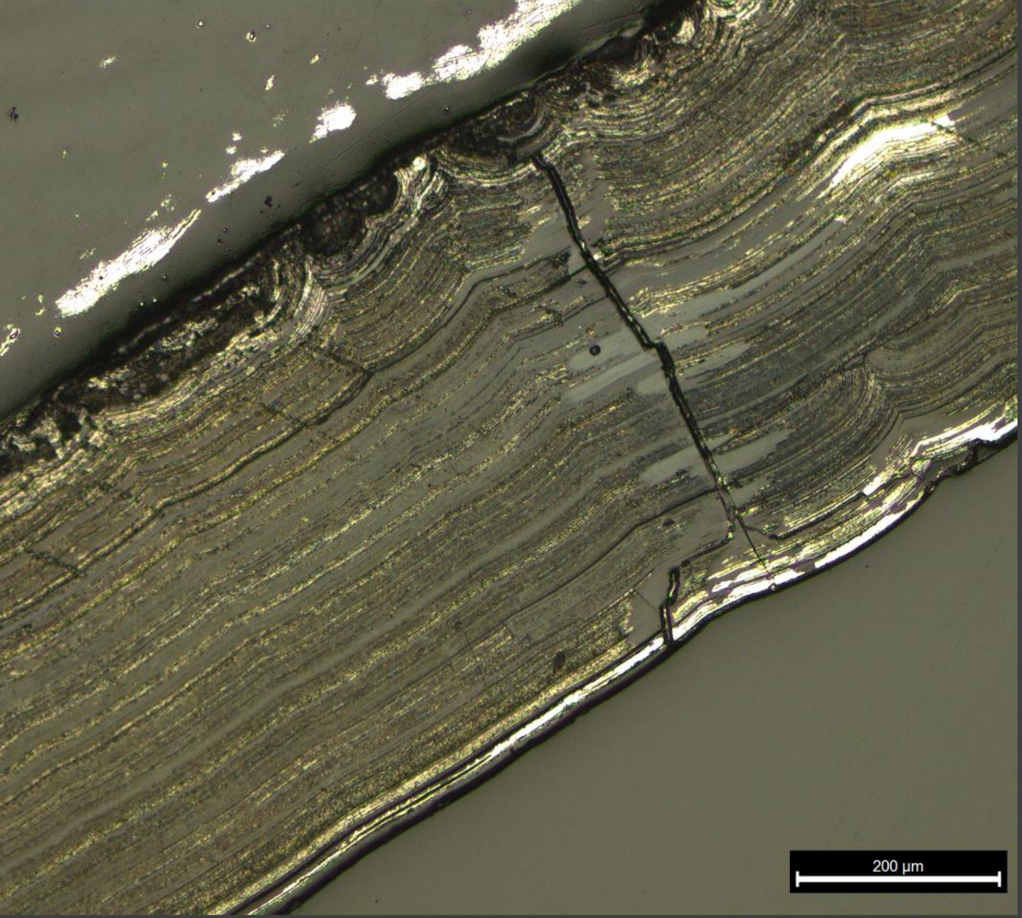
- Begins to dominate corrosion after pH 9-10 is reached
- Can etch the entire surface, but more often results in localised pitting
- Often proceeds simultaneously with leaching

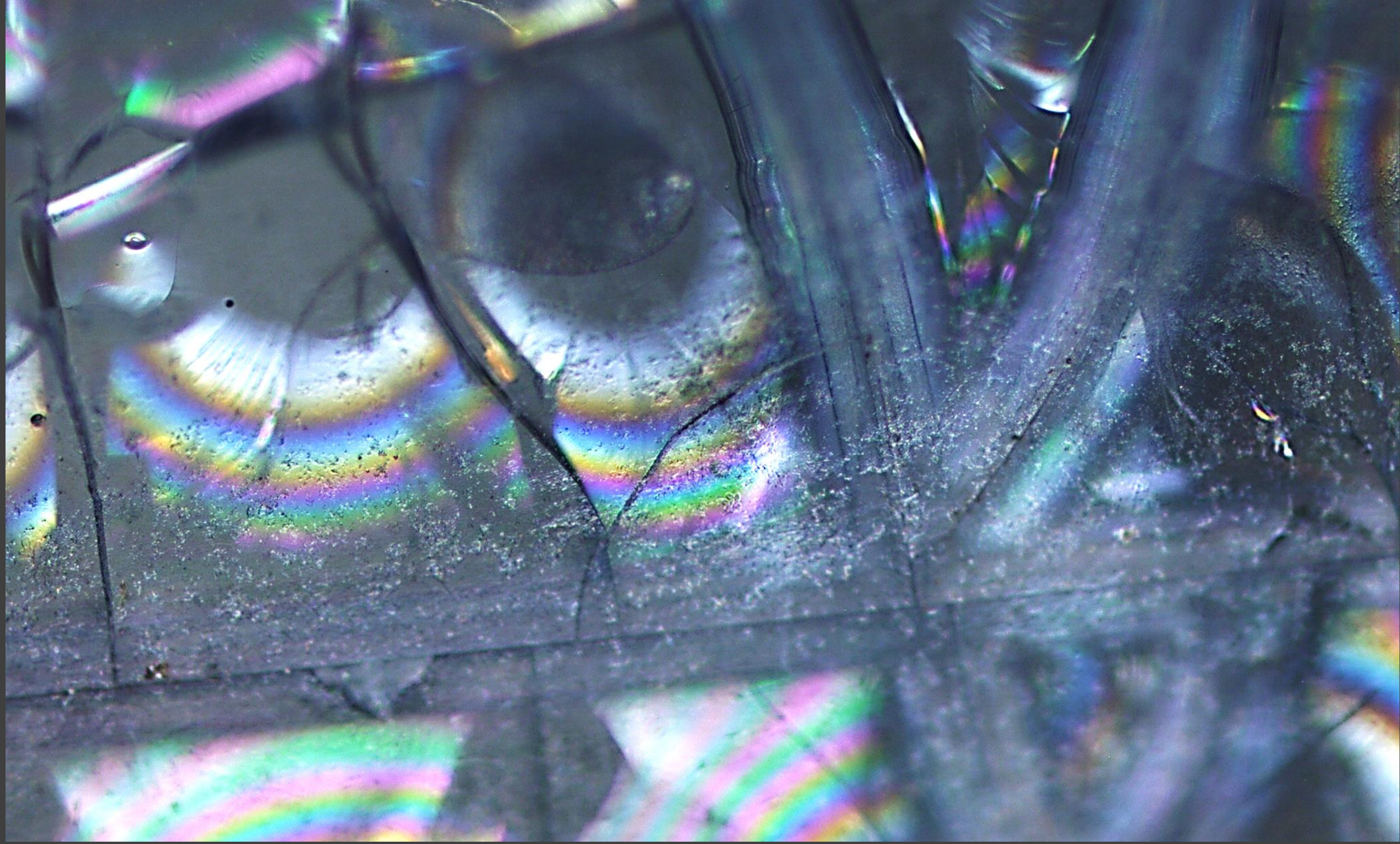






Crizzling - tiny cracks and hairline fractures that form in the weathered layer of glasses and can eventually lead to their physical collapse





Delamination

The critical relative humidity

42%

40±5%

45±2%

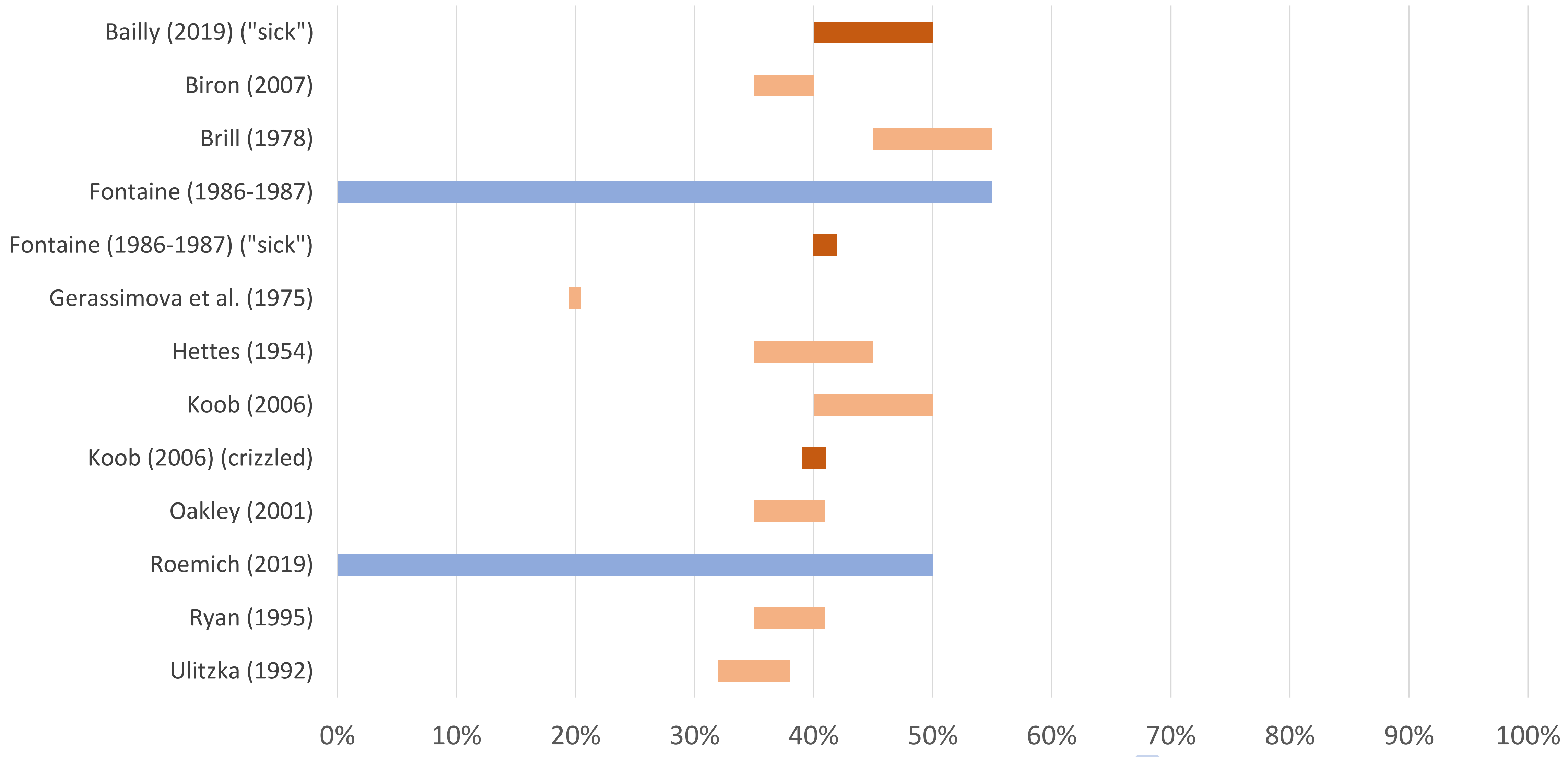
35±3%

38±3%

20%

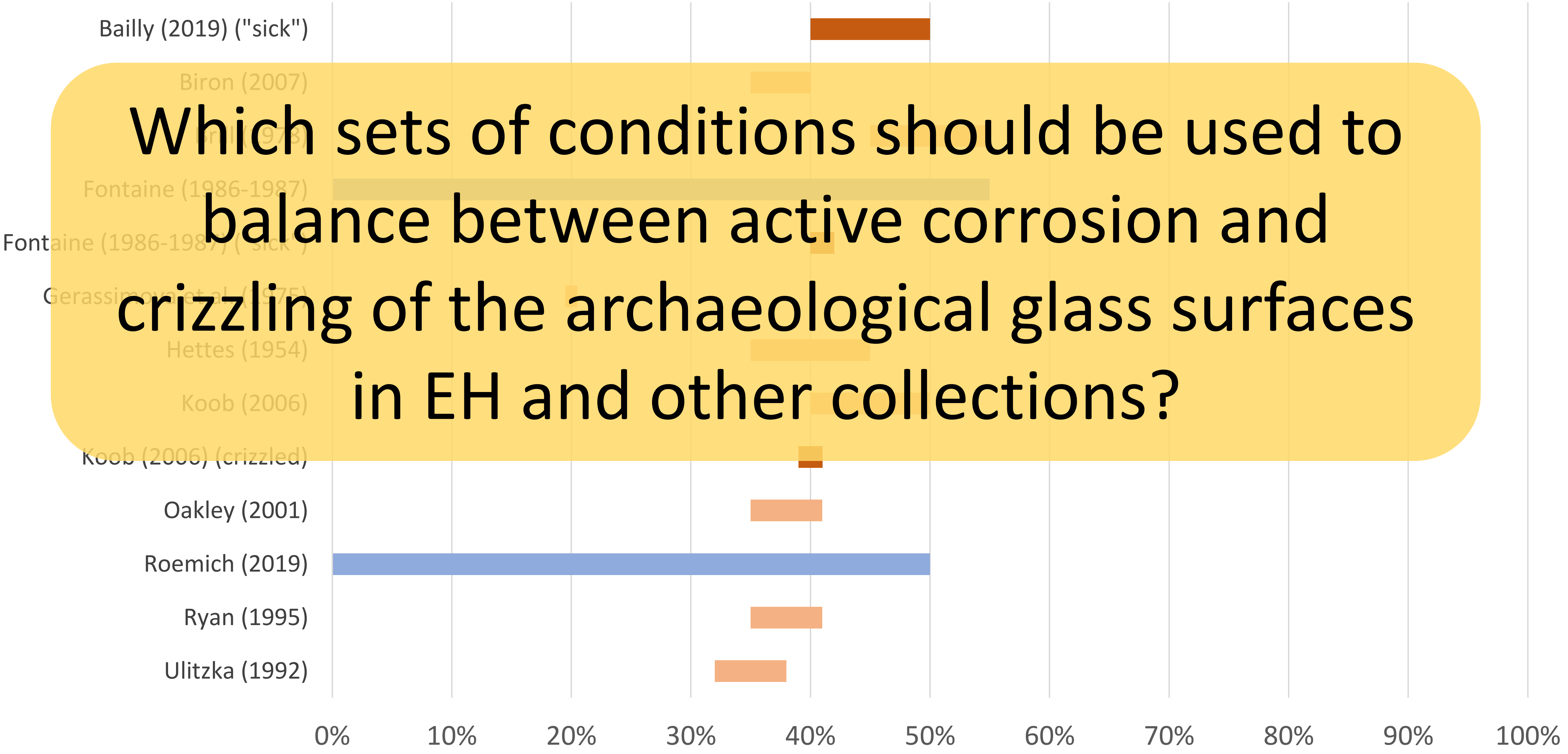
45-55%

- Exact causes of crizzling are not known, likely a consequence of excessive leaching or surface layer drying and subsequent shrinkage
- Crucial to better define a figure or range of RH that would strike a balance between leaching and crizzling, especially in archaeological glass
- RH levels of salt deliquescence cited as reference points in the past
- Conservation treatments should be reconsidered in view of newer theories of glass corrosion



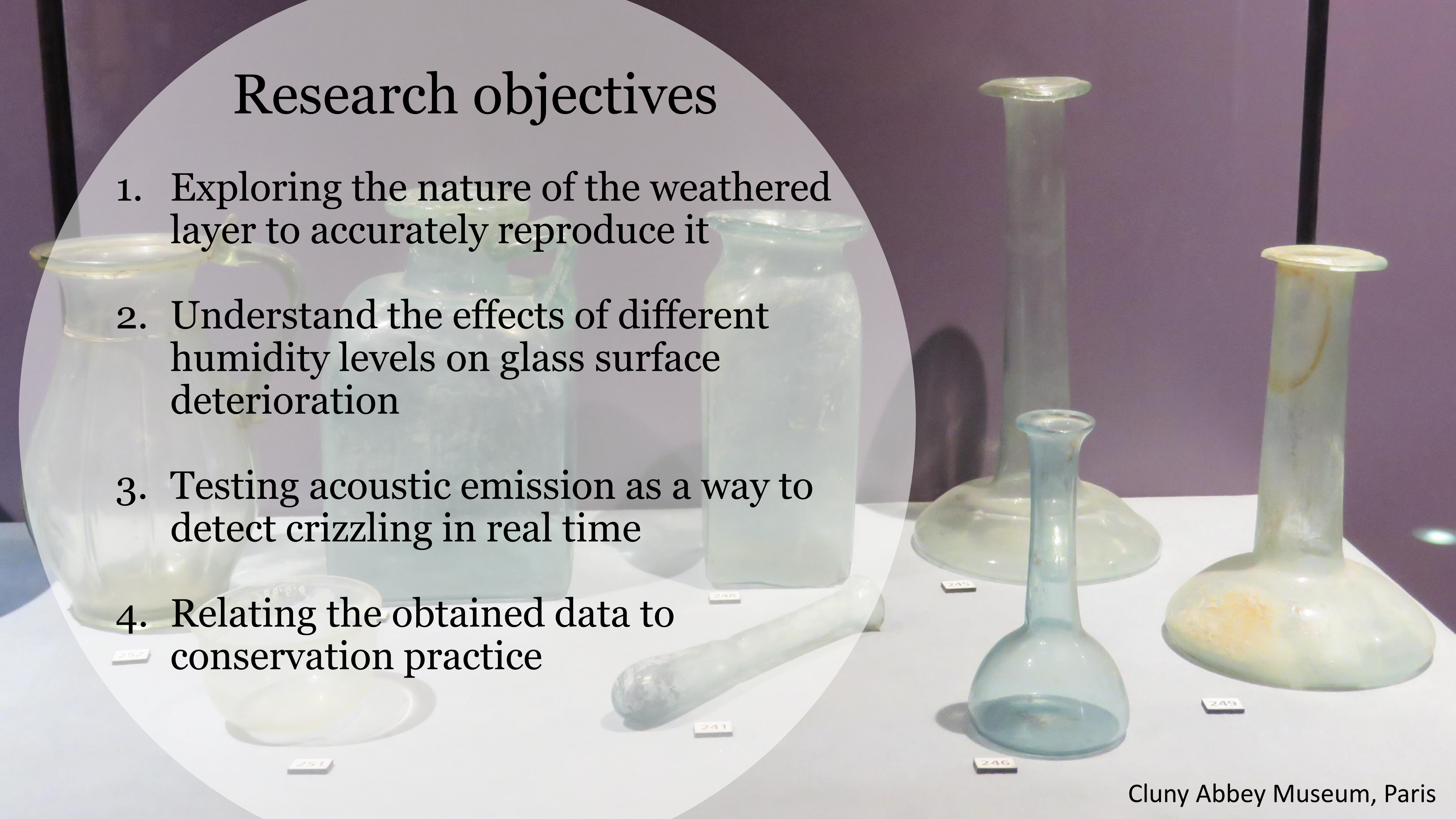
Bailly (2019) ("sick")
Biron (2007)
Brill (1978)
Fontaine (1986-1987)
Fontaine (1986-1987) ("sick")
Gerassimova et al. (1975)
Hettes (1954)
Koob (2006)
Koob (2006) (crizzled)
Oakley (2001)
Roemich (2019)
Ryan (1995)
Ulitzka (1992)
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%

Which sets of conditions should be used to balance between active corrosion and crizzling of the archaeological glass surfaces in EH and other collections?



Research objectives

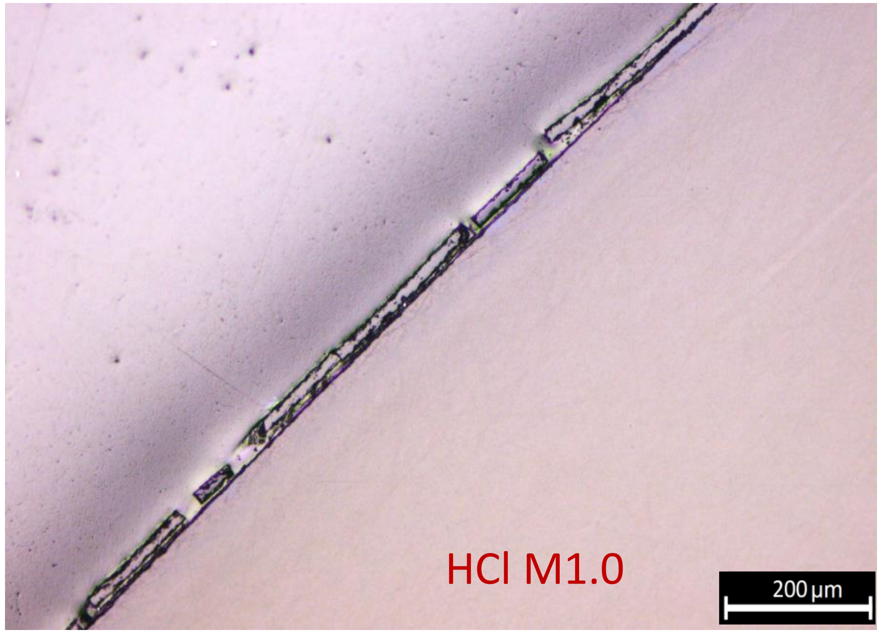
1. Exploring the nature of the weathered layer to accurately reproduce it
2. Understand the effects of different humidity levels on glass surface deterioration
3. Testing acoustic emission as a way to detect crizzling in real time
4. Relating the obtained data to conservation practice

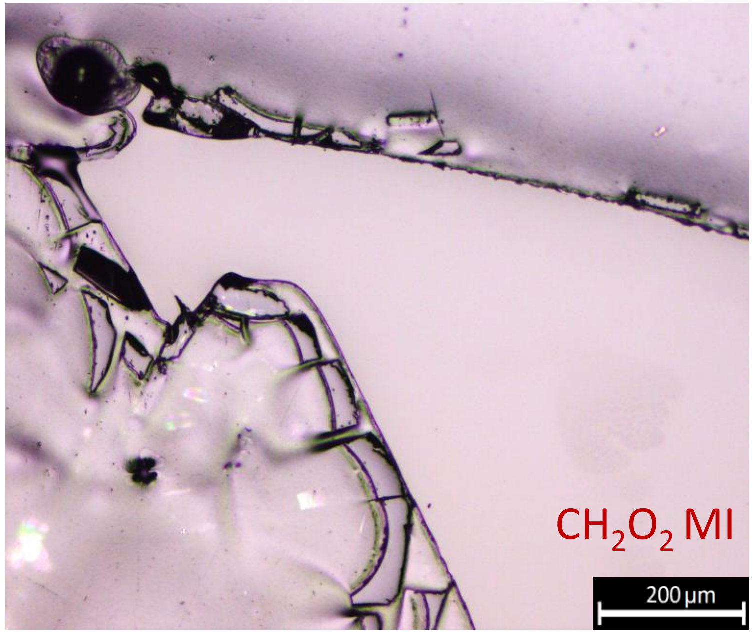


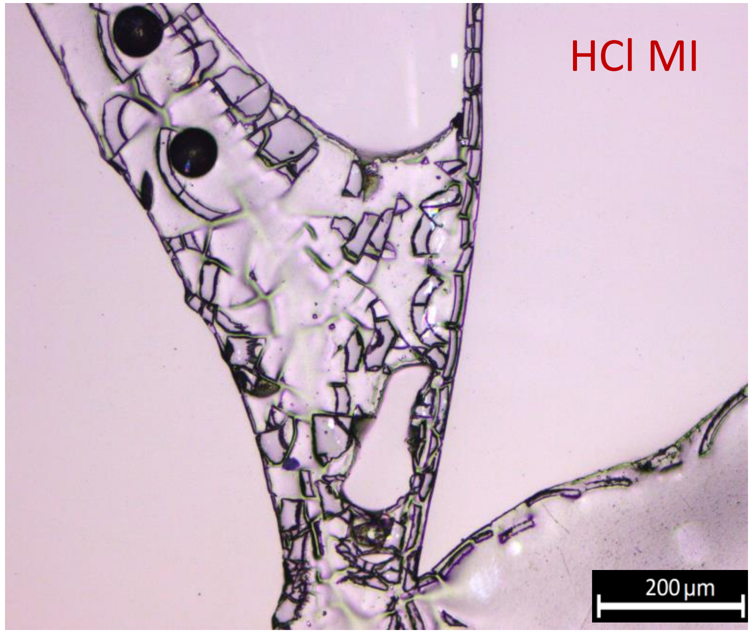
Cluny Abbey Museum, Paris

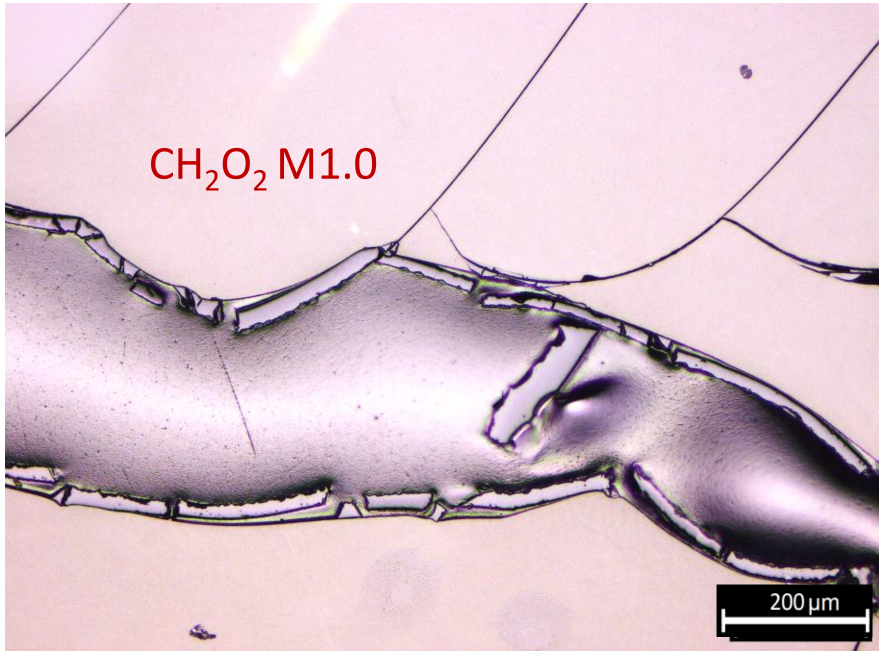
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	Cl	MnO	FeO	Sb_2O_3
MI	3.0%	3.0%	1.5%	48.0%	4.0%	23.5%	15.0%		1.0%	1.0%	
M1.0				54.2%		28.8%	17.0%				
IF P12	20.7%	0.2%	2.0%	70.0%		0.4%	4.6%	1.1%		0.3%	0.7%

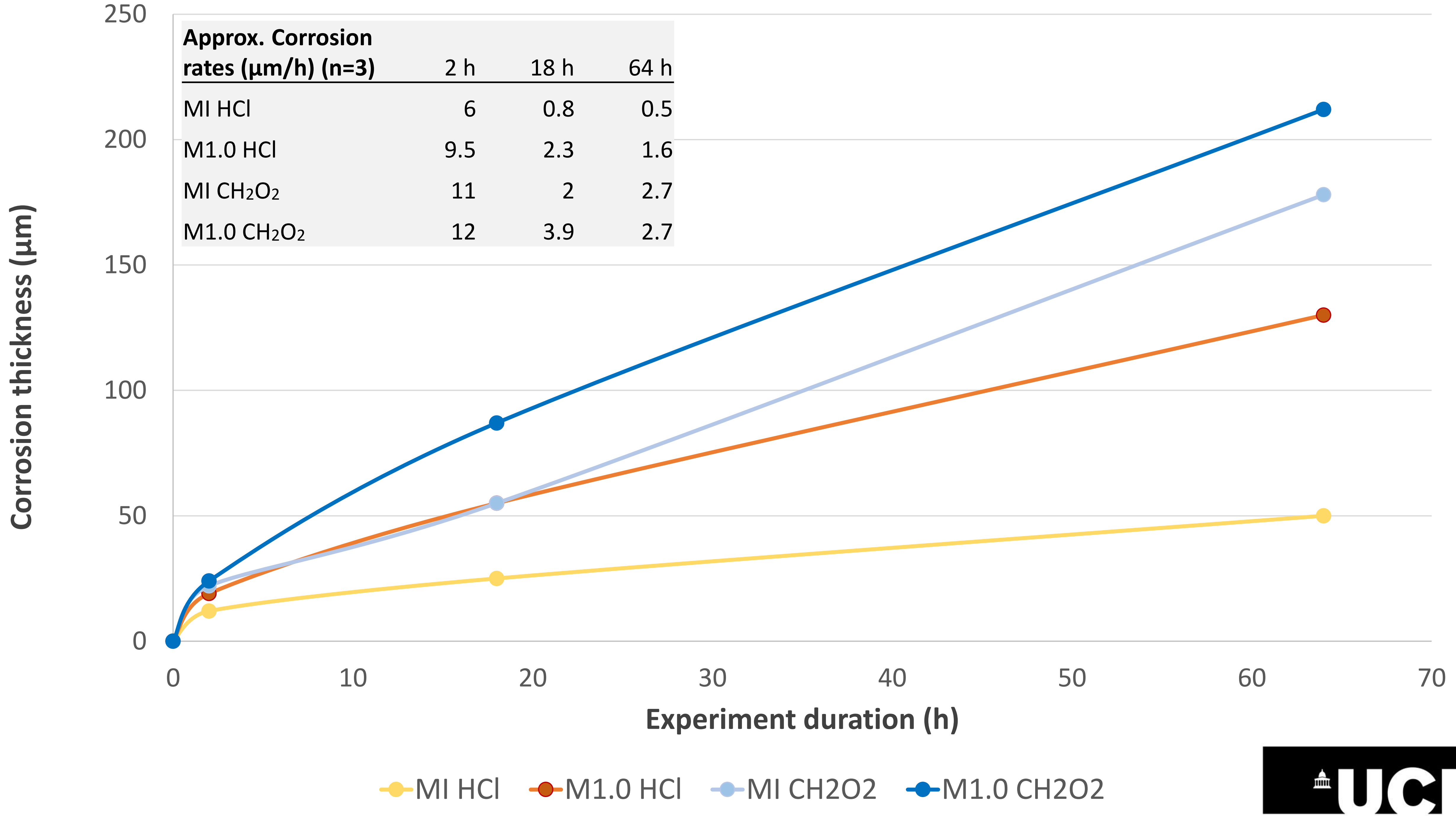
pH 1 HCl; pH 2 CH_2O_2 – 120 minutes











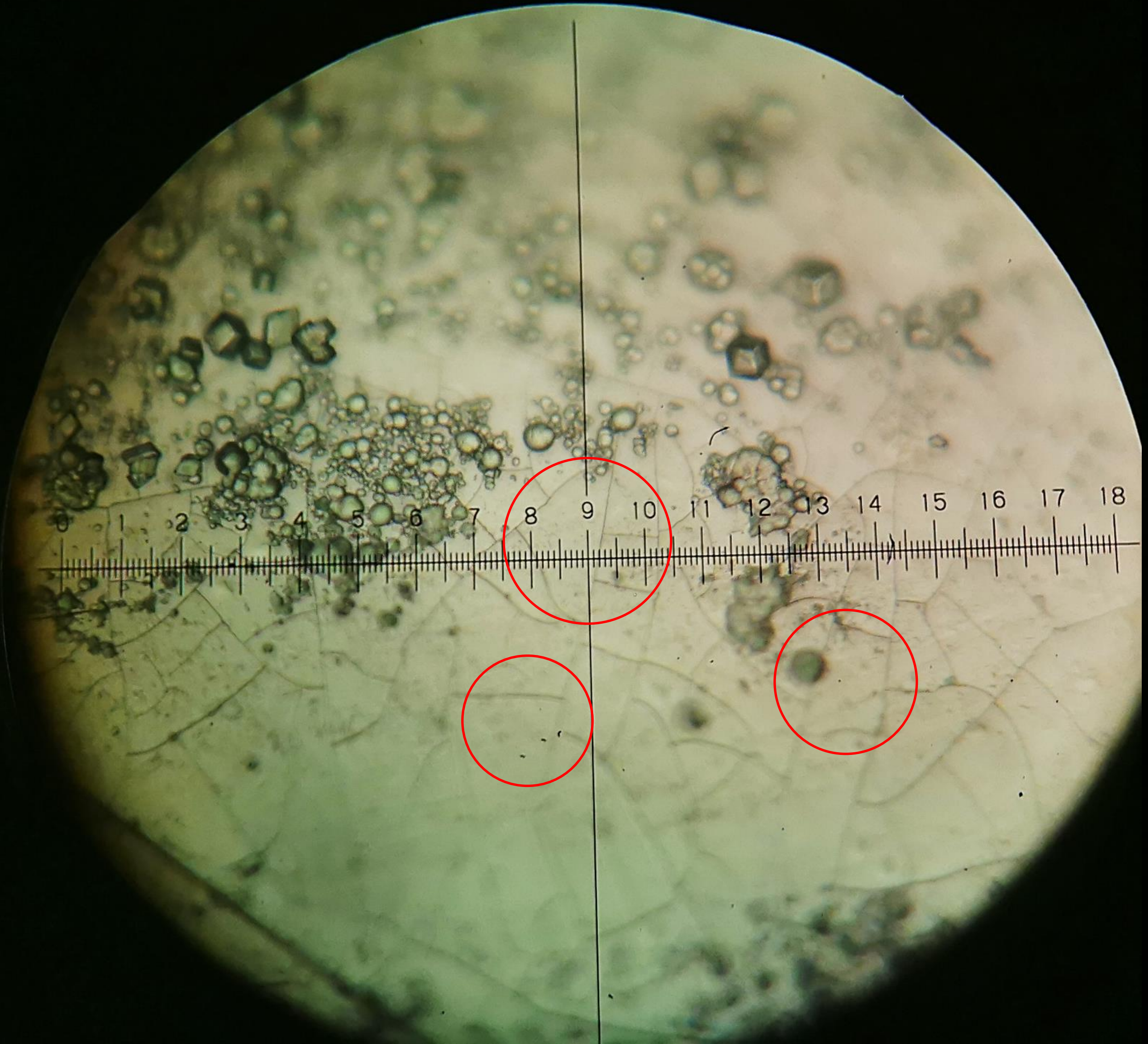
Approx. Corrosion rates (μm/h) (n=3)	2 h	18 h	64 h
MI HCl	6	0.8	0.5
M1.0 HCl	9.5	2.3	1.6
MI CH_2O_2	11	2	2.7
M1.0 CH_2O_2	12	3.9	2.7

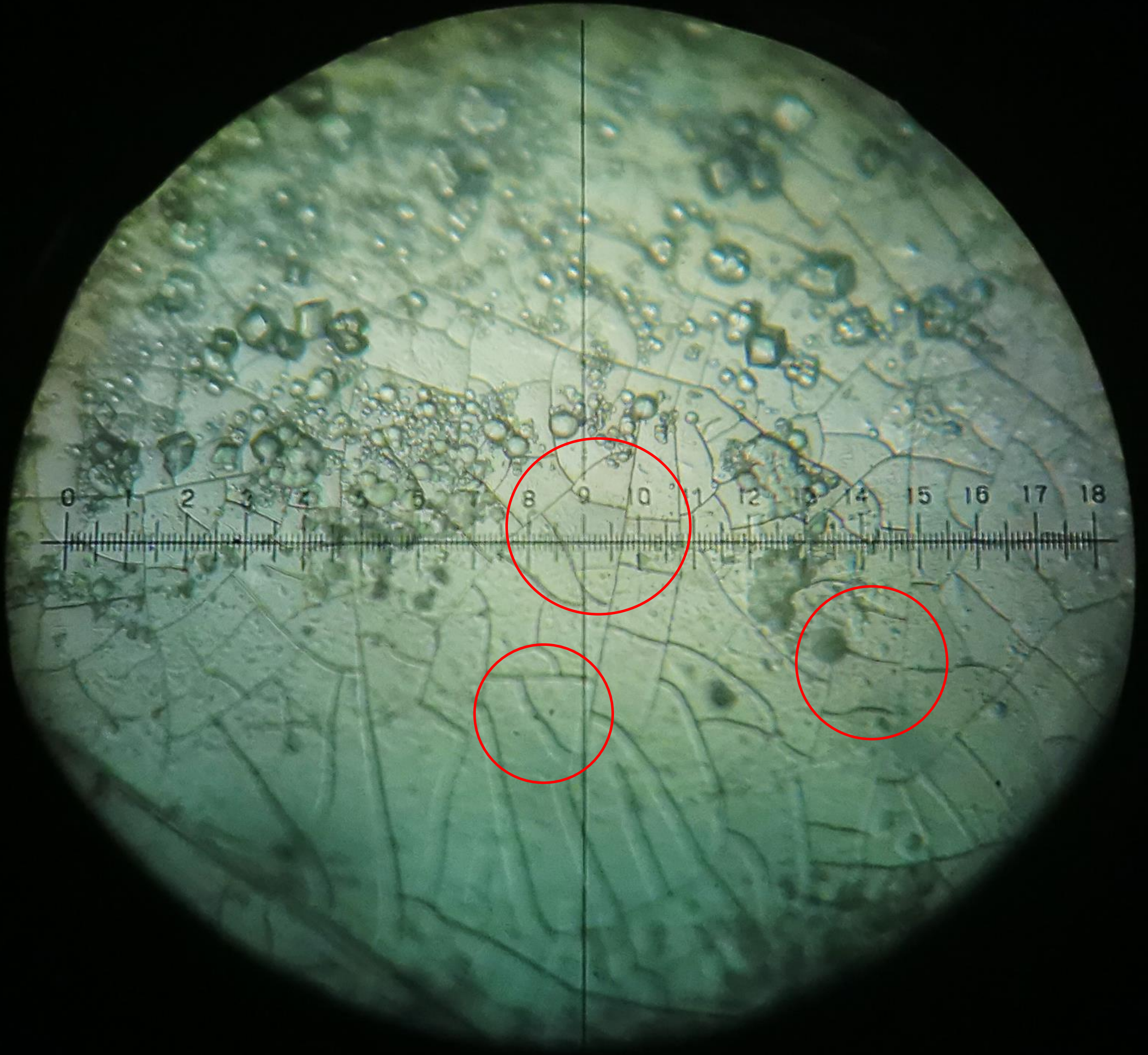
Tests in 5 g/100 ml $NaHCO_3$ solution

- Pieces ranging from ~5x5 mm to 30x30 mm immersed upright
- Smaller pieces crizzled in atmospheric conditions after 3-3.5 h leaching
- Large pieces pre-corroded in 6-8 h, M1.0 was more sensitive
- Model Roman glass nearly unaffected after four months of exposure

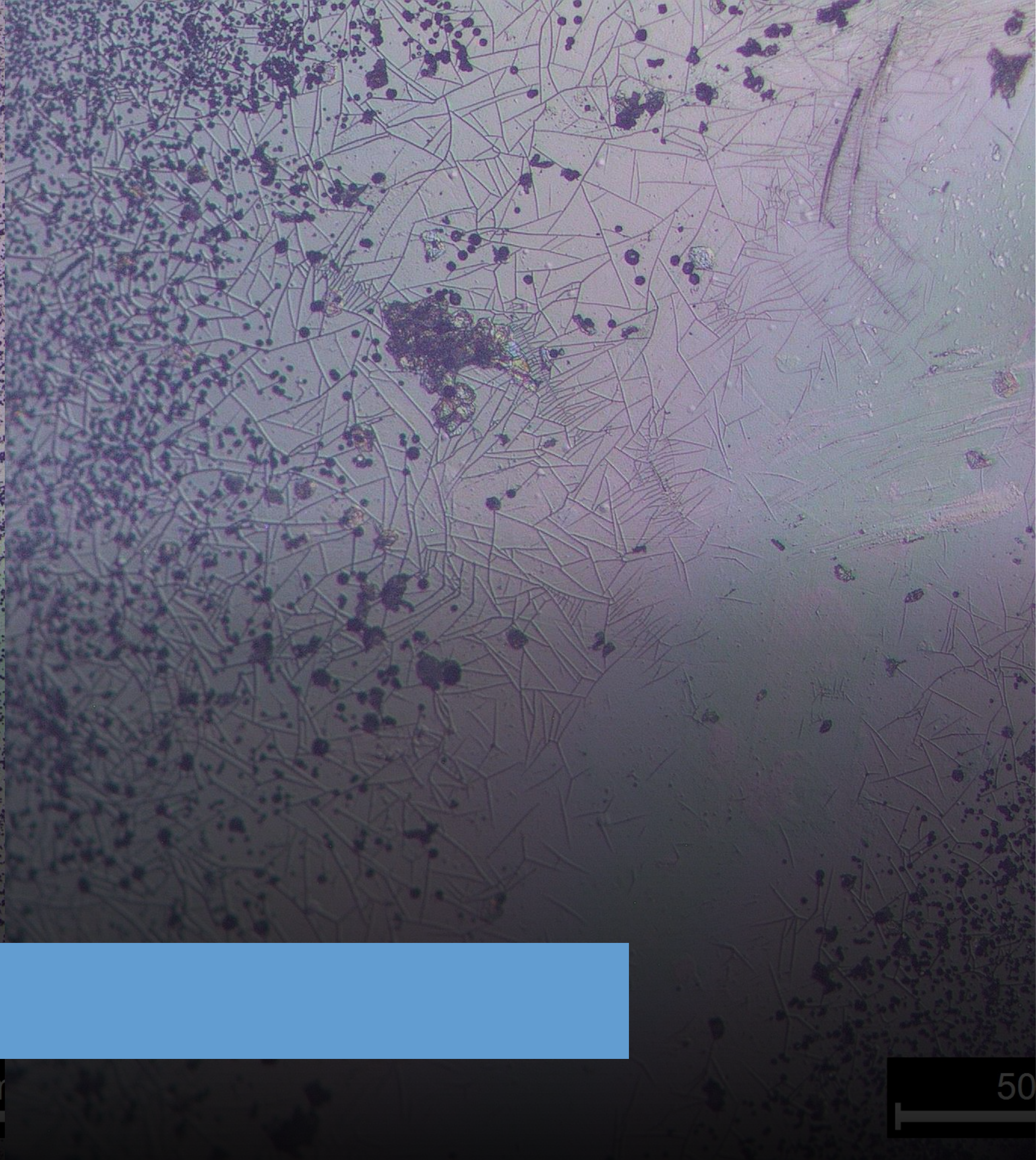
Guillot, M. 1934. Sur l'irisation du verre antique. Formation de strates de Liesegang dans le verre, au contact des solutions de bicarbonate, par précipitation rythmique de carbonate de calcium. *C.R.* 198, 2093-2095.

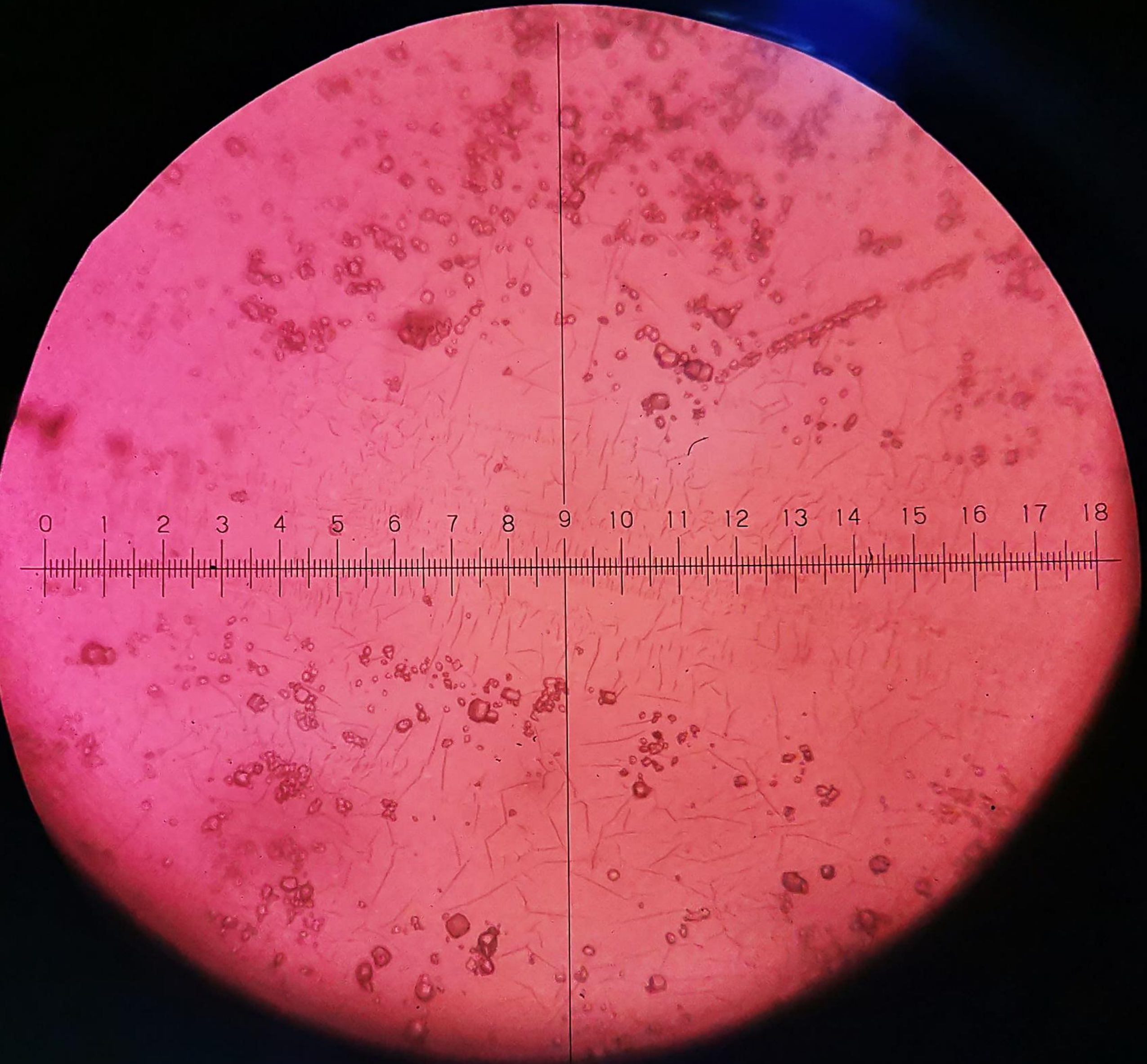
DEVELOPMENT OF CRIZZLING

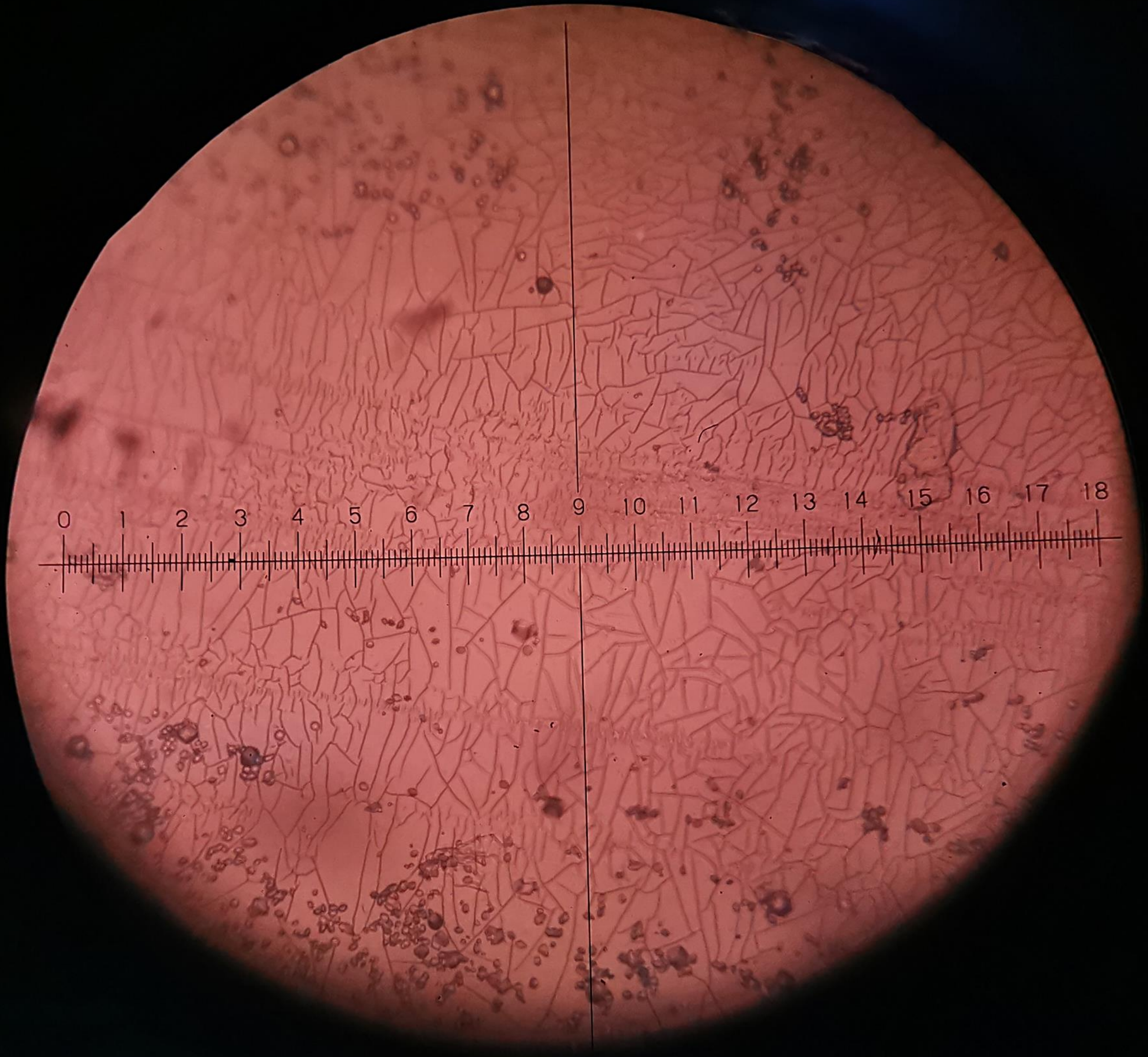


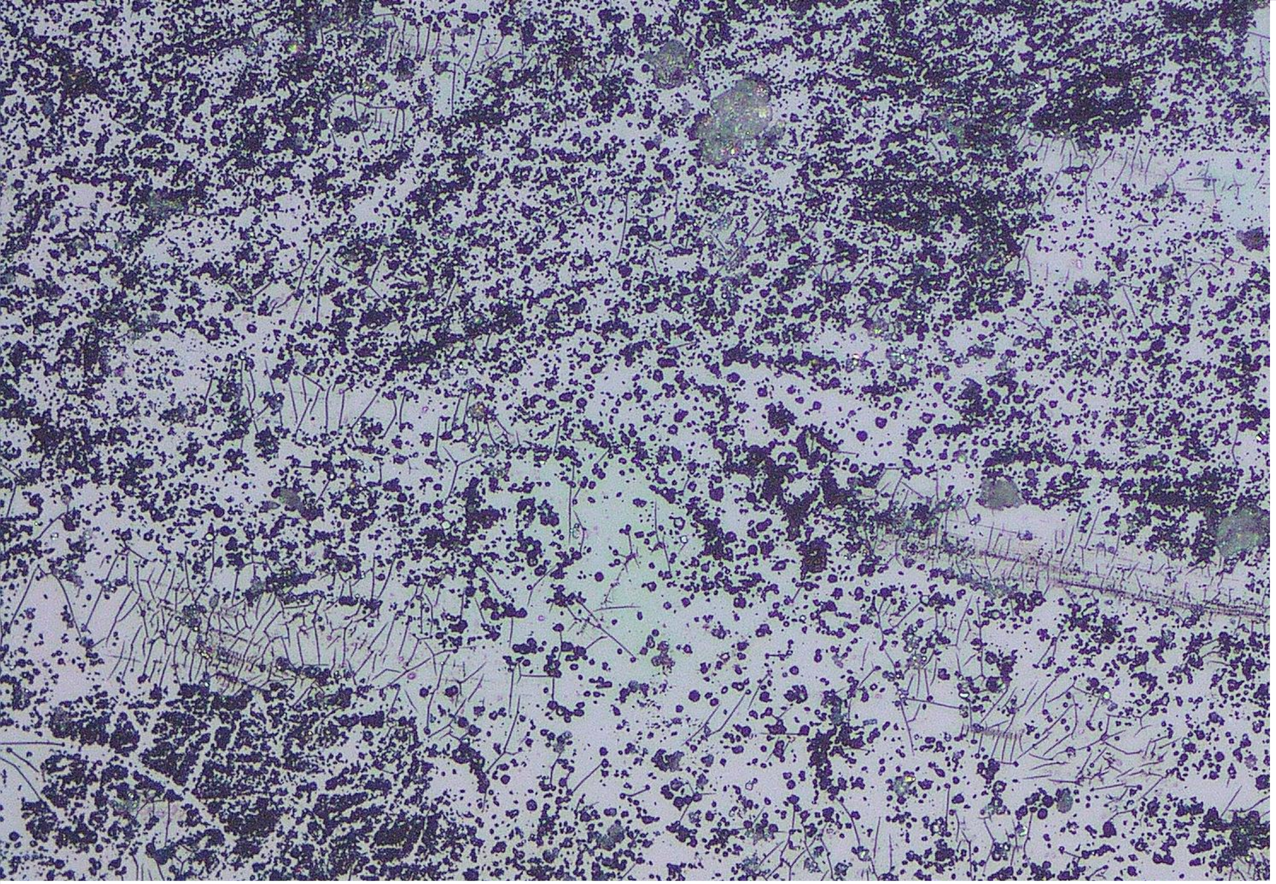
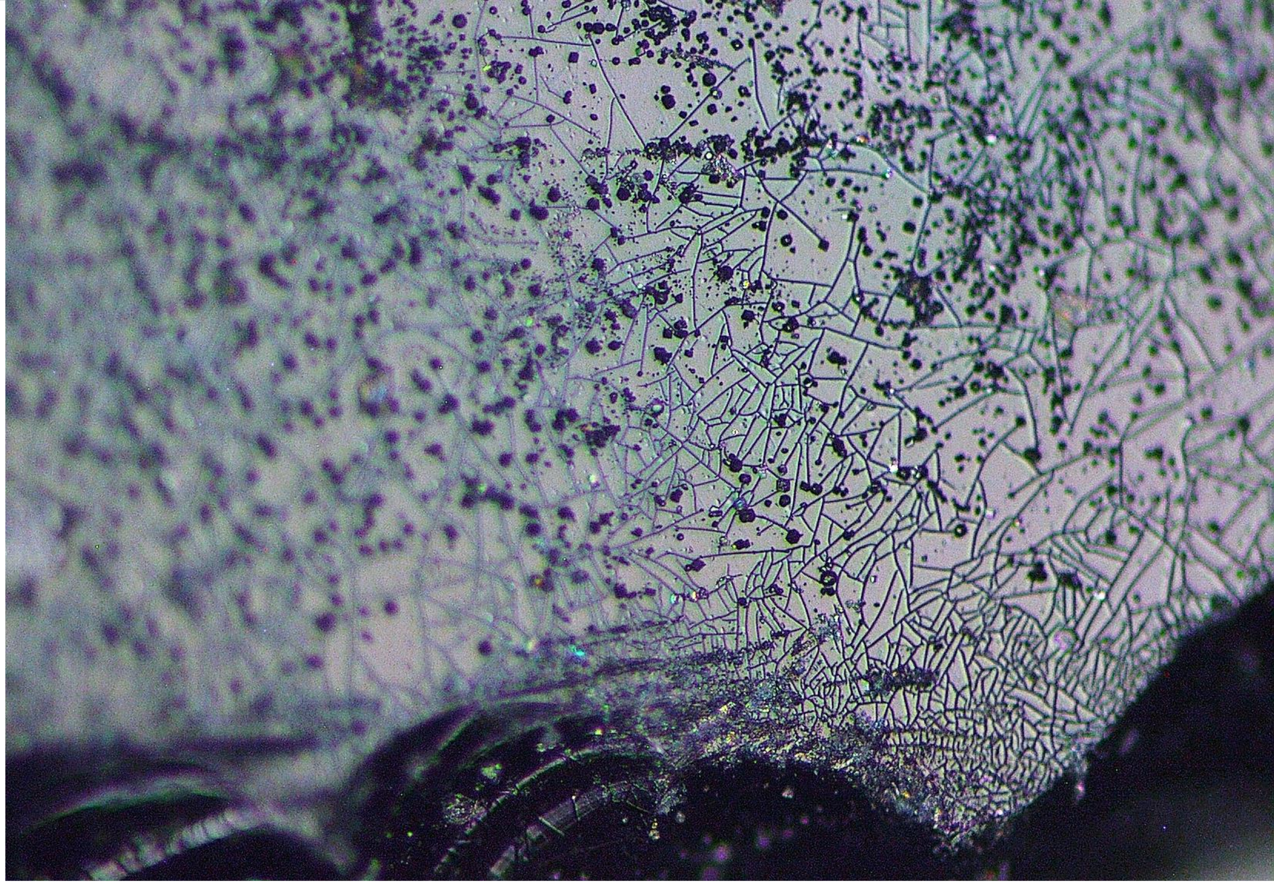


Localised deterioration



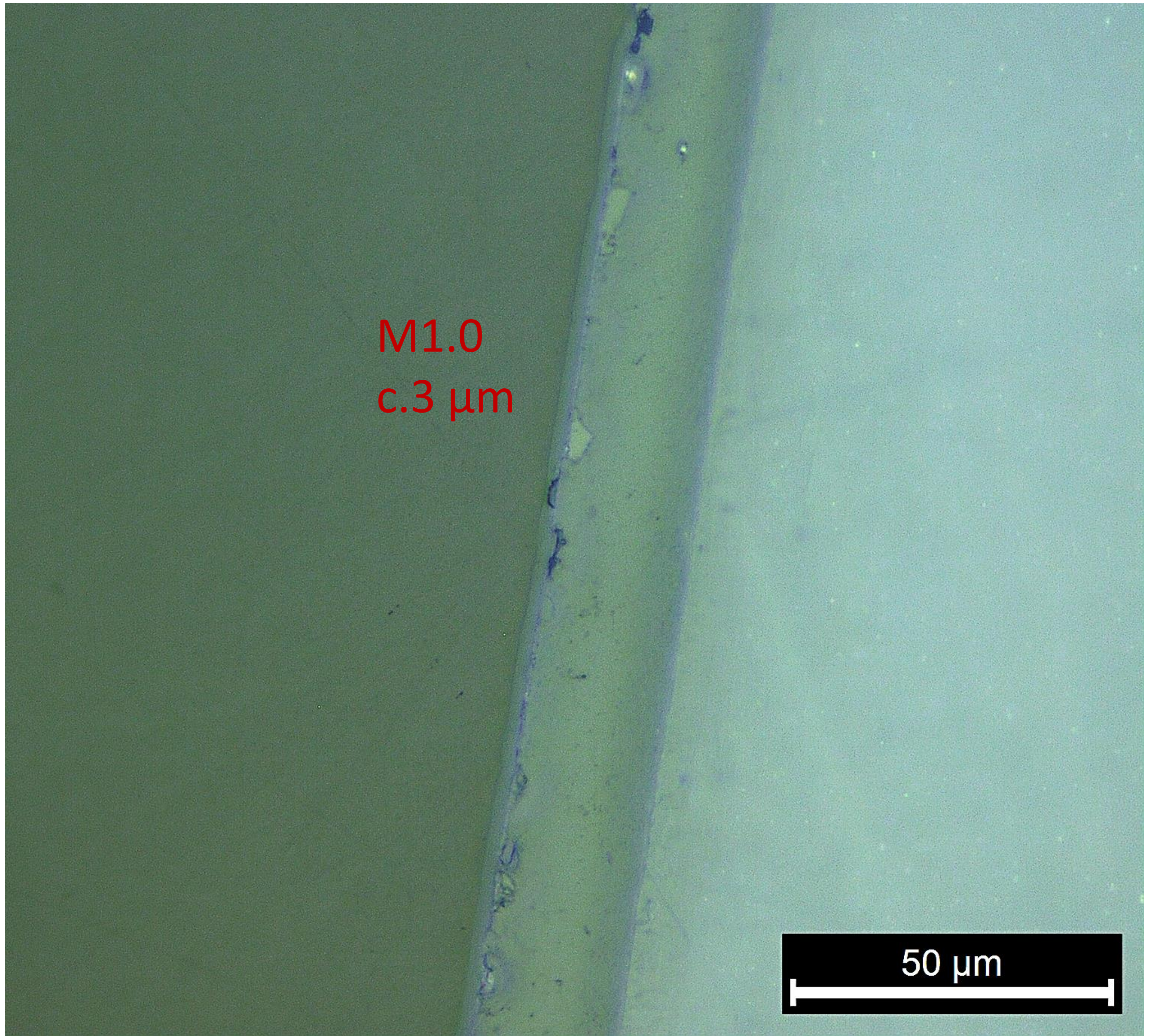

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

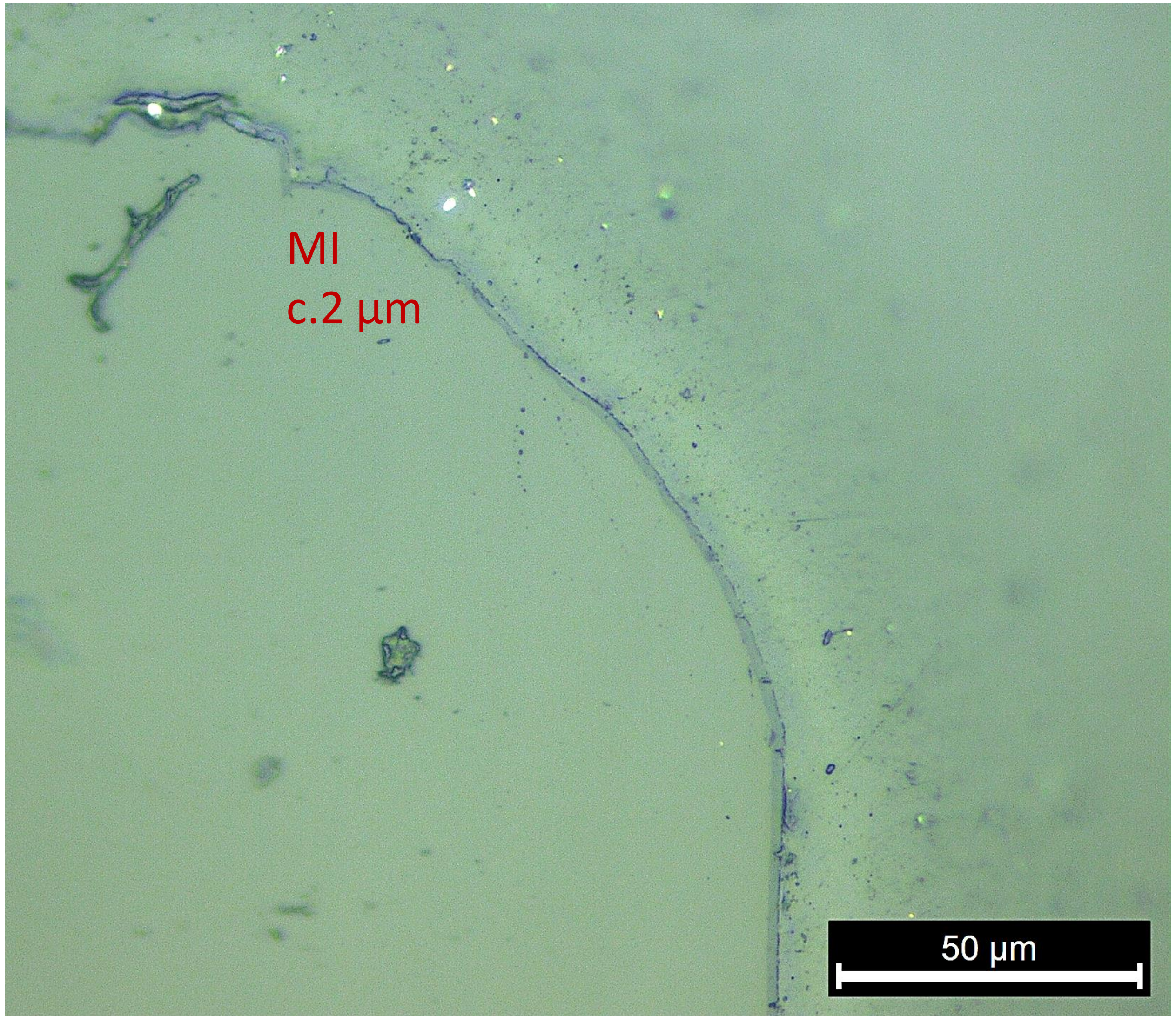

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

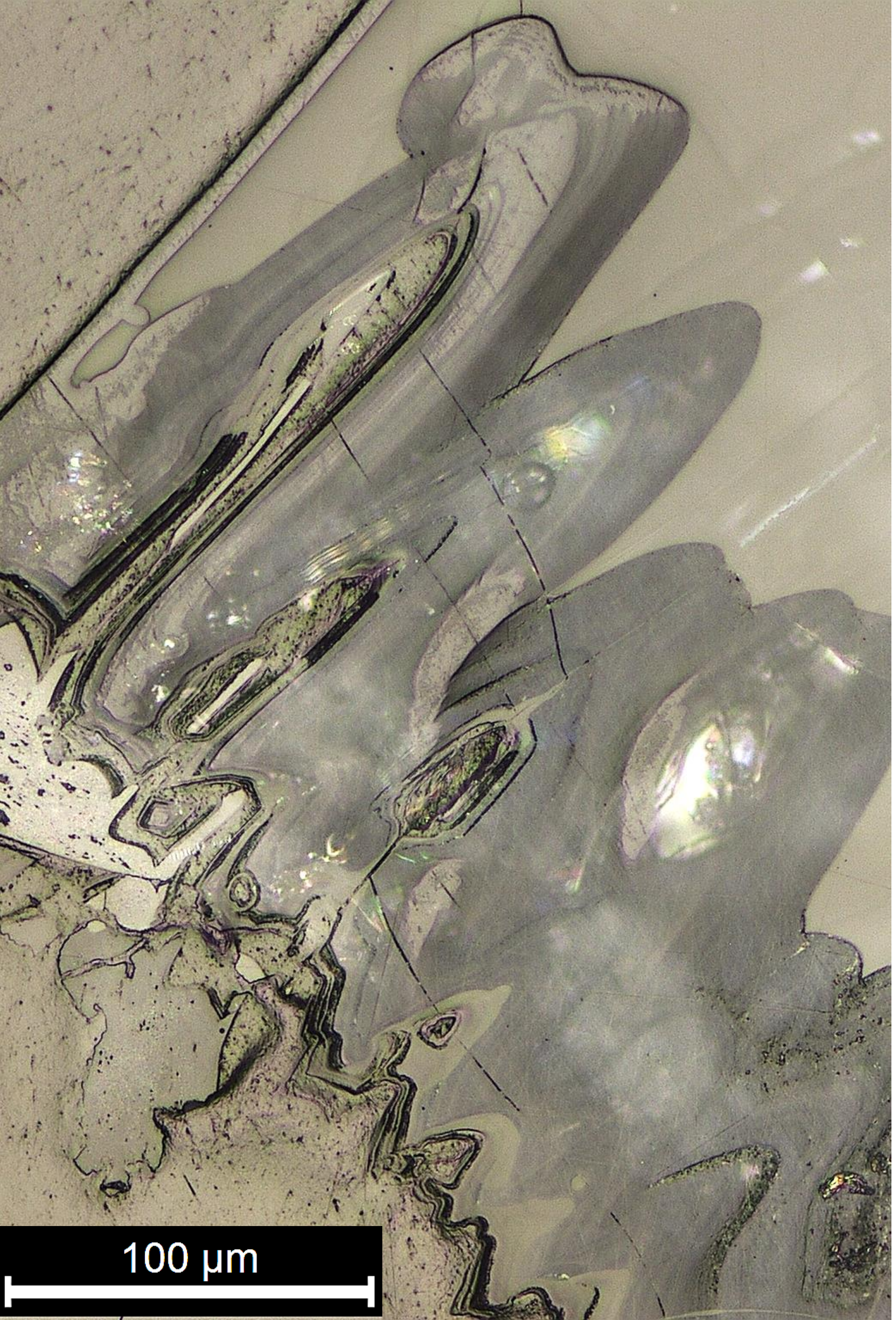



Areas of intensified crizzling

Crizzling in thin weathered layers



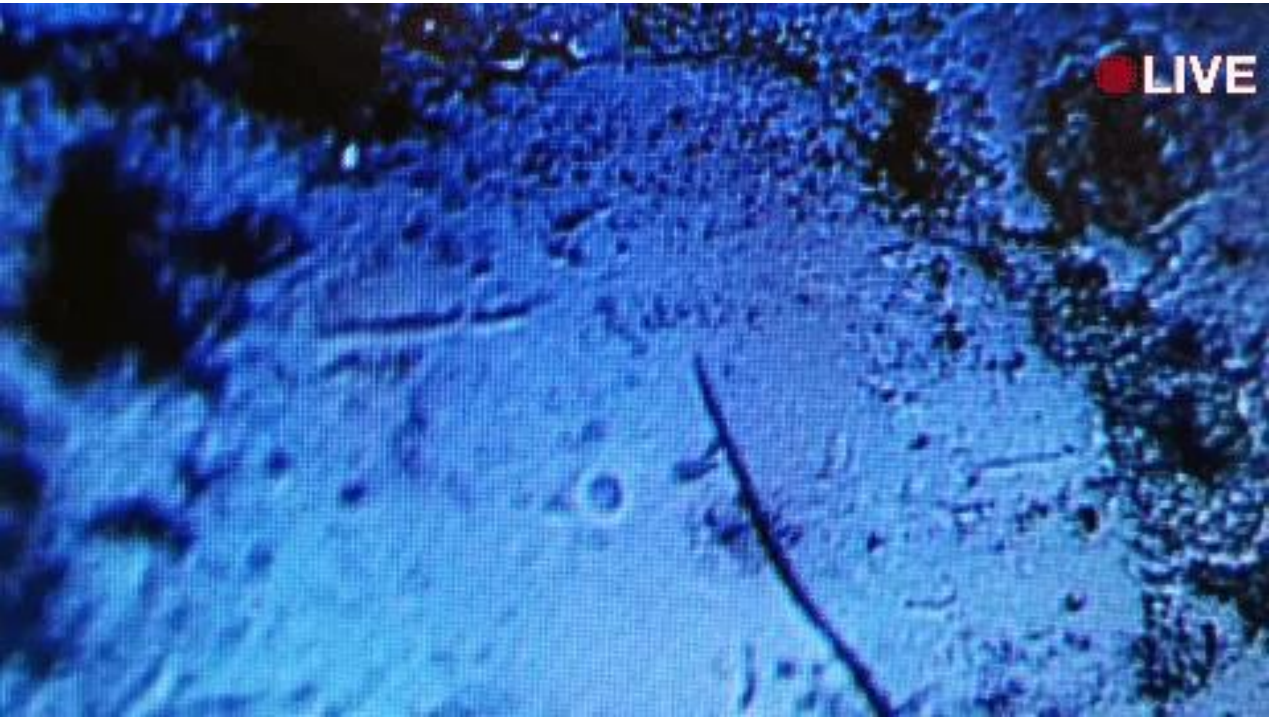


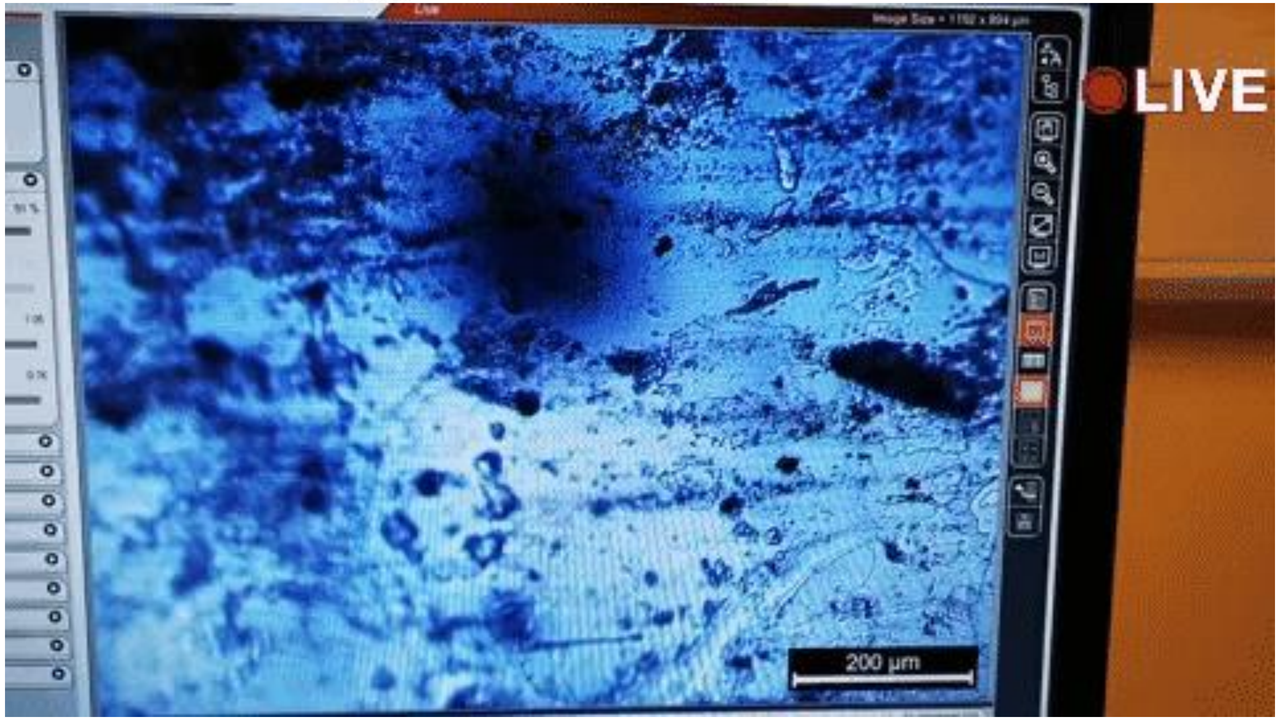


Corrosion in liquid water and high RH

- 300 days in 50 ml deionised water, 20 ^{o}C
  - M1.0 developed 10-20 μm leached layer, no crizzling, one sample shows deep stratification (left)
  - MI leaching depth approximately 5 μm, no noticeable cracking
- 300 days in near-100% RH, 20 ^{o}C
  - M1.0 leached layer 20-30 μm, crizzled, pitted, covered in water droplets and mineral accretions
  - MI almost unaffected, leached to < 5 μm, few surface crystalline deposits

Rapid crizzling during exposure to strong microscope light





Acoustic Emission (AE)

- Crizzling and delamination produces sound waves.
- Amplitude, frequency, source detected by sensor.
- Exact time and intensity of emission related to observable changes.
- Previously used to track physical changes in enamel

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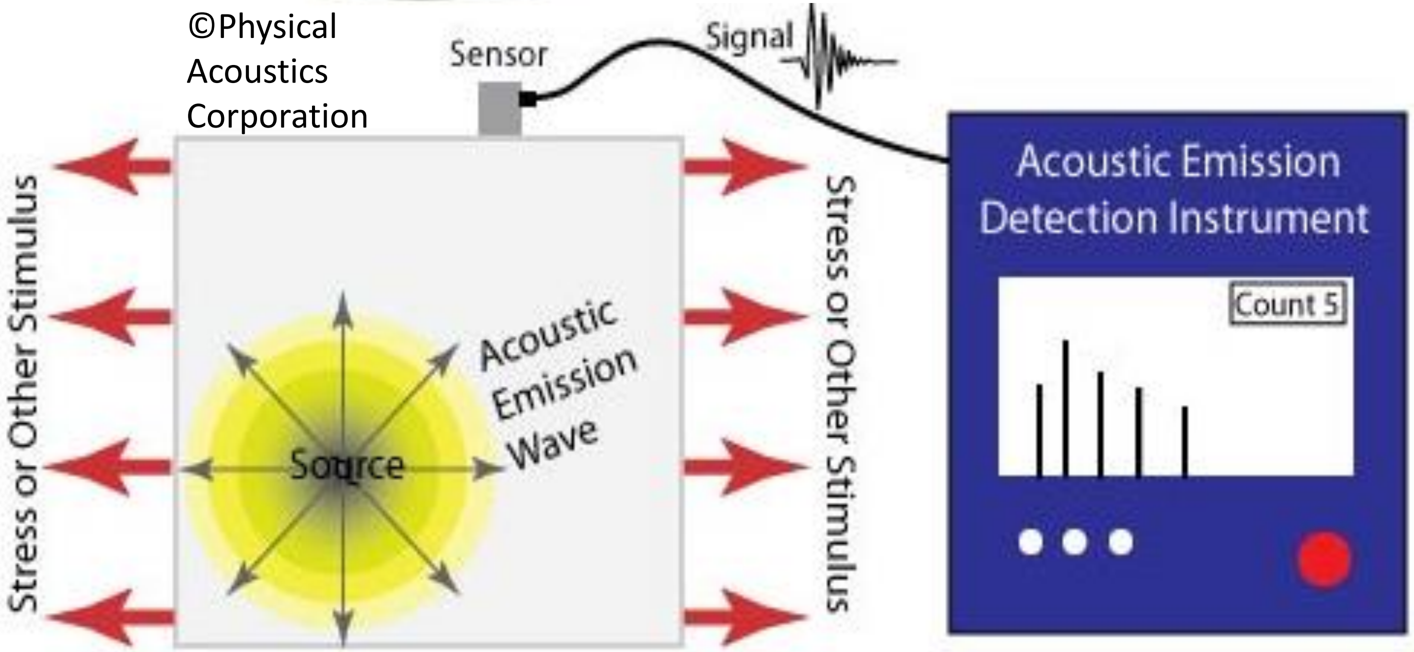

Conclusions

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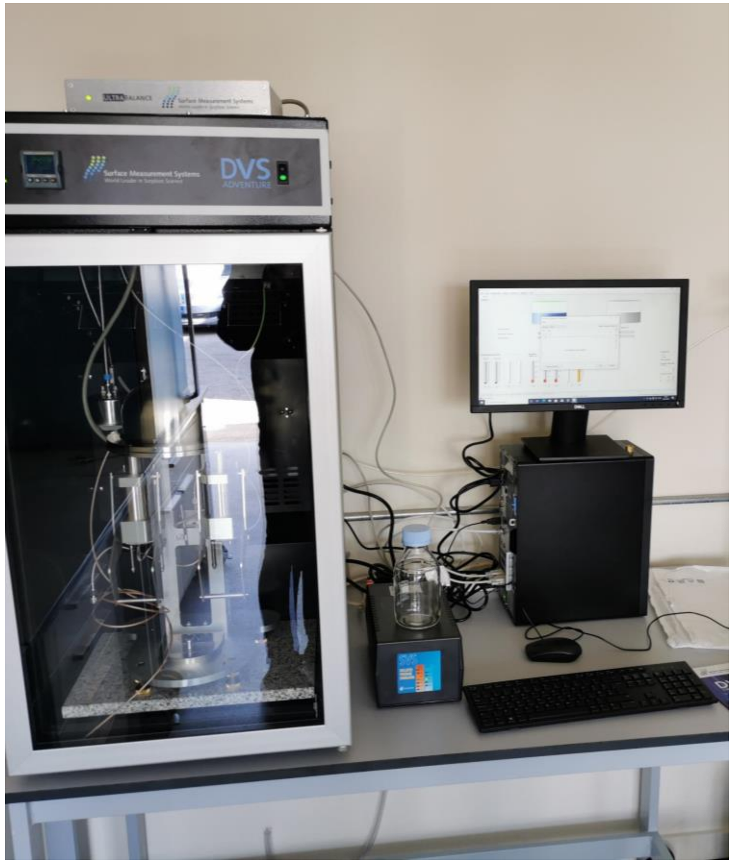
- Crizzling can also occur in extremely thin weathered layers, therefore it may not always be symptomatic of deep corrosion.
- Reducing physical disturbance to minimise delamination could be as important as tailoring storage conditions.

Current research



- Conditioning silica gel in environmental chambers (left) to 30-60% RH in increments of 5%
- Keeping pre-corroded glass in set conditions, inspecting for crizzling/delamination
- Dynamic Vapor Sorption (DVS, right) analysis to understand glass behaviour in fluctuating RH
- Repeat most successful experiments with real archaeological glass

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