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NucleUS
Immobilisation Science Laboratory

Alteration of UK Nuclear Waste Glasses; evidence from laboratory and field experiments

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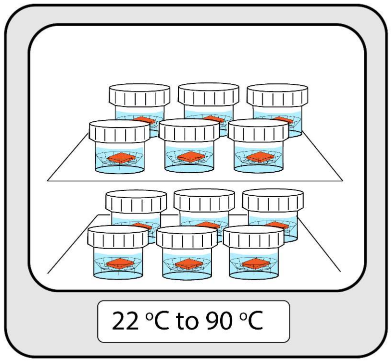
Garry Manifold, Jenny Ayling, Rachel Crawford, Professor Russell Hand.

The University of Sheffield

@ISL_Sheffield

What is this talk?

History lesson about HLW vitrification in the UK



Laboratory based durability testing of UK HLW

Field based durability testing of UK HLW in complex natural environments

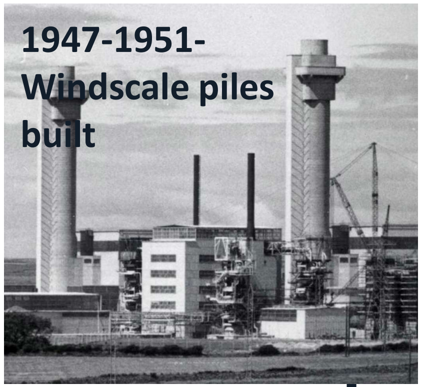
What is this talk?

History lesson about HLW vitrification in the UK

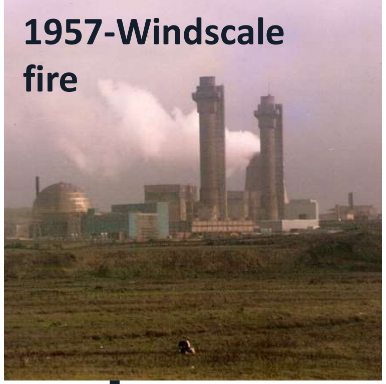
The history lesson

1940 1950 1960 1970 1980 1990 2000 2010 2020

The history lesson



1947-1951- Windscale piles built



1957-Windscale fire

1940
1950
1960
1970
1980
1990
2000
2010
2020

The history lesson

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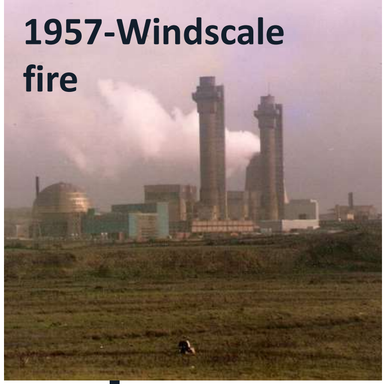
1947-1951-
Windscale piles
built


1957-Windscale
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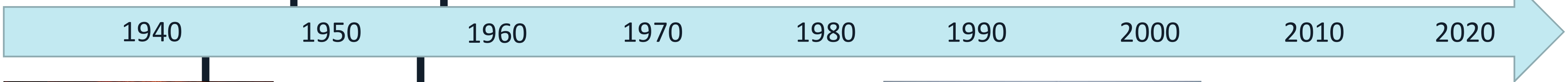
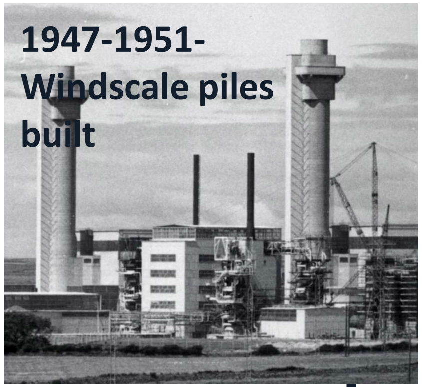



Calder Hall Civil nuclear power
station opened in 1956
“Magnox reactor”


1956- 2015 –
11 MAGNOX reactors
fleet

The history lesson



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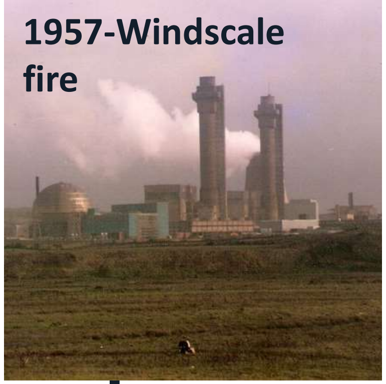
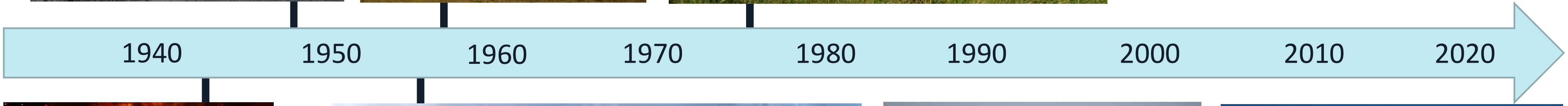


1957-Windscale
fire

1976-present -14 Advanced gas cooled reactors AGR's (8 still operational)



Calder Hall Civil nuclear power station opened in 1956
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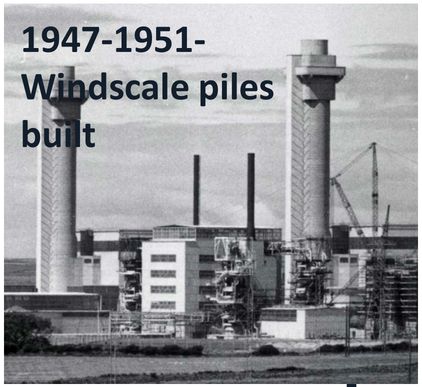
1995 – present
1 PWR reactor

The history lesson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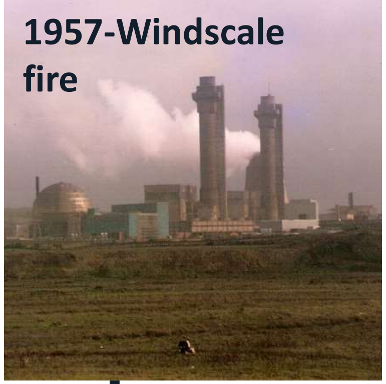
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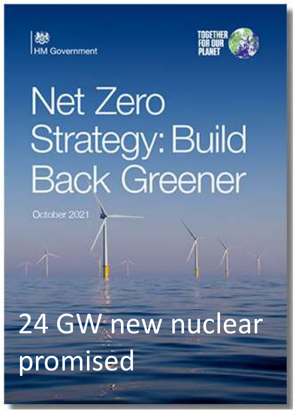
HM Government

TOGETHER FOR OUR PLANET

Net Zero Strategy: Build Back Greener

October 2021

24 GW new nuclear promised

Small Modular Reactors?

1940 1950 1960 1970 1980 1990 2000 2010 2020


Calder Hall Civil nuclear power station opened in 1956 “Magnox reactor”


1956- 2015 –
11 MAGNOX reactors fleet


1995 – present
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Spent fuel reprocessing in the UK

MAGNOX reactor fleet (1956- 2015)

Natural uranium metal based fuel in
‘**Mag**nesium-**n**on-**ox**idising’ alloy cladding

Magnox reprocessing plant (1965- 2022)

Uranium & Plutonium

Magnox High Activity Liquor
(high Mg and Al from fuel cladding)

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Uranium & Plutonium

Magnox High Activity Liquor
(high Mg and Al from fuel cladding)

Advanced Gas Cooled Reactors (AGR) (1994)

Light Water Reactor (pressurised water reactor PWR) (1994 -)

Enriched uranium oxide fuels in zirconium alloy tubes

THORP (Thermal Oxide Reprocessing Plant)

Uranium & Plutonium

Oxide High Activity Liquor (higher fission products, actinides and Gd (neutron poison))

History of vitrification of HLW in the UK

1982: second-generation French AVH processes preferred (Atelier de Vitrification La Hague).

- Higher throughput than AVM (25 vs 15 kg glass per hour)
- Elliptical rather than cylindrical melter.

1980: two-stage continuous vitrification process selected: AVM (Atelier de Vitrification Marcoule).

2002: Line 3 added

- Higher waste loading (up to 35 wt%)
- Higher throughputs (up to ~33 kg/hr)
- Wider feed envelopes (50:50 Blends, etc.).
- Product quality of "small deviations".
- Glass for Post Operational Clean Out (POCO) of the HAL storage tanks containing zirconium molybdate

1980 1990 2000 2010 2020

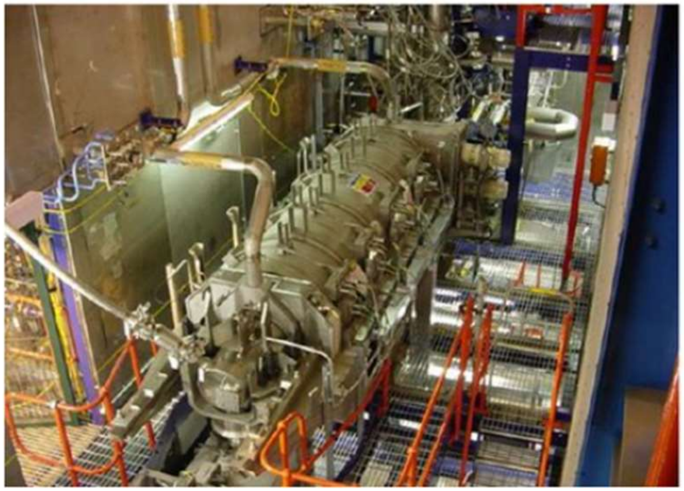
1981: Full Scale Inactive Facility (FSIF) at Sellafield

1989: Lines 1 & 2 commissioned

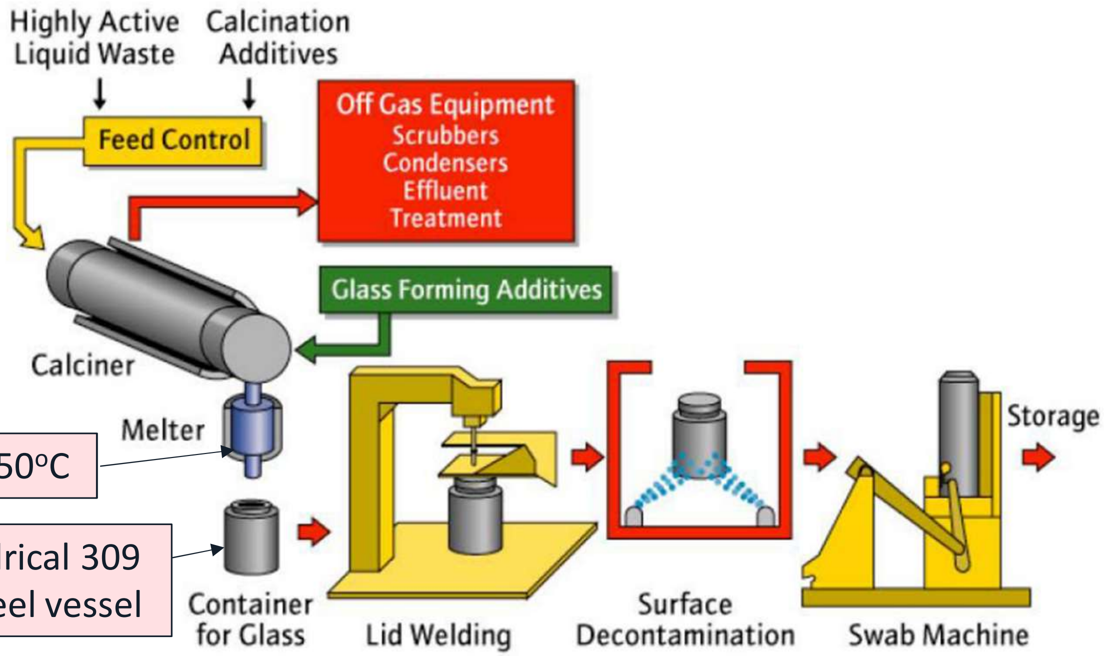
1990: First containers

2001: second full scale vitrification test rig (VTR) built for technical underpinning

1991: Full Scale Inactive Facility decommissioned



Vitrification process



~1050°C

169 L cylindrical 309 stainless steel vessel

Cooled for 24 hours

Fig. 1. Schematic of the HLW vitrification process on the Sellafield site

- Each pour is ~200 kg glass, with ~70 kg remaining in the crucible as a heel (total of 400 kg glass per container)
- Active products are not sampled but the feedstock is monitored

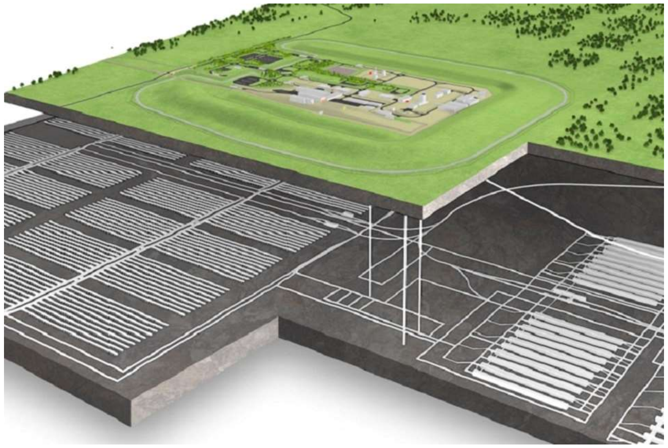
Storage conditions:

- Passive cooling to ensure glass remains well below transition temperature of ~500oC

- ~ 7,520 packages
- ~1,470 m^3 of HLW

(NDA radioactive waste inventory, 2022)

Disposal:



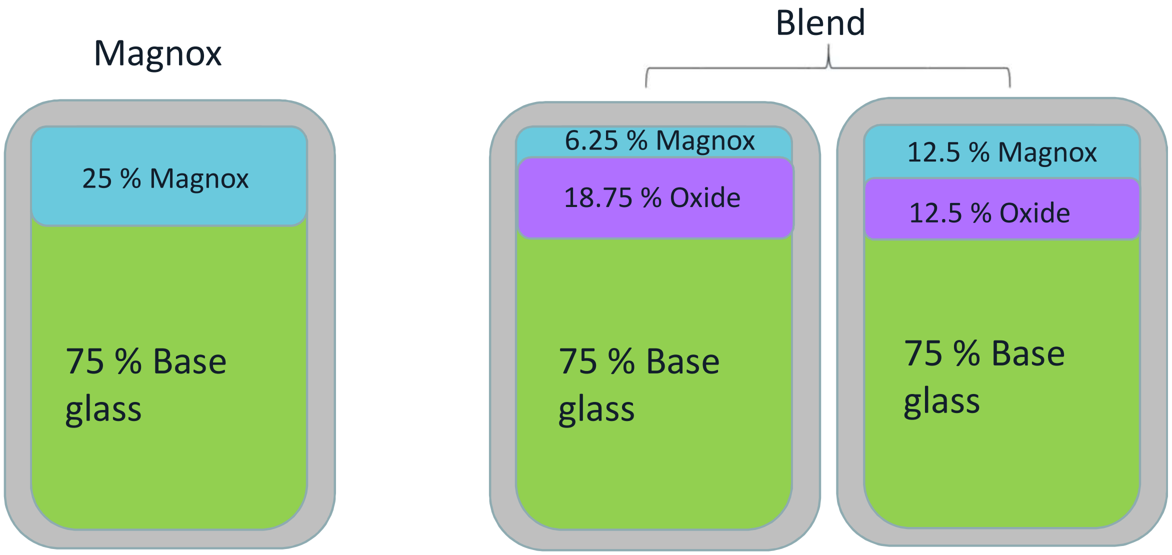
Mixture Windscale (MW) base glass

Table 2. Composition of base glasses used for the vitrification of HLW in the UK Wt %

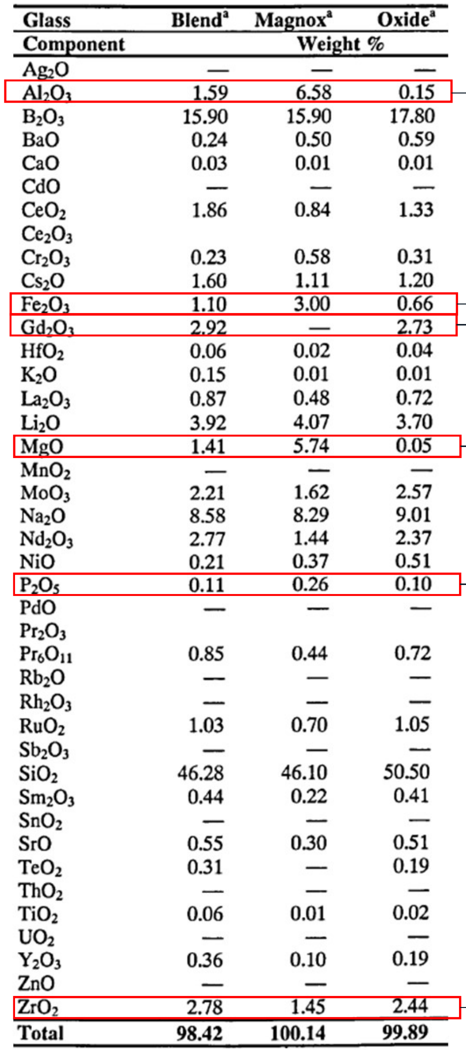
Base Glass Type	SiO_2	B_2O_3	Na_2O	Li_2O
MW	61.75	21.88	11.05	5.33
MW-½Li	63.42	22.50	11.35	2.74

- Equimolar Li and Na found to be desirable
- $LiNO_3$ added to calcine

- To ensure that vitrified Oxide HAL complies with product quality requirements, the Oxide feed is blended with Magnox liquor.
- Currently, the standard blend ratio is 75:25 Oxide:Magnox, although lower ratios, e.g. 50:50, can be implemented.



Variation in chemical composition of HLW



Glass	Blend[a]	Magnox[a]	Oxide[a]
Component		Weight %	
Ag_2O	—	—	—
Al_2O_3	1.59	6.58	0.15
B_2O_3	15.90	15.90	17.80
BaO	0.24	0.50	0.59
CaO	0.03	0.01	0.01
CdO	—	—	—
CeO_2	1.86	0.84	1.33
Ce_2O_3			
Cr_2O_3	0.23	0.58	0.31
Cs_2O	1.60	1.11	1.20
Fe_2O_3	1.10	3.00	0.66
Gd_2O_3	2.92	—	2.73
HfO_2	0.06	0.02	0.04
K_2O	0.15	0.01	0.01
La_2O_3	0.87	0.48	0.72
Li_2O	3.92	4.07	3.70
MgO	1.41	5.74	0.05
MnO_2	—	—	—
MoO_3	2.21	1.62	2.57
Na_2O	8.58	8.29	9.01
Nd_2O_3	2.77	1.44	2.37
NiO	0.21	0.37	0.51
P_2O_5	0.11	0.26	0.10
PdO	—	—	—
Pr_2O_3			
Pr_6O_{11}	0.85	0.44	0.72
Rb_2O	—	—	—
Rh_2O_3	—	—	—
RuO_2	1.03	0.70	1.05
Sb_2O_3	—	—	—
SiO_2	46.28	46.10	50.50
Sm_2O_3	0.44	0.22	0.41
SnO_2	—	—	—
SrO	0.55	0.30	0.51
TeO_2	0.31	—	0.19
ThO_2	—	—	—
TiO_2	0.06	0.01	0.02
UO_2	—	—	—
Y_2O_3	0.36	0.10	0.19
ZnO	—	—	—
ZrO_2	2.78	1.45	2.44
Total	**98.42**	**100.14**	**99.89**

Magnox HAL contains high aluminium from Mg – Al – Alloy cladding

Magnox HAL contains higher Fe

Oxide HAL contains high Gd (added as a neutron poison)

Magnox HAL contains higher Mg from residual fuel cladding

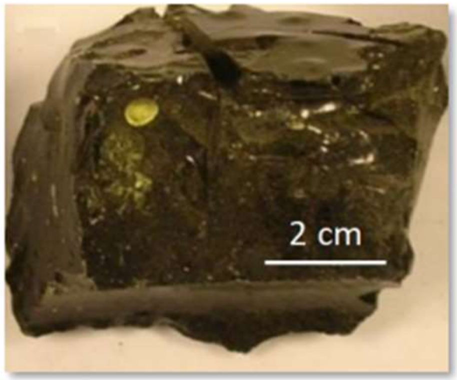
Small amount of P as Liquid-liquid solvent extraction using tributyl phophate

Oxide HAL contains higher Zr from residual fuel cladding

Chemistries for post operational clean up (POCO)

Highly active liquor (HAL) storage tanks will be emptied and washed out to remove any accumulated solids. These **solids** are expected to contain **high molybdenum**.

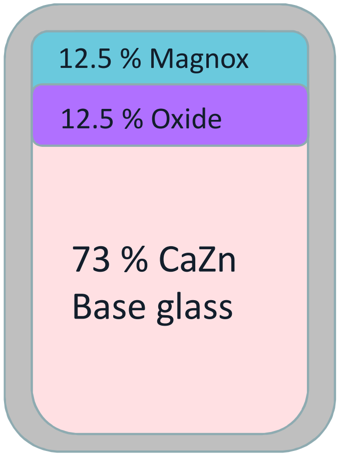
'Ca/Zn' base glass allows for significantly higher waste loadings by the formation of $CaMoO_4$ crystals when the Mo content exceeds its solubility limit in the glass.



Forcing precipitation of Mo as Ca-molybdates avoids undesirable Na-molybdates that decrease the durability of the glass

Oxide	MW base wt %	CaZn base wt %
SiO_2	60.27	56.1
B_2O_3	24.11	21.51
Li_2O	4.75	2.92
Na_2O	10.88	11.48
CaO	-	1.94
ZnO	-	6.03

The CaZn base glass has been tested using Blend HAL



12.5 % Magnox

12.5 % Oxide

73 % CaZn Base glass

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Rick Short / Procedia Materials Science 7 (2014) 93 – 100

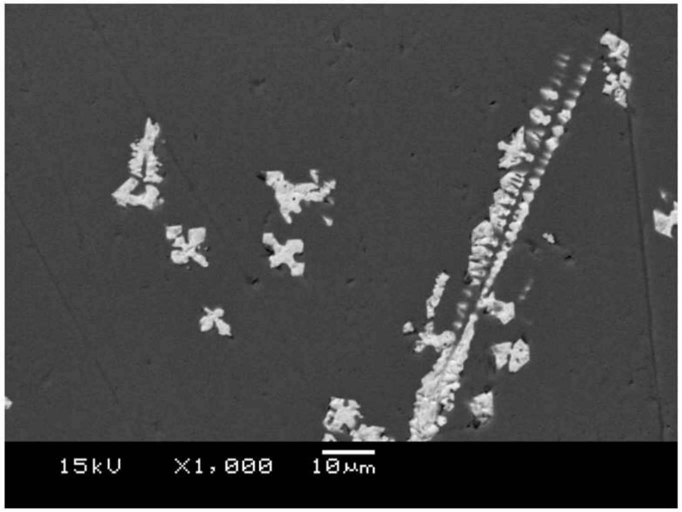

Figure 7 - Backscattered SEM picture showing $CaMoO_4$ crystals in a simulated Ca/Zn plus POCO waste glass

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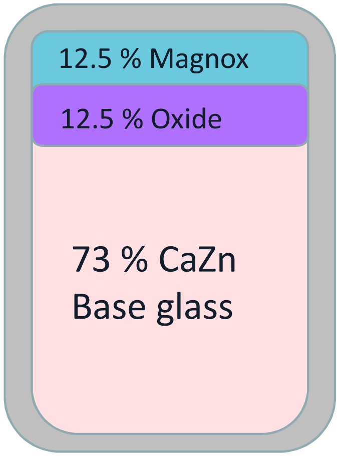

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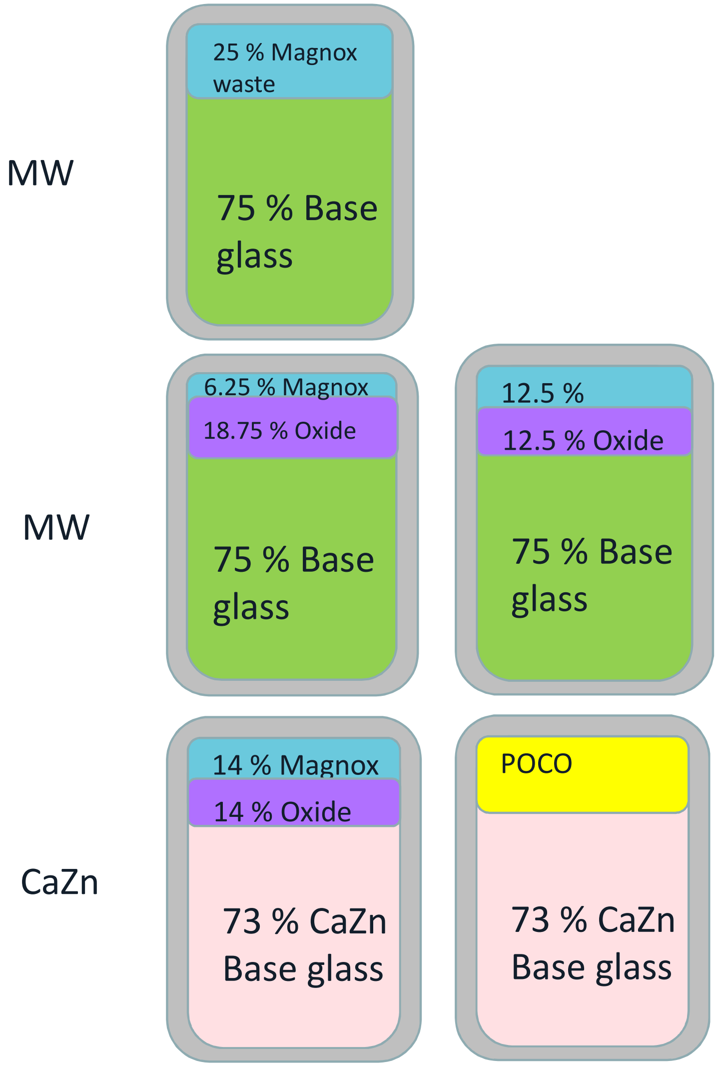
Summary of UK HLW glasses

MW25 - Blend (75:25)

Base glass　Waste Loading　Waste Type　(% oxide/magnox)

Name	Long name	Active glass produced
MW25 – Magnox	Mixture Windscale base glass 25% waste loading 100 % Magnox HAL	Yes
MW25 - Blend (75:25 or 50:50)	Mixture Windscale base glass 25% waste loading 75 % Oxide HAL: 25 % Magnox HAL	Yes
CaZn28 – Blend (50:50)	CaZn Base glass 28% waste loading 50 % Oxide HAL: 50 % Magnox HAL	Only on one active vitrification line
CaZn XX POCO	CaZn Base glass 25% waste loading 75 % Oxide HAL: 25 % Magnox HAL	Only on vitrification test rig



MW

25 % Magnox waste

75 % Base glass

MW

6.25 % Magnox

18.75 % Oxide

75 % Base glass

12.5 %

12.5 % Oxide

75 % Base glass

CaZn

14 % Magnox

14 % Oxide

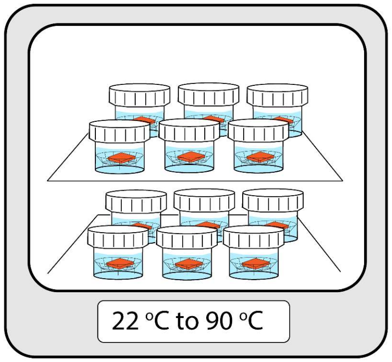
73 % CaZn Base glass

POCO

73 % CaZn Base glass

How do these glasses behave in laboratory tests

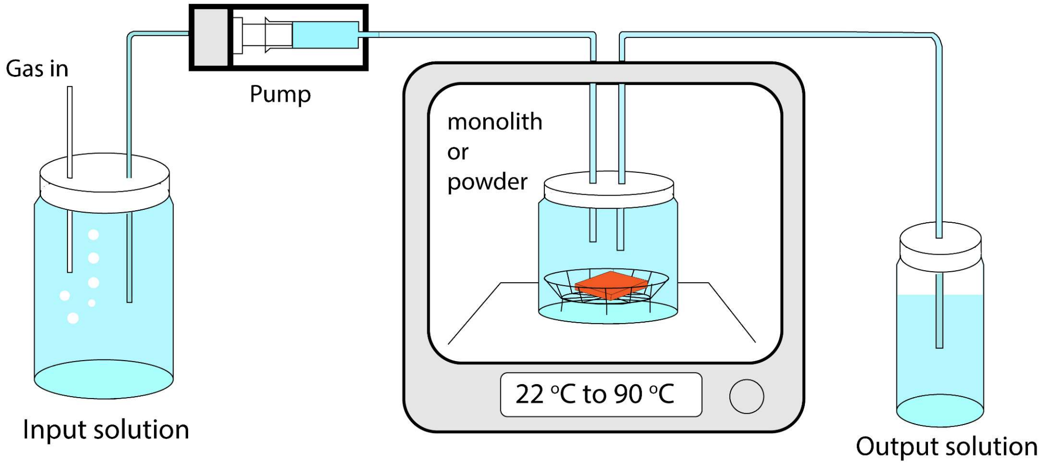
History lesson about HLW vitrification in the UK

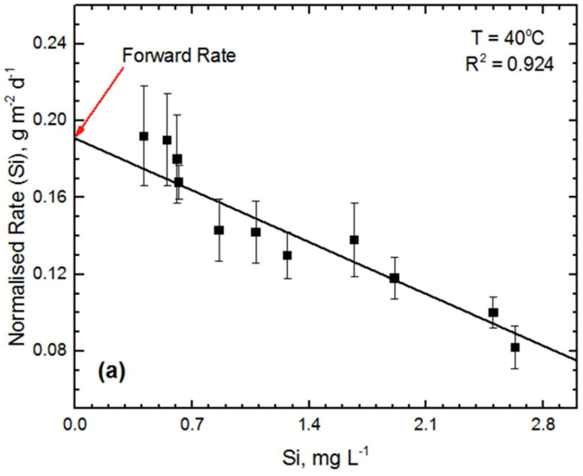


Laboratory based durability testing of UK HLW

Tests to measure the forward rate

A) Single Pass Flow Through

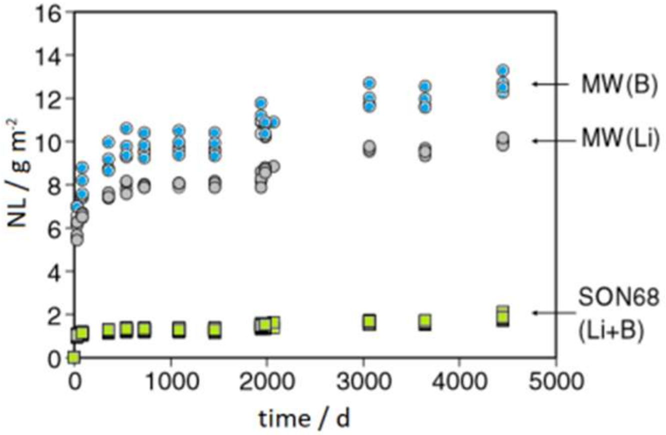




(Iwalewa et al., 2017) MW-25_magnox

Glass	Forward rate g m^2 d^1	Method & reference
MW 25	0.185 (40°C)	SPFT; Iwalawa et al., 2017.
ISG	0.026-0.006 (50°C)	SPFT/MCFT Fisher, 2020; Inagaki 2013
SON68	0.017 (50°C)	Jollivet et al., 2012

Curti et al., 2006



12.2 year PCT-B type experiment at 90 °C, SA/V = 1,200 m-1 , in UHQ water.

Is the increased Mg part of the problem?

- ^{11}B MAS NMR spectra of a simplified glass series showed a systematic increase in the amount of three-coordinated boron ([3]B) with increasing amounts of Mg.
- However, ^{11}B NMR measurements of the leached material showed that the additional [3]B was not preferentially leached.
- Despite the structural changes in the glass induced by Ca/Mg substitution, initial dissolution rates (r0) remained invariant, within error, with Ca/Mg ratio.

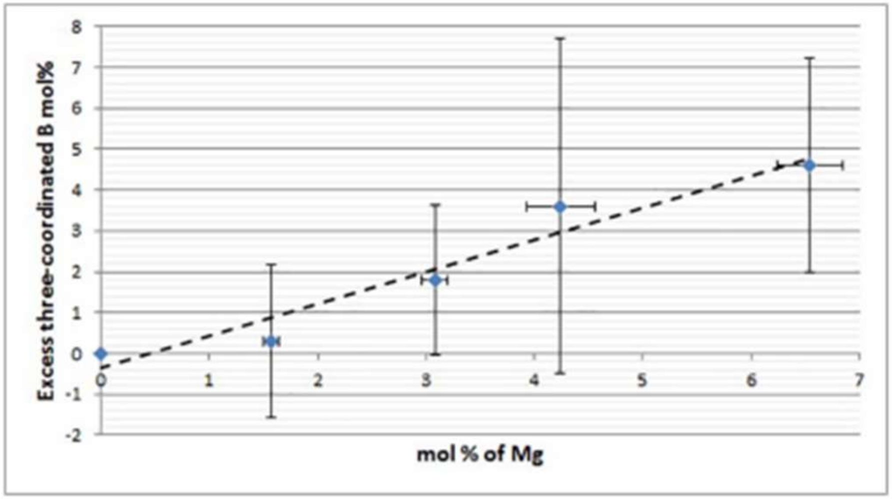


Fig. 9. The linear fit (dashed line) of the amount of boron that transform from four-fold coordination to three-fold coordination on substitution of Mg for Ca per 100 mol of cations (filled square).

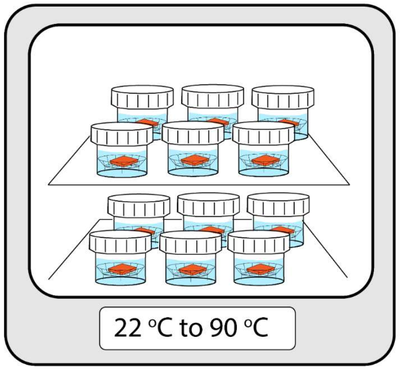
Table 5
Initial dissolution rate of the simplified glass series as determined from the rate of change in the effective thickness of dissolved glass based on Si concentration.

	CaEM	Mg25Ca75	Mg50Ca50	Mg75Ca25	MgEM
Initial dissolution rate (g/m^2/d)	2.33 ± 0.23	2.60 ± 0.26	2.54 ± 0.25	2.42 ± 0.24	2.22 ± 0.22

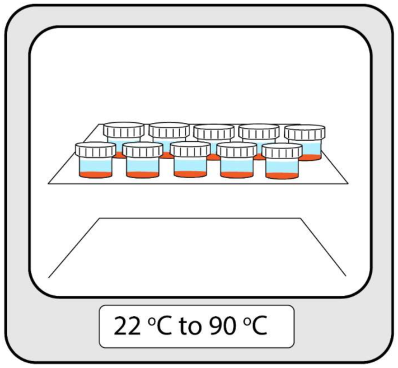
Guo et al., 2018

Comparison of the short term behaviour of MW vs CaZn

Static monolith dissolution tests
Example- ASTM C1220 (MCC-1)



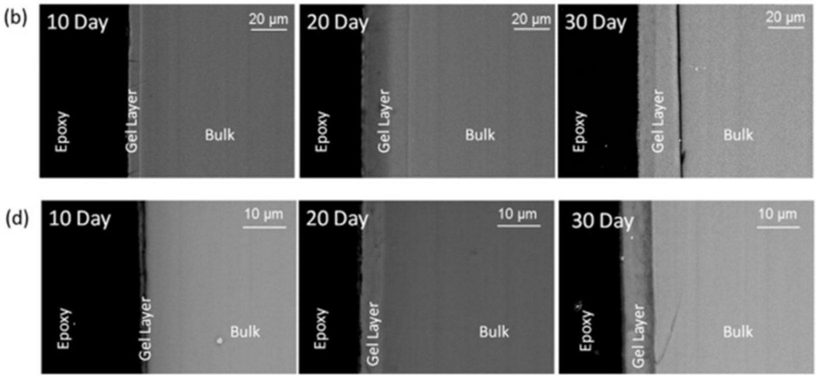
Static powder dissolution tests
ASTM- C 1285 (PCT- A/B)



Comparison of the short term behaviour of MW vs CaZn

In the short term CaZn base glass appears more durable than MW base glass:

- Addition of CaO/ZnO to the UK HLW glass reduces gel layer thickness and average alteration rate.
- Hydrated Ca- and Zn-silicates are the products of CaO/ZnO modified glass alteration.
- The average alteration rate exceeds that for the French HLW simulant, SON68.



MW_25

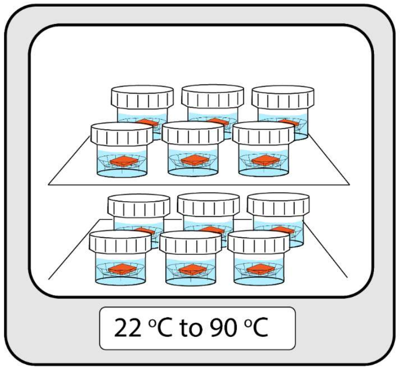
Gel layer thickness ***> 20 micron***
Rate = ***3.4*** *± 0.3 g m^{-2} d^{-1}*

CaZn_25

Gel layer thickness ***< 10 micron***
Rate = ***0.9*** *± 0.1 g m^{-2} d^{-1}*

Cassingham et al., 2016

Static monolith dissolution tests
Example- ASTM C1220 (MCC-1)



22 °C to 90 °C

Static powder dissolution tests
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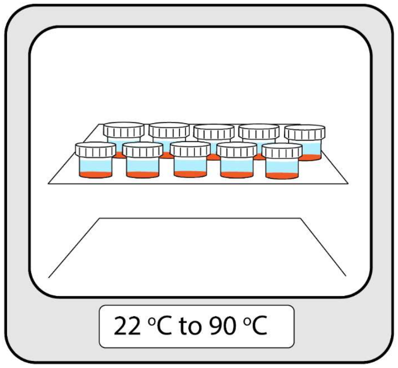


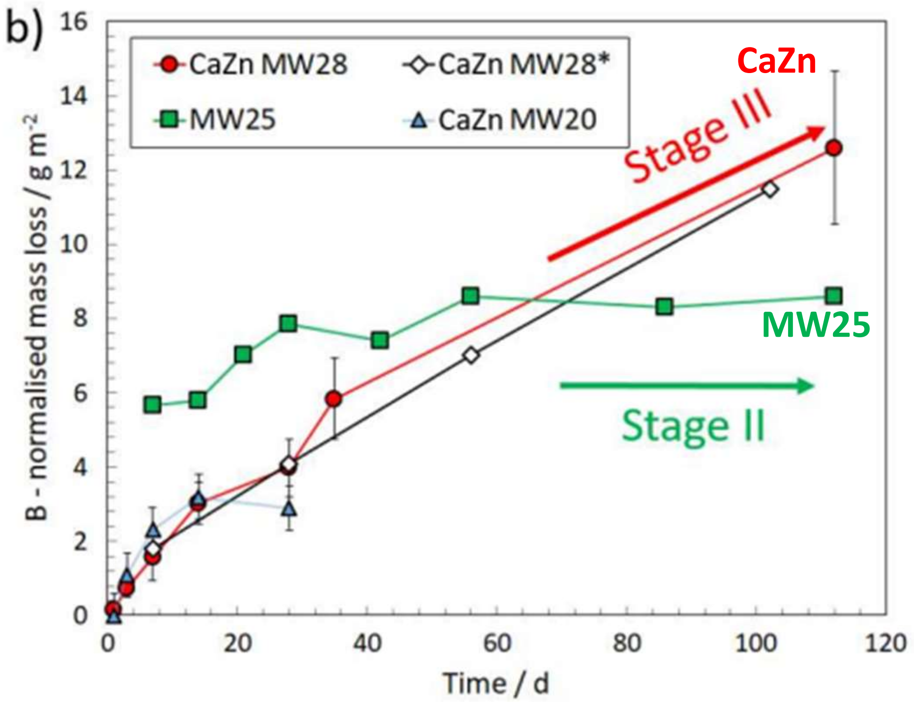
22 °C to 90 °C

Long term behaviour of MW 25 vs CaZn

Over longer time periods CaZn base glass appears less durable than MW base glass and does not display a rate drop:

- MW25 has faster dissolution rates over the short term but displays classic ‘stage II’ behaviour

- CaZn28 has faster dissolution rates over the long term and does not display a rate drop (at 90°C, 112 days in DI water



Fisher et al., 2020

Long term behaviour of MW 25 vs CaZn

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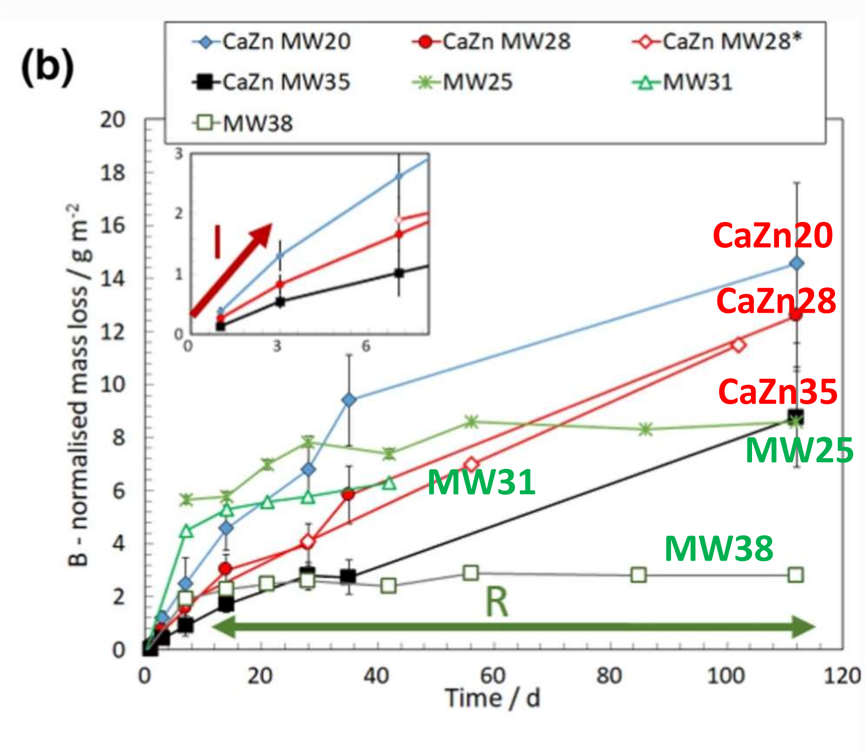
- MW25 has faster dissolution rates over the short term but displays classic ‘stage II’ behaviour
- CaZn28 has faster dissolution rates over the long term and does not display a rate drop (at 90°C, 112 days in DI water
- Increased waste loading shown not to be detrimental to glass performance
- If increasing waste loading makes a more durable glass then the evidence is pointing to component of the waste glass (e.g. Zinc)



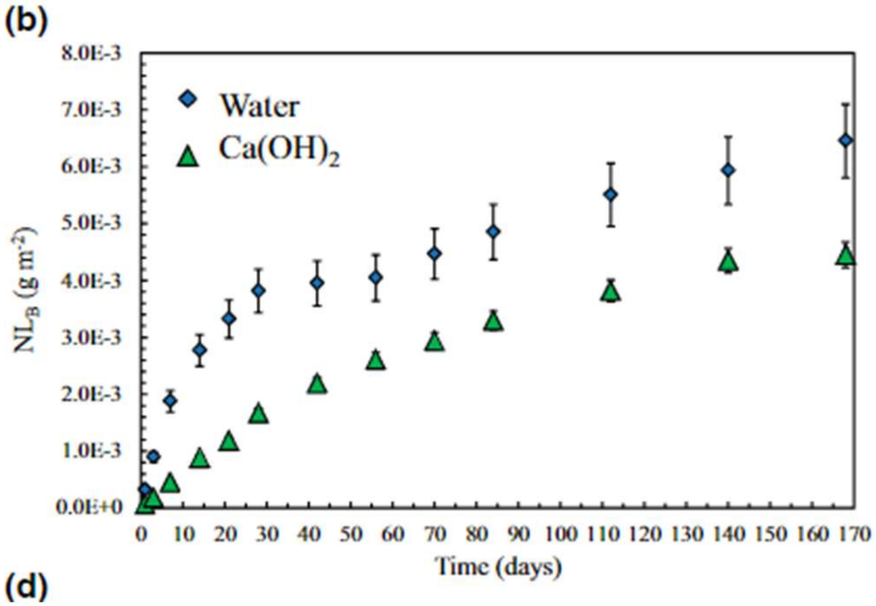
Fisher, (2021)

Behaviour of UK HLW in hyperalkaline solutions

Glass powders and monoliths were dissolved for 168 days in saturated $Ca(OH)_2$ to represent those in a co-located geological disposal facility.

Dissolution in the presence of high concentrations of Ca (>200 mg/L) was lower than dissolution in water.

A lag in Si release was observed until a Ca:Si ratio of <2 was achieved due to incorporation of Ca into the hydrated surface before precipitation of C-S-H phases that play a controlling role in future dissolution.



Corkhill et al., 2013

Backhouse, 2017

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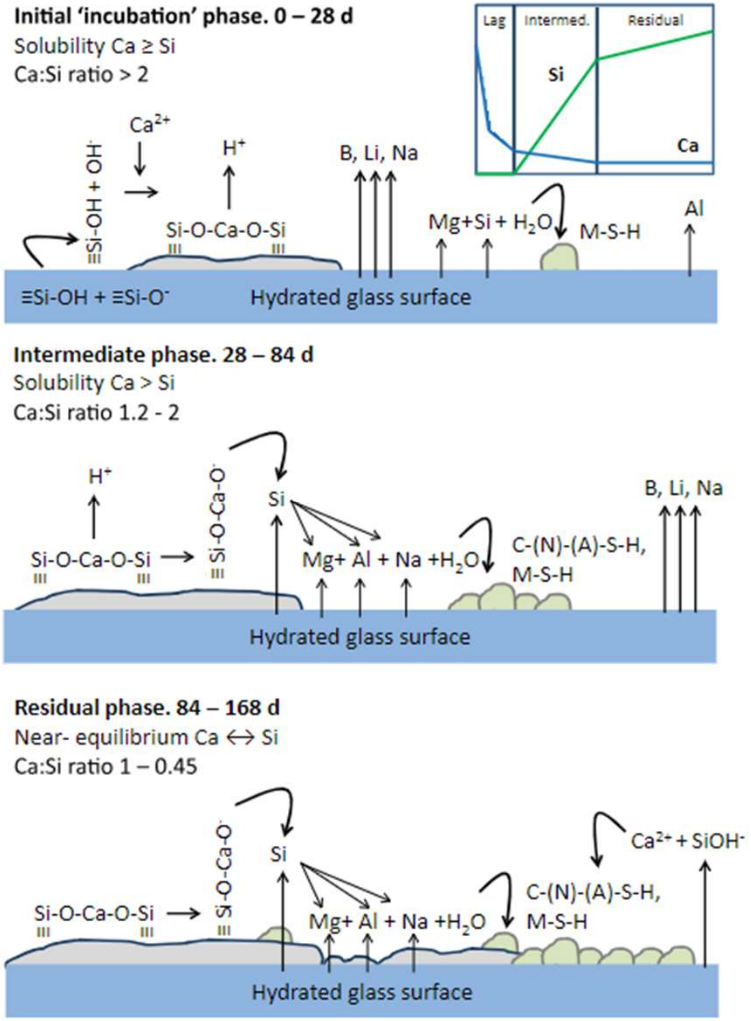
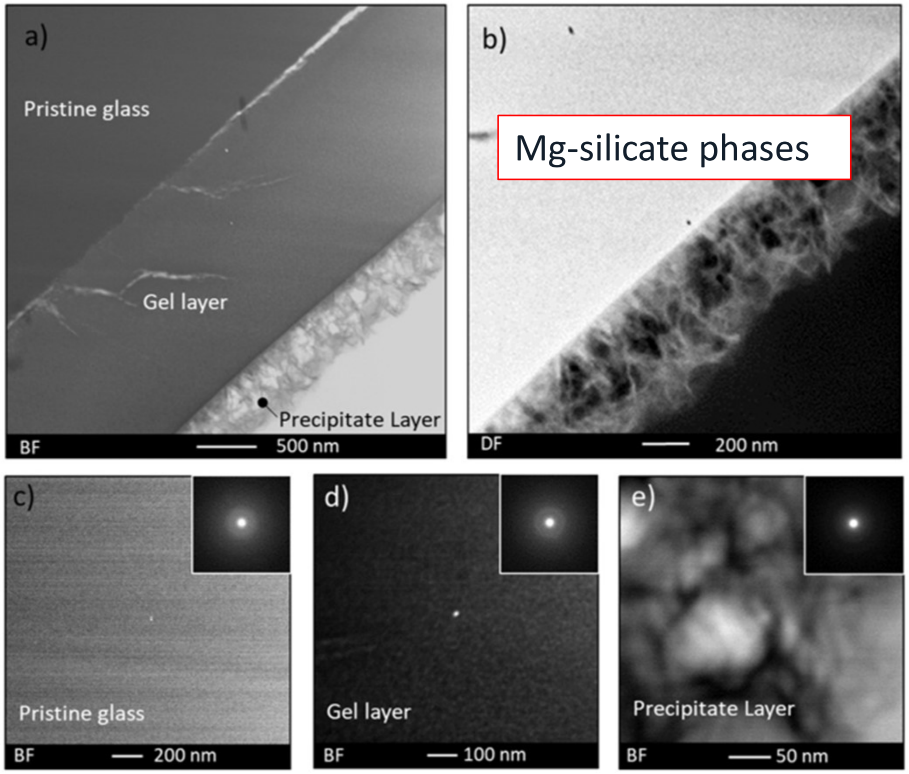


Corkhill et al., 2013

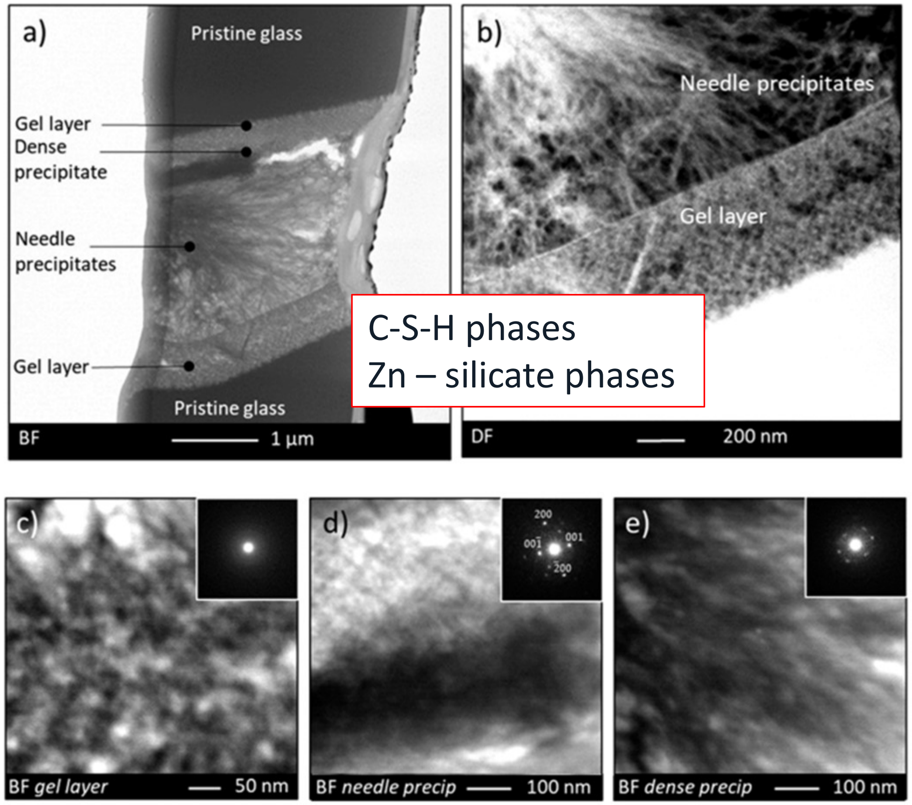
Mineralogy and morphology of the alteration layers



Mg-silicate phases

Image showing the cross section of the pristine glass, gel layer and precipitate layer; (**b**) dark field nicrograph of the gel layer and Mg-silicate rich ribbon precipitates; and high resolution bright field mages and associated selective area electron diffraction patterns of: (**c**) the pristine glass; (**d**) the gel ayer; and (**e**) the precipitates.

Fig. 5: Scanning transmission electron microscopy analysis of CaZn28 glass after 84 d of dissolution in Evolved Cement Water.

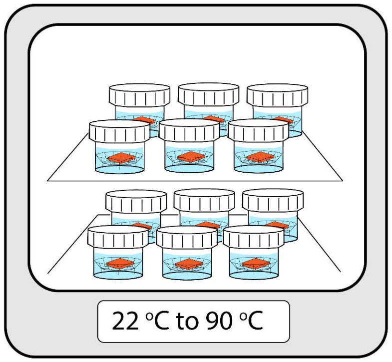


C-S-H phases
Zn – silicate phases

Corkhill et al, 2022 NPJ Mater. Degrad., 6, 67.

But what about more complex systems

History lesson about HLW vitrification in the UK



Laboratory based durability testing of UK HLW

Field based durability testing of UK HLW in complex natural environments

Purpose of field experiment and natural analogue

- Validation
- Invalidation
- Finding the ‘curveballs’
- Identifying the ‘dominant’ effect

Purpose of field experiment and natural analogue

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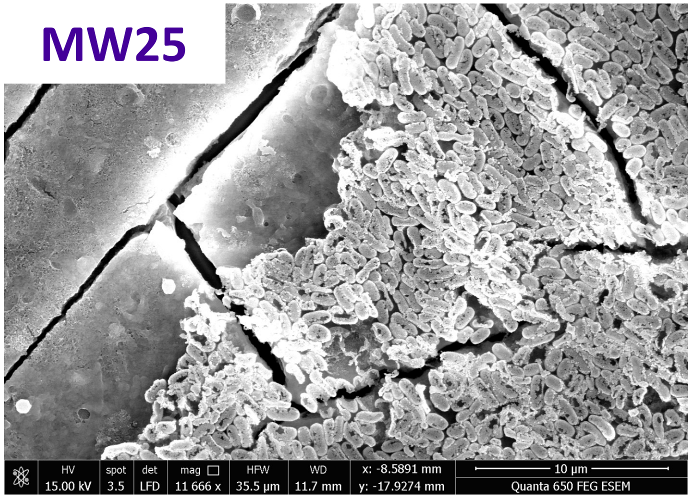
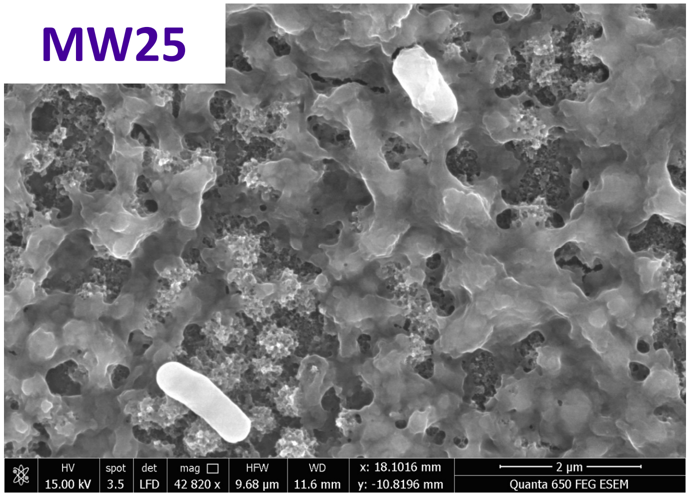
MW25



MW25



Glass dissolution in complex environments

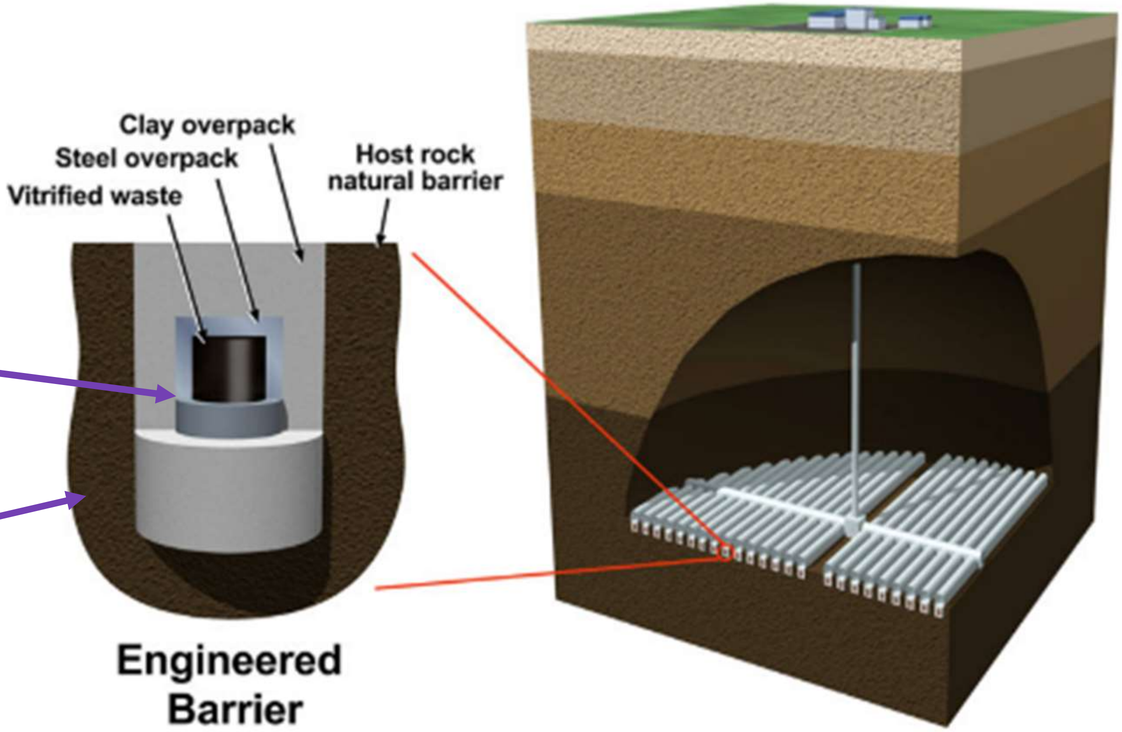
Alteration layer formation can be influenced by elements from without as well as within

Containment

Glass is cast into steel canisters. The overpack may also be composed of steel

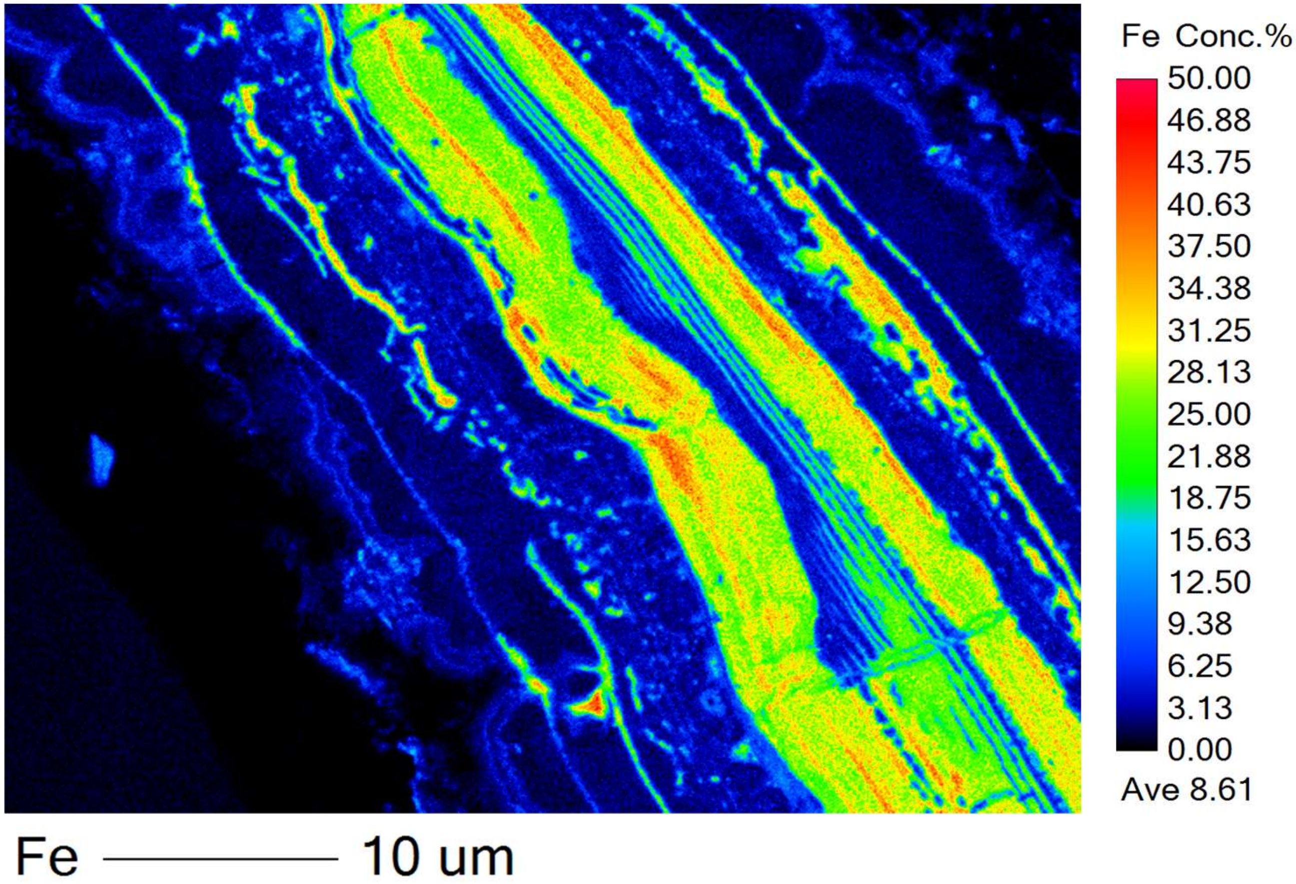
Far-field

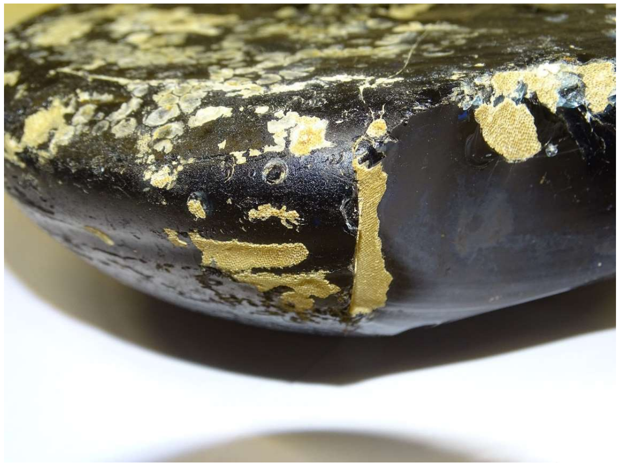
HUGE reservoir of elements present in rock-forming minerals



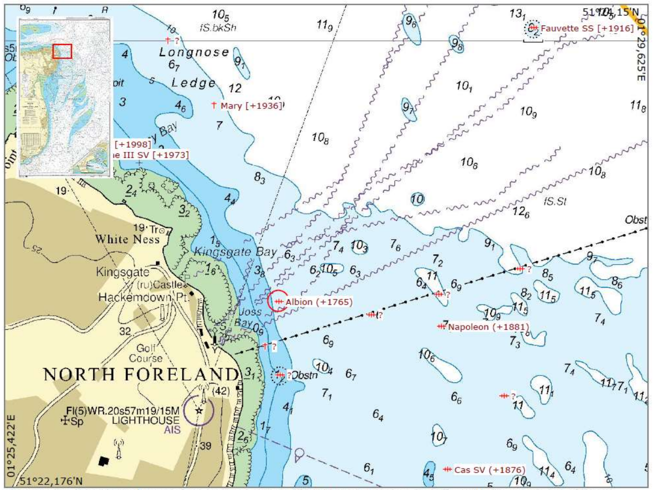
Thorpe et al.., "Forty years of durability assessment of nuclear waste glass by standard methods," npj Materials Degradation 2021

Influence of elements not in the glass



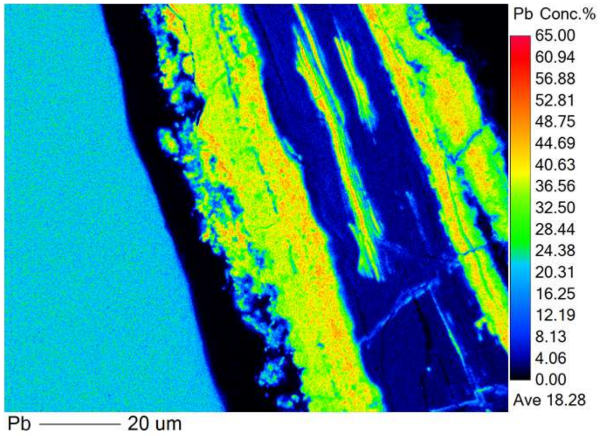


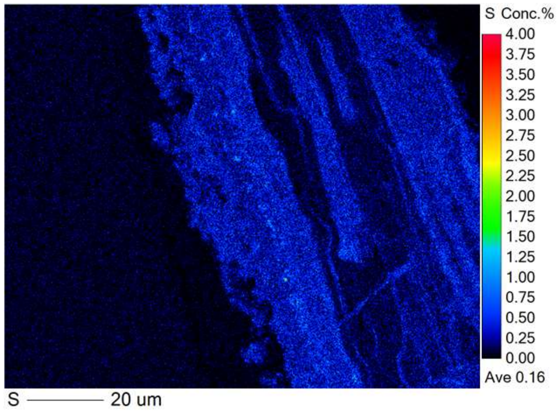
Dover to North Foreland [BA1828]

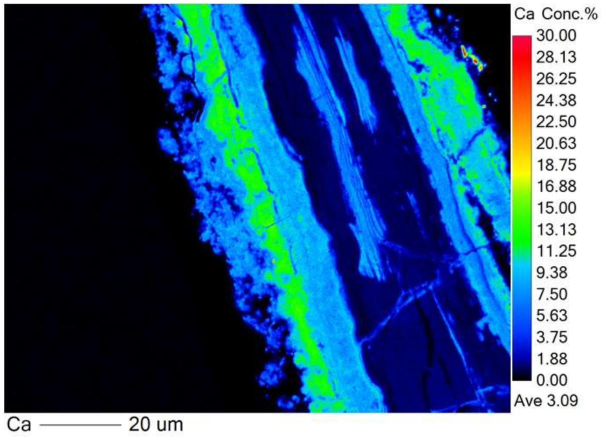


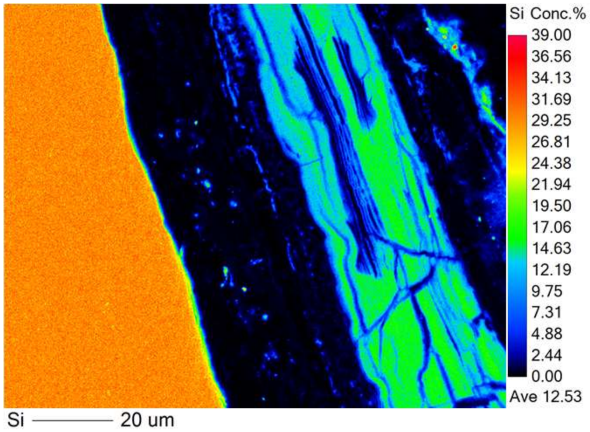
This map has been derived in part from material obtained from the UK Hydrographic Office with the permission of the UK Hydrographic Office and Her Majesty's Stationery Office and custodian authorities © British Crown Copyright, 2020.

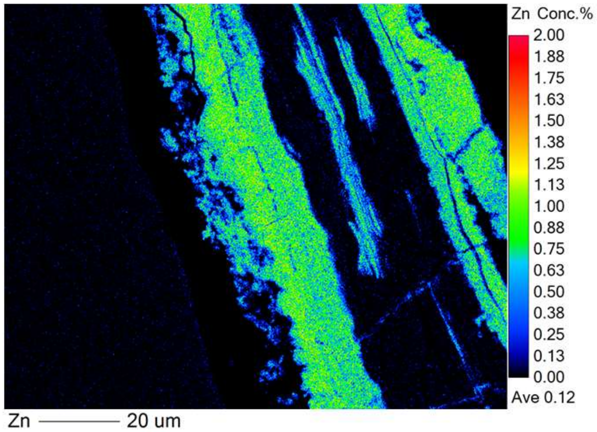
Elements sequestered for seawater and/or

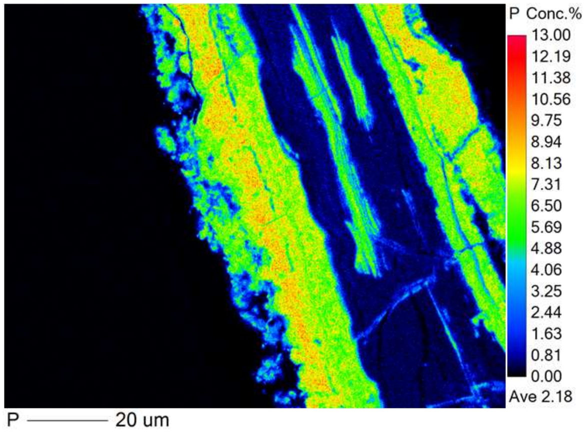










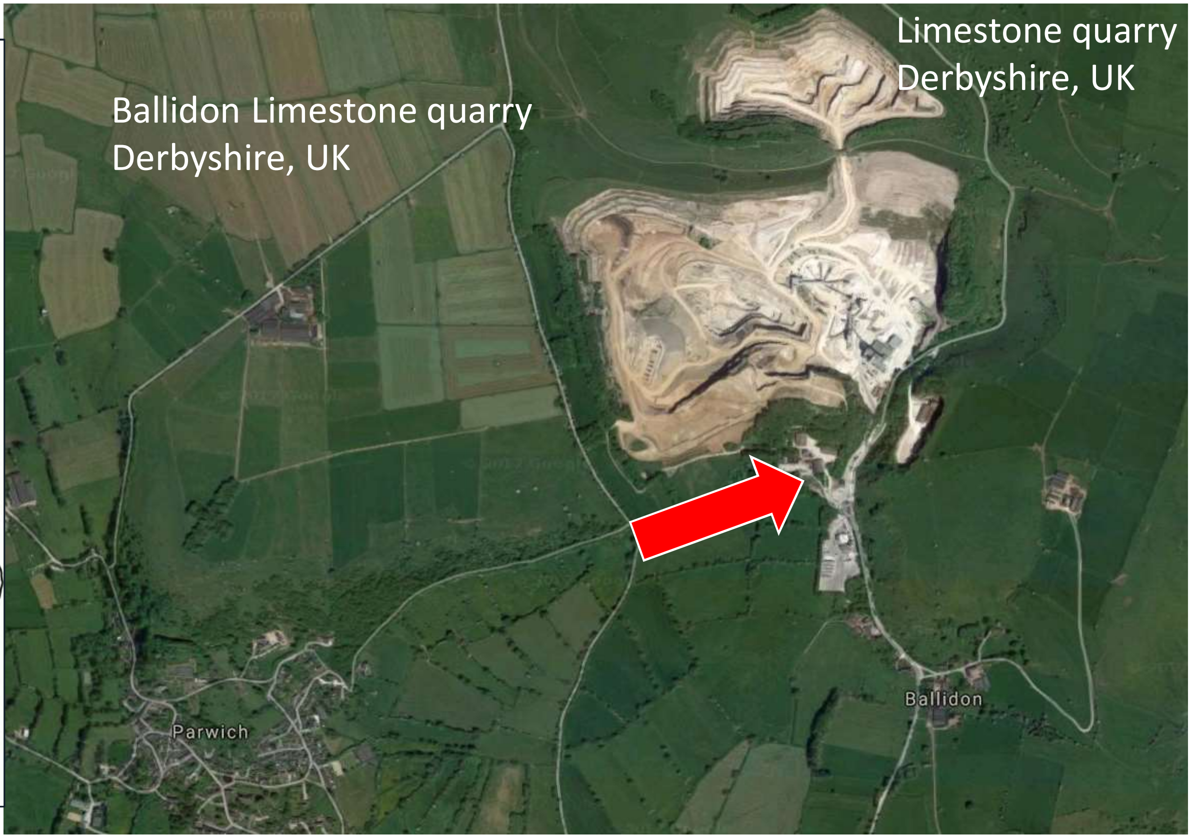


Ballidon Quarry, Derbyshire

University of Sheffield

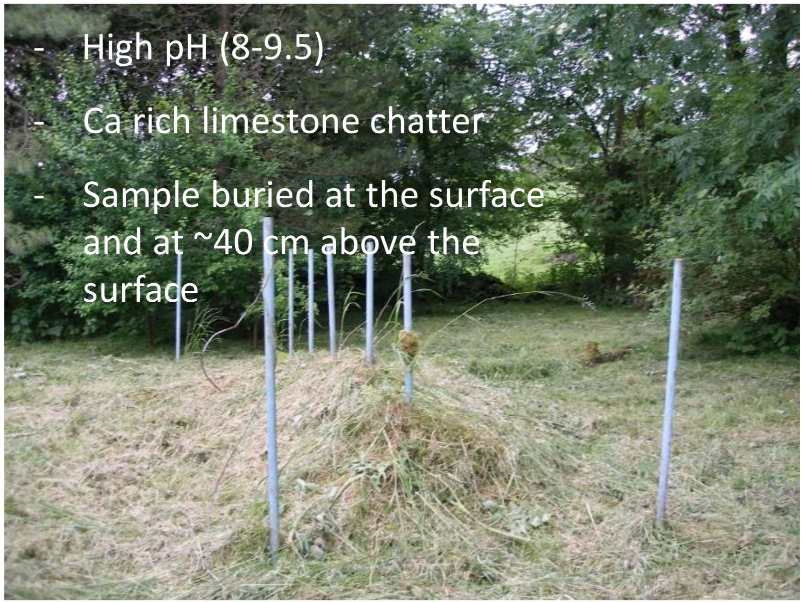
NucleUS
Immobilisation Science Laboratory

Location

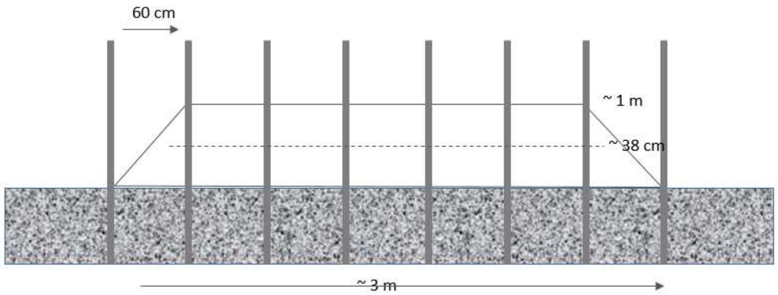

Limestone quarry
Derbyshire, UK

Ballidon Limestone quarry
Derbyshire, UK

Location



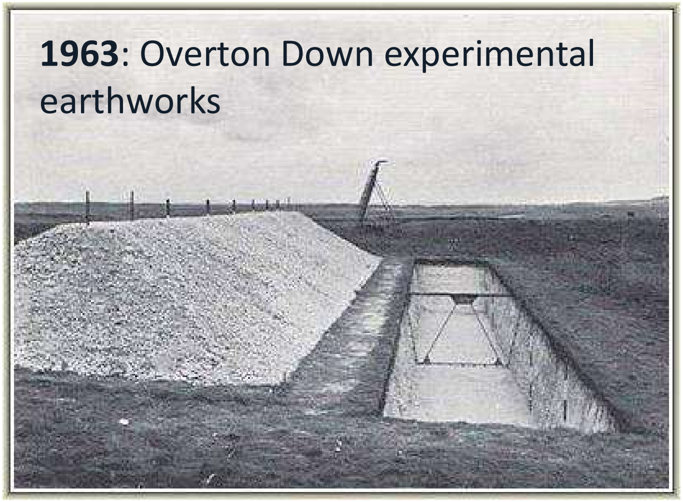
- High pH (8-9.5)
- Ca rich limestone chatter
- Sample buried at the surface and at ~40 cm above the surface



Fletcher, 1972

History

The Ballidon experiment was originally designed to test the degradation of archaeological glasses compared to modern glasses, and to be compared to previous field experiments:

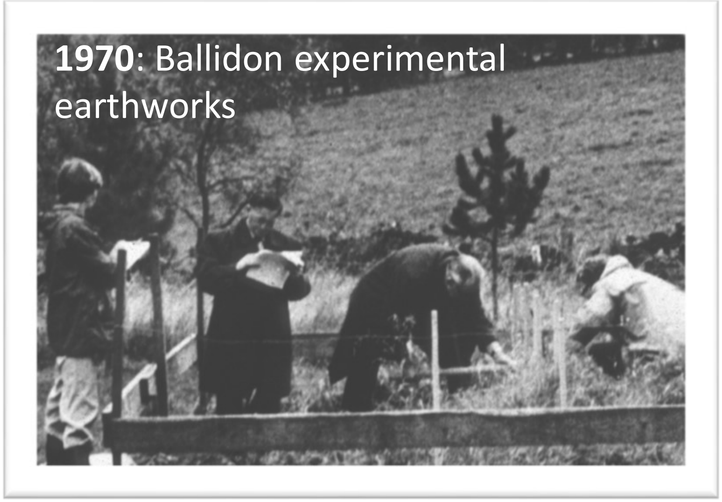


1963: Overton Down experimental earthworks

High pH (8-9) No Glass!

1963: Wareham experimental earthworks

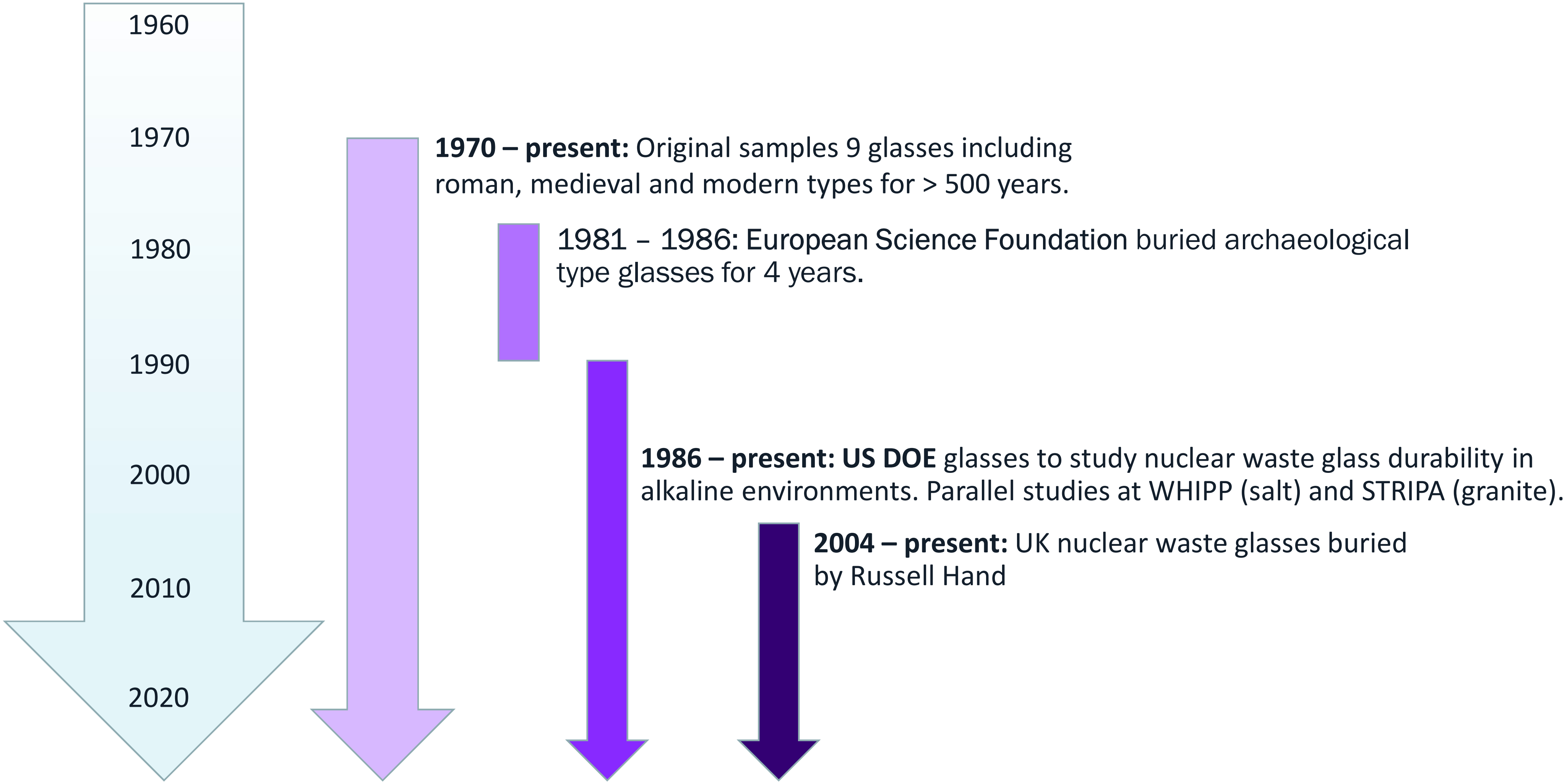
Low pH (4.5-5) – nine glasses



1970: Ballidon experimental earthworks

High pH (originally 9.7) – the same nine glass as Wareham

Four experiments at Ballidon



1970 – present: Original samples 9 glasses including roman, medieval and modern types for > 500 years.

1981 – 1986: European Science Foundation buried archaeological type glasses for 4 years.

1986 – present: US DOE glasses to study nuclear waste glass durability in alkaline environments. Parallel studies at WHIPP (salt) and STRIPA (granite).

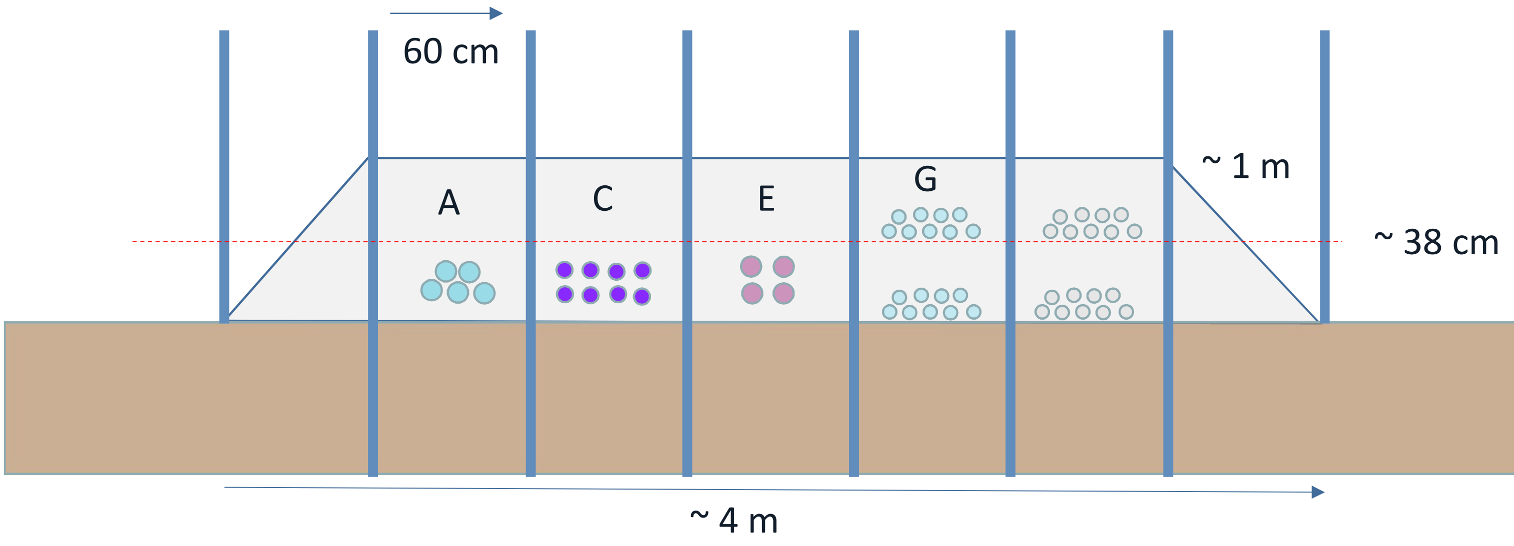
2004 – present: UK nuclear waste glasses buried by Russell Hand

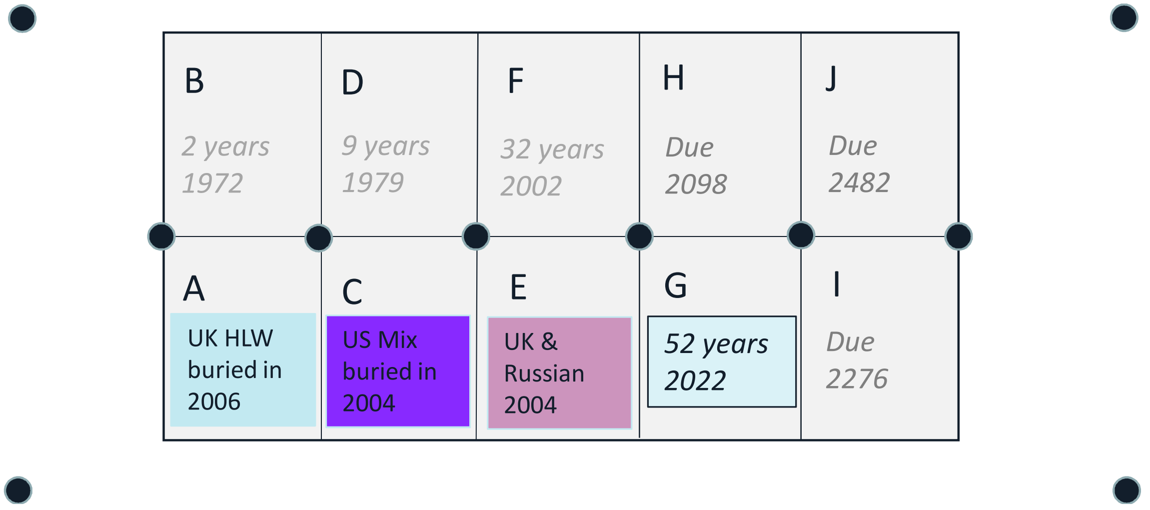
Samples removed in 2022

As original samples were removed additional samples were added in their place.

4 sets of samples were removed in 2022: **36 samples in total**

Site	Glass removed 2022	Age
A	UK HLW	18 years
C	US Compositions	18 years
E	UK HLW & Russian	16 years
G	Original samples	52 years

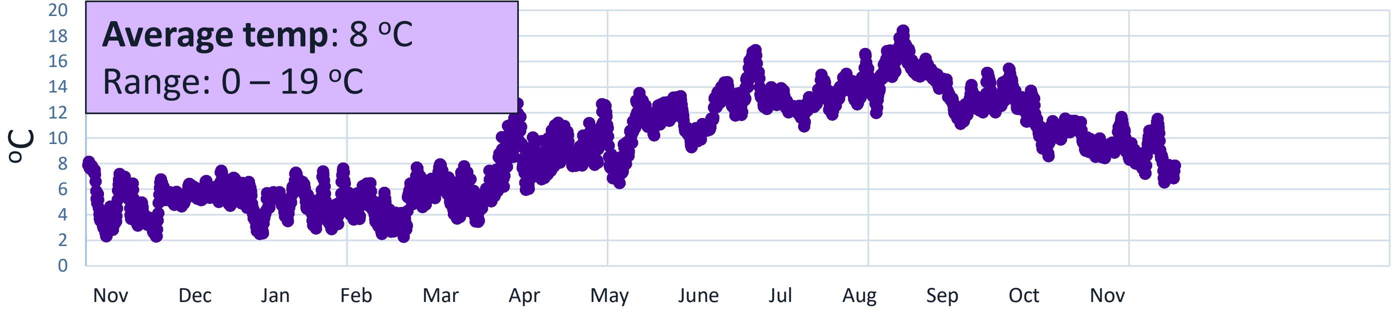




B *2 years* *1972*	D *9 years* *1979*	F *32 years* *2002*	H *Due* *2098*	J *Due* *2482*
A UK HLW buried in 2006	C US Mix buried in 2004	E UK & Russian 2004	G *52 years* *2022*	I *Due* *2276*

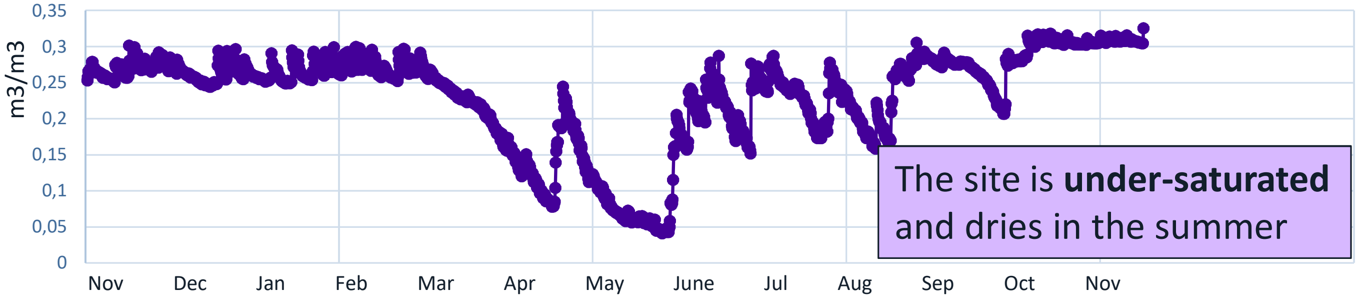
Site characterisation

Temperature °C



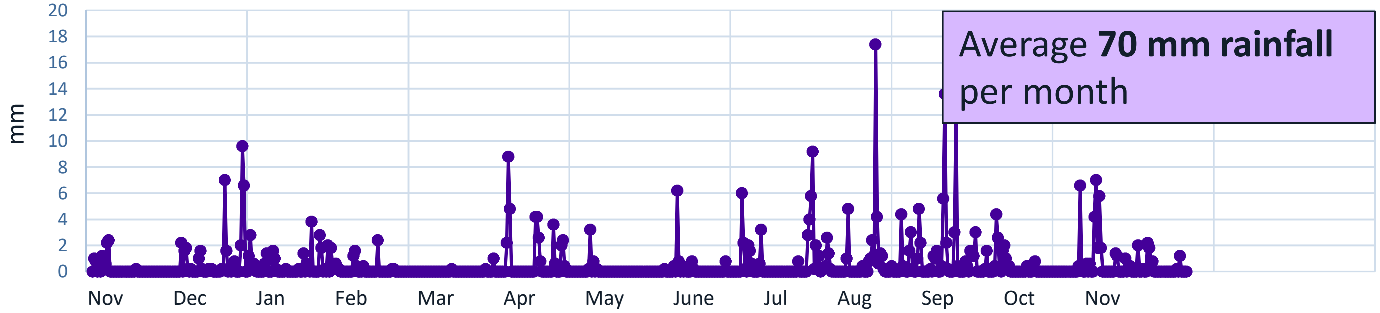
Average temp: 8 °C
Range: 0 – 19 °C

Saturation/Conductivity



The site is **under-saturated** and dries in the summer

Rainfall



Average **70 mm rainfall** per month

UK HLW glasses

1

3

5

2

4

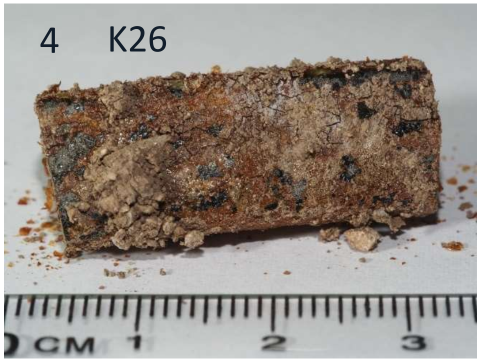
Glass	Identification
1	Magnox glass
2	Blend glass
3	NF-PRO Glass
4	75:25 iron phosphate
5	Iron phosphate + 35% $CaCl_2$

1

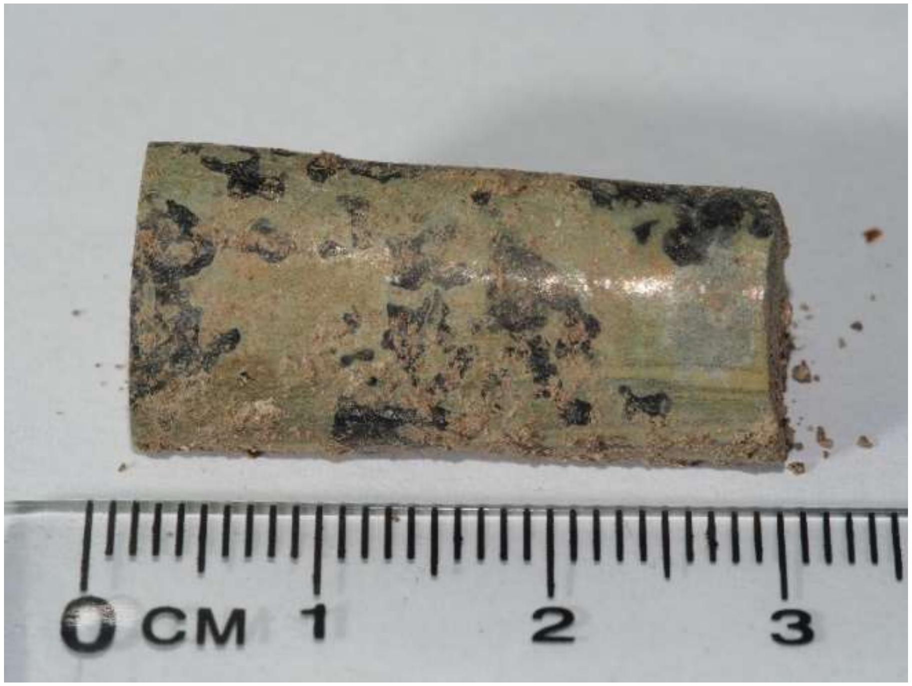
2

3

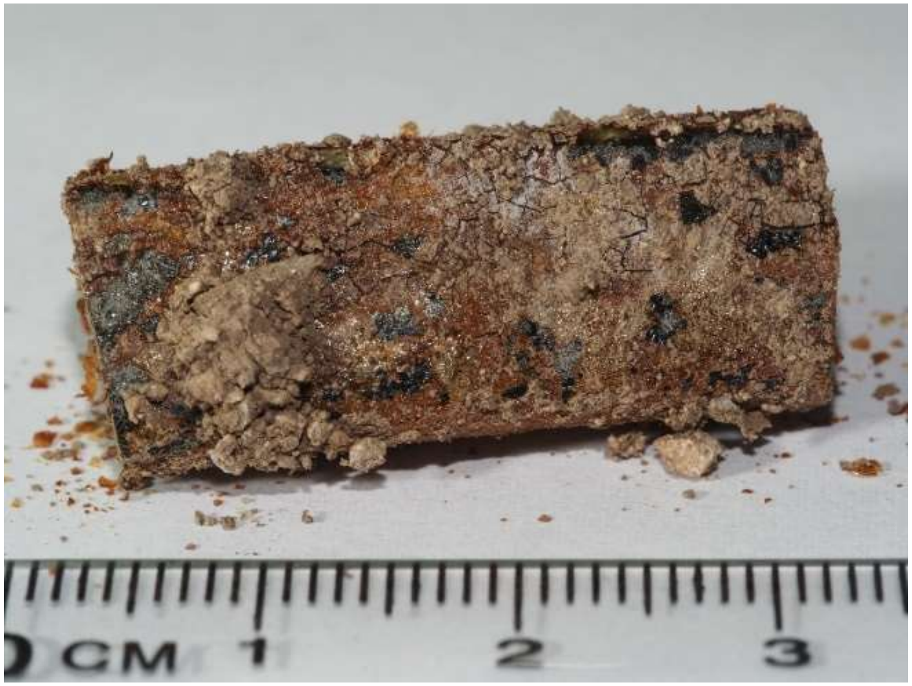
4 K26



Glass	Identification
1	V26
2	Blend MW25
3	Magnox MW25
4	Russian K26

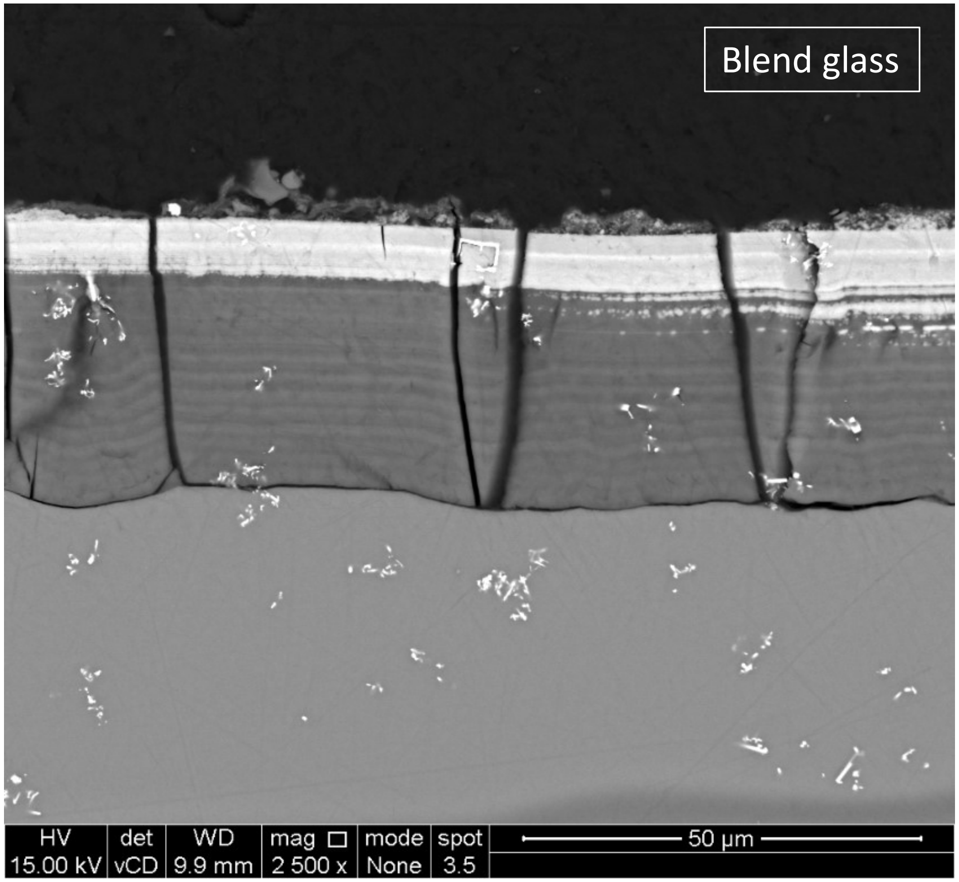


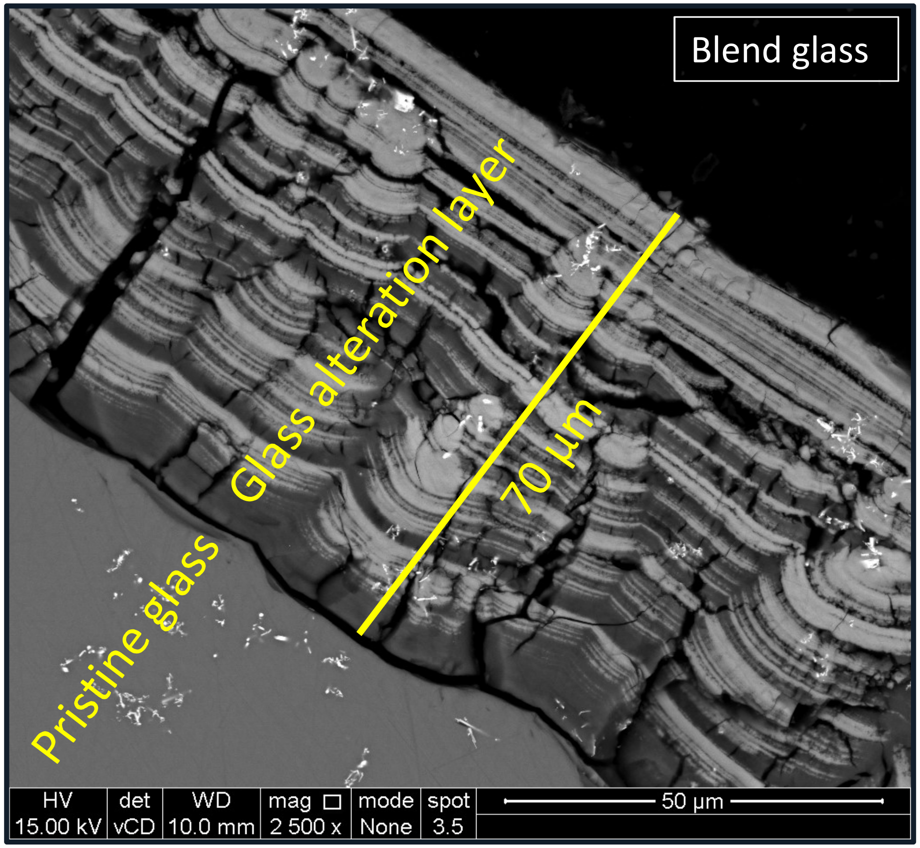
MW25 - Blend



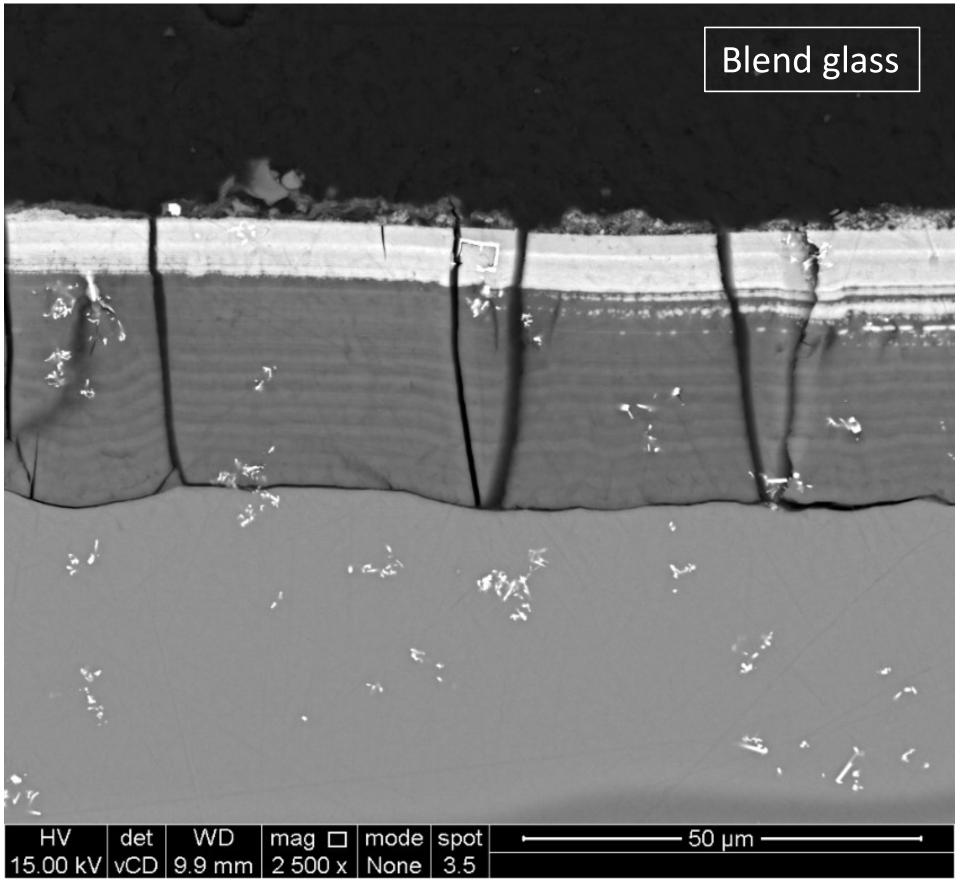
R26 (Russian)

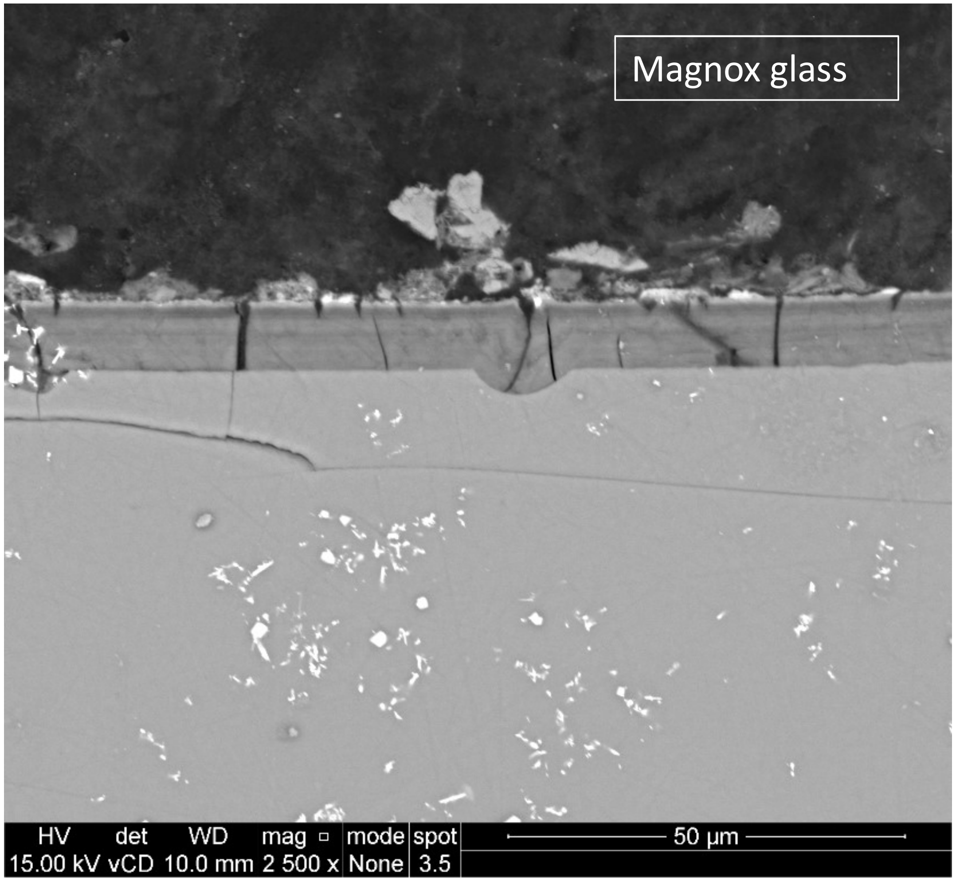
Glass Corrosion Process



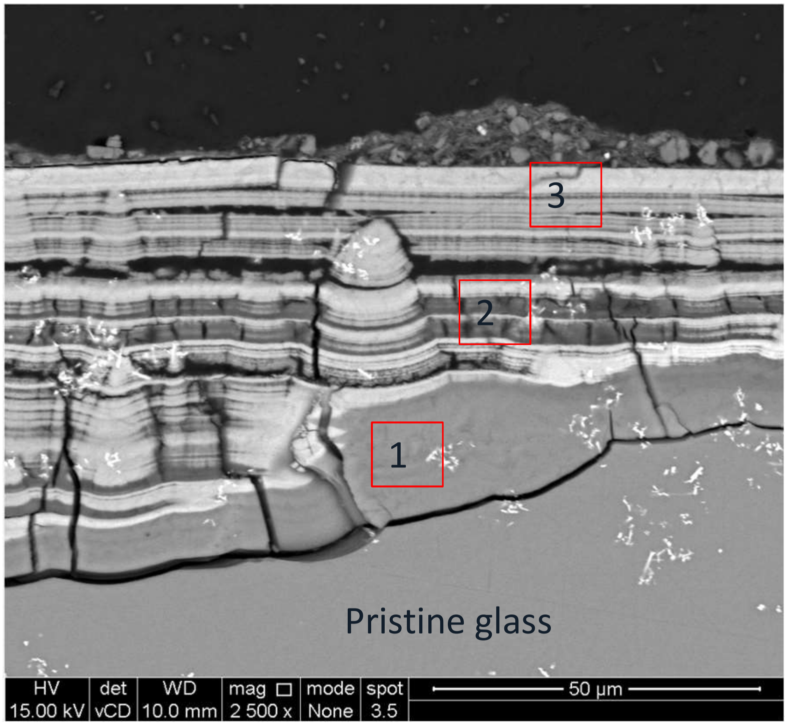


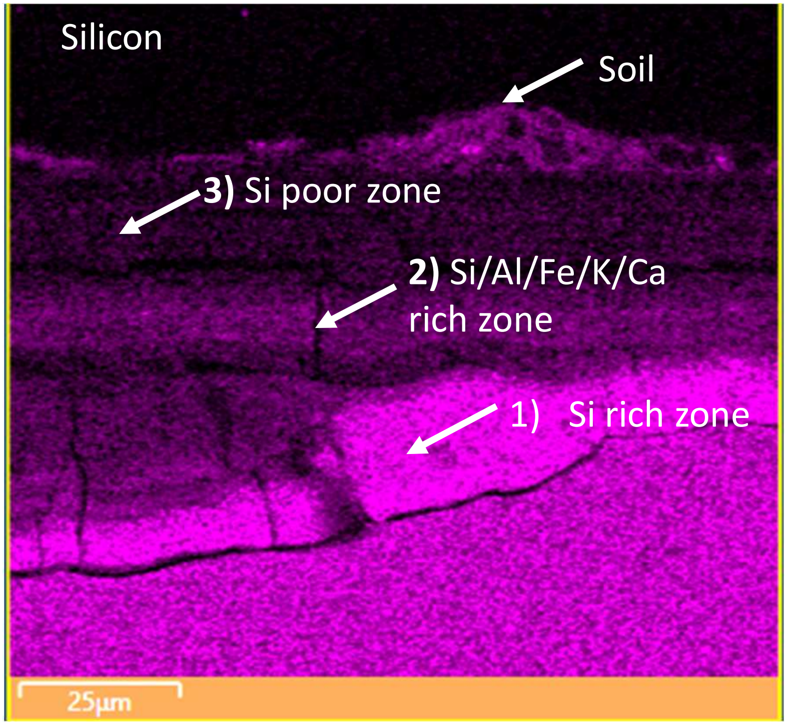
Glass Corrosion Process





UK HLW glass dissolution

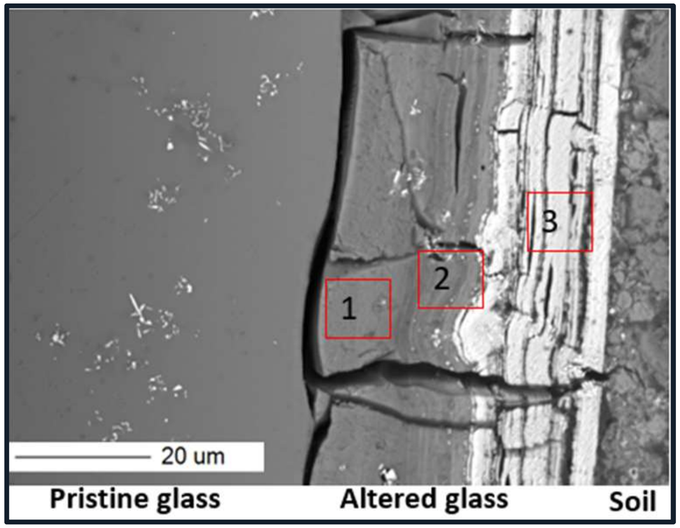


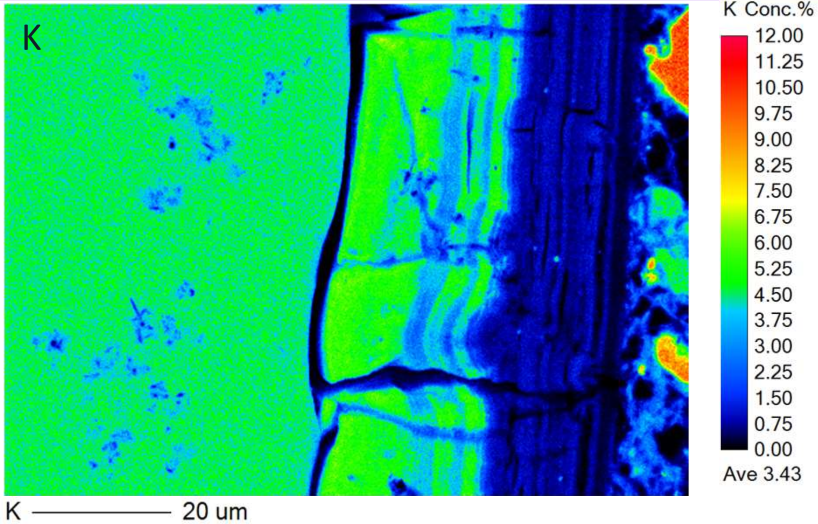


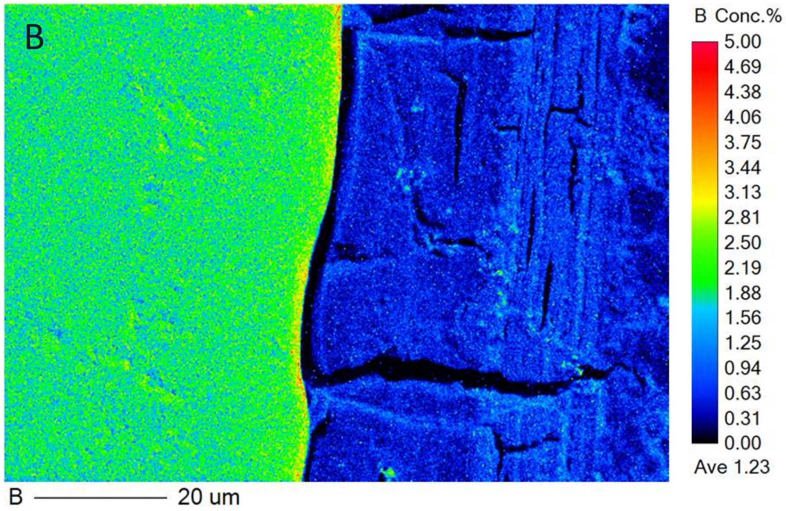
Three (possibly more) zones:

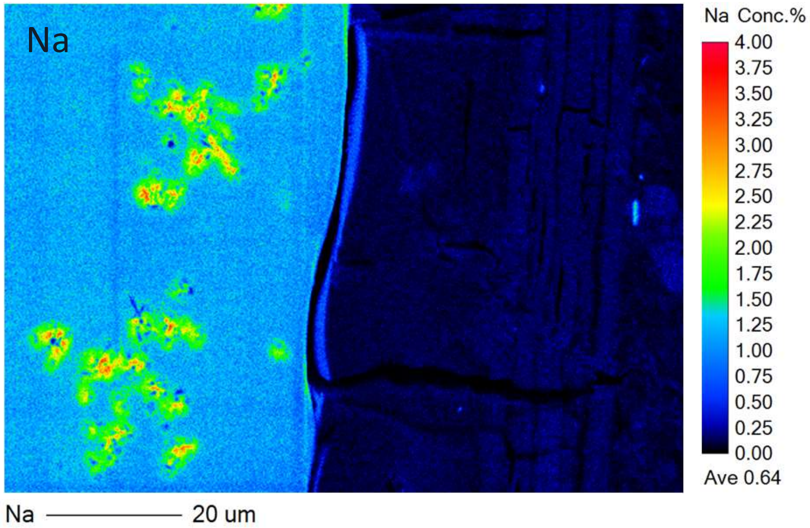
1) Si rich zone next to the pristine glass
2) Si rich layers
3) Si poor layers

Electron Probe Microanalysis (EPMA) Sample 16

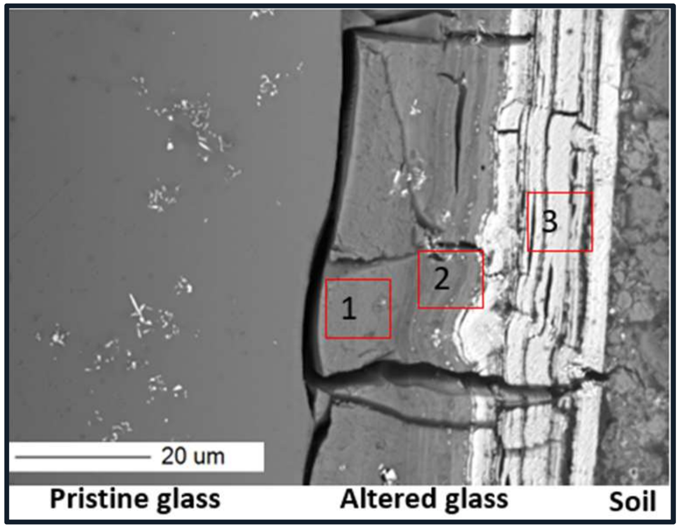


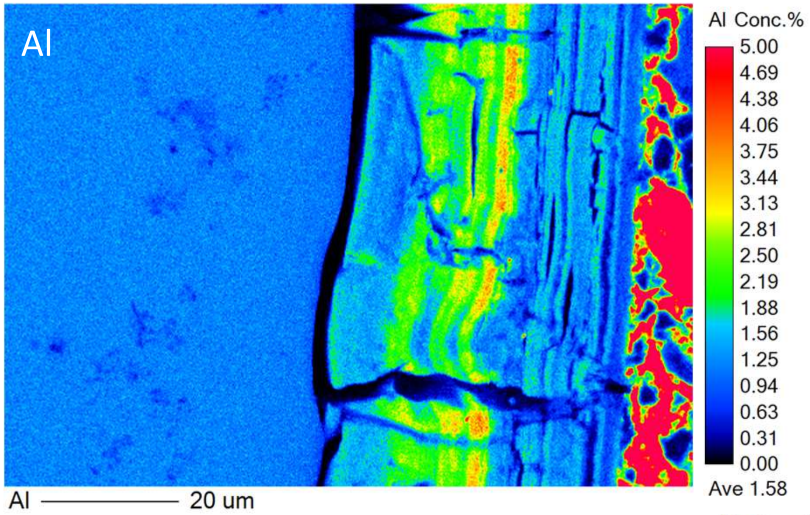


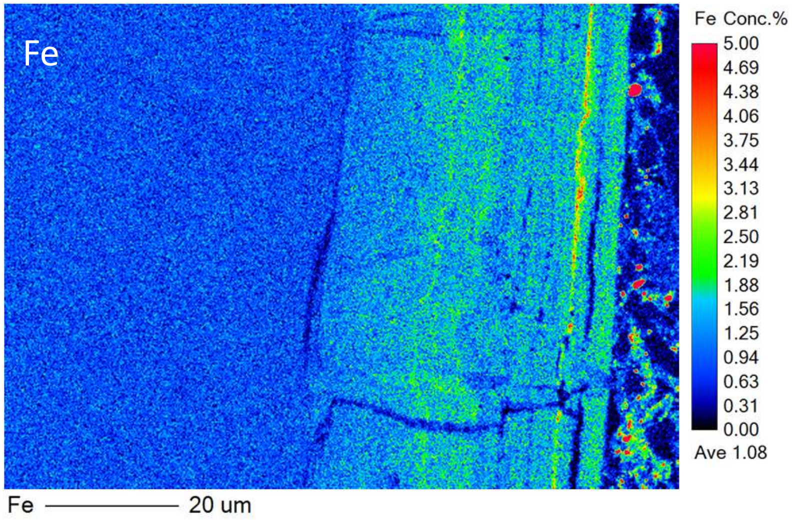


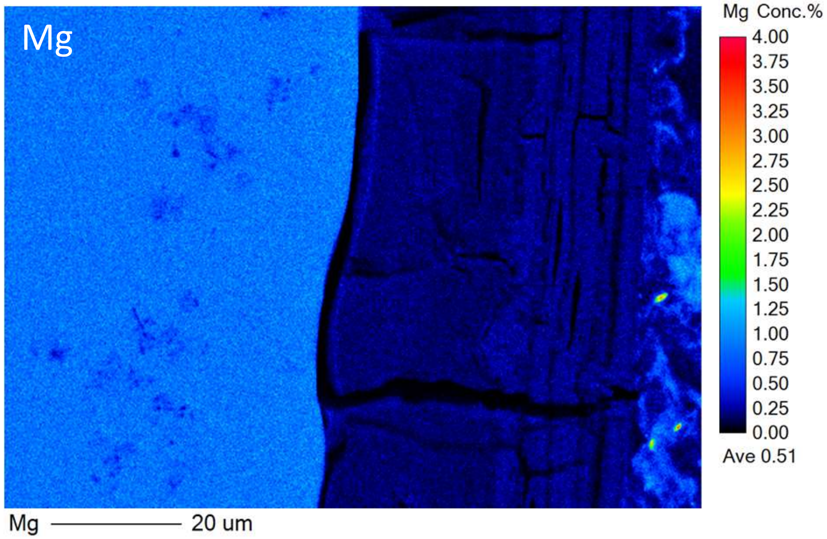


The complexities of layer 3

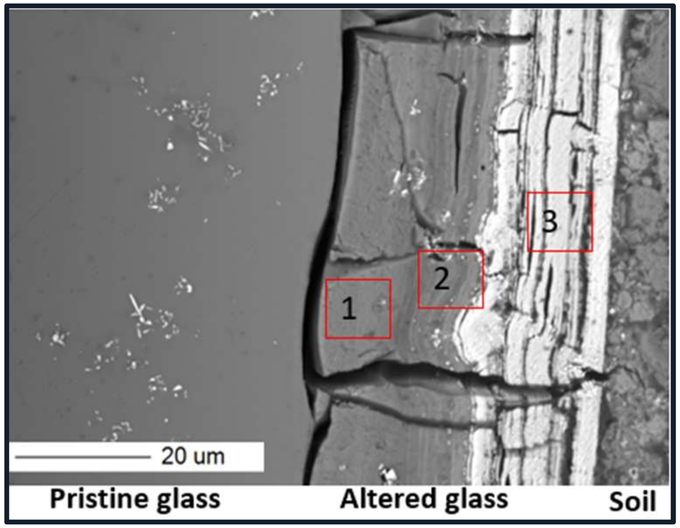


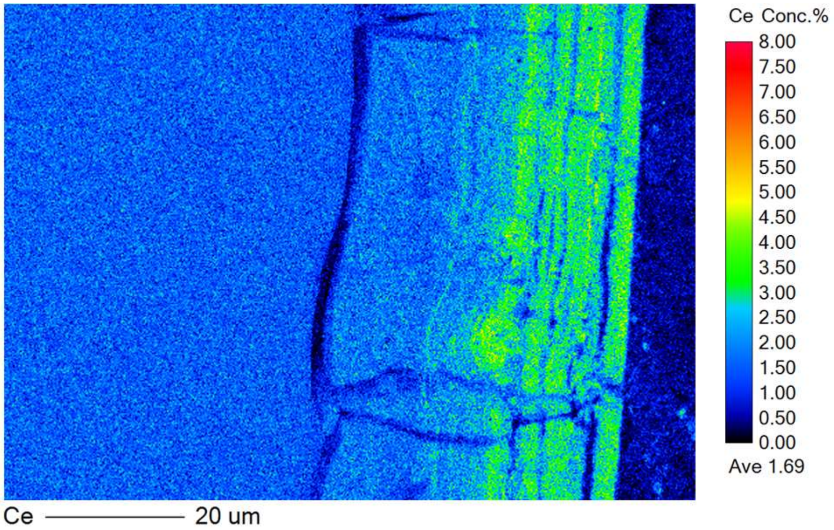


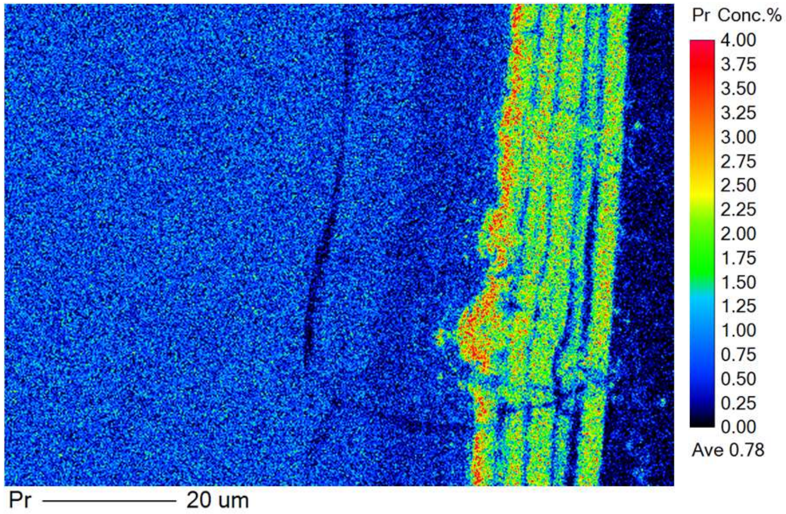


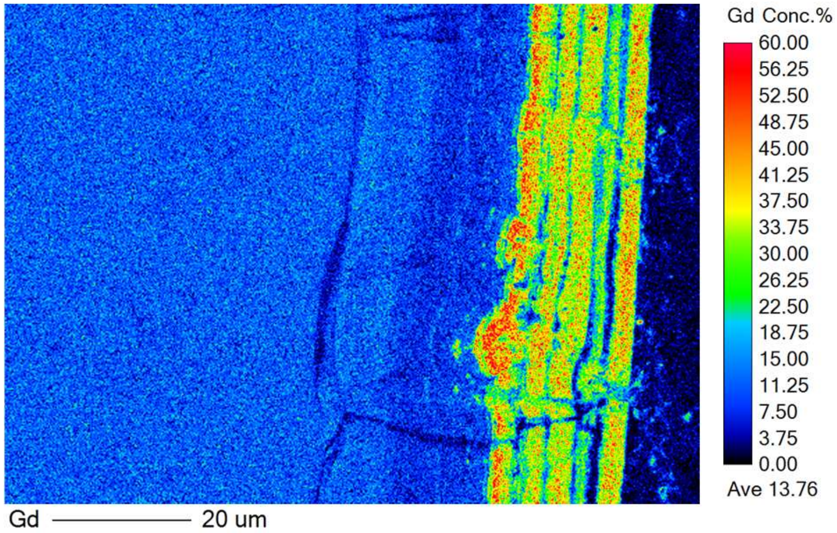


Fate of the lanthanide elements

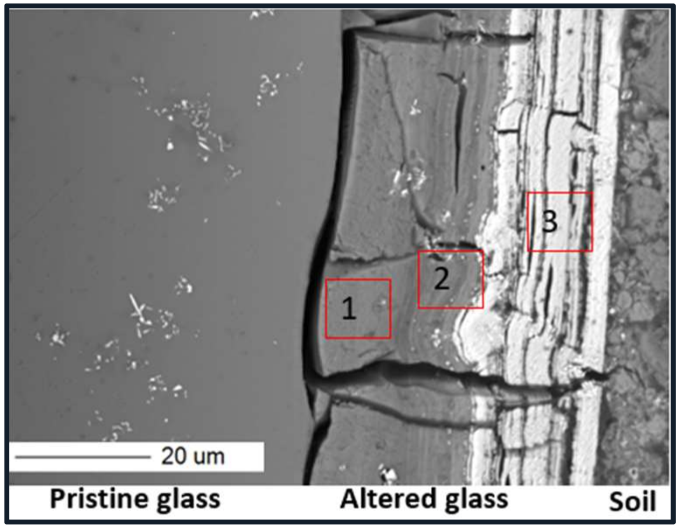


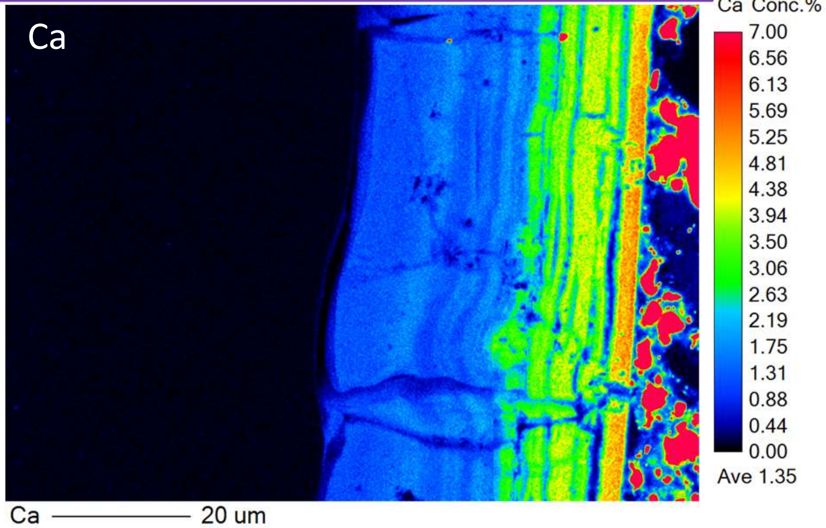


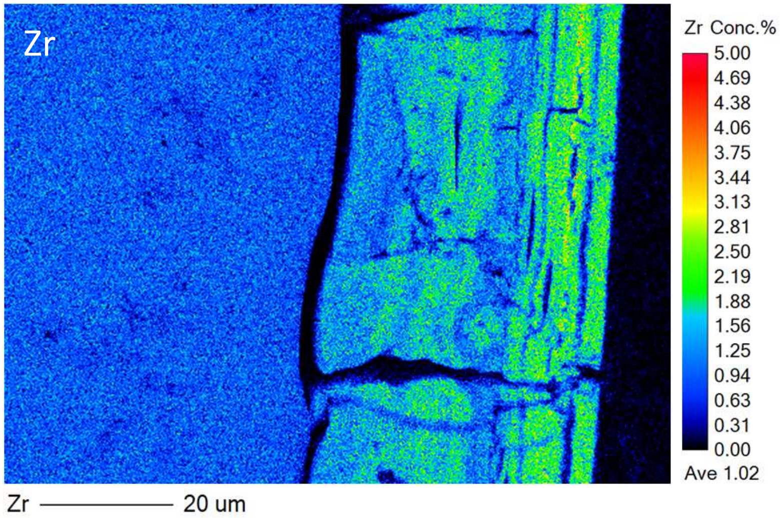


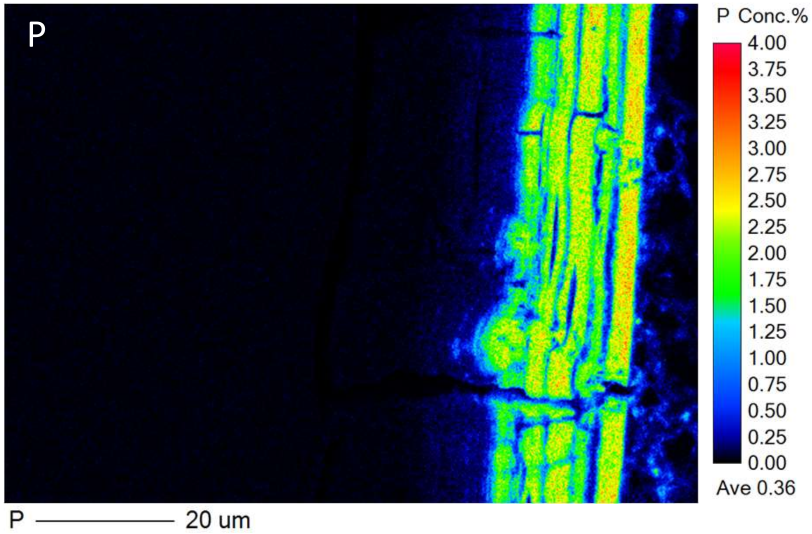


Influence of elements not found in the glass







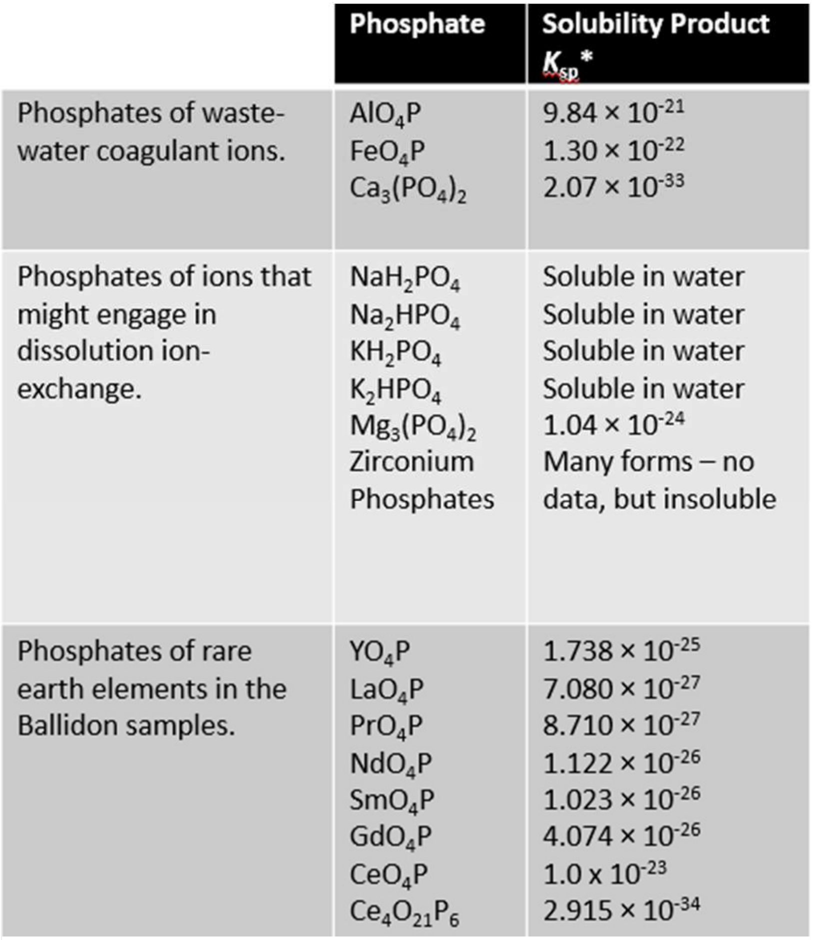


Phosphate Precipitation

Phosphate insolubility

In waste-water treatment the Ca, Fe and Al cations are all used in coagulants to remove phosphates by precipitation because their phosphates are insoluble.

- Rare earth phosphates are even more insoluble than aluminium and iron phosphate.
- Their insolubility suggests that these phases will be stable in this environment. Could they be more durable than the glass itself?



	Phosphate	Solubility Product K_{sp}*
Phosphates of waste-water coagulant ions.	AlO_4P FeO_4P $Ca_3(PO_4)_2$	9.84×10^{-21} 1.30×10^{-22} 2.07×10^{-33}
Phosphates of ions that might engage in dissolution ion-exchange.	NaH_2PO_4 Na_2HPO_4 KH_2PO_4 K_2HPO_4 $Mg_3(PO_4)_2$ Zirconium Phosphates	Soluble in water Soluble in water Soluble in water Soluble in water 1.04×10^{-24} Many forms – no data, but insoluble
Phosphates of rare earth elements in the Ballidon samples.	YO_4P LaO_4P PrO_4P NdO_4P SmO_4P GdO_4P CeO_4P $Ce_4O_{21}P_6$	1.738×10^{-25} 7.080×10^{-27} 8.710×10^{-27} 1.122×10^{-26} 1.023×10^{-26} 4.074×10^{-26} 1.0×10^{-23} 2.915×10^{-34}

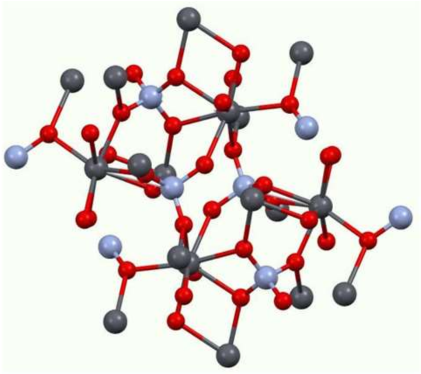
*Units vary depending upon the stoichiometric coefficients of the ions in the equilibrium.

What is the structure of these layers?

Attempts to precipitate pairs of rare earth phosphates together, in the lab, produce crystalline structures of monazite, xenotime or rhabdophane rather than discrete phosphates.

- Monazite is able to form a solid solution with the Ca bearing phosphate mineral, cheralite.
- Rhabdophane is able to incorporate Ca into its lattice.
- Xenotime prefers Yttrium and the heavier rare earth elements such as Gadolinium, but it does form mixed phases with monazite.

Small amounts of Fe, Al, Zr and Mg do occur in the monazite lattice (2). In natural deposits they are present as impurities/inclusions.

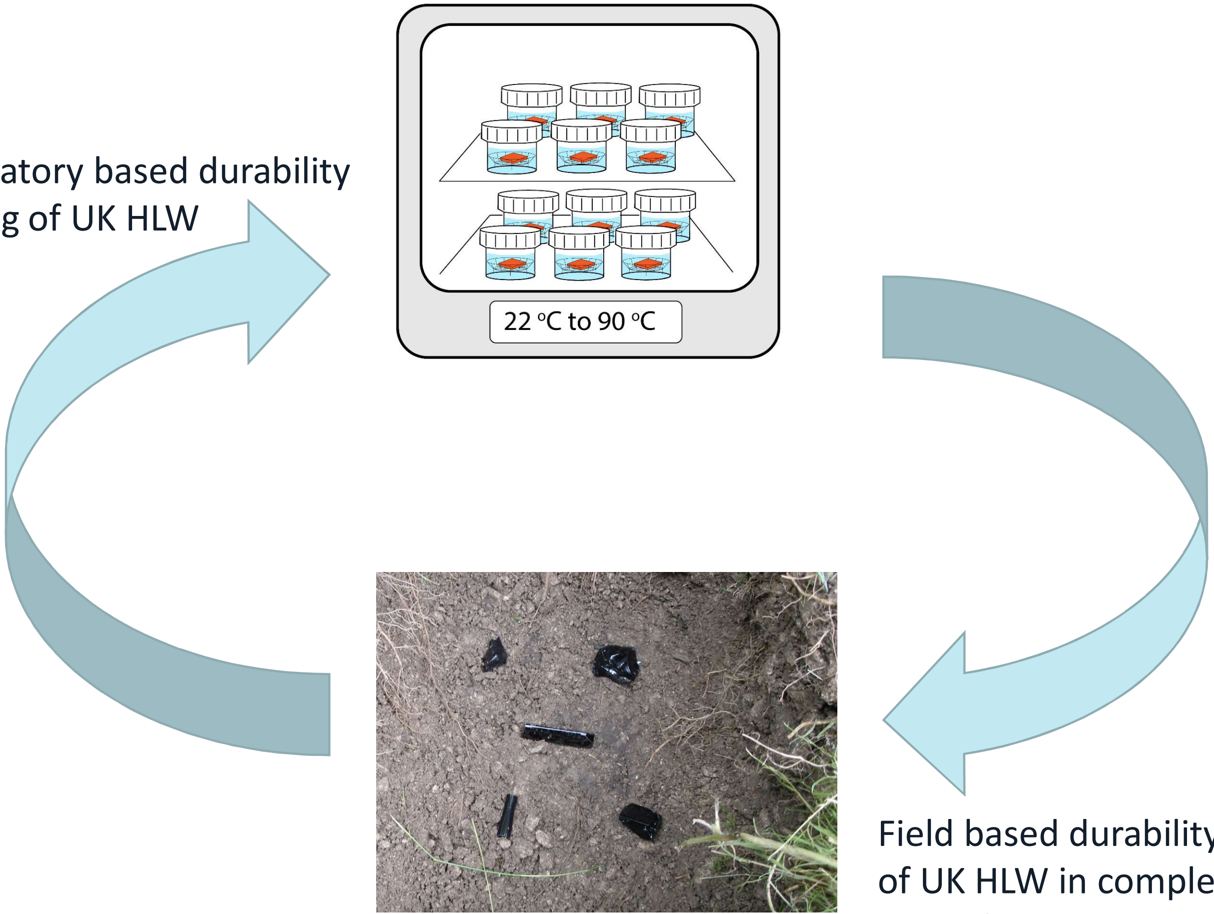


Monazite co-ordination/structure:
Red = O Pale blue = P
Dark grey = Lanthanide (rare earth)/Actinide or Calcium for charge balancing.

I18-microfocus to explore any emerging crystalline structures by µXRD, µXRF and µXANES

Diamond Lightsource, UK

Closing the circle



Laboratory based durability testing of UK HLW

Field based durability testing of UK HLW in complex natural environments

Acknowledgements

We gratefully acknowledge support from

Nuclear Waste Services

UKRI Engineering and Physical Sciences Research Council

U.S. DEPARTMENT OF ENERGY

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