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The Effect of Compositional Differences on UK Radioactive Glass Durability

Ian Farnan

Department of Earth Sciences & Cambridge Nuclear Energy Centre

RSO Launch Event 16-18 September 2020

High-level waste glass in UK

The first fleet of UK reactors (gas cooled, graphite moderated) used metallic U_{nat} fuel - **must be reprocessed**

The cladding was a magnesium-aluminium alloy called Magnox (reactors also called Magnox).

De-cladding operations leave some of the Mg-Al clad in place and this is entrained into the HLW liquor after reprocessing.

MW (Mixture Windscale) base glass has only four components: SiO_2, B_2O_3, Na_2O, Li_2O.

Vitrification Plant B355 Sellafield

Final UK glass for disposal is based on French glass, but differs in having Mg (for Ca) and high Li content. Waste loading 25wt%: MW25

Order of magnitude difference in durability of MW25

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Applied Geochemistry 21 (2006) 1152–1168
Applied Geochemistry
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Long-term corrosion of two nuclear waste reference glasses (MW and SON68): A kinetic and mineral alteration study

E. Curti [a,*], J.L. Crovisier [b], G. Morvan [b], A.M. Karpoff [b]

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[b] *Ecole et Observatoire des Sciences de la Terre, Centre de Géochimie de la Surface, UMR 7517, 1, rue Blessig, 67084 Strasbourg cedex, France*

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Available online 5 June 2006

Abstract

Powder samples of two inactive borosilicate glasses (MW and SON68), used as references for vitrified nuclear waste in Switzerland, were leached statically in pure water over more than 12a at 90 °C. Solution aliquots were taken at regular intervals in order to investigate the glass dissolution kinetics and the retention of elements representing radionuclides. At 5.7 and 12.2a, single tests were interrupted to investigate the corroded samples.

Boron and Li concentration data indicate that the glass corrosion kinetics of the MW glass is about 10 times faster than for the SON68 glass, both in the transient and asymptotic phase of the leaching process. The alteration products were studied by X-ray diffraction (XRD), scanning (SEM) and transmission electron microscopy (TEM-STEM) coupled with energy dispersive spectrometry (EDS) analyses. Alteration of the MW glass produced abundant magnesian clay minerals, as well as nanoparticles of lanthanide and Zr phosphates, whereas only small amounts Ca–Zn–Fe–Ni clay minerals were formed as alteration product of SON68.

Retention factors were above 99% for most trace elements, indicating almost quantitative fixation of many radionuclides in the secondary phases. Solution concentration data were used to calculate aqueous speciations and saturation indices of potential secondary solids. The solutions are close to saturation with respect to simple lanthanide phosphates (in agreement with the TEM data) and quartz. The presence of quartz in the altered SON68 samples is corroborated by XRD data.

In conclusion, the corrosion and radionuclide retention properties of SON68 seem to be more favorable than those of the MW glass. A major finding of this investigation was that glass degradation may strongly depend on minor compositional changes in the glass composition. The presence of Mg in the MW glass triggers the nucleation of secondary clay minerals, thereby promoting glass corrosion via silica removal. In the Mg-free SON68 glass the formation of clays, and hence the glass degradation, were considerably slower.

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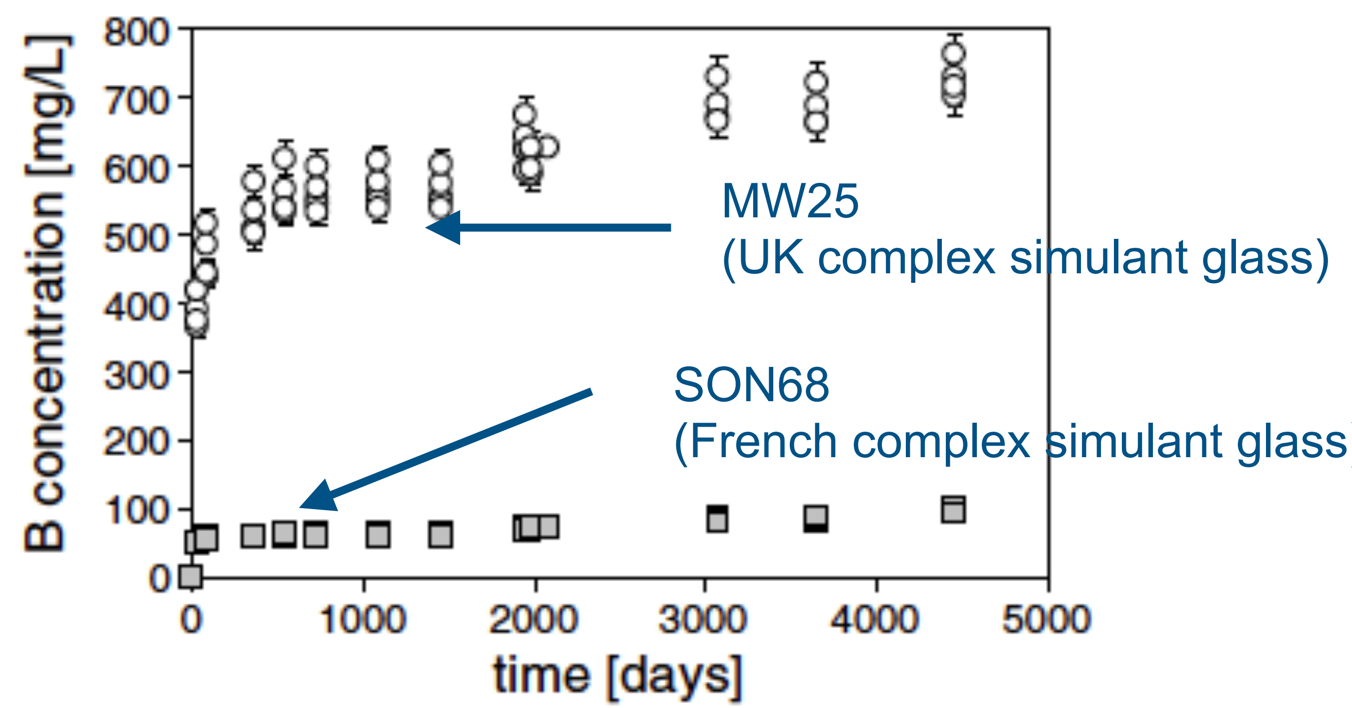
doi:10.1016/j.apgeochem.2006.03.010

Comparison measurements made by Enzo Curti (PSI) published in 2006

> 12 year experiment



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Order of magnitude difference in durability of MW25

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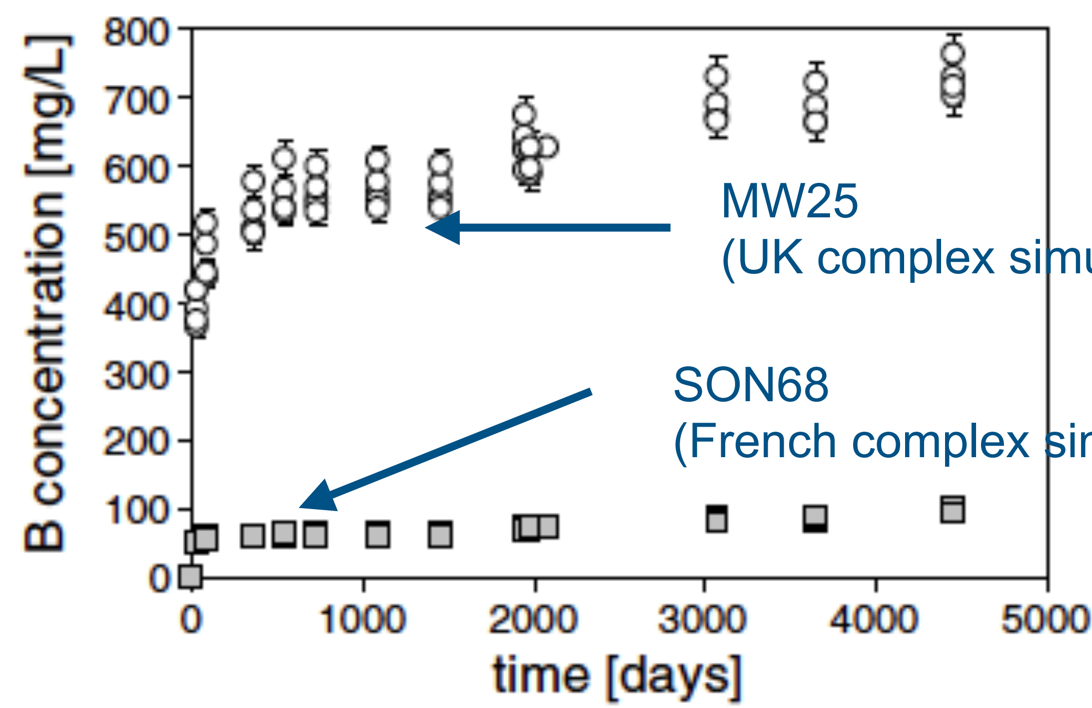

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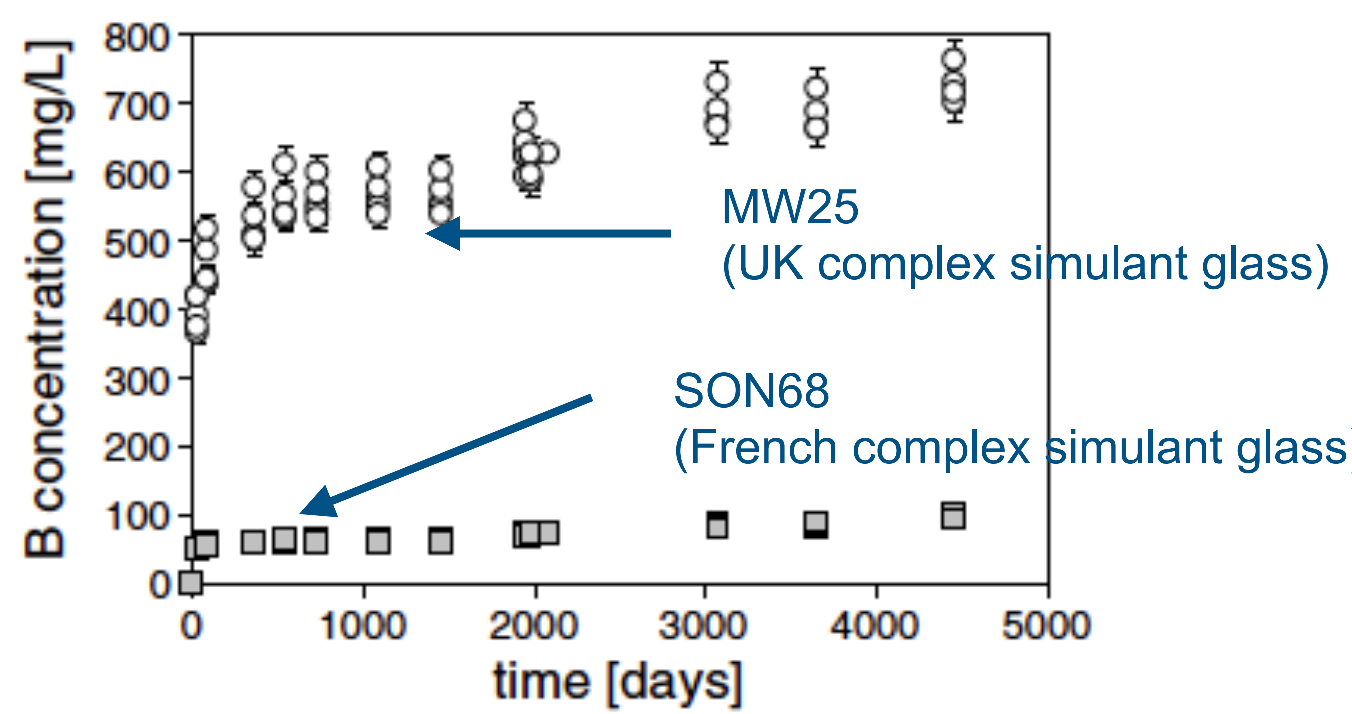
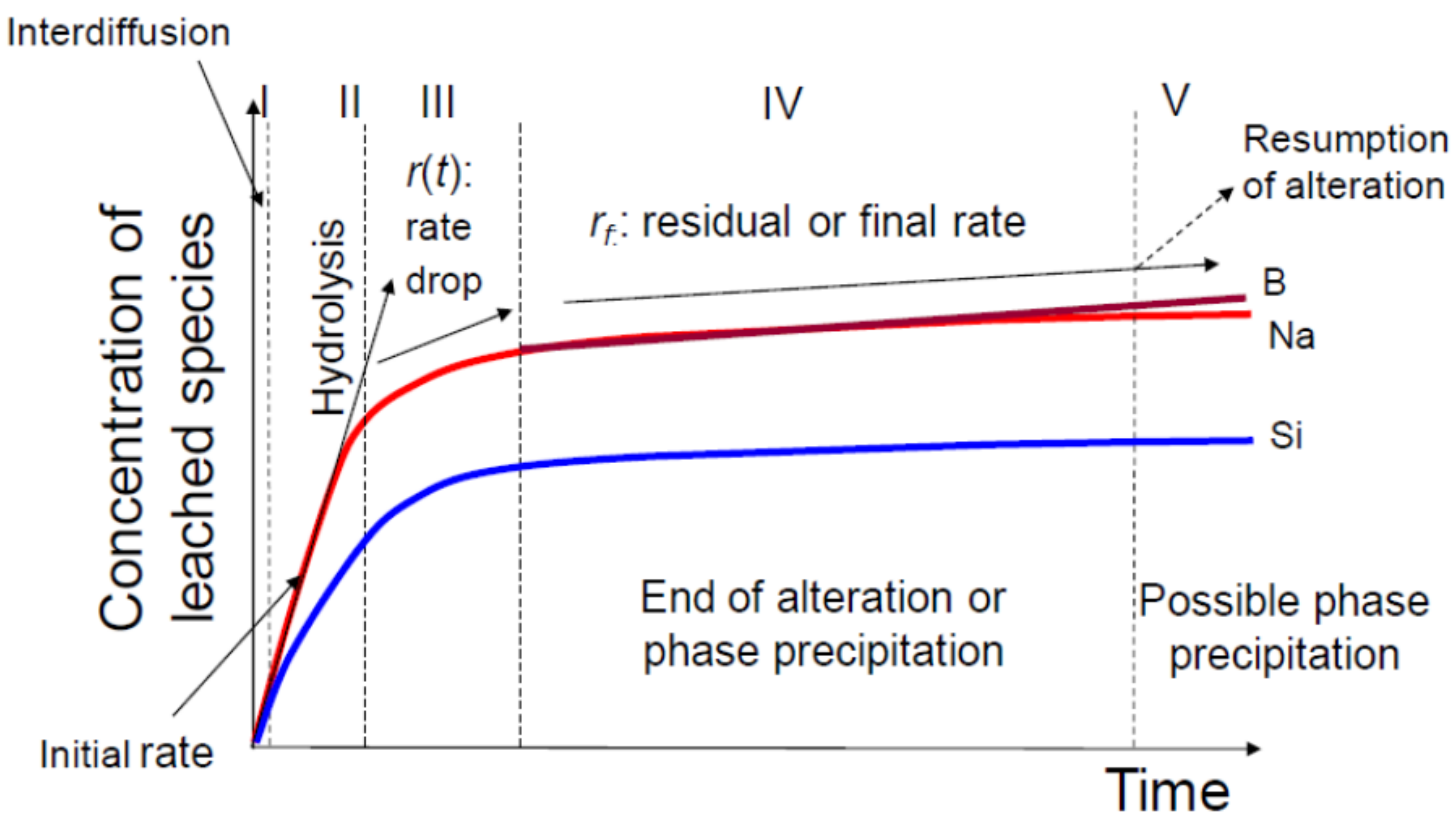


Industry Standard Model of Glass Dissolution



Complex process operating on a material of high compositional complexity

Direct Research Portfolio: Separate effect of Mg

DRAFT

amec

Experimental studies of the durability of UK HLW and ILW glasses. The effect of magnesium

To:	Radioactive Waste Management Limited
Date:	29 April 2016
From:	Amec Foster Wheeler and the University of Cambridge
Your Reference:	RWM005105
Our Reference:	AMEC/103498/01 Issue 1

AMEC/103498/01 Issue 1 draft — Page 1

DRAFT

PDRA: Clive Brigden

Cambridge Nuclear Energy MPhil: Chin Chee Tan (2013)

Cambridge Nuclear Energy MPhil: Rui Guo (2014)

Simplified glass compositions

Ratios important to glass local structure

	Si:B	B:Na	Si:(Ca/Mg)
Simulant	1.595	1.79	6.72
MW25	1.590	1.79	6.72

Series of glasses prepared with simplified composition

Element	Ca-EM	75/25 Ca/Mg	50/50 Ca/Mg	25/75 Ca/Mg	Mg-EM
Al	4.873	4.873	4.8731	4.873	4.873
B	27.579	27.578	27.578	27.578	27.578
La	1.720	1.720	1.720	1.720	1.720
Ca	6.541	4.906	3.271	1.635	-
Mg	-	1.635	3.271	4.906	6.541
Na	15.379	15.379	15.379	15.379	15.379
Si	43.908	43.908	43.908	43.908	43.908

Only difference was the variation in the Ca/Mg ratio, 6.5% in each end member

Paramagnetic ions excluded to improve resolution in NMR work

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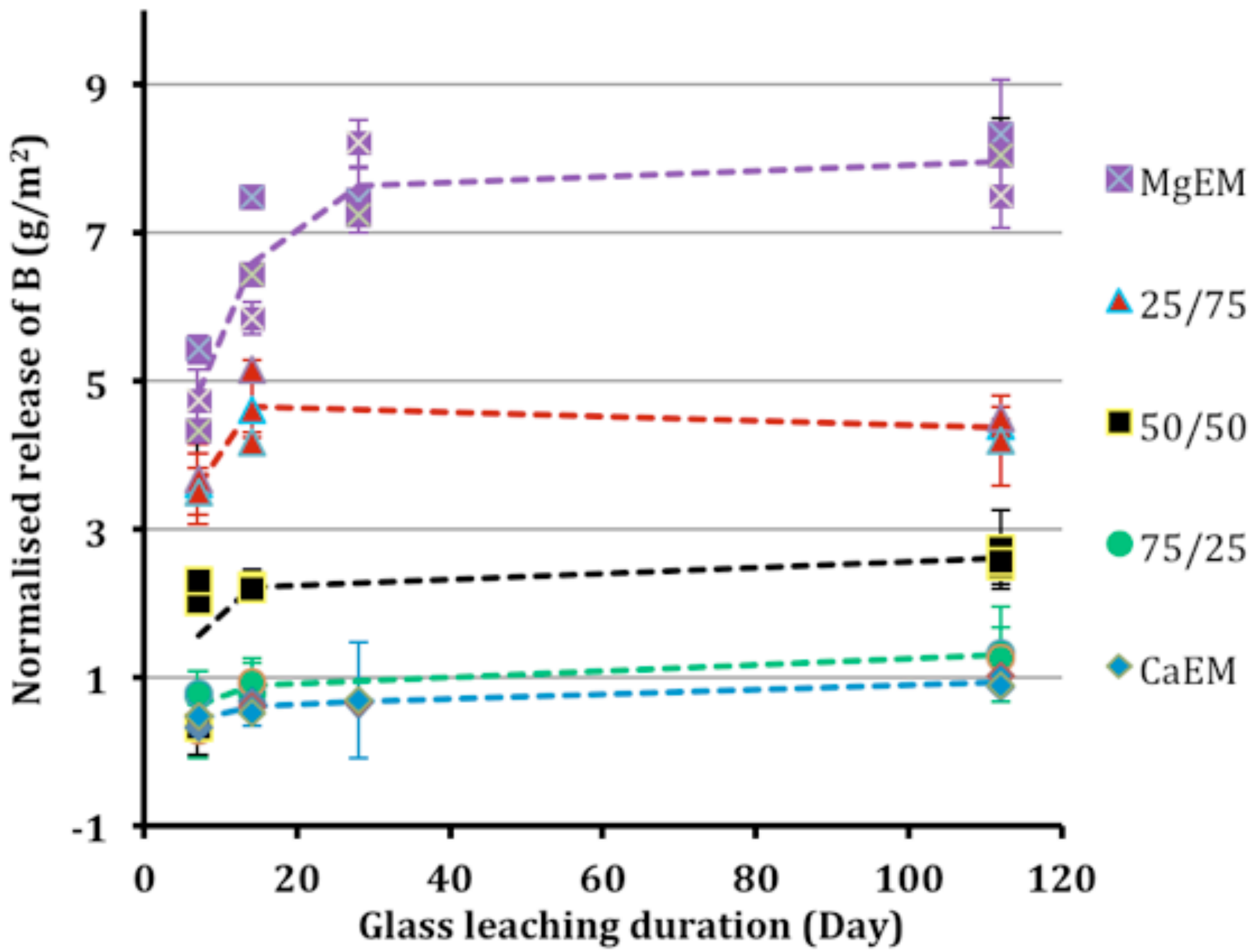
PCT-B leach test results simplified MW25 glasses

Normalised release of boron vs composition and time



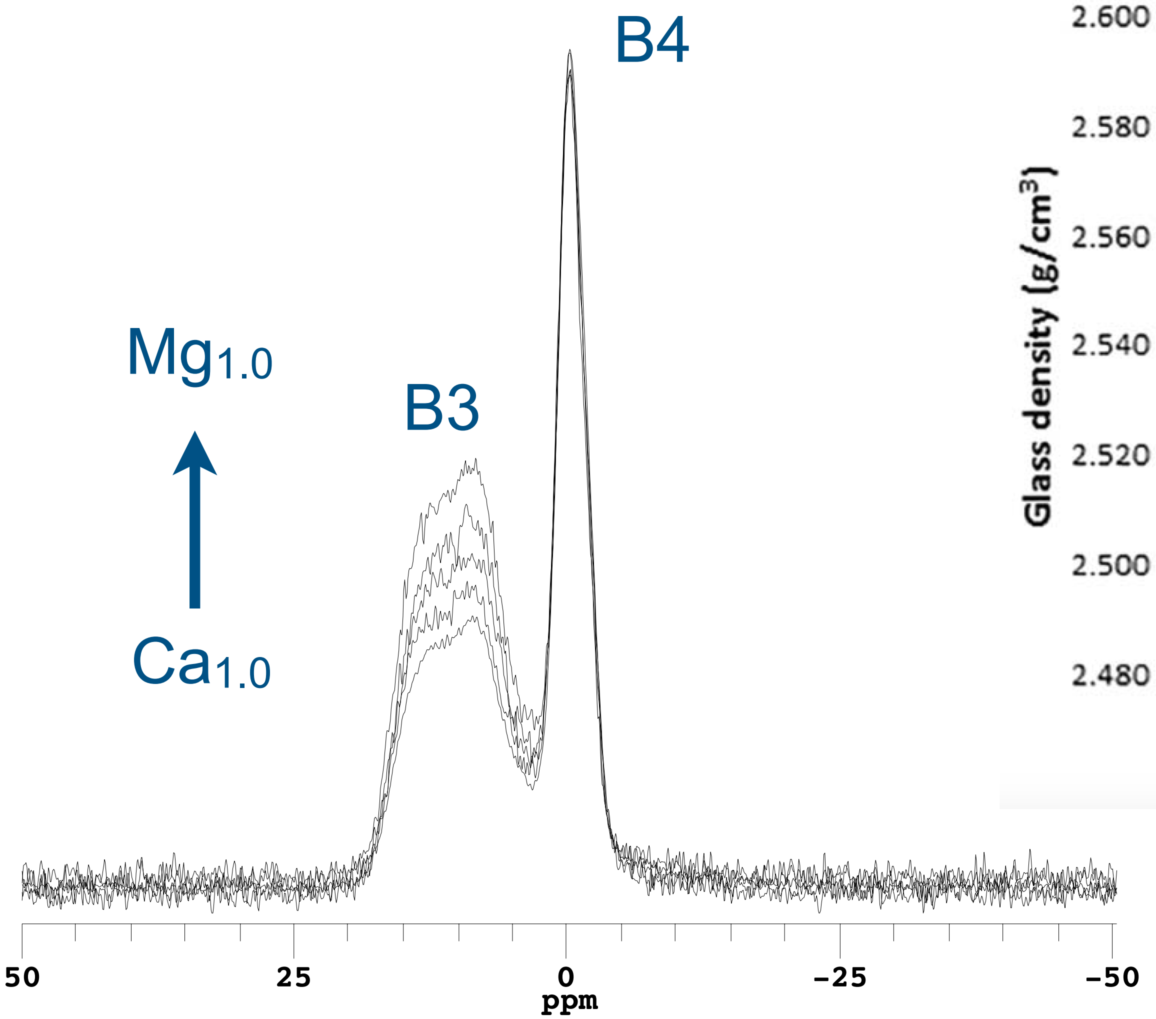
- MgEM ~ 10x Ca EM at all time periods
- ~8x after 112 days
- systematic increase with Mg content
- Ca75Mg25 glass possible exception

Simplified glasses reproduce durability differences between MW25 and SON68

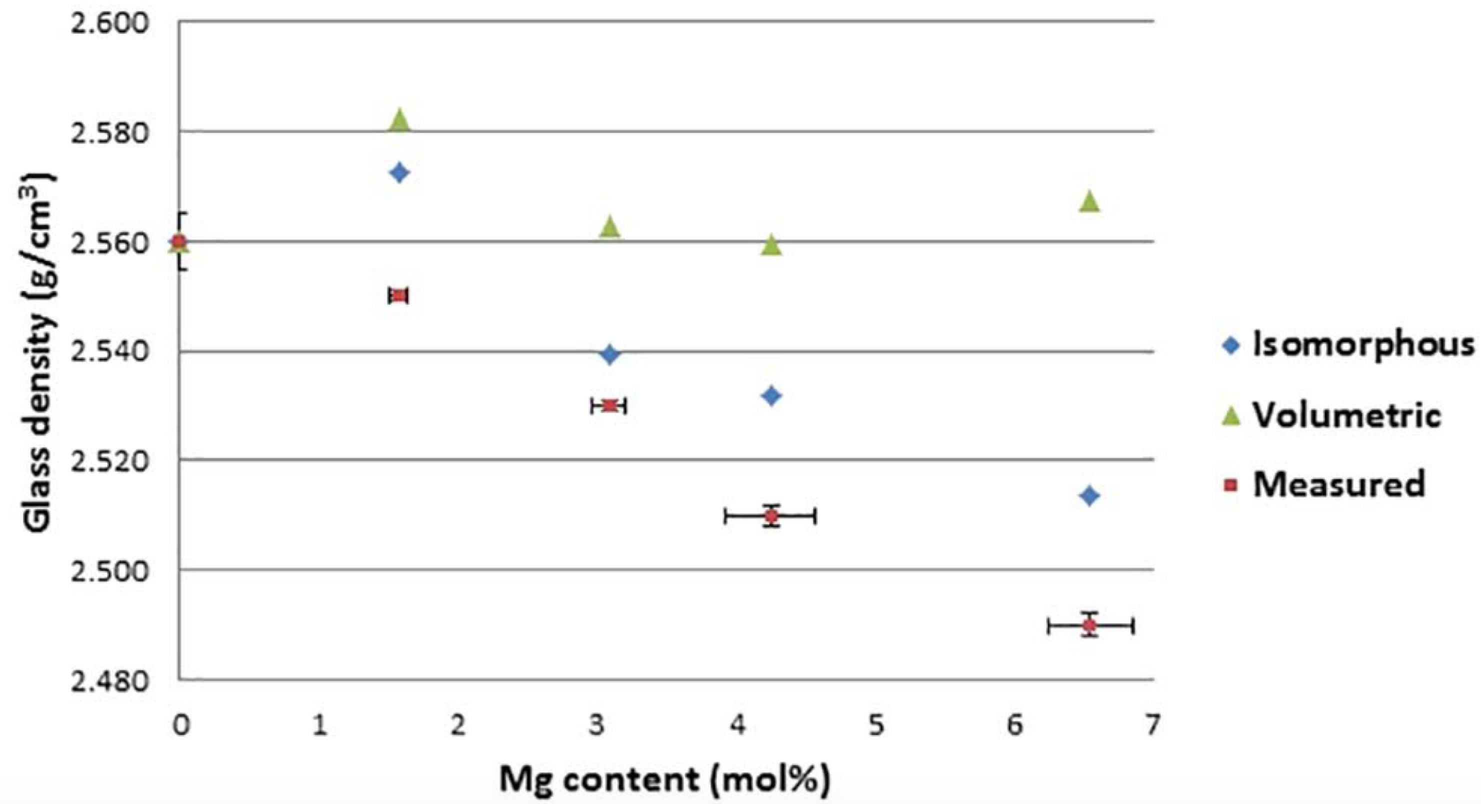
Effect of Mg on glass structure

Structural differences in MW glass due to Mg vs Ca

^{11}B MASNMR



Density



- increase in B3 vs B4 as Mg is added
- release of B increases as B3 increases
- preferential release of B3?

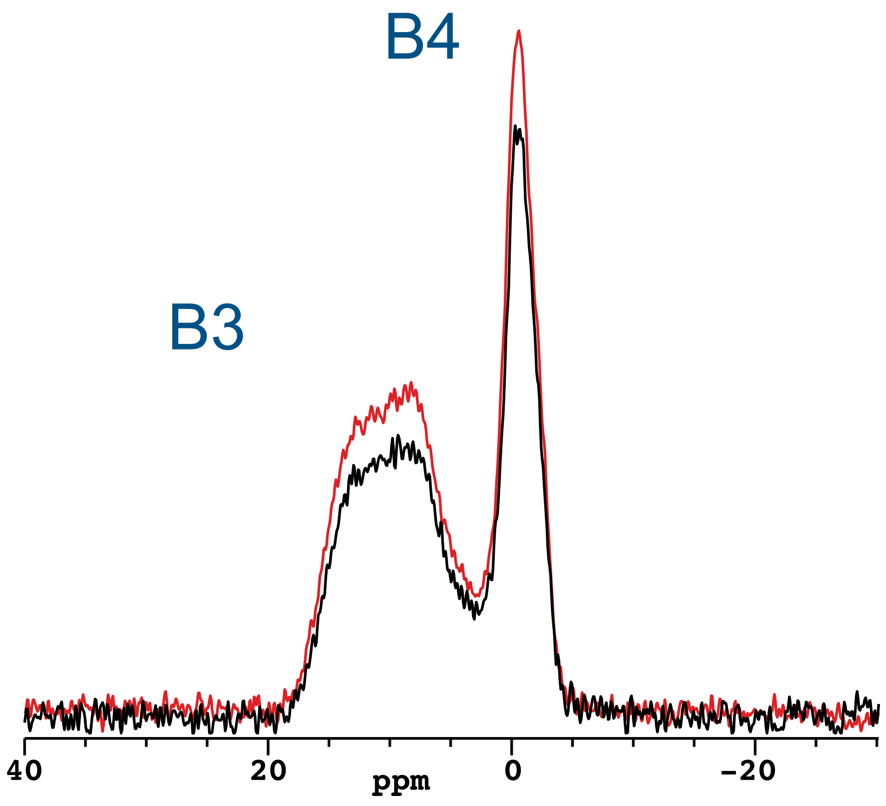
Effect of Mg on glass durability

Preferential release of B3?

^{11}B MASNMR Mg-EM, 112 day leach test

unleached

leached

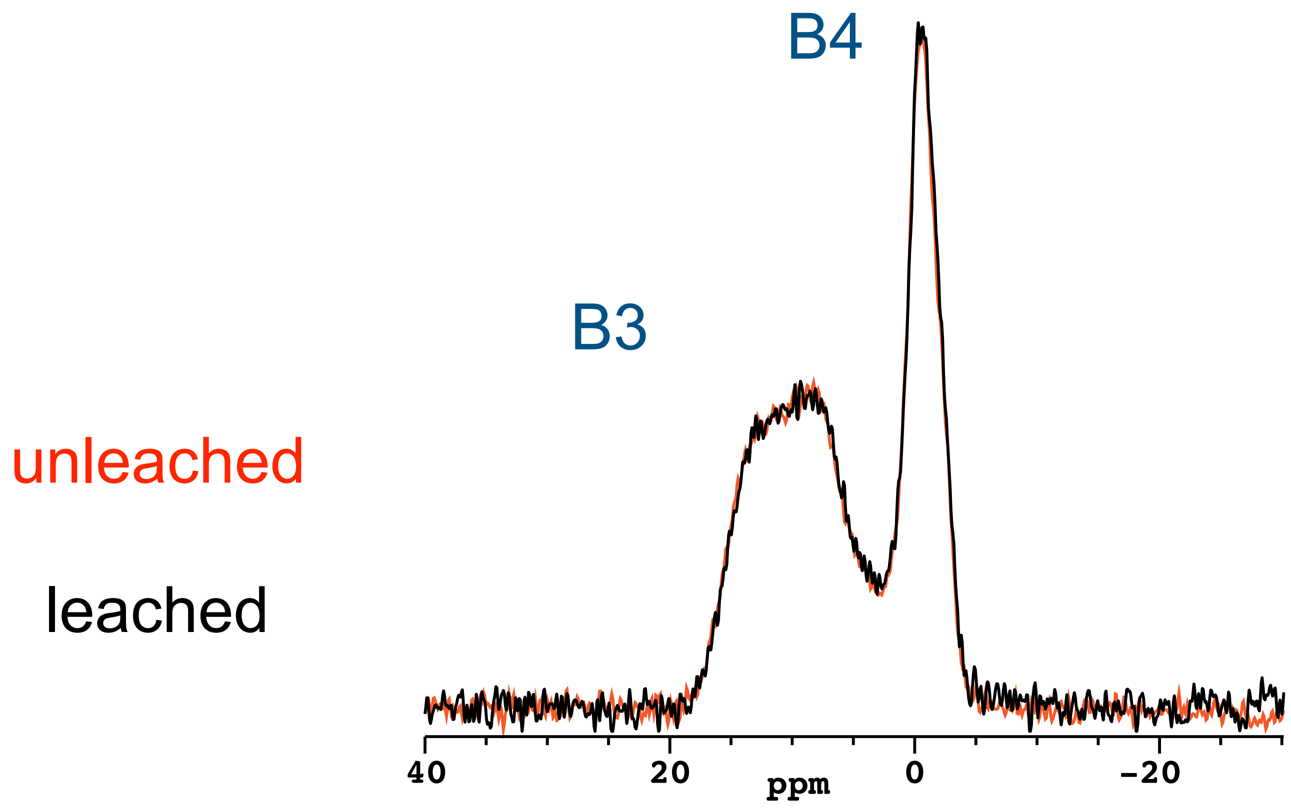


17% B released

Effect of Mg on glass durability

Preferential release of B3?

^{11}B MASNMR Mg-EM, 112 day leach test

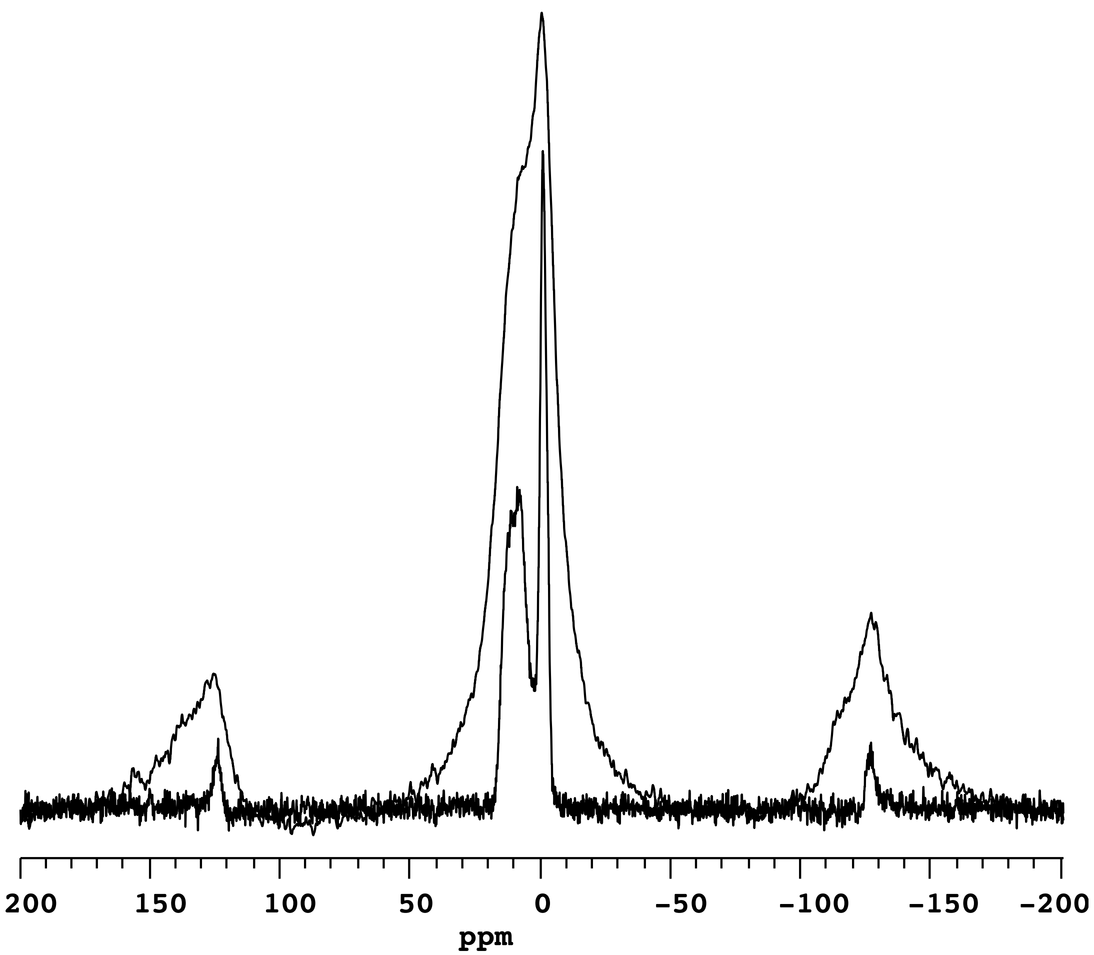


17% B released

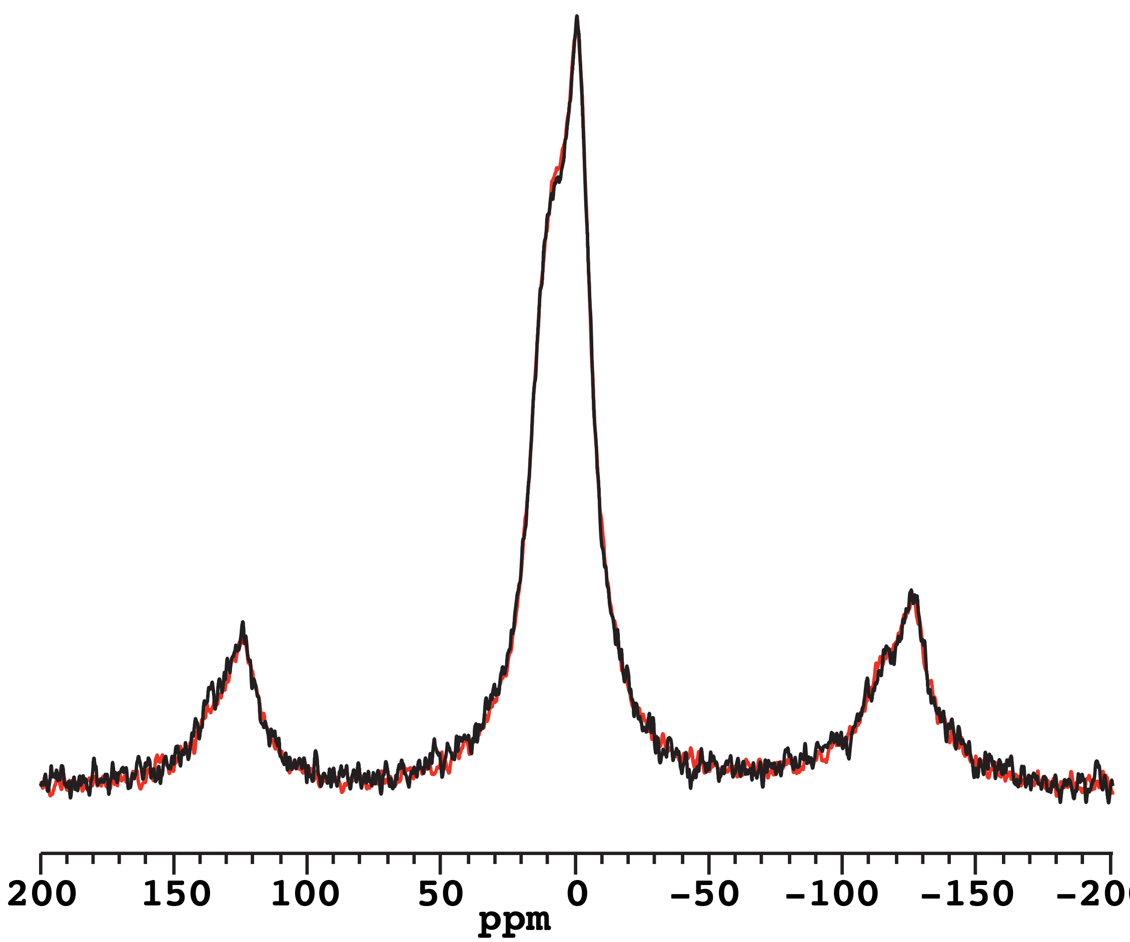
Leaching of boron is ‘congruent’ with respect to boron coordination.

Effect of Mg on glass structure

^{11}B MASNMR MW25 vs Mg-EM
MW25 paramagnetically broadened



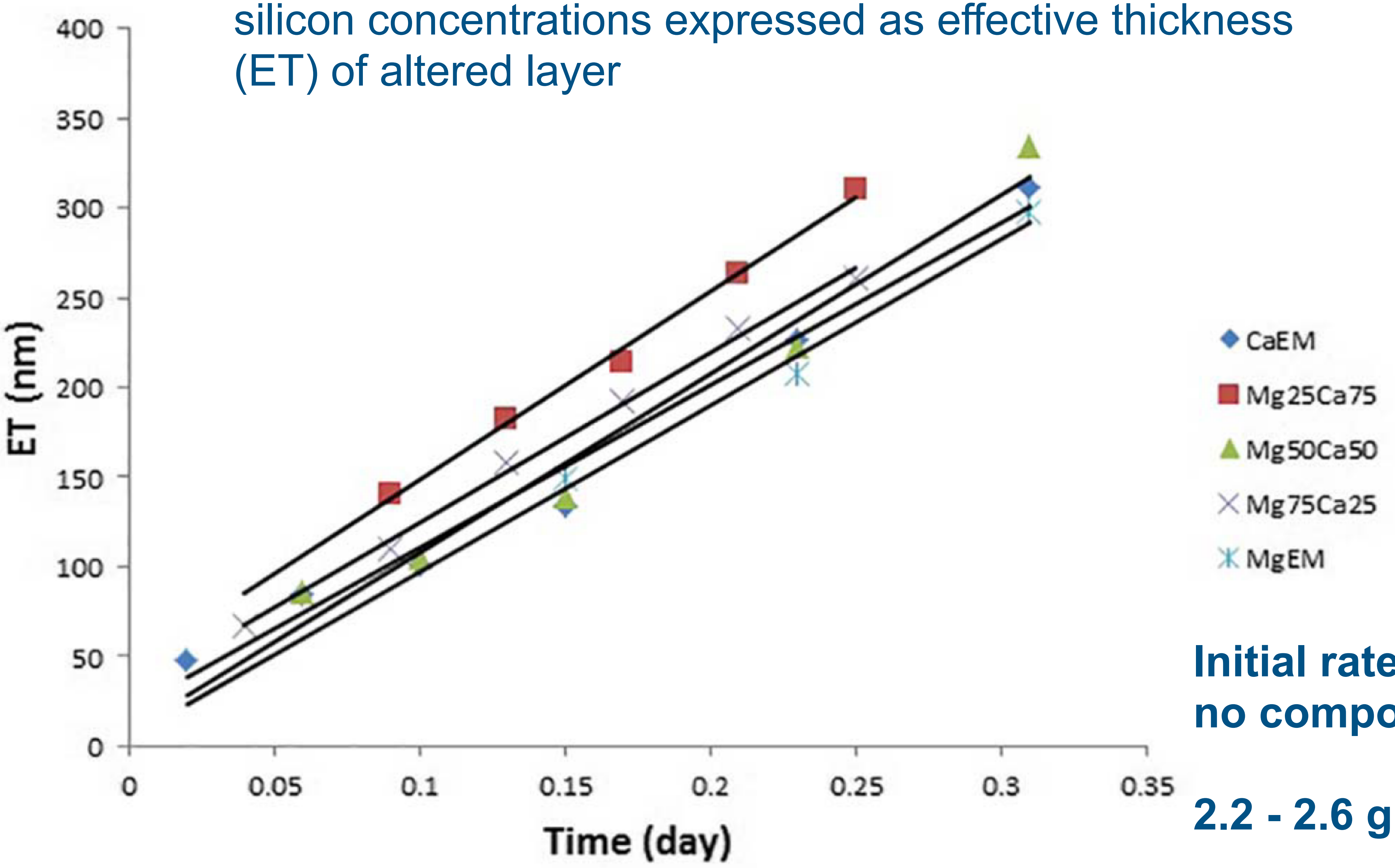
^{11}B MASNMR MW25, leached & unleached
normalised scale



Establishes boron concentration as good proxy for dissolution of UK glasses
(*already established for French glasses*)

Initial dissolution rate simplified glasses

Short duration, high dilution batch tests (SA/V = 22 m^{-1})
silicon concentrations expressed as effective thickness (ET) of altered layer



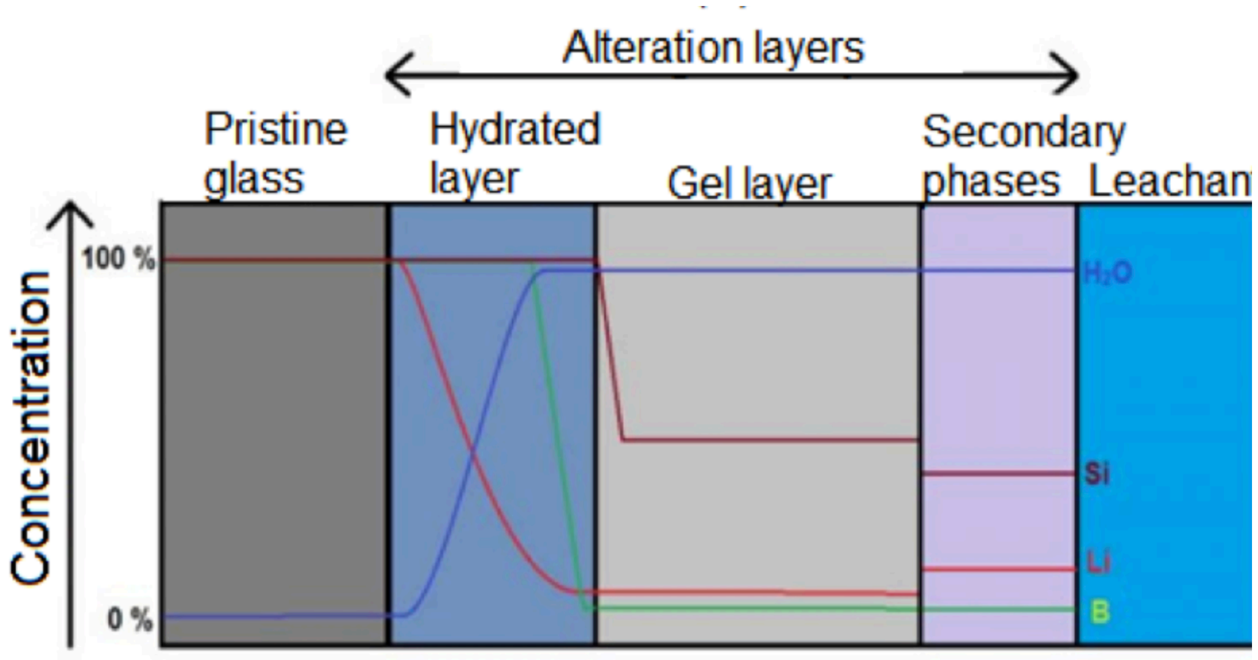
Initial rates agree within error no composition dependence

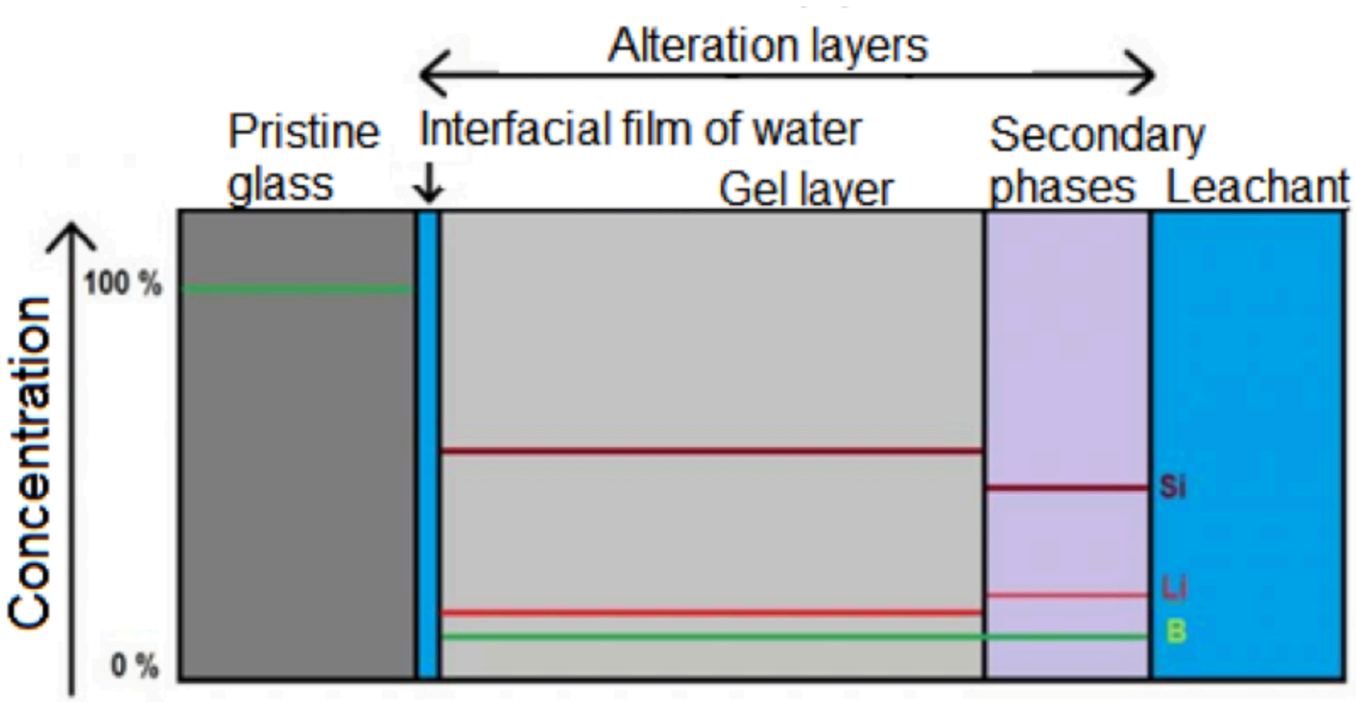
2.2 - 2.6 g m^{-2} day^{-1}

Origin of Mg causing high dissolution rates

- Initial dissolution rate not affected by composition
- structural differences (e.g. B speciation) do not affect dissolution
- **Effect must be related to passivating effect of altered layer**

Mechanisms and nature of the altered layer





RWM iCASE: Complex vs simple glasses

Cambridge Nuclear Energy MPhil: Thomas Zillhardt (2015)
(Temperature dependence of dissolution mechanisms in UK glasses)

European Nuclear Young Generation Forum 2015
June 22nd to 26th

Cambridge International Doctoral Scholarship: Rui Guo (2015)

(Nature of alteration layers in UK glasses)

EPSRC iCASE award to Tom Goût (2016) Complex vs simple glasses - mechanisms

6. Predicting radioactive waste glass dissolution with machine learning, J. N. P. Lillington, **T. L. Goût**, M. T. Harrison, I. Farnan (2020) *Journal of Non-Crystalline Solids* **533**, 119852.

5. Diffusive processes in aqueous glass dissolution, **Goût, T.L.**, S. Misra, E. T. Tipper, M. S. Bohlin, R. Guo and I. Farnan. (2019). *Nature: Materials Degradation* **3**, article 39

4. Relating Magnox and international waste glasses. **Gout, T. L.**, M. T. Harrison, and I. Farnan. (2019). *Journal of Non-Crystalline Solids* **524**. doi: 10.1016/j.jnoncrysol.2019.119647.

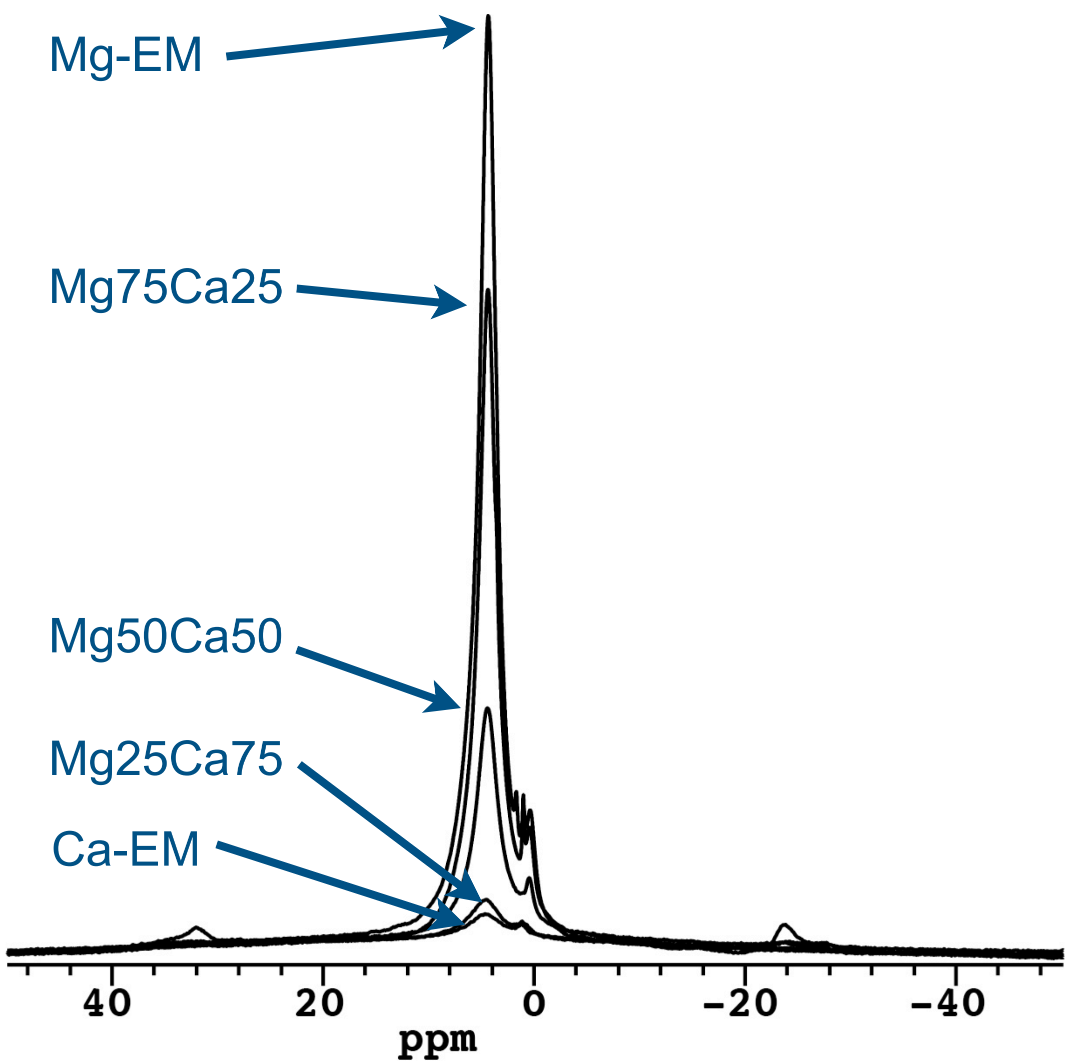
3. Evaluating the temperature dependence of Magnox waste glass dissolution. **Gout, T. L.**, M. T. Harrison, and I. Farnan**.** (2019) Journal of Non-Crystalline Solids **518**, 75-84

2.. Impacts of lithium on Magnox waste glass dissolution. Gout, T. L., M. T. Harrison, and I. Farnan. (2019) Journal of Non-Crystalline Solids **517**, 96-105

1. Experimental constraints on Li isotope fractionation during clay formation. Hindshaw, R. S., R. Tosca, **T. L. Gout**, I. Farnan, N. J. Tosca and E. T. Tipper (2019). Geochimica Et Cosmochimica Acta **250**, 219-237.

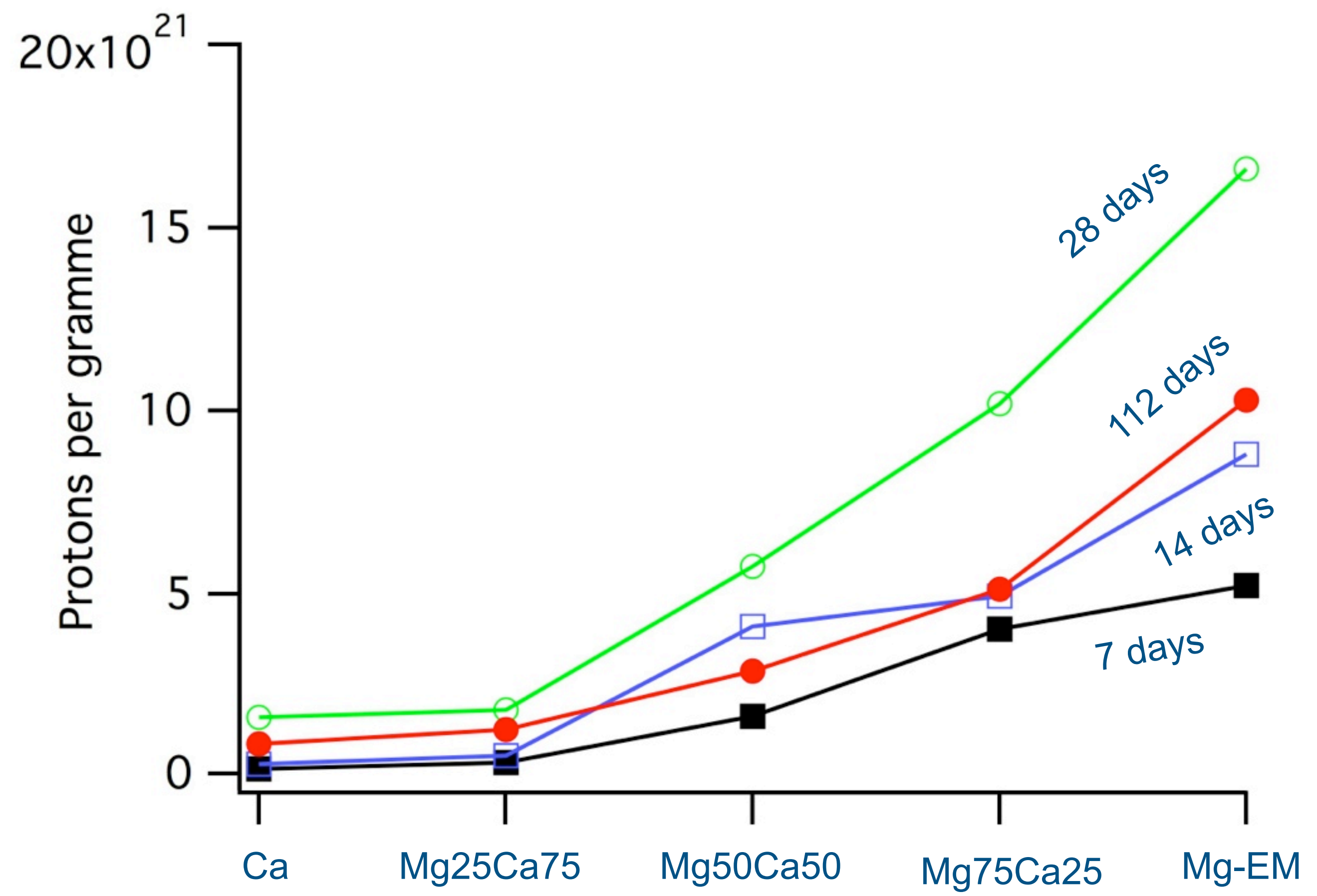
Surface alteration - ^1H NMR results

^1H MASNMR after 112 days leaching



Spectra plotted on same scale

Quantified proton contents as a function of leach time

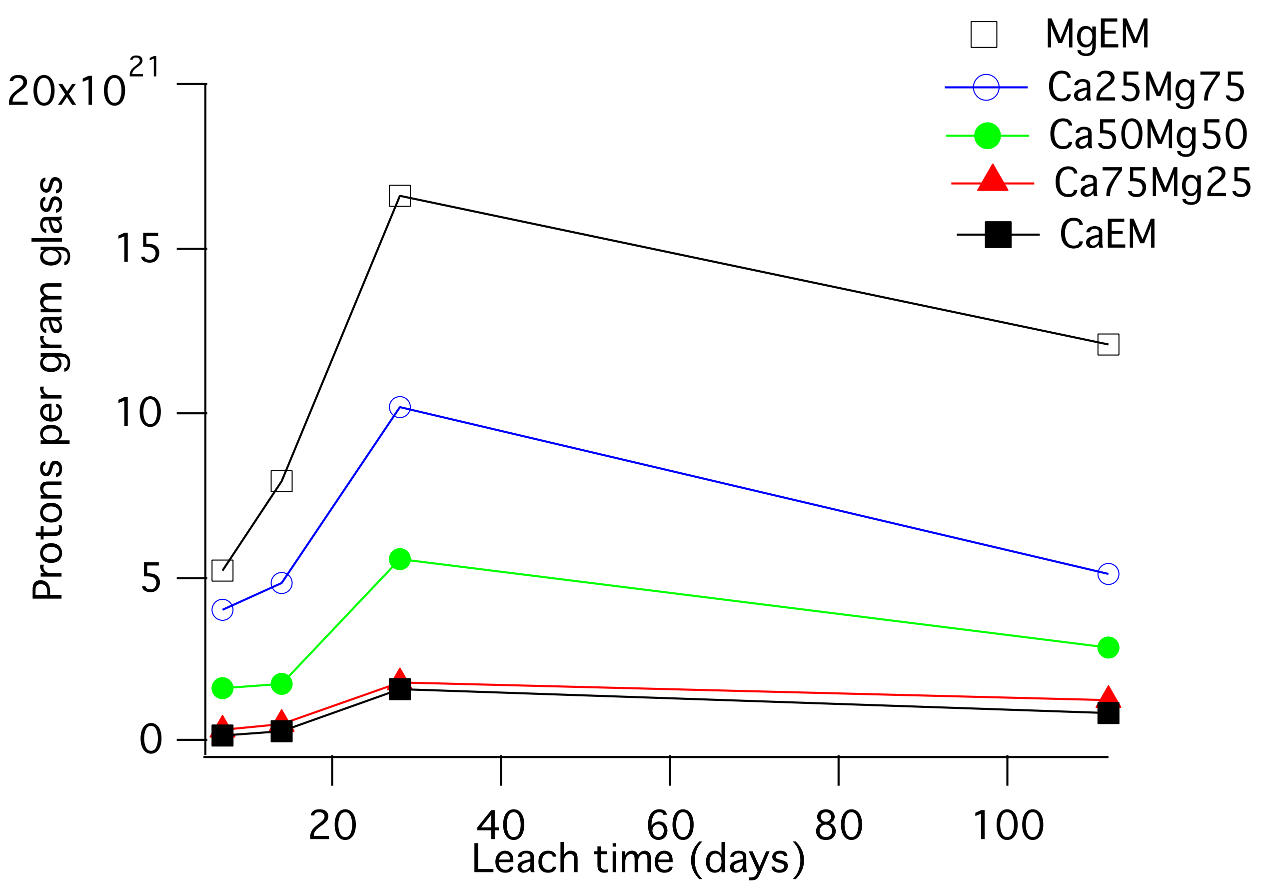


Surface alteration - ^{1}H NMR results

Spectra were integrated and background signals subtracted.

Proton content quantified by comparison with a signal of known mass of adamantane.

Expressed as the number of protons per gram of sample.



Proton content of altered layer shows clear compositional dependence on Mg content of glass.

Appears to be a maximum at 28 days.

Condensation reactions?

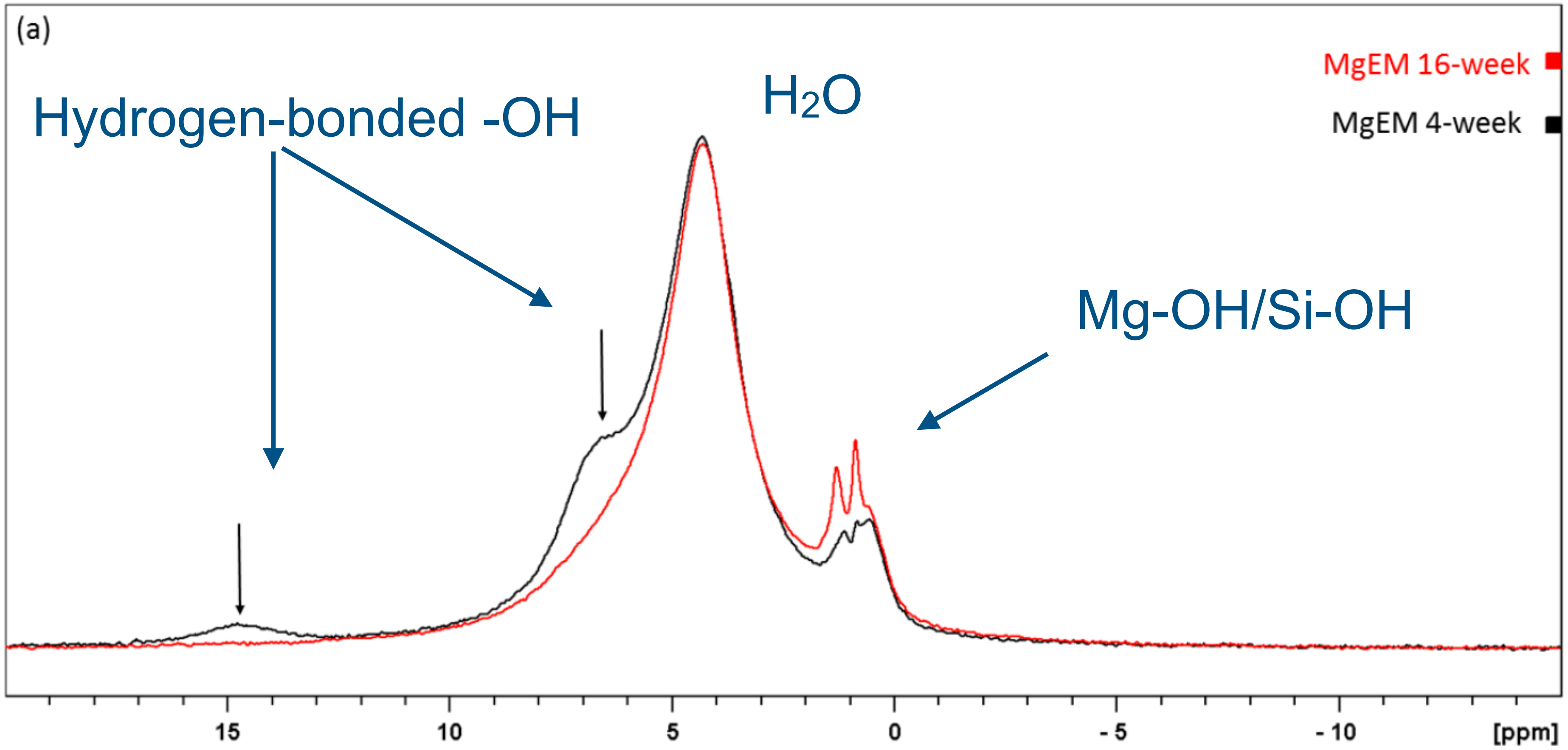
$$\text{Si-OH + SiOH} \longrightarrow \text{Si-O-Si + } H_2O$$

$$\text{Si-OH + MgOH} \longrightarrow \text{Si-O-Mg + } H_2O$$

Surface alteration - ^{1}H NMR results

Ultra-fast MASNMR (60kHz)

Resolves features not seen at lower speeds - strongly coupled to other protons



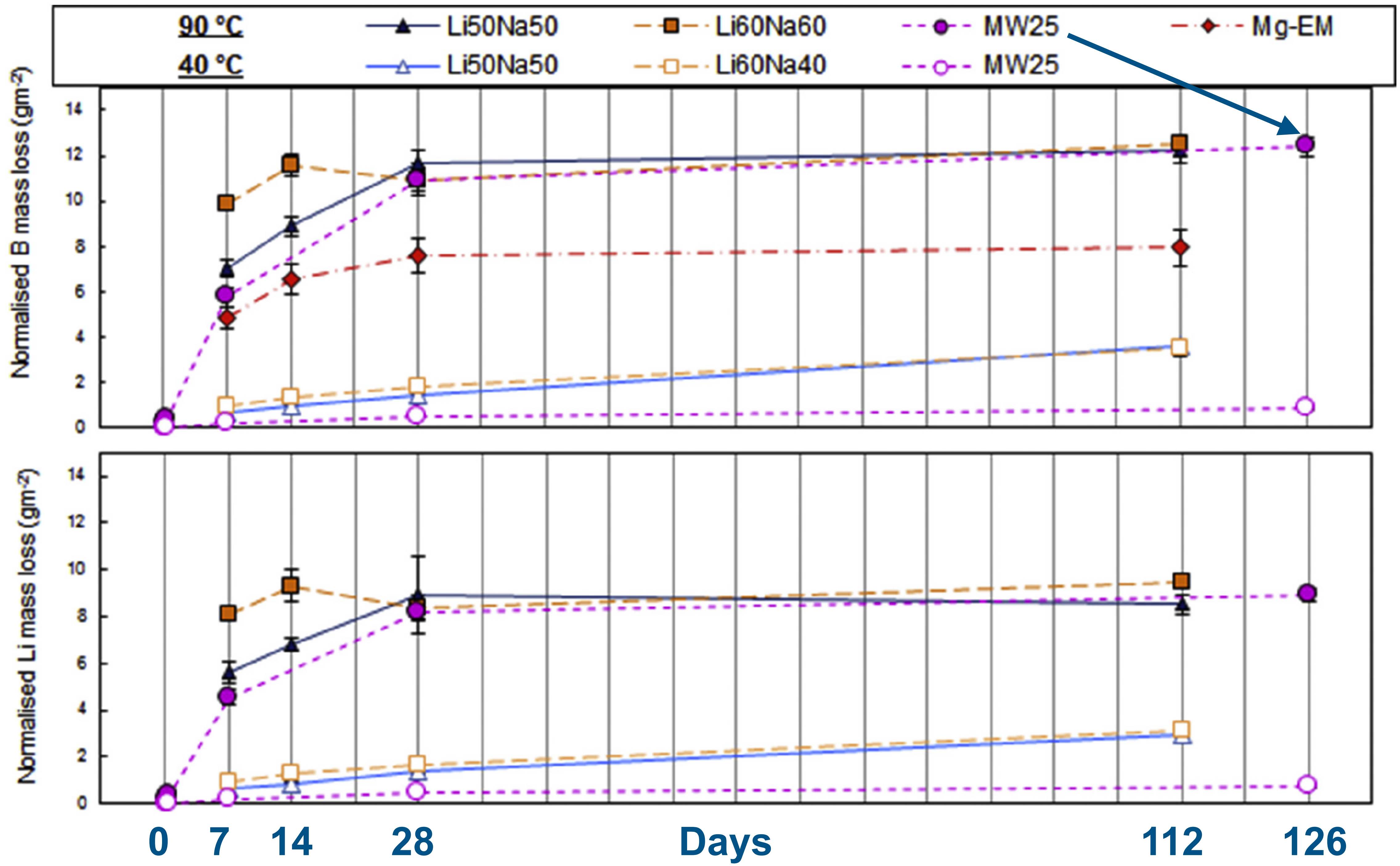
Mechanisms by time-resolved isotopic analysis

- **Temperature dependence and separate effect of Li**
- **Effect of excess Li**
- **Diffusive mechanism or not?**

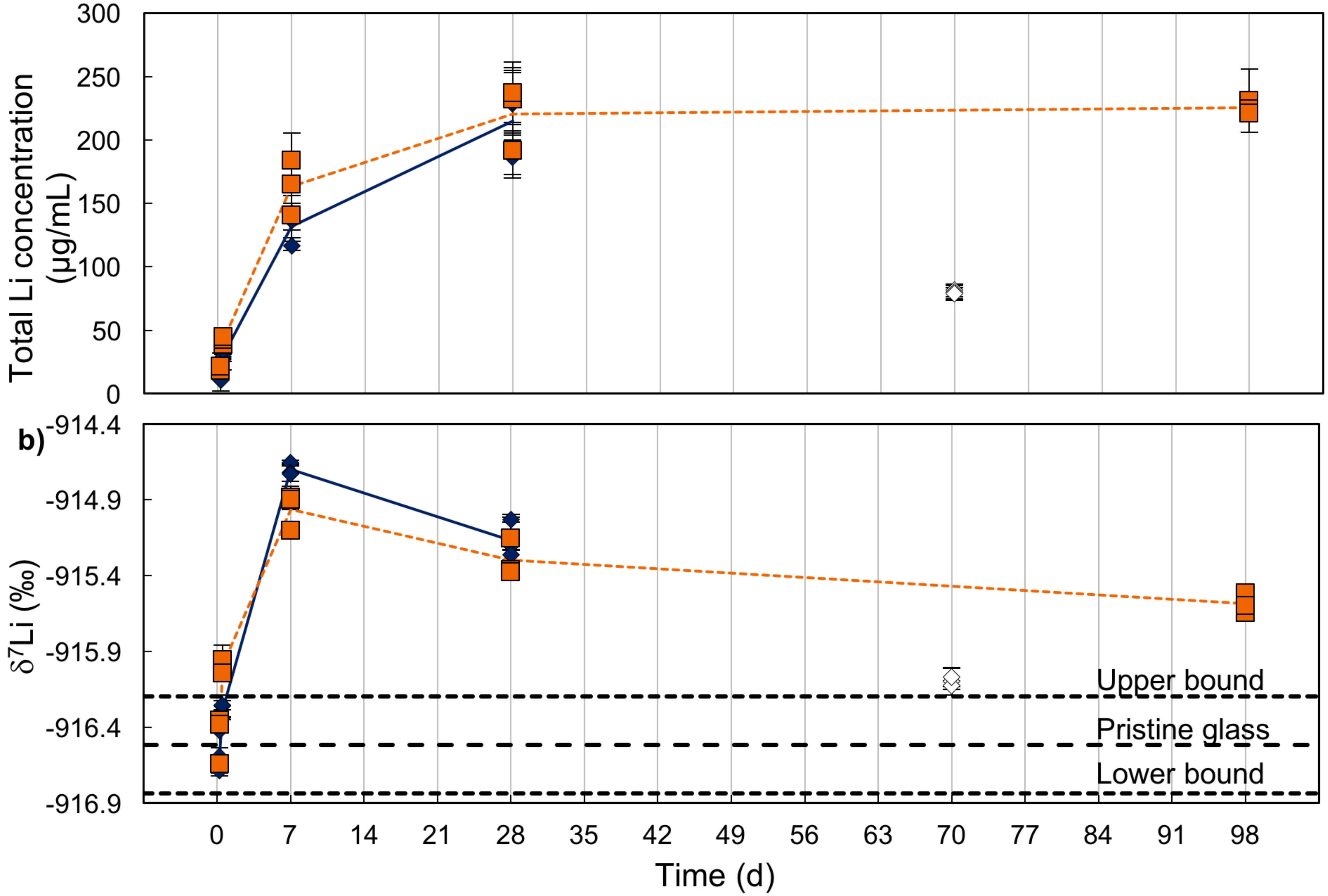
Effect of Li on MW25 dissolution

Boron

Lithium



Li isotopes as a tracer of dissolution mechanisms



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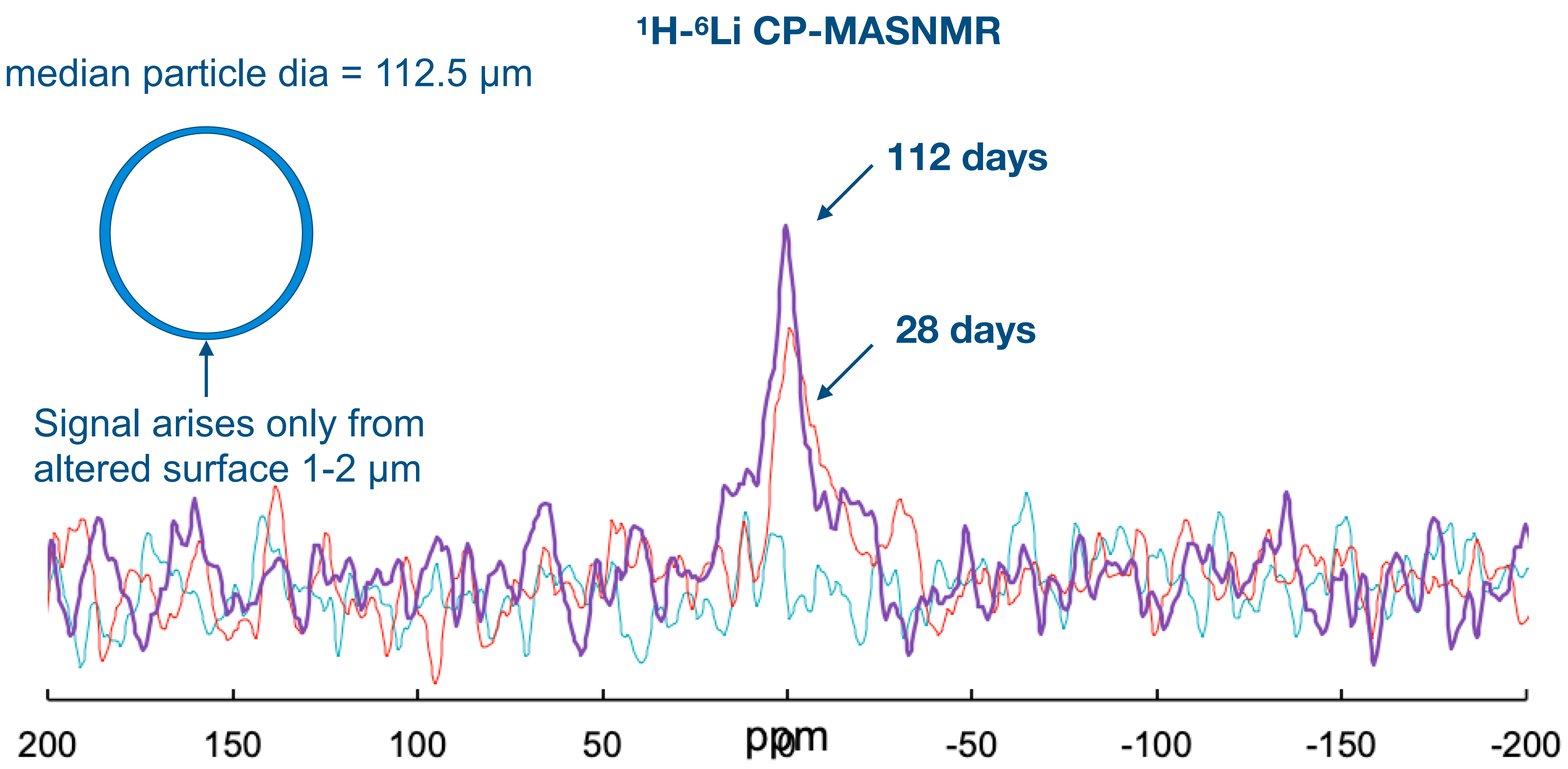

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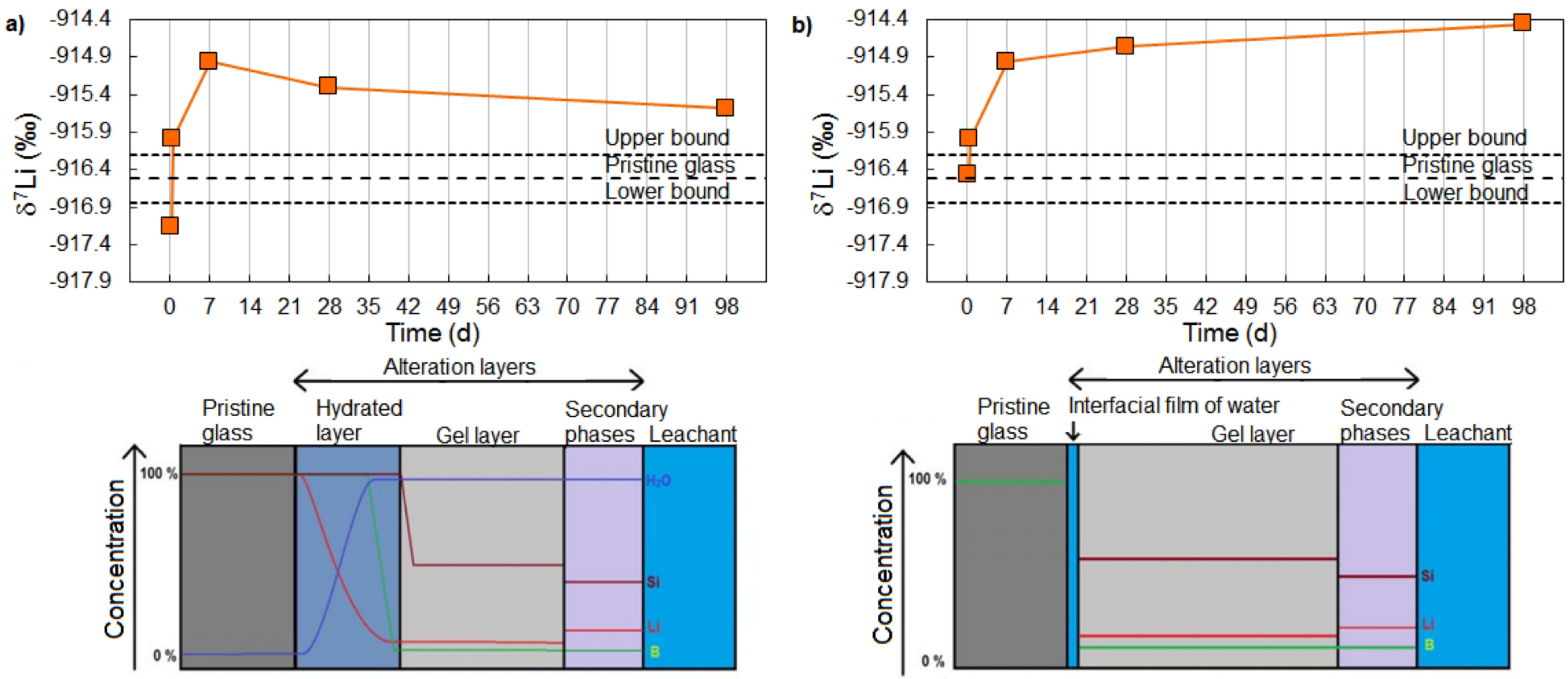

Summary

We have collaborated with RWM; as direct sponsor through RWM sponsored PhD and Masters projects, and post-doc contracts through the NDA's Direct Research Portfolio to understand teh mechanisms of UK glass dissolution to address the apliccabiity of internationally accepted models of glass dissolution to the UK case. Addressed temperature issues (GDF vs accelerated leaching)

We have used the (RWM supported) ICO Centre for Doctoral Training to provide studentships that address aspects of these issues such as adapting the GRAAL model to UK glasses to include their particular properties due to compositional variation and applying machine learning to UK glass dissolution databases (and larger international ones).