Developing an understanding of the relationship between the durability of simplified and complex UK radioactive waste glasses

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Doctor of Philosophy

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Declaration

This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the Preface and specified in the text. It is not substantially the same as any that I have submitted, or, is being concurrently submitted for a degree or diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. I further state that no substantial part of my dissertation has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. It does not exceed the prescribed word limit for the relevant Degree Committee.
Summary

Developing an understanding of the relationship between the durability of simplified and complex UK radioactive waste glasses

Thomas L. Goût

For UK radioactive waste glasses to be safely disposed of, their behaviour within a planned disposal facility over one million years must be thoroughly understood. Owing to some UK waste glasses deviating from their target Li:Na compositional ratios, the effects of Li on UK waste glasses needed to be investigated. In this thesis, the effect of Li contents on the aqueous durability of UK Magnox waste glasses was studied by fabricating and leaching two simplified analogue compositions (Li-Mg-EM) of a complex UK Magnox waste glass (MW25) with different Li:Na ratios. Further, to form a relationship between the aqueous durability of UK and French complex waste glasses, two simplified analogue compositions (Li-ISG) of a complex French waste glass (SON68) with different Li:Na ratios were fabricated and leached. To understand the effects of dissolution temperature on aqueous durability, dissolution experiments at temperatures between 40 and 90 °C took place on MW25. Additionally, isotope fingerprinting techniques were applied to investigate the mechanisms of dissolution and how these were affected by temperature; first a simplified analogue in a proof of concept experiment, then a complex Magnox waste glass. The effects of dissolution were characterised through a combination of leachate ICP-MS, MC-ICP-MS and solid state NMR experiments.

It was shown in the Li-Mg-EM analogues that the pristine B network was unaffected by changes in Li:Na ratio. The B network dissolved incongruently at 90 °C when the glass contained Li. The Li-Mg-EM analogues displayed lower aqueous durability than the Li-free analogue Mg-EM, but excess Li contents had no effect on long-term aqueous durability. The Li-ISG analogues also displayed no change in the pristine B network with the Li:Na ratio and a poorer aqueous durability than the Li-free analogue ISG. However, the B network leached congruently at 90 °C and excess Li was shown to improve aqueous durability. The proof of concept isotope fingerprinting experiments demonstrated dissolution was initially congruent, diffusive processes were taking place during the long-term dissolution of Li-Mg-EM and that this technique could be applied to the dissolution of complex waste glasses. However, these techniques showed that dissolution of MW25 was initially incongruent, as controlled through diffusive processes, and these diffusive processes were not relevant during the later dissolution regimes. The isotopic signatures of the glass leachates were consistent with the leachates concentrations in suggesting similar dissolution processes were taking place at 40 and 90 °C.
Acknowledgements

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Abstract

Safely disposing of radioactive waste glass within a geological disposal facility requires a thorough understanding of the kinetics and mechanisms of their aqueous dissolution over geological timescales. Whilst a significant number of studies have taken place on international waste glass compositions, major compositional differences between UK Magnox and international waste glasses render many of these studies inapplicable to UK Magnox glasses. Notably, one of the major compositional differences between UK and international glasses is the presence of Li. Further, the presence of excess Li concentrations in some UK vitrified products has meant the effects of Li on the aqueous durability of UK waste glasses needed to be investigated. Additionally, dissolution experiments commonly take place at a higher temperature than the expected temperature of groundwater within a geological disposal facility. As such, the effects of dissolution temperature on the mechanisms of dissolution was also investigated.

As the Li contents of complex waste glasses cannot be varied, two seven-component analogues of molar Li:Na ratios of 1.0 and 1.5 based upon a 25 wt.% loading UK Magnox waste glass with and without excess Li contents were fabricated. After characterising these glasses, they were leached in a mechanistic study to investigate the effects of Li on chemical durability. In addition to $^7$Li MAS-NMR and $^6$Li-$^1$H CP-NMR, comprehensive $^{11}$B and $^{23}$Na MAS-NMR studies and SEM imaging of the leached glass surfaces then took place to investigate the effects of dissolution on the structures of the glasses. Here we show that the proportion of $^{III}$B to $^{IV}$B units did not evolve as the Li:Na ratio was varied; suggesting that Na preferentially charge compensates the B network. However, the B network was shown to leach incongruently at 90 °C. Despite Li being shown to be detrimental to durability during the earlier dissolution regimes, the residual rates of alteration implied excess Li contents had no long-term effects on chemical durability. The observed incongruent dissolution of the B network and initially decreased chemical durability could be attributed to Li preferentially modifying the Si network, thereby promoting glass hydration and B network dissolution whilst the Na compensated $^{IV}$B units were less affected than $^{III}$B units. Additionally, Li and Na were shown to be incorporated into secondary phases at 90 °C, but these Na-bearing phases were not observed at 40 °C.

To compare the effects of Li contents on international and UK waste glass compositions, Li was substituted for Na in the well-studied Li-free French analogue “International Simple Glass” at molar Li:Na ratios of 0.4 and 0.9. These fabricated glasses were then leached and characterised in the same manner as the Magnox waste glasses. It was shown that the $^{III}$B/$^{IV}$B
ratio and the role of Na in the pristine glasses varied insignificantly with the Li:Na ratio. Further, the B network of these glasses was shown to leach congruently at both 40 and 90 °C. However, Li, Na and Mg were shown to not be incorporated into secondary phase precipitates for these glasses and the leached glass surfaces displayed only minimal evidence of surface alteration. Contrastingly, whilst Li was shown to be detrimental to aqueous durability, further substituting Li for Na improved long-term aqueous durability. This was attributable to a Li-Na mixed alkali effect which was not evident in the Magnox waste glasses.

The effects of dissolution temperature on the kinetics and mechanisms of dissolution of Magnox waste glasses still needed to be investigated. As such, a Magnox waste glass of 25 wt.% simulant waste loading was leached in static batch experiments at 40, 70, 80 and 90 °C to investigate the Arrhenius dependence of dissolution. Leached samples were characterised by EDX, SEM and XRD. It was shown that changing the dissolution temperature changed the rate of hydrolysis relative to interdiffusion. At higher temperatures, the initial release of Na deviated from Arrhenius-type behaviour and instead displayed an almost flat Arrhenius plot; demonstrating changes in temperature affect Na differently to other glass species. Whilst the activation energies of the Li and B releases were in the range of a mixed reaction, the higher activation energy of Na at lower temperatures combined with its non-Arrhenius behaviour suggested the dissolution processes of Li and Na differed. These observations were attributed to the preference of Na to charge compensate the B network.

These results highlighted a need for an additional dimension with which to probe the mechanisms by which glasses dissolve. As such, a simplistic proof of concept dissolution experiment took place at 90 °C on a simplified analogue of a complex waste glass to investigate whether the temporal evolution of the isotopic signatures of the glass leachates could provide information on glass dissolution mechanisms. Li, B and Mg isotope ratio analysis took place on the glass leachates. It was shown that dissolution was initially congruent but diffusive processes were rate limiting whilst the glass dissolved at its residual rate. These isotopic techniques were then applied to investigate the temperature dependence of dissolution of a complex Magnox waste glass. Contrastingly, it was shown that diffusive processes initially controlled dissolution but such diffusive processes were not visible at longer durations. These results suggested the same dissolution processes were taking place at both 40 and 90 °C.
# Contents

List of abbreviations ........................................................................................................... xvii

List of tables .......................................................................................................................... xxi

List of figures ......................................................................................................................... xxv

1. Introduction ......................................................................................................................... 1

   1.1. Vitrification, glass structures and waste glass compositions ........................................... 1

   1.2. Conflicting models of glass dissolution ........................................................................... 5

   1.3. Aqueous durability of radioactive waste glasses ........................................................... 10

      1.3.1. Simplified analogues of complex waste glasses ....................................................... 10

      1.3.2. Effects of composition on dissolution ..................................................................... 11

      1.3.3. Effects of temperature on dissolution .................................................................... 13

   1.4. Kinetic and equilibrium isotopic fractionation ............................................................... 13

   1.5. Scope and structure of this thesis .................................................................................. 16

2. Fabrication, dissolution and analytical methodologies ....................................................... 17

   2.1. Introduction .................................................................................................................... 17

   2.2. Sample preparation ........................................................................................................ 17

      2.2.1. In-house glass fabrication ....................................................................................... 17

      2.2.2. Production of MW25 ............................................................................................. 20

      2.2.3. Grinding, sieving and washing .............................................................................. 20

   2.3. Pre-leaching wasteform characterisation ....................................................................... 21

      2.3.1. Laser diffraction analysis ....................................................................................... 21

      2.3.2. BET surface area measurements .......................................................................... 21

      2.3.3. Density measurements .......................................................................................... 22

      2.3.4. XRD ....................................................................................................................... 22

      2.3.5. SEM and EDS ....................................................................................................... 23

      2.3.6. NMR ..................................................................................................................... 24

   2.4. Compositional characterisation .................................................................................... 31
2.4.1. EPMA ................................................................. 31
2.4.2. LA-ICP-MS .......................................................... 31
2.4.3. Digestion and ICP-OES ........................................... 32

2.5. Static batch dissolution methodology and the Li-Mg-EM experiments .......... 32
2.5.1. The ASTM product consistency test method B methodology .................. 32
2.5.2. Vessel cleaning and instrument calibrations ....................................... 33
2.5.3. Leaching experimental conditions ...................................................... 33
2.5.4. Leachate ICP-MS analysis .......................................................... 34
2.5.5. Concentration data treatment .......................................................... 38

2.6. Static batch Li-ISG dissolution ....................................................... 39
2.6.1. Equipment cleaning, preparations and calibrations ............................. 39
2.6.2. Differences in leaching experimental conditions .................................. 40
2.6.3. Leachate ICP-MS analysis conditions and data treatment ...................... 41

2.7. Static batch MW25 dissolution (70 °C and 80 °C) .................................. 41
2.7.1. Equipment cleaning, preparations and calibrations ............................. 41
2.7.2. Leaching experimental conditions ...................................................... 41
2.7.3. Leachate ICP-MS analysis conditions .............................................. 42
2.7.4. MW25 leachate data treatment ........................................................ 42

2.8. Static batch sampling MW25 dissolution (40 °C and 90 °C) ...................... 43
2.8.1. Experimental overview ........................................................................ 43
2.8.2. Equipment cleaning ........................................................................... 44
2.8.3. Preparations and calibrations ............................................................. 45
2.8.4. Beginning the experiments, taking aliquots and ending the experiments .... 46
2.8.5. Leachate ICP-OES analysis conditions and data treatment .................. 47

2.9. Static batch sampling ⁶Li-Mg-EM dissolution ......................................... 48
2.9.1. Experimental overview ........................................................................ 48
2.9.2. Equipment cleaning, preparations and calibrations ............................. 49
2.9.3. Beginning, refreshing and ending the experiments ........................................... 50
2.9.4. Leachate ICP-MS analysis conditions .......................................................... 51
2.10. Post-dissolution analyses .................................................................................. 52
   2.10.1. XRD ........................................................................................................... 52
   2.10.2. EDS and SEM .......................................................................................... 52
   2.10.3. NMR ......................................................................................................... 53
2.11. Pristine glass preparation for Li isotopic work .................................................. 54
   2.11.1. Alkali fusion of pristine powders and standards ...................................... 54
   2.11.2. Acid digestion .......................................................................................... 59
2.12. Column chromatography and B sublimation ...................................................... 59
   2.12.1. Titrations .................................................................................................. 59
   2.12.2. Cleaning ................................................................................................... 60
   2.12.3. AG MP-50 resin ....................................................................................... 60
   2.12.4. AG 50W-X12 resin and NGM (Mg) ............................................................ 66
   2.12.5. B sublimation .......................................................................................... 67
2.13. MC-ICP-MS ..................................................................................................... 67
   2.13.1. Basic background to MC-ICP-MS ............................................................. 67
   2.13.2. Instrumentation and data treatment ......................................................... 69
   2.13.3. $^7\text{Li}/^6\text{Li}$ MC-ICP-MS ........................................................................ 70
   2.13.4. $^{11}\text{B}/^{10}\text{B}$ MC-ICP-MS ................................................................. 71
   2.13.5. Mg isotope MC-ICP-MS ........................................................................... 71
   2.13.6. $^{11}\text{B}/^{10}\text{B}$ LA-MC-ICP-MS ................................................................. 72
3. Impacts of lithium on analogues of a Magnox waste glass .................................... 73
   3.1. Introduction to the Li-Mg-EM compositions ..................................................... 73
   3.2. Pristine Li-Mg-EM characterisation ................................................................. 75
      3.2.1. The formation of cristobalite in Li-Mg-EM .............................................. 75
      3.2.2. Geometric analyses ............................................................................... 78
3.2.3. Pristine glass compositions ................................................................. 80
3.3. Li-Mg-EM leachate concentrations and pH ........................................ 81
3.4. Characterisation of the glass structures and effects of dissolution ......... 85
  3.4.1. SEM and EDS .................................................................................. 85
  3.4.2. NMR .............................................................................................. 91
  3.4.3. XRD .............................................................................................. 101
3.5. Discussion ................................................................................................ 102
  3.5.1. Pristine glass structures ................................................................. 102
  3.5.2. Lithium promoting glass dissolution ............................................ 103
  3.5.3. Precipitates reducing aqueous durability ..................................... 107
  3.5.4. Suitability as an analogue ............................................................. 109
3.6. Summary ............................................................................................... 110
4. Relating Magnox and international waste glasses .................................. 111
  4.1. Introduction to the Li-ISG compositions ........................................... 111
  4.2. Fabricating amorphous Li-ISG and XRD .......................................... 113
  4.3. Pristine Li-ISG characterisation .......................................................... 113
    4.3.1. Geometric analyses .................................................................... 113
    4.3.2. Compositional analyses and final compositions ....................... 114
  4.4. Li-ISG leachate compositions and pH .............................................. 115
  4.5. Characterisation of pristine and leached glass structures .................. 120
    4.5.1. SEM .......................................................................................... 120
    4.5.2. NMR ........................................................................................ 123
    4.5.3. XRD ........................................................................................ 131
4.6. Discussion ............................................................................................ 132
  4.6.1. The structure of pristine Li-ISG ..................................................... 132
  4.6.2. Precipitates controlling aqueous durability ................................... 134
  4.6.3. Differences in dissolution of the B network and the effects of Li .... 135
5. Evaluating the temperature dependence of waste glass dissolution ......................................................... 139
  5.1. Introduction ........................................................................................................................................ 139
  5.2. Pristine MW25 characterisation ........................................................................................................ 141
    5.2.1. XRD ............................................................................................................................................. 141
    5.2.2. SEM of prepared glass powders ................................................................................................. 141
  5.3. MW25 dissolution experiments ............................................................................................................. 142
    5.3.1. Leachate concentrations and pH ................................................................................................. 142
    5.3.2. Arrhenius plots and activation energies ....................................................................................... 147
  5.4. Characterisation of leached and pristine samples ................................................................................ 149
    5.4.1. SEM and EDS ............................................................................................................................... 149
    5.4.2. XRD ............................................................................................................................................... 152
  5.5. Discussion .......................................................................................................................................... 153
    5.5.1. Temperature dependence of mobile species release ..................................................................... 153
    5.5.2. The kinetics of alteration ................................................................................................................ 161
    5.5.3. Temperature dependence of secondary phase formation .......................................................... 163
  6. Probing diffusion throughout aqueous glass dissolution ......................................................................... 165
    6.1. Introduction ....................................................................................................................................... 165
    6.2. 6Li-Mg-EM fabrication, XRD and 29Si MAS-NMR ........................................................................... 166
    6.3. Pristine 6Li-Mg-EM characterisation ............................................................................................ 167
      6.3.1. Laser diffraction and density analyses ....................................................................................... 167
      6.3.2. Compositional analyses ............................................................................................................... 167
      6.3.3. Pristine isotopic characterisation ............................................................................................. 168
    6.4. Leachate analyses ............................................................................................................................. 174
      6.4.1. Concentrations and pH ............................................................................................................... 174
      6.4.2. Li isotopes ................................................................................................................................. 178
      6.4.3. B isotopes .................................................................................................................................. 180
      6.4.4. Mg isotopes ............................................................................................................................... 182
6.5. Characterisation of leached and pristine samples ........................................ 183
  6.5.1. SEM ........................................................................................................ 183
  6.5.2. NMR ........................................................................................................ 183
6.6. Discussion ........................................................................................................ 184
  6.6.1. Initially congruent dissolution ................................................................. 184
  6.6.2. Secondary phase precipitation and adsorption ........................................ 185
  6.6.3. Interdiffusion as a rate limiting dissolution mechanism ....................... 186
7. An isotopic investigation into the temperature dependence of dissolution .... 191
  7.1. Introduction ................................................................................................... 191
  7.2. Isotopic analyses ......................................................................................... 192
    7.2.1. Li and Mg isotopes of NGM ................................................................. 192
    7.2.2. Pristine MW25 isotopic analyses ......................................................... 195
    7.2.3. MW25 leachate ratios and Li isotopes ................................................. 197
  7.3. Discussion ..................................................................................................... 199
    7.3.1. Initially incongruent dissolution ........................................................... 199
    7.3.2. Congruent dissolution with secondary phases precipitation ............... 200
8. Conclusions and future work ............................................................................. 203
  8.1. Simplified analogues and the effects of Li .................................................. 203
  8.2. Probing the dissolution mechanisms of simplified and complex glasses ...... 204
  8.3. The effects of dissolution temperature on MW25 ...................................... 205
  8.4. Concluding remarks on analogues and probing dissolution mechanisms ...... 207
  8.5. Future work .................................................................................................. 207
References ............................................................................................................. 209
Supplementary tables ............................................................................................ 226
List of abbreviations

1/T  Reciprocal of absolute temperature (K\(^{-1}\))
A   Arrhenius parameter (gL\(^{-1}\)d\(^{-1}\))
α   Alpha particle (two protons and two neutrons or He\(^{2+}\))
AVH Atelier de vitrification La Hague
AVM Atelier de vitrification de Marcoule
B\(_0\) External magnetic field (T or kg\cdot s\(^{-2}\)\cdot A\(^{-1}\))
β   Beta particle (single electron or e\(^-\))
BET Brunauer–Emmett–Teller surface area analysis
BSE Backscattered electron
CBS Centric backscatter (BSE) detector
χ   Quadrupolar coupling constant (Hz)
\(\overline{C}_i^{Blank}\) Average concentration of element I in the blanks (g/L)
\(C_i^{Sample}\) Concentration of element i in sample leachate (g/L)
CN  Coordination number
CP-NMR Cross-polarisation nuclear magnetic resonance
d  Spherical particle diameter (\(\equiv 112.5 \mu m\) herein)
\(\delta\) NMR chemical shift (ppm)
\(\delta^A X\) Delta notation for expressing changes in an isotope ratio relative to a standard (heavier isotope A to lighter isotope of element X in ‰)
DR  Double resonance
E\(_a\) Activation energy (kJmol\(^{-1}\))
EDS Energy-dispersive X-ray spectroscopy
E\(_{Lm}\) Energy of each eigenstate with spin m
EPMA Electron probe microanalysis
η   Asymmetry parameter
ETD Everhart-Thornley detector (High vacuum SE detector)
fi  Mass fraction of element i within the pristine glass
FID Free induction decay
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>Gyromagnetic ratio (NMR, rad·s$^{-1}$·T$^{-1}$) or Gamma ray (High-energy photon)</td>
</tr>
<tr>
<td>GDF</td>
<td>Geological disposal facility</td>
</tr>
<tr>
<td>GRAAL model</td>
<td>Glass reactivity with allowance for the alteration layer model</td>
</tr>
<tr>
<td>h</td>
<td>Planck's constant (6.62607004 × 10$^{-34}$ m$^2$kg·s$^{-1}$)</td>
</tr>
<tr>
<td>$\hat{H}$</td>
<td>Hamiltonian (energy operator)</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>Reduced Planck's constant (h/2$\pi$)</td>
</tr>
<tr>
<td>HAL</td>
<td>Highly active liquor</td>
</tr>
<tr>
<td>HAST</td>
<td>HAL storage tank</td>
</tr>
<tr>
<td>HLW</td>
<td>High level waste</td>
</tr>
<tr>
<td>I</td>
<td>Nuclear spin number</td>
</tr>
<tr>
<td>$\hat{I}$</td>
<td>Nuclear spin operator</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectroscopy</td>
</tr>
<tr>
<td>ISG</td>
<td>International simple glass (six-component analogue of SON68)</td>
</tr>
<tr>
<td>J</td>
<td>Intrinsic angular momentum</td>
</tr>
<tr>
<td>LA-ICP-MS</td>
<td>Laser ablation inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>LA-MC-ICP-MS</td>
<td>Laser ablation multi-collector inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength (nm)</td>
</tr>
<tr>
<td>LFD</td>
<td>Low vacuum secondary electron detector</td>
</tr>
<tr>
<td>LFi</td>
<td>Fraction of element i leached from the glass</td>
</tr>
<tr>
<td>LOI</td>
<td>Loss on ignition</td>
</tr>
<tr>
<td>M</td>
<td>Total magnetisation</td>
</tr>
<tr>
<td>m</td>
<td>Magnetic spin quantum number or Mass of glass powder</td>
</tr>
<tr>
<td>MAE</td>
<td>Mixed alkali effect</td>
</tr>
<tr>
<td>Magnox</td>
<td>Non-oxidising Mg-Al alloy cladding and type of nuclear reactor</td>
</tr>
<tr>
<td>MAS-NMR</td>
<td>Magic angle spinning nuclear magnetic resonance</td>
</tr>
<tr>
<td>MC-ICP-MS</td>
<td>Multi-collector inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>Mg-EM</td>
<td>Magnesium endmember (six component MW25 analogue)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>( \mu )</td>
<td>Magnetic moment (A(\cdot)m(^2))</td>
</tr>
<tr>
<td>( \hat{\mu} )</td>
<td>Magnetic moment operator</td>
</tr>
<tr>
<td>MW</td>
<td>Mixture Windscale</td>
</tr>
<tr>
<td>MW25</td>
<td>Inactive simulant complex Magnox waste glass of 25 wt.% waste loading</td>
</tr>
<tr>
<td>NBO</td>
<td>Non-bridging oxygen</td>
</tr>
<tr>
<td>NLI</td>
<td>Normalised releases of element i (g/m(^2))</td>
</tr>
<tr>
<td>( \omega )</td>
<td>Larmor frequency (MHz)</td>
</tr>
<tr>
<td>PCT-B</td>
<td>Product consistency test method B (ASTM International test method)</td>
</tr>
<tr>
<td>PFA</td>
<td>Perfluoroalkoxy alkane</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PUREX</td>
<td>Plutonium and uranium recovery extraction</td>
</tr>
<tr>
<td>( r )</td>
<td>Normalised release rate at 6 h of dissolution (g/m(^2)d)</td>
</tr>
<tr>
<td>R</td>
<td>Ideal gas constant (8.314 JK(^{-1})mol(^{-1}))</td>
</tr>
<tr>
<td>( r_0 )</td>
<td>Pristine spherical particle radius (( \equiv 56.25 \mu)m)</td>
</tr>
<tr>
<td>R7T7</td>
<td>French radioactive waste glass composition</td>
</tr>
<tr>
<td>REE</td>
<td>Rare-earth element (Lanthanides, Sc and Y)</td>
</tr>
<tr>
<td>RF</td>
<td>Radiofrequency</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density (g/cm(^3))</td>
</tr>
<tr>
<td>RSD</td>
<td>Relative standard deviation (ratio of standard deviation and the mean)</td>
</tr>
<tr>
<td>SA/V</td>
<td>Glass surface area to leachant volume ratio (m(^{-1}) or m(^2)/L)</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SON68</td>
<td>Inactive simulant complex R7T7 French waste glass</td>
</tr>
<tr>
<td>SSB</td>
<td>Spinning sidebands (NMR) or Standard-sample bracketing (MC-ICP-MS)</td>
</tr>
<tr>
<td>( t )</td>
<td>Altered layer thickness (( \mu)m) or Time (s)</td>
</tr>
<tr>
<td>T1 and T2</td>
<td>Longitudinal and transverse relaxation times respectively</td>
</tr>
<tr>
<td>( \theta )</td>
<td>Angle of incidence (XRD)</td>
</tr>
<tr>
<td>THORP</td>
<td>Thermal oxide reprocessing plant</td>
</tr>
</tbody>
</table>
### List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ToF-SIMS</td>
<td>Time-of-Flight Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>TR</td>
<td>Triple resonance</td>
</tr>
<tr>
<td>V</td>
<td>Frequency</td>
</tr>
<tr>
<td>$V_i$ and $V_f$</td>
<td>Initial and final volume of leachant respectively (mL or L)</td>
</tr>
<tr>
<td>VTR</td>
<td>Vitrification test rig (inactive replica of WVP)</td>
</tr>
<tr>
<td>WVP</td>
<td>Waste vitrification plant</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray powder diffraction</td>
</tr>
</tbody>
</table>
List of tables

Table 1.1: Nominal oxide mol.% compositions of MW25 and SON68..................5

Table 2.1: $^6$Li-Mg-EM with SGR-1b and $^6$Li-Mg-EM with single-element Li plasma standard mixing lines with the nominal isotopic signatures of each mixing line standard presented on the $\delta^{7}$Li and $\delta^{17}$Li scales.................................................................58

Table 2.2: Composition of NGM and masses of elements in the volumes of NGM initially loaded onto the columns.................................................................63

Table 3.1: Nominal cation atomic percent (at.%) compositions of Li50Na50-Mg-EM and Li60Na40-Mg-EM compared with Mg-EM......................................................74

Table 3.2: Measured particle size distributions of the four Li-Mg-EM batches. ........78

Table 3.3: Measured BET surface areas of the four Li-Mg-EM batches with their linear correlation coefficients.................................................................79

Table 3.4: Measured densities of the Li-Mg-EM batches........................................79

Table 3.5: Table of the nominal and measured oxide wt.% compositions of the four Li-Mg-EM batches ........................................................................81

Table 3.6: Measured elemental molar percentages of Li, Na and B in the pristine Li-Mg-EM samples (calculated from Table 3.5) alongside the fractions of $^{11}$B and $^{14}$B estimated from quantifying the pristine, 7 d leached and 112 d leached (40 and 90 °C) $^{11}$B NMR spectra. For the sake of comparison, values for Mg-EM are given (concentrations and spectrum taken from another study whilst the spectrum was quantified here using two $^{14}$B peaks.) ....................96

Table 3.7: Table comparing the percentage B released from the glass, the concentrations of Na in solution estimated from this B fraction released, the measured concentrations of Na in solution, the difference between the estimated and measured concentrations presented in mg/l and mg and the quantification of the leached and pristine $^{23}$Na MAS-NMR spectra. ..........100

Table 4.1: Nominal cation atomic percent (at.%) compositions of Li29Na71-ISG and Li47Na53-ISG compared with ISG. For comparison, the nominal at.% compositions of Mg-EM and the Li-Mg-EM compositions (Table 3.1) are shown.................................................................112

Table 4.2: Measured particle size distributions of the four Li-ISG batches compared with the distributions acquired for the full-Li MW base glass during this run and previously in the Li-Mg-EM run (Table 3.2).................................................................114
Table 4.3: Measured densities of the Li-ISG batches. For comparison, the density of ISG is displayed. ................................................................. 114

Table 4.4: The measured oxide wt.% compositions of the two batches of each Li-ISG composition given next to their respective nominal compositions and the technique used to measure that oxide. ................................................................. 115

Table 4.5: Estimated percentage of B leached from each Li-ISG and Li-Mg-EM composition for each leaching duration at each temperature. ................................................................. 119

Table 4.6: Measured elemental molar percentages of Li, Na and B in the pristine Li-ISG samples (calculated from Table 4.4) alongside the fractions of $^{\text{III}}$B and $^{\text{IV}}$B estimated from quantifying the pristine, 7 d leached and 112 d leached (40 and 90 °C) $^{11}$B NMR spectra. For the sake of comparison, the nominal composition of ISG and the results of the curve fitting are given. ................................................................................................. 128

Table 4.7: Table comparing the percentage of B released from the glass, the concentration of Na in solution estimated from the fraction of B released, the measured concentration of Na in solution and the difference between the measured and estimated Na concentrations presented in mg/l and mg. ................................................................................................. 131

Table 5.1: Nominal oxide wt.% composition of MW25. ................................................................. 139

Table 5.2: Table of the activation energies (Ea) obtained from the non-linear least squares regressions (Figure 5.5b) for B, Li and Mo. The Ea for Na was instead obtained through linear regression of the 40 and 70 °C points........................................................................................................ 149

Table 6.1: Nominal cation atomic percent (at.%) composition of $^6$Li-Mg-EM compared with Li50Na50-Mg-EM (Chapter 3) and Mg-EM........................................................................................................ 166

Table 6.2: Table of the nominal and measured oxide wt.% compositions of $^6$Li-Mg-EM presented alongside the technique used to measure the concentration of that oxide, the recoveries for each oxide and the RSD associated with each average measurement. ............. 168

Table 6.3: Table showing the Li isotope MC-ICP-MS results for the four $^6$Li-Mg-EM alkali fusions, the $^6$Li-Mg-EM digest run in duplicate and the SGR-1b digest run in duplicate. ..... 170

Table 6.4: Table showing the Li isotope MC-ICP-MS results for the duplicate BCR-1, duplicate BCR-2 and quintuplicate SGR-1b alkali fusions relative to NIST 8545 L-SVEC. ............ 171
Table 6.5: Table showing the Li isotope MC-ICP-MS results relative to NIST 8545 L-SVEC for the samples eluted through the columns twice. ................................................................. 172

Table 7.1: Table of the mass of Li in the prepared NGM standards loaded onto the AG MP-50 columns and eluted for Li. δ⁷Li values represent average values from the duplicate measurements for the variable Li load samples and the triplicate measurements for the 5 ng Li load samples and Aristar Li. ........................................................................................................... 193

Table 7.2: Table of the mass of Mg in the prepared NGM standards loaded onto the AG MP-50 columns (first set of standards) and the AG 50W-X12 columns (second set of samples), eluted for Mg and analysed for Mg isotopes by MC-ICP-MS........................................................................... 194

Table 7.3: Table showing the Li isotope MC-ICP-MS results for the four MW25 alkali fusions, the MW25 digest and the SGR-1b digest. ........................................................................................................ 196
List of figures

Figure 1.1: Abstraction of the two-stage AVH vitrification process employed at the waste vitrification plant at Sellafield Ltd. ................................................................. 3

Figure 1.2: Abstractions of the local structure of a Na silicate glass (a) and a Ca-Mo-Na-Zn alumino-borosilicate glass (b). ................................................................. 4

Figure 1.3: Cartoon depicting the temporal evolution of theoretical leachate Na and Si concentrations throughout the five dissolution regimes. ........................................... 6

Figure 1.4: Cartoons of elemental profiles within altered glass at high reaction progress according to an interdiffusion-based model of dissolution (a) and an interfacial dissolution-precipitation model (b). ................................................................. 9

Figure 2.1: Abstraction of an ICP-MS................................................................. 35

Figure 2.2: Abstraction of an ICP torch. ............................................................... 35

Figure 2.3: Concentrations of Li and counts/s of Na measured for the IAPSO standard seawater calibration of the AG MP-50 columns. ............................................ 62

Figure 3.1: XRD spectra of the fines of the four Li-Mg-EM batches (a) and the washed and sized fractions of the four Li-Mg-EM batches presented alongside crushed International Simple Glass (Background corrected) (b) ................................................................. 75

Figure 3.2: $^{29}$Si MAS-NMR spectra of: the full-Li MW base glass fines (Cyan) and the full-Li MW base glass fines mixed with 1 wt.% cristobalite (Magenta) (a); Li50Na50-Mg-EM-1 fines (Cyan) and Li60Na40-Mg-EM-1 fines (Magenta) (b) ................................................................. 76

Figure 3.3: XRD spectra of the resulting powders from cristobalite tests three to six. ........... 78

Figure 3.4: Normalised releases of B, Li, Na and Si measured in the Li-Mg-EM leachates using ICP-MS. For comparison, the normalised releases measured in the Mg-EM leachates at 90 °C and MW25 at both 40 °C and 90 °C (from Chapter 5) are also given. ..................................................... 82

Figure 3.5: Normalised releases of Mg measured in the Li-Mg-EM 40 °C (primary vertical axis) and 90 °C (secondary vertical axis) leachates using ICP-MS. For comparison, the normalised Mg releases measured for Mg-EM at 90 °C and MW25 at both 40 °C and 90 °C (from Chapter 5) are also given ........................................................................................................ 84

Figure 3.6: pH of the Li-Mg-EM leachates. ..................................................................... 85
Figure 3.7: Secondary electron SEM images of Li50Na50-Mg-EM (top row) and Li60Na40-Mg-EM (bottom row) leached at 90 °C for: pristine (a and f), 7 d (b and g), 14 d (c and h), 28 d (d and i) and 112 d (e and j). ................................................................. 86

Figure 3.8: Secondary electron SEM images of Li50Na50-Mg-EM (a) and Li60Na40-Mg-EM (b and c) leached for 112 d at 90 °C, and Li60Na40-Mg-EM leached for 14 d at 90 °C (d). 86

Figure 3.9: Backscattered electron SEM images of pristine Li50Na50-Mg-EM (a), and Li50Na50-Mg-EM and Li60Na40-Mg-EM leached for 112 d at 90 °C (b and c respectively). .......................................................................................................................... 87

Figure 3.10: EDS spectra of 112 d 90 °C leached Li50Na50-Mg-EM (a) and Li60Na40-Mg-EM (b). .......................................................................................................................... 88

Figure 3.11: Secondary electron SEM images of Li50Na50-Mg-EM (top row) and Li60Na40-Mg-EM (bottom row) leached at 40 °C for: pristine (a and f), 7 d (b and g), 14 d (c and h), 28 d (d and i) and 112 d (e and j). ................................................................. 89

Figure 3.12: Secondary electron SEM images of Li50Na50-Mg-EM (a) and Li60Na40-Mg-EM (b) leached for 112 d at 40 °C. .......................................................................................................................... 89

Figure 3.13: Backscattered electron SEM images of Li50Na50-Mg-EM (a) and Li60Na40-Mg-EM (b) leached for 112 d at 40 °C. .......................................................................................................................... 90

Figure 3.14: EDS spectra of 112 d 40 °C leached Li50Na50-Mg-EM (a) and Li60Na40-Mg-EM (b). .......................................................................................................................... 90

Figure 3.15: 7Li MAS-NMR spectra of fines of the four Li-Mg-EM batches (a), Li50Na50-Mg-EM leached at 40 and 90 °C for 112 d (b) and Li60Na40-Mg-EM leached at 40 and 90 °C for 112 d (c). .......................................................................................................................... 90

Figure 3.16: Static 6Li-1H CP-NMR spectra of Li50Na50-Mg-EM leached at 40 °C (a) and 90 °C (b). Lines correspond to the washed and sized pristine glass (Magenta), the 7 d leached glass (Cyan) and the 112 d leached glass (Gold). .......................................................................................................................... 91

Figure 3.17: 11B MAS-NMR spectra of washed and sized pristine: Li50Na50-Mg-EM-1 (Blue), Li50Na50-Mg-EM-2 (Green), Li60Na40-Mg-EM-1 (Orange), Li60Na40-Mg-EM-2 (Red) and Mg-EM (Black; taken from another study for comparison46). .......................................................................................................................... 93
Figure 3.18: $^{11}$B MAS-NMR spectra of Li50Na50-Mg-EM leached at 40 °C (a), Li50Na50-Mg-EM leached at 90 °C (b), Li60Na40-Mg-EM leached at 40 °C (c) and Li60Na40-Mg-EM leached at 90 °C (d).

Figure 3.19: Quantification of the washed and sized Li50Na50-Mg-EM $^{11}$B MAS-NMR spectrum using one $^{11}$B peak (a) and two $^{11}$B peaks (b).

Figure 3.20: $^{23}$Na MAS-NMR spectra of the pristine washed and sized Li-Mg-EM batches.

Figure 3.21: $^{23}$Na MAS-NMR spectra of pristine and leached 40 °C leached Li50Na50-Mg-EM (a), 90 °C leached Li50Na50-Mg-EM (b), 40 °C leached Li60Na40-Mg-EM (c) and 90 °C leached Li60Na40-Mg-EM (d).

Figure 3.22: Example of a $^{23}$Na MAS-NMR spectrum (90 °C 112 d leached Li50Na50-Mg-EM) fit using three peaks in the Igor Pro software.

Figure 3.23: XRD spectra of the Li-Mg-EM compositions leached for 112 d.

Figure 4.1: X-ray diffractograms from the test run of the Li29Na71-ISG pour (a) and the fabricated Li-ISG batches (b).

Figure 4.2: Normalised elemental releases of B (a), Li (b), Na (c) and Si (d) for the Li-ISG compositions. For comparison, the normalised releases for ISG and SON68 at 90 °C taken from another study are displayed.

Figure 4.3: Measured pH of the Li-ISG leachates.

Figure 4.4: Secondary electron SEM images of Li29Na71-ISG (top row) and Li47Na53-ISG (bottom row) leached at 90 °C for: 7 d (a and e), 14 d (b and f), 28 d (c and g) and 112 d (d and h).

Figure 4.5: Secondary electron SEM images of Li29Na71-ISG (top row) and Li47Na53-ISG (bottom row) leached at 40 °C for: 7 d (a and e), 14 d (b and f), 28 d (c and g) and 112 d (d and h).

Figure 4.6: Secondary electron SEM images of Li29Na71-ISG leached for 112 d at 90 °C (a) and 40 °C (c), and Li47Na53-ISG leached for 112 d at 90 °C (b) and 40 °C (d).

Figure 4.7: $^7$Li MAS-NMR spectra of the four pristine Li-ISG batches.

Figure 4.8: $^7$Li MAS-NMR spectra of pristine and 112 d leached Li29Na71-ISG (a) and Li47Na53-ISG (b).
Figure 4.9: Static $^6$Li-$^1$H CP-NMR spectra of Li29Na71-ISG leached for 112 d at 40 °C (Magenta) and 90 °C (Cyan). ................................................................. 124

Figure 4.10: $^{11}$B MAS-NMR spectra of the four pristine Li-ISG batches with ISG (a) and the two Li-ISG compositions compared with the two Li-Mg-EM compositions (b) ........... 126

Figure 4.11: $^{11}$B MAS-NMR spectra of Li29Na71-ISG leached at 40 °C (a), Li47Na53-ISG leached at 40 °C (b), Li29Na71-ISG leached at 90 °C (c) and Li47Na53-ISG leached at 90 °C (d). .................................................................................................................. 127

Figure 4.12: Example of curve fitting the Li-ISG $^{11}$B MAS-NMR spectra as demonstrated using Li29Na71-ISG leached at 40 °C for 112 d ................................................................. 127

Figure 4.13: $^{23}$Na MAS-NMR spectra of pristine ISG and the pristine Li-ISG batches (a) and the two Li-ISG compositions compared with the two Li-Mg-EM compositions (b). ....... 129

Figure 4.14: $^{23}$Na MAS-NMR spectra of Li29Na71-ISG leached at 40 °C (a) and 90 °C (b), and Li47Na53-ISG leached at 40 °C (c) and 90 °C (d) ................................................................. 130

Figure 4.15: XRD spectra of the Li-ISG compositions leached for 112 d ........................................ 132

Figure 5.1: X-ray diffractogram of pristine washed and sized MW25 acquired using 10 ± 1 mg of sample on a low-background plate .................................................................................. 141

Figure 5.2: Secondary electron SEM images of pristine washed and sized MW25 ................. 141

Figure 5.3: Normalised elemental releases for Li (Squares), B (Triangles), Na (Circles) and Mo (Diamonds) measured using ICP-OES in the 40 °C (Blue) and 90 °C (Red) leachates and ICP-MS in the 70 °C (Green) and 80 °C (Orange) leachates .................................................. 144

Figure 5.4: Normalised Si releases (a), normalised Te releases (b) and leachant pH (c) for the 90 °C (Red triangles), 80 °C (Orange squares), 70 °C (Green circles) and 40 °C (Blue diamonds) leachates .................................................................................................................. 146

Figure 5.5: Normalised Ba, Cr and Cs releases (a), normalised lanthanide (Ce, La, Nd and Pr) releases (b) and normalised Y releases (c) for the 70 °C (vacant markers) and 80 °C (filled markers) leachates .................................................................................................................. 147

Figure 5.6: Arrhenius plots (a) and concentration plots (b) of the 6 h dissolution rates of B, Li, Mo and Na at 40, 70, 80 and 90 °C against the reciprocal of absolute temperature (1/T) ... 148
Figure 5.7: Secondary electron SEM images of pristine MW25 (Leftmost); MW25 leached at 70 °C for 6 h (a), 1 d (b), 7 d (c), 14 d (d) and 28 d (e); and MW25 leached at 80 °C for 6 h (f), 1 d (g), 7 d (h), 14 d (i) and 28 d (j). .......................................................... 149

Figure 5.8: Secondary electron SEM images of MW25 leached for 28 d at 70 °C (a) and 80 °C (b). .......................................................... 150

Figure 5.9: Backscattered electron SEM images of pristine MW25. .......................................................... 150

Figure 5.10: EDS spectra of pristine MW25. .......................................................... 151

Figure 5.11: Backscattered electron SEM images of MW25 leached for 28 d at 70 °C (a) and 80 °C (b). .......................................................... 152

Figure 5.12: EDS spectra of MW25 leached for 28 d at 70 °C (a) and 80 °C (b). ............... 152

Figure 5.13: X-ray diffractograms of MW25 leached for 28 d at 40, 70, 80 and 90 °C. ...... 153

Figure 6.1: XRD spectra of the fines and washed and sized fraction of $^{6}$Li-Mg-EM (a) and the $^{29}$Si MAS-NMR spectrum of the fines of $^{6}$Li-Mg-EM (b). .......................................................... 166

Figure 6.2: Particle size distribution for washed and sized $^{6}$Li-Mg-EM. ..................... 167

Figure 6.3: Measured (Orange) and nominal (Blue) standard addition mixing lines for $^{6}$Li-Mg-EM mixed with SGR-1b (a) and $^{6}$Li-Mg-EM mixed with a Li plasma standard (b). .......... 173

Figure 6.4: Normalised releases of $^{6}$Li and $^{7}$Li (a), and B and Na (b) measured in the $^{6}$Li-Mg-EM leachates by ICP-MS. .......................................................... 176

Figure 6.5: Measured pH of the leachants from vessel 1 and vessel 2 in the $^{6}$Li-Mg-EM experiments.......................................................... 177

Figure 6.6: The Li/Na (a), Li/B (b), Li/Mg (c) and Li/Al (d) ratios calculated from their respective concentrations ($\mu$g/ml) measured in the $^{6}$Li-Mg-EM leachates. ...................... 178

Figure 6.7: Temporal evolution of the Li isotopic signature of the $^{6}$Li-Mg-EM leachates (a) and evolution of the Li isotopic signature of the leachates as a function of Li concentration (blank and mass loss corrected) change (b). .......................................................... 179

Figure 6.8: Temporal evolution of the B isotopic signature of the $^{6}$Li-Mg-EM leachates (a) and evolution of the B isotopic signature of the leachates as a function of B concentration (blank and mass loss corrected) change (b) ............................................. 181
Figure 6.9: Temporal evolution of the Mg isotopic signatures ($\delta^{26}\text{Mg}$ (a) and $\delta^{25}\text{Mg}$ values (b)) of the $^6\text{Li}$-Mg-EM leachates. .............................................................. 182

Figure 6.10: Secondary electron SEM of $^6\text{Li}$-Mg-EM leached for 98 d in the refreshed leachant experiment (a) and the experiment without refreshing the leachant (b). ....................................... 183

Figure 6.11: $^{11}\text{B}$ MAS-NMR spectra of pristine $^6\text{Li}$-Mg-EM and $^6\text{Li}$-Mg-EM leached for a total of 98 d after refreshing the leachant after 28 d (Blue) and without refreshing the leachant. 183

Figure 6.12: $^6\text{Li}$-$^1\text{H}$ CP-NMR (a) and $^6\text{Li}$ MAS-NMR with $^6\text{Li}$-$^1\text{H}$ CP MAS-NMR (b and c) of $^6\text{Li}$-Mg-EM fines and 98 d leached $^6\text{Li}$-Mg-EM without refreshing the leachant................. 184

Figure 6.13: Cartoons depicting theoretical plots of temporal evolutions of the Li isotopic signatures of the leachates alongside theoretical elemental profiles of cross-sections of leached glass at high reaction progress. The theoretical alteration layer structures and leachate isotopic signatures were based upon an interdiffusion-based model (the GRAAL model) (a) and the interfacial dissolution-precipitation model (b) .............................................................. 187

Figure 7.1: Leachate pH (a), Li/Na ratios (b) and Li/B ratios (c)............................................................... 198

Figure 7.2: Temporal evolution of the Li isotopic signature of the MW25 leachates......... 199
1. Introduction

Nuclear power is an invaluable low-carbon energy source. However, a planned increase in global nuclear power capacity, particularly in China and India\(^1\), demands safe nuclear waste reprocessing and disposal strategies. Notably, the disposal of high level waste (HLW) presents a challenge internationally due to the significant concentrations of long lived radionuclides of actinides, fission products and unextracted U and Pu present in these wastes generating large amounts of heat over the course of hundreds of years through $\beta$ and $\gamma$ decay processes\(^2,3\).

Vitrification of HLW, which is typically a by-product arising from the reprocessing of spent nuclear fuel from nuclear reactors, into a durable borosilicate or phosphate glass matrix is often internationally regarded as the preferred method of waste immobilisation\(^4,5\). Vitrification not only reduces the volume of HLW by approximately one third\(^6\), but also, owing to the structural flexibility of the amorphous glass networks affording the incorporation of a vast array of elements, provides a chemically durable solid wasteform to reduce many of the hazards associated with waste disposal\(^5,7,8\). After an interim storage period, the internationally accepted method for permanent waste disposal is disposal deep underground within a geological disposal facility (GDF)\(^9,10\), with HLW or spent fuel GDFs being planned for Canada, France, Japan, Sweden, Switzerland, the USA and the UK\(^4\). However, groundwater is expected to eventually breach the GDF, contact the waste package and corrode the vitrified waste.

1.1. Vitrification, glass structures and waste glass compositions

In the UK, spent nuclear fuel has been reprocessed following the PUREX (Pu and U recovery extraction) process: the cladding is first mechanically stripped from the fuel pellets before they are dissolved in nitric acid and then Pu and U are recovered through liquid-liquid solvent extraction using tributyl phosphate. However, the PUREX process results in the formation of a nitric acid-based HLW stream, or highly active liquor (HAL)\(^8\), which consists of fission products, unextracted Pu and U, actinides, corrosion products, residual cladding, fuel additives, fuel impurities and neutron poisons\(^11\). The HAL is then concentrated through evaporation and temporarily stored in HAL storage tanks (HAST) prior to vitrification. The exact composition of the HAL is dependent upon a number of factors, such as the type of fuel and fuel burn up. Owing to the variety of gas cooled and light water reactor designs, and consequently fuel types, used across other countries which employ the PUREX process, such as France and the USA,
the composition of the HAL differs significantly between countries as well\textsuperscript{12}. In the UK, HAL compositions vary based upon whether they were reprocessed in the Magnox plant (for waste from Magnox reactors) or the THORP plant (thermal oxide reprocessing plant, for waste from advanced gas cooled reactors and light water reactors)\textsuperscript{8}.

The first generation UK and French Magnox reactors in the 1950s used fuels consisting of a non-oxidising Mg-Al alloy cladding (termed Magnox) coating metallic U bars, employing CO\textsubscript{2} coolant flowing through holes in graphite moderators to transfer heat\textsuperscript{13}. Around this time, research began into the vitrification of radioactive wastes, initially employing natural soils as a base material for vitrification\textsuperscript{14}. In the 1960s and 1970s vitrification focussed on the “fixation in glass of active liquors” process and the “highly active residue vitrification experimental studies” respectively, both of which involved “in-can” batch vitrification. By the 1980s vitrification of Magnox waste had begun on an industrial scale using the AVM (atelier de vitrification Marcoule) process, but this was soon replaced by the AVH (atelier de vitrification La Hague) process\textsuperscript{8}.

The waste vitrification plant (WVP) at Sellafield Ltd. still employs the two-step AVH vitrification process (Figure 1.1). The HAL is first passed alongside a sucrose solution (to act as a reducing agent to minimise the volatilisation of Ru) through a rotating (20 to 30 rpm), 1.73 ° inclined calciner at 600 to 840 °C to evaporate and partially denitrate the HAL\textsuperscript{8}. The calcined HAL then flows out of the calciner into the melter, where is it mixed with a “mixture windscale” (MW) Li-Na borosilicate base glass frit and heated to at least 1000 °C\textsuperscript{11}. Once all the calcined material and MW base glass have been added to the melter, the glass is poured into stainless steel containers, welded shut, decontaminated and then checked for contamination before being transferred to the air-cooled vitrified product store for interim storage\textsuperscript{11}. By 2025, the UK is expected to have a packaged vitrified HLW inventory volume of approximately 1500 m\textsuperscript{3} (approximately 6770 waste packages)\textsuperscript{6,8}. Typically, a Magnox waste loading of 25 wt.% with a LiO\textsubscript{2} concentration of approximately 4.1 wt.% was targeted in the final vitrified product, which may be considered to be the “standard” Magnox waste glass composition\textsuperscript{8,15}. Further, a Li:Na ratio of approximately 1.0 was targeted in both the MW base glass and the final vitrified product to optimise the properties of the base glass during vitrification and to improve the aqueous durability of the vitrified product through the mixed alkali effect respectively\textsuperscript{8,16}. As the vitrified products cannot be characterised, campaigns on a full-scale inactive replica of the WVP, the
vitrification test rig, produced simulant waste glasses for experimentation\textsuperscript{17,18}; most notably, a full-component inactive simulant “standard” Magnox waste glass of 25 wt.% waste loading, herein referred to as MW25 (Table 1.1).

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\textbf{Figure 1.1: Abstraction of the two-stage AVH vitrification process employed at the waste vitrification plant at Sellafield Ltd.}\textsuperscript{8}, reproduced from Harrison (2014)\textsuperscript{8}.

It was later found that the addition of LiNO\textsubscript{3} to the HAL inhibited the formation of refractory oxides during calcination\textsuperscript{11}. To accommodate this extra Li contents, an MW base glass composition with half the molar Li\textsubscript{2}O removed, named MW-½Li base glass, was fabricated. For a Magnox waste glass of 25 wt.% waste loading, this resulted in an equimolar split of Li between the LiNO\textsubscript{3} added to the HAL and the MW-½Li base glass being required to achieve a LiO\textsubscript{2} concentration of 4.1 wt.% and an equimolar Li\textsubscript{}:Na ratio in the final vitrified product; where the initial Li contents of the HAL-LiNO\textsubscript{3} mixture was measured to ensure it was of the target Li concentration\textsuperscript{8,11,16}. However, owing to the operational requirements of the WVP, this method resulted in too high LiNO\textsubscript{3} concentrations being added to the HAL for some vitrified products; producing some Magnox waste glasses of target 25 wt.% waste loading with Li concentrations exceeding 4.1 wt.% and molar Li:Na ratios greater than one\textsuperscript{16,19,20}. Consequently, the safety cases for the permanent disposal of both “standard” and “excess Li” 25 wt.% Magnox vitrified products needed to be considered.

The degree of incorporation of the calcined HAL into the glass matrix depends upon its pristine structure. Whilst glasses lack long-range order, short and intermediate-range order are still present. Oxide glasses consist of a glass network of network forming species modified or charge compensated by network modifying species, as shown in Figure 1.2\textsuperscript{21,22}. Network forming species are high field strength cations, such as Al, B and Si, which form chains of bridging
covalent bonds with O to create a glass network. Network modifying species, such as alkali and alkaline earth metals, either modify the glass network through forming non-bridging O (NBO) ionic bonds or charge compensate tetrahedral network forming units\textsuperscript{23–25}.

**Figure 1.2:** Abstractions of the local structure of a Na silicate glass (a) and a Ca-Mo-Na-Zn alumino-borosilicate glass (b), reproduced from Ojovan and Lee (2005)\textsuperscript{21} and Calas et al. (2003)\textsuperscript{22} respectively. Although not displayed in (b), the other alkali metals (Cs, K and Li) or alkaline earth metals (Ba and Sr) could be expected to fulfil similar structural roles to Na and Ca respectively.

In alkali silicate glasses (Figure 1.2a), the glass network is composed of tetrahedral SiO$_4$ units with the degree of network connectivity of the glass network represented by Q$^n$, where n gives the average number of bridging O bonds (covalent Si-O-X bonds, where X is a network forming cation). In such a system, network modifying alkali species create NBO (Si-O$^-$ M$^+$ ionic bonds, where M is a network modifying cation) which reduce the connectivity of the glass network and the value of n to below four\textsuperscript{23}. Where alkaline earth metals are included in the glass composition, these species form two neighbouring NBO\textsuperscript{24}. In a modified random network with sufficient network modifier concentration, alkali species cluster to form ionic channels of depolymerised glass which facilitate their transport through the glass network\textsuperscript{26–29}. In an alkali alumino-borosilicate system (Figure 1.2b), as is common for radioactive waste glasses, B and Al fulfil a network forming role. Al alone is unable to form a glass network but forms tetrahedral units with network bonds to Si and B. Owing to the lack of charge balancing of the Al tetrahedra and Al$_2$O$_3$ only providing 1.5 O atoms per Al tetrahedron, a network modifying cation and its O atom charge compensate the Al tetrahedra\textsuperscript{24}. Contrastingly, B is able to form a glass network alone through creating trigonal B (BO$_3$ groups, $^{\text{III}}$B) units. In borosilicates, B exists in both trigonal and tetrahedral ([BO$_4$]$^{-}$ groups, $^{\text{IV}}$B) coordination with B-O-X bonds, where $^{\text{IV}}$B units
require charge compensation from network modifying species\textsuperscript{24,30,31}. It has been shown that in Li-Na borosilicates, Li preferentially modifies the Si network whilst Na preferentially charge compensates IV\textsubscript{B} units\textsuperscript{25,32}. The flexibility of the borosilicate glass matrix affords the incorporation of the majority of radionuclides present in a variety of HAL compositions and is capable of accommodating high waste loadings, whilst remaining producible on an industrial scale at relatively low melting temperatures\textsuperscript{5,8,33}. However, some elements commonly present in HAL compositions, such as Mo and platinoids, have an inherently low degree of solubility in borosilicate glasses and in sufficient concentration can form crystalline secondary phases such as RuO\textsubscript{2} crystallites or alkali molybdates and chromates (yellow phase)\textsuperscript{15,22,34–36}.

Table 1.1: Nominal oxide mol.% compositions of MW25 and SON68\textsuperscript{15,37}.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>MW25</th>
<th>SON68</th>
<th>Oxide</th>
<th>MW25</th>
<th>SON68</th>
<th>Oxide</th>
<th>MW25</th>
<th>SON68</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag\textsubscript{2}O</td>
<td>0.00</td>
<td>0.01</td>
<td>La\textsubscript{2}O\textsubscript{3}</td>
<td>0.12</td>
<td>0.20</td>
<td>RuO\textsubscript{2}</td>
<td>0.37</td>
<td>0.00</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>2.80</td>
<td>3.38</td>
<td>Li\textsubscript{2}O</td>
<td>8.93</td>
<td>4.59</td>
<td>SiO\textsubscript{2}</td>
<td>50.50</td>
<td>52.63</td>
</tr>
<tr>
<td>B\textsubscript{2}O\textsubscript{3}</td>
<td>15.86</td>
<td>14.01</td>
<td>MgO</td>
<td>7.52</td>
<td>0.00</td>
<td>Sm\textsubscript{2}O\textsubscript{3}</td>
<td>0.07</td>
<td>0.00</td>
</tr>
<tr>
<td>BaO</td>
<td>0.20</td>
<td>0.28</td>
<td>MnO\textsubscript{2}</td>
<td>0.00</td>
<td>0.31</td>
<td>SnO</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>CaO</td>
<td>0.00</td>
<td>5.01</td>
<td>MoO\textsubscript{3}</td>
<td>0.65</td>
<td>0.85</td>
<td>SrO</td>
<td>0.18</td>
<td>0.23</td>
</tr>
<tr>
<td>CeO\textsubscript{2}</td>
<td>0.43</td>
<td>0.39</td>
<td>Na\textsubscript{2}O</td>
<td>8.84</td>
<td>11.37</td>
<td>TeO\textsubscript{2}</td>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>Cr\textsubscript{2}O\textsubscript{3}</td>
<td>0.26</td>
<td>0.24</td>
<td>Nd\textsubscript{2}O\textsubscript{3}</td>
<td>0.36</td>
<td>0.42</td>
<td>Y\textsubscript{2}O\textsubscript{3}</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>Cs\textsubscript{2}O</td>
<td>0.25</td>
<td>0.27</td>
<td>NiO</td>
<td>0.32</td>
<td>0.40</td>
<td>ZnO</td>
<td>0.00</td>
<td>2.14</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>1.19</td>
<td>1.31</td>
<td>Pr\textsubscript{2}O\textsubscript{3}</td>
<td>0.11</td>
<td>0.10</td>
<td>ZrO\textsubscript{2}</td>
<td>0.74</td>
<td>1.54</td>
</tr>
</tbody>
</table>

With the exception of aluminophosphate glasses in Russia, a borosilicate glass matrix has been internationally adopted for the vitrification of HLW\textsuperscript{4}. However, owing to differences in HAL compositions, there are significant differences between the radioactive waste glass compositions of different countries. Notably, Magnox waste glasses contain high Mg concentrations (MW25 nominally contains 4.68 wt.% MgO\textsuperscript{15}) whilst other waste glass compositions, such as the French inactive simulant R7T7-type full-component waste glass SON68 (produced following the AVH process)\textsuperscript{37–45}, contain no Mg but high concentrations of Ca (Table 1.1). Vitrified waste glass compositions have been shown to significantly affect the kinetics and mechanisms of aqueous dissolution, with Mg effecting significant differences in dissolution behaviour between UK Magnox and international waste glasses\textsuperscript{46–50}.

1.2. Conflicting models of glass dissolution

After interim storage in a vitrified product store, it is planned that the vitrified products will be disposed of in a GDF. Whilst as of yet there is not planned location for a UK GDF, a depth of
200 to 1000 m and lifespan of at least one million years must be considered\textsuperscript{51–54}. However, after tens to hundreds of thousands of years groundwater at approximately 40 °C (assuming a 1 km deep GDF with an average UK surface temperature of \(~15\) °C and geothermal gradient of \(~25\) °C/km\textsuperscript{53,55}) is expected to breach the GDF and stainless steel waste containers to contact the waste and corrode the glass; potentially releasing radionuclides into the geosphere which could diffuse or advect into the biosphere. Consequently, the optimal waste disposal strategy and safety case for disposing of these radioactive waste glasses within a GDF depends upon developing a thorough understanding, and subsequently robust models, of the kinetics and mechanisms of their aqueous dissolution over geological timescales. However, the inherently disordered structure of glasses and the sensitivity of glass dissolution to waste glass composition and experimental conditions means that the mechanisms of waste glass dissolution are still currently debated.

Broadly speaking, a set of dissolution mechanisms involving interdiffusion processes (herein collectively referred to as interdiffusion-based models) have been agreed upon in the nuclear glass community to describe waste glass dissolution in initially dilute aqueous solutions\textsuperscript{9,56–61}. In such cases, the temporal evolution of the leachate concentrations may be described by five agreed-upon distinct dissolution regimes\textsuperscript{4,37,57,62}, as given in Figure 1.3. It should also be considered that the dissolution mechanisms occur simultaneously throughout glass dissolution, with the rate of each mechanism significantly varying depending upon numerous factors such as glass and leachant composition, leachant temperature and pH and glass surface area to leachant volume ratio\textsuperscript{43,49,63}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1_3.png}
\caption{Cartoon depicting the temporal evolution of theoretical leachate Na and Si concentrations throughout the five dissolution regimes: I initial interdiffusion, II initial hydrolysis, III rate drop regime, IV residual rate regime and V potential resumption of the initial dissolution rate. Reproduced from Frugier et al. (2008)\textsuperscript{37}.}
\end{figure}
Dissolution is initially controlled by interdiffusion reactions: the coupled mechanisms of glass hydration through the inward diffusion of water species, ion-exchange reactions between protonated water species (H$_3$O$^+$ or H$^+$) and glass modifying alkali species (M$^+$) (Equations 1-1 and 1-2) and the subsequent outward diffusion of glass species. In near-neutral pH aqueous solutions, interdiffusion initially controls dissolution (Regime I in Figure 1.3). As it is a diffusive process, the theoretical concentrations of the alkalis in solution should increase proportionally with $t^{0.5}$. Whilst the rate of interdiffusion of Na at near-neutral pH is expected to be faster than the release of B, B is a network former and is not expected to leach through interdiffusion reactions. However, B is frequently observed to be released alongside the alkali metals, sometimes also proportionally with $t^{0.5}$. This may be attributed to B rapidly leaching through network hydrolysis reactions (as in Equation 1-3) owing to the low energy barrier associated with hydrolysis of the X-O-B bonds (where X is a network forming cation).

\[
\equiv Si - O^-M^+ + H_3O^+ \rightarrow \equiv Si - OH + M^+ + H_2O \quad \text{Equation 1-1}
\]

\[
\equiv Si - O^-M^+ + H^+ \rightarrow \equiv Si - OH + M^+ \quad \text{Equation 1-2}
\]

The time for which interdiffusion initially controls the rate of dissolution is highly pH and temperature dependent, with higher pH and temperatures shortening this time. As the rate of interdiffusion rapidly decreases and the concentrations of alkalis within solution rapidly increase the leachant pH, hydrolysis of the glass network (Equations 1-3) is favoured and quickly becomes the dominant dissolution mechanism. The combined rates of interdiffusion and hydrolysis cause the glass to dissolve at its most rapid forward rate, referred to as the initial dissolution rate (regime II in Figure 1.3), with apparently congruent glass dissolution. As such, regimes I and II are collectively referred to as the initial rate regime.

\[
\equiv Si - O - X \equiv +H_2O \rightarrow \equiv Si - OH + \equiv X - OH \quad \text{Equation 1-3}
\]

Hydrolysis results in an increase in the concentrations of network formers and orthosilicic acid (H$_4$SiO$_4$) in the leachant. Subsequently, the slowing rate of network hydrolysis and high concentrations of Si in solution result in in-situ condensation reactions in the hydrolysed glass (Equation 1-4) alongside a significant number of H$_4$SiO$_4$ resorption and precipitation reactions (Equations 1-5 and 1-6) controlling the rate of dissolution. These reactions result in a depleted layer of reorganised glass consisting of Si and low solubility elements, commonly referred to as the gel layer, forming as dissolution progresses. These mechanisms characterise the rate drop regime (regime III in Figure 1.3). Previously, it was debated whether the slowing of
the dissolution rate was caused by the increasing concentration of H₄SiO₄ in solution decreasing affinity for Si network hydrolysis⁷⁵ or whether this decrease was caused by the gel layer having a passivating effect as it developed⁶⁹,⁷⁶. Whilst it was demonstrated that the reactive transport of water species through the gel layer played a significant role in the rate drop regime⁷⁷, it was concluded both decreasing affinity and passivating gel layer effects should be considered in models of glass dissolution⁶⁹,⁶⁰.

\[
\equiv Si - OH + \equiv Si - OH \leftrightarrow \equiv Si - O - Si \equiv + H₂O \quad \text{Equation 1-4}
\]

\[
H₄SiO₄ + \equiv Si - OH \leftrightarrow \equiv Si - O - Si(OH)₃ + H₂O \quad \text{Equation 1-5}
\]

\[
H₄SiO₄ + H₄SiO₄ \leftrightarrow 2SiO₂ + 4H₂O \quad \text{Equation 1-6}
\]

Eventually, the Si concentration in solution reaches a steady state apparent solubility limit where the rates of Si network hydrolysis and secondary phase precipitation are equal⁷⁸. The glass dissolution rate then slows to its residual rate (residual rate regime, regime IV in Figure 1.3), with the significantly abated rate of network hydrolysis then allowing interdiffusion reactions to become relevant once more. Significant amounts of Si-bearing phases could also precipitate to fuel a resumption of the initial dissolution rate (regime V in Figure 1.3)⁷⁹. In some interdiffusion-based models, part of the gel layer undergoes in-situ condensation reactions to the extent that it densifies into a highly passivating nanoporous interphase. Water species are forced to reactively diffuse through this interphase to reach the pristine glass interface, with glass species similarly reactively diffusing outwards through this layer into solution. In this view, the residual rate regime is controlled by the rate limiting reactive interdiffusion of water species across this passivating interphase coupled with the precipitation of Si-bearing secondary phases controlling the rate of hydrolysis of the glass network³⁸,⁴⁸,⁵⁸,⁵⁹,⁷³,⁸⁰,⁸¹. Such a model, the GRAAL (glass reactivity with allowance for the alteration layer) model, has been the most successful in predicting glass dissolution rates⁵⁷,⁵⁷,⁸². The GRAAL model couples interdiffusion reactions across a passivating reactive interphase of hydrated glass with the consumption of this layer through hydrolysis-precipitation reactions to create a non-passivating depleted gel layer and secondary phase precipitates (Figure 1.4a)³⁷.

In the last decade, a model of silicate mineral weathering, herein referred to as the “interfacial dissolution-precipitation model”, was extended to silicate glasses. This model not only challenged the alteration layer structures put forward by interdiffusion-based models, but also the hypothesis that interdiffusion reactions are rate-limiting during the initial moments of
dissolution and again during the residual rate regime\textsuperscript{83–86}. In the interfacial dissolution-precipitation model, dissolution is consistently congruent at a single reaction front in a thin interfacial film of water contacting the pristine glass interface with no interdiffusion reactions or preferential dissolution taking place (Figure 1.4b). Further, rather than being relict glass structures, the alteration layers are formed through the coupled precipitation of a porous amorphous silica phase regardless of whether the bulk solution is dilute\textsuperscript{83}. Initial dissolution in this model is congruent through hydrolysis of the glass network (Equation 1-3) without interdiffusion reactions. H\textsubscript{4}SiO\textsubscript{4} then polymerises in solution through condensation reactions and, when the film of water at the pristine glass interface becomes supersaturated with respect to silica, amorphous silica precipitates from solution behind the congruent dissolution front. This layer then develops through the aggregation of silica spheres which in turn grow through either continued silica precipitation or Ostwald ripening. Subsequently, the rate of dissolution slows as this precipitated layer develops due to the inhibited percolation-controlled transport of water species towards the supersaturated thin film\textsuperscript{83–87}. A later version of this model added that, under apparent silica saturation conditions, a dense gel layer could form behind the congruent dissolution front which subsequently limits transport to volume diffusion\textsuperscript{86}. Recently, seemingly contradictory nanoscale elemental profiles of leached glass cross-sections and investigations into the passivating nature of the alteration layers suggested the mechanisms of dissolution are highly dependent upon the experimental conditions used, with neither incongruent or congruent models of dissolution being strictly correct\textsuperscript{38,57,74,84}.

Figure 1.4: Cartoons of elemental profiles within altered glass at high reaction progress according to an interdiffusion-based model of dissolution (a) and an interfacial dissolution-precipitation model (b)\textsuperscript{37,57,83}.
1.3. Aqueous durability of radioactive waste glasses

1.3.1. Simplified analogues of complex waste glasses

Full-component inactive simulant waste glasses provide an accurate representation of the final vitrified product and are invaluable tools for understanding how radioactive waste glasses will behave in a GDF over geological timescales. However, these complex glasses generally contain in excess of 20 oxide components as well as insoluble crystalline phases likely present in the vitrified products. Owing to the multiple parameters contributing to the aqueous dissolution of these complex glasses, their dissolution mechanisms are likely convoluted. Further, as MW25 was fabricated on a full-scale inactive replica of the waste vitrification plant at Sellafield Ltd., it would not be viable to vary the composition of MW25. Instead, dissolution experiments on simplified analogues provide a mechanistic understanding of their dissolution processes, thereby affording an improved interpretation of the dissolution processes of the complex glasses they aim to represent. Further, simplified analogues can easily be fabricated in-house with an array of subtle compositional substitutions and different fabrication conditions for detailed mechanistic studies on the effects of pristine glass structure on aqueous durability.

Owing to the significant dependence of dissolution behaviour on glass composition, ISG (international simple glass) was put forward as a common benchmark composition to relate dissolution experiments and models from different research groups internationally. The composition of this six-component glass (Al, B, Ca, Na, Si and Zr) was designed such that the nominal molar elemental ratios of ISG would be the same as in SON68 excluding the REEs and paramagnetics present in SON68. Consequently, ISG may be considered a simplified analogue of SON68. Notably, numerous sophisticated aqueous dissolution experiments and structural studies under a variety of conditions spanning up to three decades have focussed on investigating the dissolution processes of SON68 and ISG. Further, it has been shown that during the dissolution of ISG a highly passivating densified alteration layer interphase forms. Many studies have taken place using leachant compositions enriched in Si to understand and model the structure of this passivating layer and subsequently how it will protect the glass over geological timescales. However, it has been shown that the release of elements from ISG, in particular Na, differ from SON68.

As part of a Radioactive Waste Management task sub-contracted to the University of Cambridge through Amec Foster Wheeler (currently Jacobs), a series of six or seven-
component glasses (Al, B, Ca or Mg, La, Na and Si) were produced with various Mg:Ca molar ratios and underwent accelerated dissolution experiments at 90 °C for between 7 and 112 d. Notably, the first composition and Ca-free simplified analogue, referred to as Mg-EM, was fabricated with the aim of being a simplified analogue of MW25. In fabricating Mg-EM, the molar ratios of all elements within Mg-EM were the same as those of MW25 with La representing the REEs on a charge for charge basis and paramagnetic elements being excluded. Structural studies and dissolution experiments on Mg-EM and MW25 demonstrated Mg-EM was an excellent simplified analogue of MW25.

1.3.2. Effects of composition on dissolution

Although Mg-EM has been shown to be an excellent analogue of MW25, ISG and Mg-EM are both Li-free compositions whilst SON68 and MW25 nominally contain 4.59 and 8.93 % Li2O respectively (Table 1.1). However, based upon the GRAAL model (Figure 1.4a) and elemental profiles within cross-sections of 25.75 year altered SON68, the dissolution behaviour of Li is expected to differ from other alkali metals. This difference is attributable to the preference of Li to modify the Si network coupled with the small ionic radius of Li permitting its easier diffusion from the glass resulting in a wide Li interdiffusion curve. Contrastingly, Na is more tightly bonded to the B network in its preferential charge compensation role and as such leaches alongside the sharp B hydrolysis front behind the Li interdiffusion curve (Figure 1.4a). In many studies on the effects of elements on aqueous durability, elements are simply added to the glass. However, it should be considered this might decrease the contents of elements beneficial to aqueous durability (such as Si and Zr) or increase contents of elements detrimental to aqueous durability (such as B and the alkali metals). Generally, a glass of higher alkali metal contents may be expected to have a lower aqueous durability owing to the increased depolymerisation of the glass network. Whilst Li is expected to be detrimental to aqueous durability, the effect of Li on aqueous durability is convoluted.

In Magnox waste glasses of various waste loadings (ranging from 25 to 38 wt.% with approximately constant Li contents), aqueous durability was shown to increase with the fraction of waste loaded. This may be attributed to the total alkali metal contents of the glass decreasing and concentrations of some beneficial or low solubility elements increasing (such as Al and Zr) as the waste load was increased. However, it must also be considered that as the waste loading is increased, Mo might cluster in sufficient concentration to form crystalline yellow phase with chromates to significantly reduce the aqueous durability of the glass.
Following an experiment which demonstrated the addition of 1% Li$_2$O to a 28 wt.% waste loading Magnox glass had a significant detrimental impact on aqueous durability, it was demonstrated that increasing the Li$_2$O contents of both 25 wt.% and 32 wt.% waste loading Magnox glasses decreased aqueous durability$^{16,92,93}$. It was noted that increasing the Li$_2$O contents from 4.0 to 4.5% decreased aqueous durability significantly more than increasing Li$_2$O contents from 4.5 to 5.0%. Further, the aqueous durability of the 32 wt.% waste loading glass appeared significantly more sensitive to the increase in Li contents than that of the 25 wt.% waste loading glass. However, decreasing the Li$_2$O contents from 4.0 to 3.5% improved aqueous durability significantly more for the 25 wt.% waste loading glass than the 32 wt.% waste loading glass. It should be considered that the authors could not solely attribute these effects to Li based upon variations in the concentrations of other elements$^{16,92,93}$.

Contrastingly, the addition of Li to an ISG composition containing Ce resulted in an increased initial dissolution rate but improved long-term (13.6 year) aqueous durability$^{20}$. Again, this effect may not be solely attributed to Li as the concentrations of other elements varied with the addition of Li. However, these studies do well to highlight that the effects of Li on aqueous durability appear to be highly dependent upon pristine glass composition. Further, they show the importance of substituting in elements, rather than simply adding them to the composition, during mechanistic elemental studies on aqueous durability.

When the Li contents of glasses are varied, the Li:Na ratio of the pristine glass and a mixed alkali effect (MAE) on aqueous durability should also be considered. The MAE is a diffusion-related phenomenon which results in non-linear variations in glass properties such as electrical conductivity, viscosity and aqueous durability when one element is substituted for another at various ratios (in this case Li for Na)$^{94,95}$. Whilst the mechanisms of the Li-Na MAE are still debated, it could be attributed to “type specific pathways” and energy mismatches between sites occupied by Li and Na resulting in the slowed diffusion of these alkali metals through the glass network$^{29,96-101}$. As such, minima in the diffusivities of Li and Na may be expected at an equimolar Li:Na ratio. As the MAE is a diffusive effect, it is expected to be most relevant to aqueous durability when interdiffusion is the dominant mechanism of dissolution$^{94}$. The presence of Mg in Magnox waste glasses results in their B releases being an order of magnitude higher than from their Mg-free equivalent SON68 throughout dissolution$^{49,89}$. However, similar initial dissolution rates were observed for Ca-EM (Mg-EM with Mg:Ca ratio
of zero) and Mg-EM\textsuperscript{46}. This demonstrated that rather than being attributable to differences in pristine glass structure, the poorer aqueous durability of Mg-containing glasses is caused by the precipitation of significant amounts of Mg-bearing silicate secondary phases throughout dissolution; likely an amorphous precursor to a smectite clay mineral such as a hectorite\textsuperscript{47,49}. The precipitation of this Mg-bearing silicate phase consumes significant amounts of Si from solution to fuel further hydrolysis of the glass network and increase the glass dissolution rate. Such an effect would be particularly important during the residual rate regime, where, according to interdiffusion-based models, the rate of dissolution is controlled by interdiffusion and secondary phase precipitation. As such, a significant drop in aqueous durability has been observed in studies where SON68 or ISG have been leached in leachants containing Mg\textsuperscript{47,50,102}.

1.3.3. Effects of temperature on dissolution

Whilst a 1 km deep UK GDF could be expected to eventually contain groundwater at approximately 40 °C, a significant number of experiments have taken place at an accelerated dissolution temperature of 90 °C assuming the underlying dissolution mechanisms would be the same as those at 40 °C but accelerated\textsuperscript{16,46,103,104}. Dissolution temperature has been shown to have a significant effect on the rate of dissolution in both initially dilute or Si-enriched leachant compositions\textsuperscript{63,105,106}. Many of these studies aimed to investigate the effects of temperature on the initial dissolution rates and the Arrhenius-type behaviour of these initial releases\textsuperscript{63,107–109}. From Arrhenius plots, activation energies for B hydrolysis, interdiffusion and Si hydrolysis can be calculated to better understand which processes are initially rate-limiting during dissolution\textsuperscript{107}. However, these temperature studies also highlighted a need for a new angle with which to understand the mechanisms of dissolution and how this is affected by dissolution temperature. From an initial dissolution rate study on MW25 at 40 and 90 °C, it was shown that the initial dissolution rate at 90 °C was approximately an order of magnitude higher than at 40 °C\textsuperscript{108}. Similar releases were observed for Al, Mg and Si at both temperatures, which suggested the fraction of these leached elements incorporated into secondary phases at 90 °C was significantly higher than at 40 °C. Consistent with temperature studies on a Magnox waste glass leached at pH 12.1, these initial rate dissolution experiments on MW25 gave activation energies within the range of a surface-controlled reaction\textsuperscript{108,110}.

1.4. Kinetic and equilibrium isotopic fractionation

The fractionation of stable isotopes during natural processes provides an exceptionally powerful
tool for geochemists studying an array of subjects such as palaeoceanography, fluid-rock interactions and silicate mineral weathering. Notably, Li may be considered a ‘non-traditional’ element for stable isotope geochemistry as precise measurements through multicollector-inductively coupled plasma mass spectrometry (MC-ICP-MS) were not attainable until relatively recently (circa 1999). Similarly, whilst B isotope geochemistry has myriad applications, it was considered “non-conventional” in light stable isotope geochemistry. The relative mass difference between the heavy and light isotopes of Li and B (approximately 17 and 10 % respectively) results in a large range of isotopic fractionation factors, particularly in low temperature environments. Isotope effects may be divided into kinetic and equilibrium isotope effects.

Kinetic isotope effects tend to be associated with rapid, unidirectional processes such as evaporation or diffusion. In these cases, isotopic fractionation arises due to the higher velocity of the lighter isotope across a phase boundary or through a phase (diffusion and evaporation respectively) resulting in the preferential transport of the lighter isotope. As these differences in velocity arise from differences in mass, kinetic isotope effects should be present at all temperatures. In the case of diffusion, this results in the source eventually becoming enriched in the heavier isotope. The difference in mass between the isotopes of Li and B result in the magnitude of isotopic fractionation for these processes being extremely large. Additionally, kinetic isotopic fractionation can arise due to the dissociation energy of covalently bonded molecules containing the heavier isotope being higher and consequently requiring more energy to break.

Equilibrium isotope effects may occur due to differences in isotopic masses effecting differences in bond energy preferences. In this case, molecules with the heavier isotope have a higher reduced mass, a lower frequency as defined by Hooke’s law, a lower zero-point energy and so are more stable than molecules containing lighter isotopes. As such, the heavier isotope is preferentially partitioned to higher bond energy sites. For some species (such as Li), bond energy is inversely proportional to the site coordination number (CN) and as such the lighter isotope is preferentially partitioned into higher coordination number phases. Li isotopes potentially fractionate during the weathering of natural systems through two processes: kinetic isotopic fractionation during mineral dissolution and equilibrium isotopic fractionation due to Li being incorporated into or adsorbed onto secondary phases. Whilst
no kinetic isotopic fractionation accompanied dissolution of the primary phase during the
dissolution of basaltic glasses\textsuperscript{118–121}, these studies and numerous others found consistent
evidence that Li fractionates significantly during smectite clay formation\textsuperscript{122–125}. This isotopic
fractionation arises from a number of sources, with the magnitude of isotopic fractionation
being the sum of the isotopic fractionation from all Li sites within the clay\textsuperscript{126}. Most notably, Li
can substitute for Mg in octahedral sites in smectite clays owing to their similar ionic radii.
Alternatively, Li can adsorb onto the surface of the clay and into interlayer sites (collectively
referred to as ‘exchangeable Li’) or be incorporated into pseudo-hexagonal (ditrigonal) sites
within the tetrahedral clay layers\textsuperscript{126}. \(^6\)Li is preferentially incorporated into the ditrigonal and
octahedral sites with isotopic fractionation varying depending upon the difference in bonding
energy between Li in solution and that site. This is attributable to Li having a CN of four in
aqueous solutions, causing \(^7\)Li to preferentially remain in solution due to the higher
coordination ditrigonal (CN of six) and octahedral sites (CN of six) having a lower energy and
consequently \(^6\)Li to be preferentially incorporated into these sites\textsuperscript{113,127}. Despite having the same
CN, differences in bonding environment appear to effect significant differences in isotopic
fractionation between the ditrigonal and octahedral sites\textsuperscript{126}. As the exchangeable Li has a CN
of four in smectites, there is not expected to be any associated isotopic fractionation with these
sites\textsuperscript{119,126}. Changes in pH are expected to affect clay nucleation and growth rates, the rate of
crystallisation and the speciation of Li in solution to subsequently affect the magnitude of
isotopic fractionation. Further, equilibrium isotopic fractionation theoretically observes a
reciprocal of temperature squared dependence\textsuperscript{126}. However, for hectorites with a low degree of
crystallinity, only a small change in isotopic fractionation with temperature between 25 and 90
\(^\circ\)C was observed\textsuperscript{118}. Additionally, as Na is expected to compete with Li for exchangeable sites,
Li isotopic fractionation is also dependent upon leachant composition\textsuperscript{126}.

Similar to Li, \(^{10}\)B is preferentially adsorbed onto interlayer surface sites in smectite clay
minerals\textsuperscript{123,128,129}. At acidic and near-neutral pH, B is largely present in solution as B(OH)\textsubscript{3}
(trigonal coordination) which has a lower affinity for adsorption onto clays than B(OH)\textsubscript{4}\textsuperscript{−}
tetragonal coordination) which is present in alkaline solutions. Owing to bond energy effects,
\(^{11}\)B is preferentially partitioned into B(OH)\textsubscript{3} and \(^{10}\)B is preferentially partitioned into B(OH)\textsubscript{4}\textsuperscript{−}
due to their lower and higher CNs respectively. As B is generally tetrahedrally coordinated in
clays, the adsorption of B results in the enrichment of \(^{10}\)B in the interlayer sites of secondary
phases and an enrichment of $^{11}$B in solution. Consequently, this equilibrium isotope effect has a very strong pH dependency$^{117,123,129,130}$. Notably, there is a linear temperature dependence for the isotopic fractionation of B adsorbed or incorporated into smectites such that the values for melt-fluid interactions at 1100 °C can be extrapolated to adsorption at 25 °C$^{129,131}$.

1.5. Scope and structure of this thesis

To begin this work, Chapter 2 describes the experimental methods employed herein. The unique role of Li alluded to by elemental profiles combined with the potential for a Li:Na MAE suggested that a simplified analogue of MW25 should contain Li. Further, whilst it has been shown that the addition of Li to MW25 effected poorer aqueous durability, this has convoluted the effects of Li on aqueous durability$^{92}$. As such, Chapter 3 aimed to fabricate and leach Li-containing analogues of MW25 produced by substituting Li for Na in Mg-EM at two ratios to represent MW25 and excess-Li contents MW25. Comparisons of NMR studies and dissolution experiments afforded an interpretation of the effects of Li contents on aqueous durability as well as the suitability of the Li-Mg-EM analogues as a representation of MW25. Similarly, whilst Li has been added to a composition similar to ISG$^{40}$, the effect of Li on ISG has yet to be investigated. In Chapter 4, Li-containing analogues were fabricated by substituting Li for Na in ISG at two Li:Na ratios with the aims of providing a simplified analogue of SON68 and an analogue representing excess-Li contents SON68. Comparisons of the effects of Li on ISG and Mg-EM aimed to understand the relationship between complex glasses and simplified analogues as well as compare the effects of excess Li contents on MW25 and SON68 through their respective analogues.

Whilst the experiments in Chapters 3 and 4 took place at 40 and 90 °C to investigate the consistency of the effects of Li across a range of temperatures, Chapter 5 aimed to investigate the temperature dependence of the aqueous durability of MW25 through leaching MW25 powders at 40, 70, 80 and 90 °C. However, these results highlighted a need for a new method to understand how glasses dissolve. Therefore, Chapter 6 focussed on applying Li and B isotope fingerprinting techniques to probe whether diffusive processes took place during the dissolution of a Li-Mg-EM analogue in a simplistic dissolution experiment at 90 °C. Chapter 7 subsequently focussed on applying the same Li isotope fingerprinting techniques to investigate the temperature dependence of the dissolution mechanisms of MW25 at 40 and 90 °C. Finally, Chapter 8 summarises the main findings of this work.
2. Fabrication, dissolution and analytical methodologies

2.1. Introduction

In this chapter, the compositions investigated are briefly presented alongside the methods of their fabrication, characterisation and aqueous dissolution. Pristine fabricated analogue glasses were characterised through a combination of laser diffraction analysis, BET (Brunauer–Emmett–Teller) analysis, Archimedes principle, X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), and magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR) of various isotopes, whilst the pre-fabricated complex waste glass MW25 underwent XRD, SEM and EDS analyses. The compositions of the fabricated samples were obtained through combinations of electron probe microanalysis (EPMA), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and acid digestion followed by ICP optical emission spectrometry (ICP-OES). Samples were then leached in deionised water, before the glass leachates underwent ICP-MS or ICP-OES analysis and leached glass powders underwent further analyses. Additionally, for the experiments detailed in Chapters 6 and 7, leachates were prepared and analysed for Li, Mg and B isotope ratios through multi-collector ICP-MS (MC-ICP-MS). In such experiments, the Li and B isotopic compositions of the pristine glasses were obtained through alkali fusion, acid digestion and LA-MC-ICP-MS.

2.2. Sample preparation

2.2.1. In-house glass fabrication

Four sets of compositions were investigated: a complex simulant Magnox waste glass of 25 wt.% waste loading (MW25), two seven-component simplified analogues of MW25 with different Li:Na ratios (Li-Mg-EM), a Li-Mg-EM composition with an equimolar Li:Na ratio enriched in $^6$Li to a target $^7$Li/$^6$Li of one ($^6$Li-Mg-EM) and two Li-containing seven-component analogues of different Li:Na ratios based upon the Li-free ISG composition (Li-ISG). With the exception of MW25, all compositions were fabricated in-house. A Mettler AJ100 analytical balance was used to weigh out all dried precursor powders, which were then heated in a 90 % Pt 10% Rh 200 mL crucible using a Lenton UAF 16/10 laboratory chamber furnace.

2.2.1.1. Li-Mg-EM fabrication

The six-component Li-free borosilicate glass Mg-EM was formulated to be a simplified analogue of MW25 following discussions between operators of the waste vitrification plant at...
Sellafield, Jacobs and the University of Cambridge. The molar ratios of all elements except La had been fixed to their molar ratios within the MW25, with La representing all REEs on a charge-for-charge basis and all other constituents of MW25 were omitted. To isolate and investigate the effects of Li on aqueous durability for the mechanistic study described in Chapter 3, Li was substituted for Na in Mg-EM on an atom for atom basis at elemental molar ratios of 1.0 and 1.5 to form Li50Na50-Mg-EM and Li60Na40-Mg-EM respectively; keeping the molar elemental fractions of other glass species and the total alkali metal contents of the glasses constant.

Precursor powders were dried at 90 °C for 2 h in Al trays before being weighed, mixed in the crucible and placed into the furnace: Al₂O₃ (Sigma Aldrich, 99.99 %), B₂O₃ (Alfa Aesar, 99.98 %), La₂O₃ (Alfa Aesar REacton, 99.999 %), Li₂CO₃ (Alfa Aesar Puratronic, 99.998 %), MgO (Alfa Aesar, 99.99 %), Na₂B₄O₇ (Alfa Aesar, 99.95 %), and SiO₂ (Alfa Aesar, 99.9 %).

Precursors were heated at 10 °C/min to 750 °C, held for 3 h to allow for the release of CO₂, heated to 1150 °C at 10 °C/min and then heated as quickly as possible to 1500 °C, at which time the glass was poured onto ambient temperature steel plates coated with a graphite release agent. The poured glass was crushed to a fine powder using an agate mortar and pestle, placed back into the crucible and heated using the same procedure without the 3 h dwell. This time, the glass was poured onto pre-heated 250 °C steel plates, held for 2 h and cooled to ambient temperatures. The glass was annealed at 550 °C (just below its estimated glass transition temperature) for 2 h, then cooled slowly to room temperature inside the furnace over the course of 16 h. This yielded approximately 38.5 g of glass per batch. Due to the dissolution experiments taking place at two temperatures and the 200 ml crucible only accommodating enough precursor powders to yield enough glass for one temperature, it was necessary to produce each composition in two identical batches. These batches were never mixed and were characterised as if they were separate compositions. A number suffix appended to the sample name was used to distinguish between batches.

2.2.1.2. Li-ISG fabrication
The six-component Li-free borosilicate glass ISG was formulated to provide a common benchmark simplified waste glass composition for researchers to study internationally. The molar elemental ratios of ISG were identical to those of the French complex simulant waste glass SON68, with the REE and paramagnetic elements of SON68 omitted. Unlike Mg-EM, ISG contained no Mg or La but contained Ca and Zr. In Chapter 4, the effects of Li on the
aqueous durability of ISG were investigated through substituting Li for Na in ISG on an atom for atom basis. As SON68 contains a lower Li:Na ratio than MW25, elemental molar Li:Na ratios of 0.4 and 0.9 were targeted when fabricating Li29Na71-ISG and Li47Na53-ISG respectively. The elemental molar ratios of other glass species of the Li-ISG batches remained the same as in ISG and SON68. Based upon tests which took place to minimise cristobalite production (see Section 3.2.1), SiO₂ was dried at 250 °C for 16 h and all Li-ISG precursor powders except SiO₂ were dried at 110 °C for 16 h in Al weighing trays. Precursors (Al₂O₃ (Sigma Aldrich, 99.99 %), B₂O₃ (Alfa Aesar, 99.98 %), CaCO₃ (Sigma Aldrich, 99.995 %), Li₂CO₃ (Alfa Aesar Puratronic, 99.998 %), Na₂CO₃ (Alfa Aesar, 99.5 %), SiO₂ (Alfa Aesar, 99.9 %) and ZrO₂ (Sigma Aldrich, 99.99 %)) were weighed, mixed in the crucible and heated in the furnace.

The Li-ISG test pour followed an adaptation of the ISG heating procedure: precursors were heated to 750 °C at 10 °C/min, held for 3 h, heated to 1150 °C at 5 °C/min, then heated as quickly as possible to 1300 °C for pouring onto stainless steel plates. The glass was crushed to a fine powder and this procedure was repeated once more, whereafter the glass was annealed at 520 °C for 6 h and left to cool in the furnace over 16 h. This procedure differed from the original ISG procedure through the addition of a dwell at 750 °C, and removing the 4h dwell at 1300 °C. However, this procedure yielded a significant amount of muscovite (see Section 0). Following this test pour, the Li-ISG batches were instead fabricated using a modified Li-Mg-EM procedure. Dried precursors were heated to 700 °C at 10 °C/min, held for 3 h, heated to 1100 °C at 10 °C/min, then heated as quickly as possible to 1450 °C where the crucible was water quenched to ambient temperature. The quenched glass was crushed to a fine powder using an agate mortar and pestle, then underwent the same heating procedure without the 3 h dwell. Li29Na71-ISG and Li47Na53-ISG batches were then annealed at 510 °C and 500 °C respectively for 2 h before being cooled in the furnace over 16 h. As with the Li-Mg-EM glasses, two batches of each Li-ISG composition were fabricated.

2.2.1.3. ⁶Li-Mg-EM fabrication

⁶Li-Mg-EM was fabricated with the aims of providing a composition enriched in ⁶Li for NMR studies and to undergo the proof of concept isotope fingerprinting experiments in Chapter 6. The nominal molar elemental composition of ⁶Li-Mg-EM was identical to that of Li-Mg-EM with an equimolar Li:Na ratio, but was enriched in ⁶Li to a nominal equimolar ⁷Li/⁶Li ratio (δ⁷Li of -918.90 ‰, relative to NIST SRM 8545 L-SVEC at a ⁷Li/⁶Li ratio of 12.330¹²,¹³) with
all other isotopes assumed to be at natural abundance. A single batch of $^6$Li-Mg-EM was produced using the same precursor powders as in fabricating the Li-Mg-EM compositions, with the addition of $^6$Li$_2$CO$_3$ (Euriso-top, 95.77 % $^6$Li atoms). It was assumed the other Li$_2$CO$_3$ precursor (Alfa Aesar Puratronic, 99.998 %) contained Li at natural abundance (92.41 % $^7$Li atoms, 7.59 % $^6$Li atoms). $^6$Li-Mg-EM was fabricated and annealed following the same methodology as the Li-Mg-EM compositions (Section 2.2.1.1).

### 2.2.2. Production of MW25

As active vitrified waste products cannot be directly characterised, the WVP at Sellafield Ltd is supported by the vitrification test rig (VTR). The VTR operates as a full scale inactive replica of the WVP, producing simulant vitrified products to be characterised and optimising the waste loading and throughput of the WVP\(^8\). The ‘Mixture Windscale’ complex simulant Magnox waste glass of 25 wt.% waste loading (MW25) was fabricated to provide inactive samples representative of a ‘standard’ UK waste glass composition\(^16\). MW25 from pour 36 VTR campaign 10 was produced on the VTR following process parameters used in the production of active canisters on the WVP\(^15\). A description of the AVH vitrification process by which MW25 was fabricated is presented in Section 1.1. Typically, this process yields a 200 kg pour per waste container\(^15\). MW25 appeared free from yellow phase (devitrified alkali or alkaline earth metal molybdates and chromates), but some other crystalline phases were noted (RuO$_2$ and Cr-Fe-Mg-Ni spinels, see Chapter 5) which accounted for approximately 1.3 % of the glass. In addition to a void under the top surface of the pour, bubbles accounted for between 1.2 % and 1.9 % of the glass\(^15\). These fractions of bubbles and crystalline phases were considered standard for this type of vitrified product.

### 2.2.3. Grinding, sieving and washing

The fabricated batches were placed into a sample bag and struck once with a hammer to obtain pieces for density, EPMA and LA-ICP-MS analyses. All glasses were crushed, sieved and washed to the same size fraction (75 to 150 µm) using the same methodology. Glass pieces were crushed in an agate mortar and pestle set and sieved using a nest of 75 and 150 µm stainless steel test sieves with a lid and catchpan: the nest of sieves was tapped at an incline for one minute, the sieves were rotated and tapped again, with this process being repeated until all of the glass had passed through the 150 µm sieve. The 75 µm sieve was then removed from the nest and tapped until no visible fines came from the sieve. Any visible contaminants were removed from the sized glass and the fines using a pair of tweezers before magnetic particles
were removed by passing a magnet in a sample bag through the powder repeatedly. Sized powders were then washed to remove adhering fines following an adaptation of the ASTM product consistency test method B procedure\textsuperscript{134}. As washing the glass in deionised water may result in roughening of the glass surfaces, the glass was washed solely using ethanol. The sized glass powders were placed into clean 60 ml glass beakers, where absolute ethanol (Fisher Scientific, analytical grade) was forcefully squirted into the beakers in a circular motion to disturb the glass and fill the beaker to 1.5 times the sample volume. The beakers were then swirled for 10 s, left to settle for 15 s, then the ethanol was decanted. This process was repeated twice more, but on the final time the ethanol was decanted after the beaker was ultrasonically agitated for 2 min. This washing procedure was repeated until the decanted ethanol after the ultrasonic bath step appeared clean or a minimum of four times in total. The glass was then dried at 90 °C for 16 h, checked with a magnet again and finally placed into clean sample vials.

2.3. Pre-leaching wasteform characterisation

2.3.1. Laser diffraction analysis
Laser diffraction analysis took place to obtain particle size distributions of the washed and sized (75 to 150 µm) Li-Mg-EM, 6Li-Mg-EM and Li-ISG batches to ensure the sized fractions were free from fines and close to the geometric mean spherical particle diameter of 112.5 µm. To ensure consistency between runs, a batch of washed and sized MW base glass was also analysed along each set of batches. A Malvern Instruments Mastersizer E (Department of Materials Science and Metallurgy, University of Cambridge) was used. A small enclosed cell with glass windows containing a PTFE magnetic stirrer was filled with absolute ethanol, before being placed in front of a lens of a 300 mm focal length. A beam length of 14.3 mm was used to analyse a particle distribution of 1.2 to 600.0 µm. Ethanol was as the dispersant as water resulted in the samples forming colloids. The laser was aligned, the ethanol was stirred and a background was acquired. For each sample, 50 to 100 mg of washed and sized powder was analysed (approximately 25000 to 55000 particles, depending upon the density of the glass and assuming a spherical particle size with a diameter of 112.5 µm). An obscuration value of 0.0750 to 0.1500 of the volume distribution and a residual of less than 2.0000% were targeted per measurement. The cell was dismantled and cleaned thoroughly with lens tissues and ethanol after each measurement.

2.3.2. BET surface area measurements
BET analysis took place for all four pristine washed and sized Li-Mg-EM batches and for one
pristine washed and sized Li29Na71-ISG batch to provide a specific surface area. A target sample mass of 1.000 g was analysed, which had first been degassed inside a box oven at 150 °C for over 16 h to remove adsorbed surface water and CO2. BET surface areas were measured with a Micromeritics TriStar 3000 automated gas-adsorption analyser (Department of Materials Science and Metallurgy, University of Cambridge) using 77 K N2 gas adsorption under a high vacuum and a partial pressure range of between 0.01 and 0.99.

2.3.3. Density measurements
To investigate how glass composition affected density and to calculate geometric glass surface area to leachant volume ratios in the dissolution experiments, Archimedes’ principle was used to measure the density of all Li-Mg-EM and Li-ISG batches and 6Li-Mg-EM. Each batch was analysed in triplicate using pieces of annealed glass which weighed more than 0.25 g and were free from any visible defects. An Ohaus Pioneer analytical balance with weigh-below hook mounted onto a steel frame was used for the measurements with a piece of wire and beaker of ambient temperature (21.0 to 28.0 °C) type one deionised water (18.2 MΩ.cm at 25.0 °C). The temperature of the water was measured throughout each density measurement. The wire was first weighed using the weigh-below hook in the air before it was weighed whilst submerged in water. The sample was then suspended from the wire and weighed in the air before it was submerged fully in deionised water, weighed, removed from the water and dried. The sample was weighed twice more in the water for a triplicate in-water mass, before it was removed and dried a final time then weighed in the air for a duplicate in-air mass. The average mass of the sample in the water subtracted from the average mass of the sample in air yielded the volume of the sample, which was then divided by the average mass of the sample in the air and multiplied by the calculated density of the deionised water to yield a sample density.

2.3.4. XRD
In-house fabricated pristine glass powders (Li-Mg-EM, 6Li-Mg-EM and Li-ISG) underwent XRD analysis to ensure they were amorphous, whilst pristine MW25 was analysed to investigate its crystalline phases. Analysis took place on a Bruker D8 Advance powder X-ray diffractometer with a solid-state detector and monochromator using Cu Kα1 radiation (λ = 0.15046 nm) and a near sample aperture slit size of 0.600 mm. A range of 10 ° to 60 ° (2θ) was analysed in 978 steps of 0.05 °, with a dwell time of 7 s per step. Characteristic peaks in the diffractograms were referenced to the International Centre for Diffraction Data (ICDD) database using DIFFRAC.EVA software.
Initially, approximately 100 mg of fine particles (<75 µm) of each Li-Mg-EM batch and ⁶Li-Mg-EM were analysed using a circular glass slide on an acrylic sample holder. As crystalline phases were found in the pristine Li-Mg-EM and ⁶Li-Mg-EM fines, the analysis was repeated using approximately 100 mg of washed and sized glass powder. Analysis also took place on the SiO₂ precursor used in the fabrication of all batches as well as pristine MW base glass frit, which was expected to be amorphous. Additionally, quantitative comparisons of the crystallinity of the Li-Mg-EM and ⁶Li-Mg-EM fines took place using 20 ± 1 mg of sample on a low background sample holder. Pristine Li-ISG fines underwent analysis using approximately 100 mg of sample with a low background sample holder. For the pristine MW25 samples, 10 ± 1 mg of washed and sized sample was analysed with a low background sample holder.

2.3.5. SEM and EDS

To assess the efficacy of the washing procedure, secondary electron (SE) images of one pristine washed and sized batch of each Li-Mg-EM composition and the washed and sized MW25 powders were acquired on a FEI QEMSCAN 650F SEM. Samples were analysed uncoated. Images were acquired at low vacuum using a 20 kV beam, a working distance of 13.0 mm and a spot size of 4.0 with a low vacuum secondary electron detector (LFD) as to facilitate EDS spot analysis during the same run. To identify areas of interest for EDS analysis, backscattered electron (BSE) images were taken at a half-field width of either 190 or 212 µm under the same conditions using a Centric BackScatter (CBS) detector. BSE images were also useful for identifying areas of potential contamination and crystalline phases in MW25. At least two SE and BSE images were acquired for each sample. EDS spot analysis of the pristine washed and sized Li-Mg-EM batches and MW25 took place on three or four spots selected from each BSE image using a Bruker X Flash 6 | 30 silicon drift detector, for a total of between six and eight spots analyzed for each sample. Peaks in the EDS spectra were then assigned elements using ESPIRIT 2 software.

As a crystalline phase was found in the Li-Mg-EM fines but not the washed and sized fractions, this suggested that this crystalline phase was easier to grind than the amorphous phase and therefore there could be an enrichment of Si in fines. To qualitatively assess this, EDS spot analysis also took place on the fines of each Li-Mg-EM batch using the same conditions as the washed and sized batches. After assigning elements to each peak in the EDS spectra, ESPIRIT 2 software was then used to quantify the oxide wt.% of each peak. As the powders had not been ground and polished and standards were not used, this comparison was purely qualitative. As
such, the SiO$_2$:Oxide wt.% ratios of the fines and washed and sized fractions were compared.

2.3.6. NMR

2.3.6.1. Background to single-pulse MAS-NMR experiments

The sensitivity of NMR spectroscopy to changes in local chemical environments makes it an invaluable tool in probing the structures of both amorphous and crystalline materials; affording in-depth studies into the roles of elements within glasses, how elements in different environments are leached from glasses, sample crystallinity and the structure of secondary phase precipitates. To investigate these local environments, NMR employs nuclear spin, which is a property intrinsic to some nuclei and is characterised by a spin number $I$. Nuclear spin is related to the intrinsic angular momentum, $J$, through Equation 2-1 where $h$ is Planck’s constant and $I$ may take integer or half-integer values.

$$J = \frac{h}{2\pi} \sqrt{I(I + 1)}$$  \hspace{1cm} \text{Equation 2-1}

The intrinsic angular momentum of a nucleus effects a magnetic moment, $\mu$, which are related through the gyromagnetic ratio, $\gamma$ (Equation 2-2). $\gamma$ is a unique constant for each nuclide. The sensitivity of a nucleus during NMR spectroscopy is dependent upon $\gamma$, such that nuclei with a nuclear spin of zero ($I = 0$) have no magnetic moment and are not detectable by NMR. The total magnetisation of a sample, $M$, is equal to the vectorial sum of the magnetic moments.

$$\mu = \gamma J$$  \hspace{1cm} \text{Equation 2-2}

Nuclear spin is quantised such that for nuclei with a non-zero spin, $2I + 1$ degenerate energy levels exist. Each discrete energy level takes a magnetic spin quantum number, $m$, such that there are $2I + 1$ values for $m$. In the presence of a uniform magnetic field in the $z$-axis ($B_0$), dipoles precess around the magnitude field with an angular frequency, $\omega$, dependent upon the gyromagnetic ratio (Equation 2-3). Commonly, the $\omega$ of a type of nucleus may be referred to as its Larmor frequency.

$$\omega_0 = -\gamma B_0$$  \hspace{1cm} \text{Equation 2-3}

Whilst the energy levels are degenerate (of the same energy) in the absence of a magnetic field, these energy levels experience a Zeeman interaction in the presence of $B_0$ to remove the degeneracy and create $2I + 1$ equally spaced discrete energy levels described by $m$. The Zeeman interaction and nuclear spin quantisation occur in the direction of the magnetic field (in this case defined as along the $z$-axis). At equilibrium, the spin system is in a number of possible eigenstates. The energy operator of the system in $B_0$ applied along the $z$-axis assuming no other
interactions, $\hat{H}$, is given by the nuclear magnetic moment operator, $\hat{\mu}$, and $B_0$ (Equation 2-4). Defining the relationship between $\hat{\mu}$ and the nuclear spin operator, $\hat{I}$, to be Equation 2-5 and through applying $\hat{I}$ in the z-axis, $\hat{I}_z$, on the eigenfunction to yield $m$, the energy of each eigenstate for each value of $m$, $E_{I,m}$, can be represented using Equation 2-6.

$$\hat{H} = -\hat{\mu}B_0$$  \hspace{1cm}  \text{Equation 2-4}
$$\hat{\mu} = \gamma \frac{\hbar}{2\pi} \hat{I}$$  \hspace{1cm}  \text{Equation 2-5}
$$E_{I,m} = -\gamma \frac{\hbar}{2\pi} B_0 m$$  \hspace{1cm}  \text{Equation 2-6}

The nucleus may only change its energy level to an adjacent energy level through absorbing or emitting a photon. As $m$ has $2I + 1$ values ranging from $-I$ to $+I$ in intervals equal to one ($I, I-1...-I$), from Equation 2-6 it is shown that the energy gap between two neighbouring energy states is equal to the absolute value of $\gamma \frac{\hbar}{2\pi} B_0$. Using the Planck equation with the reduced Planck constant, $\hbar$, ($E = \hbar \nu$) with Equation 2-3 and the energy gap between two Zeeman states ($E = |\gamma \frac{\hbar}{2\pi} B_0|$), it can be shown that the nucleus in the presence of $B_0$ along the z-axis will emit or absorb a photon of frequency, $\nu$, equal to its Larmor frequency, $\omega$. These frequencies are in the radiofrequency (RF) range and are measured during an NMR experiment.

Single-pulse NMR experiments may be described in the classical picture, where the frequency at which the magnetic moment of the nucleus precesses around the magnetic field and the resonance frequency of the energy gap described by the Planck equation are both equal to $\omega$. Net magnetisation, $M$, is parallel to $B_0$ in the z-axis rotating at $\omega$, such that the spin system appears stationary in the rotating frame. The sample is then irradiated using a microsecond pulse of polarised RF radiation at the Larmor frequency to create a magnetic field in the X-Y plane, $B_1$. $B_1$ causes $M$ to nutate perpendicular to $B_0$ towards the X-Y plane to an angle dependent upon the length of the RF pulse. In many experiments, the RF pulse length is such that $M$ fully nutates by a $\pi/2$ angle into the X-Y plane and this is referred to as a $\pi/2$ pulse. After the RF pulse has ended, $M$ aligns back towards $B_0$ along the z-axis (referred to as $T_1$ spin-lattice relaxation) and individual spins lose coherence such that $M$ dephases in the X-Y plane (referred to as $T_2$ spin-spin relaxation). The decay of $M$ during dephasing results in a change in magnetic flux from the sample which is recorded as a function of time to yield a free induction decay (FID). After the spin system returns to the z-axis, this process is repeated and the signals are
accumulated. As signal builds linearly whilst noise increases with the square root of the number of acquisitions, the signal to noise ratio of the spectrum increases proportionally with the square root of the number of acquisitions. The FID is then Fourier transformed to convert it from the time domain into the frequency domain to yield a spectrum with one or more peaks depending upon the environments of the probed nuclei\textsuperscript{136,137}.

In practice, the $B_0$ experienced by different nuclei within the same sample may vary slightly as nearby electrons and neighbouring nuclei produce their own magnetic fields. Consequently, the same nuclei in different chemical environments will observe slightly different resonance frequencies. The shift in frequency is measured relative to a known reference material to yield a chemical shift, $\delta$ (Equation 2-7). As these differences in frequency can be quite subtle, $\delta$ is presented on the parts per million (ppm) scale. Increased negative $\delta$ correspond to a larger degree of shielding of the nucleus\textsuperscript{137}. As the electrons defining the chemical bonds within a material are influenced by $B_0$ and can yield a range of $\delta$ values, NMR is a powerful technique for quantitatively probing the structure of materials on an atomistic scale.

$$\delta = \left( \frac{V_{\text{Sample}} - V_{\text{Standard}}}{V_{\text{Standard}}} \right) \times 10^6 \quad \text{Equation 2-7}$$

Owing to the atomic motion in liquid samples generally occurring at frequencies far exceeding the Larmor frequency, the nuclei in liquid samples experience the same average magnetic field, the electron distribution anisotropy of the nucleus averages to zero and the different chemical shifts observed by molecules in different orientations average to near a single value. Consequently, the peaks of the spectra of liquid samples are generally very narrow. However, a number of factors which influence the magnetic field experienced by nuclei within solid samples effect broad peaks and render obtaining high resolution spectra during solid-state NMR experiments somewhat challenging. Notably, this is caused by dipole-dipole interactions between nuclei, chemical shift anisotropy arising from anisotropic electronic shielding at each individual site and, for $I \geq 1$ nuclei, interactions between the nuclides quadrupole moment and the electric field gradient (EFG) across the nucleus. These effects are particularly relevant for powdered crystalline samples, which essentially contain a large number of crystallites locked into an array of different crystallographic orientations.

To overcome these solid broadening effects, powdered samples are loaded into narrow zirconia or silicon carbide sample holders referred to as “rotors”. The sample is then spun rapidly (usually between 4 and 50 kHz) at the “magic angle” of 54.7° from the direction of $B_0$ in the
Fabrication, dissolution and analytical methodologies

z-axis and as such is named magic angle spinning (MAS)-NMR. This is because these anisotropic interactions are dependent upon molecular orientations which include the term $3\cos^2\theta - 1$, where $\theta$ gives the angle between $B_0$ along the z-axis and the rotor (the principal axis of interaction). As such, when $\theta$ is equal to the magic angle (54.7 °), these interaction terms tend to zero. Consequently, this results in the dipole-dipole, chemical shift anisotropy and first-order quadrupole interactions tending to zero, a single isotropic value and zero respectively. Peaks subsequently narrow because the average $\theta$ experienced by each nucleus over time is 54.7 ° and directionally dependent chemical shielding is removed\textsuperscript{137}. Fundamentally, this replicates the molecular motion in liquids which removes dipolar coupling and directionally dependent chemical shielding. Where the spinning speed of the sample is less than the anisotropic interactions in Hz, modulation of the $B_1$ RF frequency effects spinning sidebands (SSB). SSB appear in the spectra at frequencies dictated by the spinning speed and as such can often be easily distinguished from the isotropic chemical shift.

Nuclei with $I \geq 1$ (here $^6$Li, $^7$Li, $^{11}$B and $^{23}$Na) have multiple energy gaps and are referred to as quadrupolar nuclei. However, the quadrupole moments of these nuclei, arising from a nonspherical charge distribution on the nucleus, interact with the EFGs in their surroundings. This quadrupolar interaction can be a stronger effect than the RF pulse and as such quadrupolar lineshapes tend to be broader than $I = \frac{1}{2}$ non-quadrupolar nuclei. Whilst MAS-NMR can reduce the first-order quadrupole interactions to zero to significantly narrow the quadrupolar lineshape, $3\cos^2\theta - 1$ is absent from the second order quadrupolar interaction terms. When these second order interactions are sufficiently large, the central transition observes a poor degree of symmetry and is shifted from the “true” $\delta$ value, $\delta_{CS}$. Powder MAS-NMR spectra of quadrupolar nuclei are characterised by the quadrupolar coupling constant $\chi$, an asymmetry parameter $\eta$, and a centre of gravity of the line $\delta_{CG}$; where $\chi$ provides a measure of the strength of the quadrupole interaction (by extension the magnitude of the EFG at the nucleus) and $\eta$ provides a measure of the deviation from axial symmetry for the EFG. Generally, increasing the strength of $B_0$ decreases these quadrupolar broadening effects, increasing $\chi$ intensifies these broadening effects and changing $\eta$ significantly changes the lineshape. In MAS-NMR experiments, $\delta_{CS}$ appears on the left edge of the peak whilst the $\delta_{CG}$ is present to the right at a more negative chemical shift\textsuperscript{137–139}. 
2.3.6.2. Background to cross polarisation NMR experiments

Cross polarisation (CP) NMR experiments involve double resonance: two nuclei are excited in the same experiment through transferring polarisation (or magnetisation) from one nucleus to another, typically to increase the sensitivity for nuclei which have low abundance or sensitivity through transferring polarisation from a highly abundant and sensitive nucleus such as $^1$H. Further, CP-NMR allows for the selective probing of certain environments to provide additional structural information; as is the case here, where $^6$Li-$^1$H CP-NMR was used to selectively probe Li in the alteration layers due to negligible $^1$H polarisation from the pristine glass (Section 2.10.3.2). Initially, $^1$H is irradiated using the proton channel with a $\frac{\pi}{2}$ RF pulse at its Larmor frequency to nutate the M of $^1$H into the X-Y plane. A short on-resonance ‘contact pulse’ is then applied to both $^1$H and the other nuclide, i, to create a ‘spin-lock field’ $B_{1}^{H}$ to maintain magnetisation for $^1$H in the X-Y plane. The nuclide i simultaneously also experiences a $B_{1}^{i}$ field in this plane. The contact pulse amplitude is such that the Hartmann-Hahn matching condition is fulfilled (Equation 2-8), where $\alpha$ is coefficient which is a function of I and m.

$$\alpha_{H} \gamma_{H} B_{1}^{H} = \alpha_{i} \gamma_{i} B_{1}^{i}$$

Equation 2-8

When this condition is met, both nuclei precess at the same frequency $\omega$ about $B_{1}$ such that the energy gaps for each rotating frame are equal for $^1$H and i. As both $^1$H and i are quantised in the X-Y plane perpendicular to $B_{0}$, the dipole coupling operator (which describes the dipolar coupling between $^1$H and i) cannot affect the total energy or magnetisation of the spin system such that energy and angular momentum are conserved. As the energy gaps for $^1$H and i are equal, the dipolar coupling allows for energy to be redistributed between the $^1$H and i spins. Whilst the magnitude of the initial $B_{1}^{H}$ was large enough to nutate M into the X-Y plane, the $B_{1}^{H}$ spin-lock field is significantly weaker than $B_{0}$ such that the $^1$H magnetisation reduces. As the energy and magnetisation are conserved, this leads to a large increase in the i magnetisation in the $B_{1}^{i}$ direction. However, it should also be considered that there is some redistribution of energy due $^1$H-$^1$H dipolar coupling. Subsequently, the decay of the i magnetisation is recorded as in a single-pulse experiment. The relaxation time of i then becomes that of $^1$H and as such is often greatly reduced. Combined with the greatly enhanced signal for i, CP-NMR affords significantly enhanced signal to noise ratios$^{136,137,140,141}$. Whilst $^6$Li is quadrupolar, it has a low quadrupolar moment and a spin of 1. As such, considerations for CP-NMR experiments of half-integer quadrupolar nuclei are not applicable to $^6$Li-$^1$H CP-NMR experiments.
2.3.6.3. **Single-pulse MAS-NMR experiments**

To study the effects of varying the Li:Na ratio on the structures of the pristine Li-Mg-EM and Li-ISG glass networks, single-pulse MAS-NMR Li ($^6$Li or $^7$Li), $^{11}$B, $^{23}$Na and $^{29}$Si experiments took place on these compositions. Additionally, $^6$Li single-pulse MAS-NMR experiments on pristine $^6$Li-Mg-EM took place to further investigate the role of Li in Li-Mg-EM, alongside further $^{11}$B experiments. NMR experiments did not take place on MW25 as the paramagnetic contents of MW25 effects broad peaks with poor signal to noise ratios. All NMR experiments took place at room temperature on either a Chemagnetics Infinity spectrometer with a 9.4 T magnet or a Varian Infinity Plus spectrometer with an 11.7 T magnet ($^1$H Larmor frequencies of 400 MHz or 500 MHz respectively). Chemagnetics solid-state MAS probes accommodated rotors of external diameters between 2.5 and 9.5 mm and were either double-resonance (DR) or triple-resonance (TR) MAS probes, depending upon availability. Rotors were made of zirconia, with the exception of some 7.5 and 9.5 mm rotors which were made of silicon nitride.

2.3.6.3.1. **$^6$Li MAS-NMR**

Pre-leaching single-pulse $^6$Li Bloch decay experiments took place on the fines ($<75 \, \mu m$) of each Li-Mg-EM batch and $^6$Li-Mg-EM to investigate the role of Li within the glass. For Li-Mg-EM, spectra were acquired on the Chemagnetics Infinity spectrometer at a Larmor frequency of 58.87 MHz using a 4.0 mm DR MAS probe. Between 70 and 100 mg of fines were analysed in 4.0 mm rotors spun at 10.0 kHz. T1 saturation recovery experiments yielded a T1 of 516.8 s for a $\frac{\pi}{2}$ pulse (5.1 µs) for the Li-Mg-EM samples. As this relaxation time was too long, spectra were instead acquired by accumulating between 300 and 780 Bloch decays following a $\frac{3\pi}{20}$ pulse (1.5 µs) with a recycle delay of 60.0 s. For $^6$Li-Mg-EM, experiments took place on the Varian Infinity Plus spectrometer at a Larmor frequency of 73.54 MHz. A 7.5 mm DR MAS probe with zirconia 7.5 mm rotor was used to analyse 1160 mg of fines spun at 4.0 kHz. Spectra consisted of 52 Bloch decays following a $\frac{\pi}{2}$ pulse (5.0 µs) with a recycle delay of 1650.0 s (T1 found to be 329.8 s). All spectra were referenced to $^6$Li in 1.0 M $^6$LiCl (95.77 % $^6$Li atoms) in type one deionised water (18.2 MΩ.cm at 25 °C) at 0.0 ppm.

2.3.6.3.2. **$^7$Li MAS-NMR**

As the low natural abundance of $^6$Li made the Li-Mg-EM $^6$Li MAS-NMR experiments challenging, single-pulse $^7$Li Bloch decay experiments also took place on the fines ($<75 \, \mu m$) of all Li-Mg-EM and Li-ISG batches. All spectra were acquired on the Varian Infinity Plus
Fabrication, dissolution and analytical methodologies

spectrometer at a Larmor frequency of 194.21 MHz. A 4.0 mm DR probe was used, with between 80 and 120 mg of sample loaded into 4.0 mm zirconia rotors and spun at 10.0 kHz. Each spectrum consisted of 30 Bloch decays following a \( \frac{\pi}{2} \) pulse (4.8 µs) with a recycle delay of 132.5 s, with T1 saturation recovery experiments yielding similar T1 values for \( ^{6}\text{Li-Mg-EM} \) and \( ^{29}\text{Na71-ISG} \) (26.5 ± 0.6 s and 25.2 ± 0.5 s respectively). Spectra were referenced to \( ^{7}\text{Li} \) in 0.5 M LiCl in type one deionised water (18.2 MΩ.cm at 25 °C) at 0.0 ppm.

2.3.6.3.3. \( ^{11}\text{B MAS-NMR} \)
The well-resolved peaks of \( ^{\text{III}}\text{B} \) and \( ^{\text{IV}}\text{B} \) species in \( ^{11}\text{B MAS-NMR} \) spectra allow for the quantification of the \( ^{\text{III}}\text{B}/^{\text{IV}}\text{B} \) ratios of the pristine glasses. \( ^{11}\text{B Bloch decay experiments took place on the washed and sized fractions of } ^{6}\text{Li-Mg-EM, all batches of Li-Mg-EM and all batches of Li-ISG. A Varian Infinity Plus spectrometer was used at a Larmor frequency of 160.32 MHz with a 4.0 mm TR MAS probe. Between 50 and 120 mg sample was loaded into a 4.0 mm zirconia and spun at 10.0 kHz for the experiments. T1 saturation recovery experiments yielded similar T1 values for the Li-Mg-EM and Li-ISG batches at 5.5 s and 6.5 s respectively. Spectra consisted of 240 Bloch decays after a \( \frac{\pi}{14} \) pulse (0.4 µs) with a 6.0 s recycle delay, after confirming these were non-saturating conditions through comparing spectra acquired with recycle delays of 6.0 and 26.0 s. Spectra were referenced to 15% BF\(_3\).OEt\(_2\) in CDCl\(_3\) at 0.00 ppm using a secondary reference of powdered NaBH\(_4\) at -42.05 ppm. To compare the evolution of the \( ^{\text{III}}\text{B}/^{\text{IV}}\text{B} \) ratio with the changing Li:Na ratio, \( ^{11}\text{B spectra of the Li-Mg-EM, } ^{6}\text{Li-Mg-EM} \) and Li-ISG batches were quantified using DMFIT\(^{142}\) software.

2.3.6.3.4. \( ^{23}\text{Na MAS-NMR} \)
\( ^{23}\text{Na MAS-NMR experiments on the washed and sized Li-Mg-EM and Li-ISG batches took place on a Varian Infinity Plus spectrometer at a Larmor frequency of 132.18 MHz. Between 70 and 140 mg of sample was loaded into 4.0mm zirconia rotors and spun at 10.0 kHz in a 4.0 mm DR MAS probe. } ^{23}\text{Na spectra consisted of 1200 to 1800 Bloch decays following a } \frac{\pi}{15} \) pulse (1.2 µs) with a recycle delay of 6.0 s. A small pulse angle was used to ensure the conditions were non-saturating and quantitative, as later \( ^{23}\text{Na MAS-NMR experiments on the leached glasses (Section 2.10.3.1) revealed a second well-resolved Na site. } ^{23}\text{Na spectra were referenced to 0.1 M NaCl in type one deionised water (18.2 MΩ.cm at 25 °C) at 0.0 ppm.} \)

2.3.6.3.5. \( ^{29}\text{Si MAS-NMR} \)
\( ^{29}\text{Si MAS-NMR experiments took place on the fines of one batch of each Li-Mg-EM} \)
composition, the fines of $^6$Li-Mg-EM, MW base glass frit fines and base glass frit fines spiked with 1 wt.% cristobalite to compare the coordination of the Si network and to attempt to quantify the crystallinity of the Li-Mg-EM fines through comparisons with the unsiked and spiked MW base glass $^{29}$Si spectra. Spectra were acquired using a Chemagnetics Infinity spectrometer at a Larmor frequency of 79.48 MHz. A 9.5 mm DR probe was used, with 800 to 1000 mg of sample inside 9.5 mm rotors made of either zirconia or silicon nitride spun at 4.4 kHz. $^{29}$Si spectra were acquired as 3700 to 4700 Bloch decays following a $\pi/8$ pulse (1.0 µs) with a recycle delay of 21.0 s. Spectra were referenced to RTV silicone at -22.3 ppm.

2.4. Compositional characterisation

Fabricated compositions underwent a combination of compositional analyses to ensure they were close to their respective nominal target compositions. EPMA and LA-ICP-MS analyses took place in-house, whilst ICP-OES after acid digestion took place in collaboration with the Department of Chemistry, University of Sheffield. For EPMA or LA-ICP-MS analysis, three (Li-Mg-EM and $^6$Li-Mg-EM) or four (Li-ISG) pieces of each batch were mounted in two-part epoxy resin and polished with successive diamond pastes of particle sizes 9, 6, and 3 µm before being carbon coated for EPMA analysis.

2.4.1. EPMA

EPMA was used to obtain the oxide wt.% concentrations of La, Mg and Si in the Li-Mg-EM batches, Si in the Li-ISG batches and all elements except B and Li in $^6$Li-Mg-EM. A Cameca SX100 electron microprobe with 15 keV acceleration voltage, beam current of 20 nA and 10 µm beam diameter were used. Mineral standards were used to calibrate the instrument: jade for Na, diopside for Ca and Si, periclase for Mg, corundrum for Al, lanthanum hexaboride for La and zircon for Zr. Analysis took place using 12 or 10 randomly selected points on each piece of glass for a total of 36 (Li-Mg-EM and $^6$Li-Mg-EM) or 40 (Li-ISG) points respectively.

2.4.2. LA-ICP-MS

LA-ICP-MS analysis took place on all Li-Mg-EM batches and $^6$Li-Mg-EM to obtain the concentrations of B and Li, which were too light to analyse using EPMA. Concentrations were normalised using the SiO$_2$ concentration measured using EPMA as an internal standard to account for any analytical bias. Later acid digestion then ICP-OES analysis of the Li-Mg-EM batches provided concentrations with better recoveries than the LA-ICP-MS analysis. As such, the concentrations measured for the Li-Mg-EM batches by LA-ICP-MS did not contribute to
their final compositions and the Li-ISG batches did not undergo LA-ICP-MS analysis. An ESI NWR193UC laser ablation system with a 193 nm Excimer laser using ArF gas connected to a Perkin-Elmer NexION 350D ICP-MS was used for LA-ICP-MS. Glitter software was used to normalised the results to the EPMA SiO$_2$ values. NIST610 was analysed to calibrate the elemental sensitivity of the run using certified values and NIST614, NIST612 and BCR-2G standards were analysed to confirm the accuracy of this calibration. Additionally, NIST 610 was analysed at the start and end of each set of samples to monitor drift. Spot analysis took place by ablating nine randomly selected 50 by 50 µm squares per sample. A fluence of 10 Jm$^{-2}$, integration time of 5000 ms and dwell of 10 ms were used; taking 41 s per spot.

2.4.3. Digestion and ICP-OES

2.4.3.1. Digestion and analysis conditions
Approximately 0.25 g of each Li-Mg-EM and Li-ISG batch was sent to the Department of Chemistry, University of Sheffield for acid digestion then ICP-OES analysis to obtain the concentrations of all glass species. In this collaboration, 0.12500 g and 0.03125 g of glass was digested inside PFA (perfluoroalkoxy alkane, Savillex) vials. As the digested 0.12500 g sample would precipitate out of the solution faster than the 0.03125 g sample, if both samples returned identical concentrations then it may be concluded that precipitation did not occur. The PFA vials were then filled with 9 ml concentrated HCl and 3 ml concentrated HNO$_3$, heated to 150 °C for 30 minutes, 1 ml concentrated HF was then added to each vial, heated for 10 minutes at 150°C, another 1 ml concentrated HF and 1 ml concentrated HNO$_3$ were then added to each vial, and the vials were finally heated for a further 10 minutes. The digested samples were then diluted to 50 ml using 1 % HNO$_3$. A portion of this diluted sample was also further diluted to obtain 20 and 200 fold dilutions for ICP-OES analysis. Samples were then analysed alongside certified reference materials for each constituent glass element using a Spectro Ciros Vision ICP-OES. Although it was not possible to extract the RSD values or standard deviations for each measurement, all reported RSD values were less than 2 %.

2.5. Static batch dissolution methodology and the Li-Mg-EM experiments

2.5.1. The ASTM product consistency test method B methodology
The ASTM product consistency test (PCT) methods A and B provide robust guidelines for assessing the chemical durability of nuclear waste glasses. Whilst test method A is a fixed 7 d leaching test at 90 °C in type one deionised water inside stainless steel leaching vessels, test method B is a static batch dissolution experiment with more flexibility with regards to duration,
temperature, particle size, glass surface area to leachant volume ratios, leachant compositions and leaching vessel materials. This methodology outlines methods for preparing the glass, setting up the dissolution experiments and treating the leachate concentration data.

2.5.2. Vessel cleaning and instrument calibrations
Leaching vessels (stainless steel reaction vessels with 5ml PTFE liners) were cleaned following an extension to the ASTM PCT-B cleaning methodology. In the Li-Mg-EM experiments, all PTFE liners used were new. The stainless steel vessels and the new PTFE liners were first rinsed thrice with deionised water, soaked in 1% HNO$_3$ at 90 °C for 1 h, rinsed with deionised water, then soaked in 1% HNO$_3$ at 90 °C for 16 h. This procedure was then repeated using deionised water instead of 1% HNO$_3$, before the vessels were dried at 90 °C for at least 16 h. Analysis of PTFE liners had previously shown the F concentrations were negligible after minimal cleaning.

Al heater blocks were placed into Grant Instruments QBD2 or QBH2 dry block heaters and were preheated at 24 h before the experiments; the temperature of each block was checked using a leaching vessel connected to an external thermocouple to ensure it was within 2 °C of the target temperature. An Eppendorf Research Plus 0.5 to 5.0 ml pipette was calibrated by pipetting deionised water of a measured temperature at the maximum, minimum and intermediate volumes of the pipette five times into a glass beaker on an Ohaus Pioneer analytical balance. An Ohaus Pioneer analytical balance was used for masses below 110 g, with a Cole-Parmer Symmetry ECII-400 balance (two decimal place) used for heavier masses. A Mettler Toledo LE438 pH electrode with FE20 Fiveeasy benchtop pH meter was calibrated using buffer solutions which bracketed the expected pH of the solution: pH 4.00 and 7.00 ± 0.01 NIST traceable buffer solutions were used for the deionised water and blank leachates, whilst NIST traceable 7.00 and 10.00 ± 0.01 buffers were used for the sample leachates. Automatic temperature correction was used for all pH measurements.

2.5.3. Leaching experimental conditions
The Li-Mg-EM compositions were leached following the static batch ASTM product consistency test method B methodology: 0.390 to 0.400 ± 0.001 g of washed and sized glass (75 to 150 µm) was leached in 4.00 ± 0.08 ml of type one deionised water (18.2 MΩ.cm at 25.0 °C) per leaching vessel at 40.0 ± 0.1 °C and 90.0 ± 0.1 °C for 7, 14, 28 and 112 d (± 2% of each duration). A leachant volume to glass mass ratio (V/m) of 10.0 ± 0.5 ml/g was targeted, which resulted in a glass surface area to leachant volume ratio (SA/V) of between 1948 and
2200 m$^{-1}$ (assuming a spherical particle size with 112.5 µm diameter) which depended upon the density of the glass used. The deionised water was unbuffered and the pH of the leachant was allowed to vary freely throughout the experiment. Each duration at each temperature for each composition consisted of samples leached in triplicate with duplicate blank vessels. The first batches of each composition were used for durations of 28 and 112 d at 40 °C and 90 °C, and the second for 7 and 14 d; future experiments would use the same batch for all durations.

Leaching vessels consisted of 5 ml PTFE liners with PTFE caps inside stainless steel reaction vessels with Swagelok lids. The stainless steel vessel created a ‘closed system’ which prevented the solubilisation of CO$_2$ into the leachant. The masses of assembled vessels were taken whilst empty, after adding the glass powder (which was also weighed separately beforehand) and after pipetting in the leachant. The pH of the type 1 18.2 MΩ.cm DI leachant was measured in triplicate. SA/V ratios were calculated for each vessel using the mass of sample weighed on the weighing paper and the calculated volume of leachant used. The sealed leaching vessels were then placed into the pre-heated Al heater blocks inside Grant Instrument block heaters and were maintained at either 40 or 90 °C for the desired duration. After 4 to 16 h had passed, the tightness of the vessels was checked. Leaching experiments were set up so that all four leaching durations would end on the same day.

After the desired leaching durations had elapsed, the leaching vessels were weighed to calculate the volume of leachant lost. Mass loss exceeded 5 % of the initial leachant volume in only one vessel and this leachate was not analysed. Leachates were filtered using a piece of Savillex PFA tubing attached to a Whatman Puradisc 0.45 µm pore-size nylon filter and a BD Plastipak 10 ml syringe. Approximately 1.1 ml of the filtered leachate underwent pH analysis. As it was noted that moving the pH meter between the blank and sample leachates resulted in unstable blank measurements, the sample leachates were recorded first. The filtered leachate was dispensed into a 4 ml polypropylene (PP) scintillation vial, from which a 1.00 ml aliquot was taken and then diluted 5 times in a 15 ml PP centrifuge tube using 4.00 ml of 1 % HNO$_3$ (Teflon double distilled) for ICP-MS analysis. Leached glass powders were dried at 90 °C for 16 h.

2.5.4. Leachate ICP-MS analysis

2.5.4.1. Basic principles of ICP-MS

Whilst many of the features of an ICP-MS can differ significantly depending on the design of the instrument, the basic principles remain the same as summarised in Figure 2.1. For liquid samples, the sample is aspirated using a peristaltic pump into a nebuliser. Argon gas flowing
into the nebuliser then converts the sample into a fine aerosol, which is sprayed into a spray chamber. The spray chamber acts to separate the fine and large droplets of the aerosol which are transported to the ICP torch via a sample injector and discarded as waste respectively. Further, the spray chamber smooths out the ‘pulses’ which occur during sample nebulisation.

A combination of a plasma torch, an RF coil and an RF generator are used to create the inductively coupled plasma (ICP), as shown in Figure 2.2. Plasma gas (usually argon) is passed through the outer tube of the plasma torch, whilst the auxiliary gas (used to change the position of the plasma, often also argon) and nebuliser gas carrying the sample are passed through the middle tube and sample injector respectively. The RF generator passes an alternating current through the Cu RF coil, creating a strong magnetic field at the top of the plasma torch. A high-voltage spark at the tip of the torch then introduces electrons which are accelerated by the magnetic field to ionise argon atoms. This ionisation process continues to form the ICP discharge in a chain reaction which is sustained by the RF coil. In ICP-MS this torch is mounted horizontally and is used to ionise the sample ions, whilst in ICP-OES this torch is mounted vertically and is used to generate photons through exciting electrons from their ground states. The sample aerosol then passes through the sample injector and into the plasma. The sample is then desolvated, vaporised, atomised and finally ionised as it moves through the plasma\textsuperscript{143,144}.

Figure 2.1: Abstraction of an ICP-MS, reproduced from Thomas (2004)\textsuperscript{143}.

Figure 2.2: Abstraction of an ICP torch, reproduced from Thomas (2004)\textsuperscript{141}.
The sample ions are then transported through the MS interface which lies between the sampler and skimmer cones. Whilst the torch is at atmospheric pressure, the MS analyser region is at a pressure of approximately $10^{-6}$ Torr as maintained by a turbomolecular pump. The small orifices of the cones allow for a mechanical pump to maintain a pressure of approximately 1 to 4 Torr in the MS interface. However, capacitive coupling between the coil and plasma creates a secondary discharge between sampler cone and plasma. This discharge detrimentally affects the kinetic energy of ions passing through the MS interface and can produce doubly-charged interfering species. For efficient focussing in the ion optics, it is important that the sample ions entering the spectrometer have similar kinetic energies; as would be the case for a neutral plasma, but is significantly disturbed by a secondary discharge. The sampler cone is therefore designed with a grounding mechanism (such as a grounded shield between the coil and torch or two opposing RF coils) to minimise secondary discharge for a variety of common operating conditions\textsuperscript{143,144}.

After passing through the skimmer cone, the samples ions pass into the ion optics system. To ensure the composition of the beam is not compromised, it is extremely important that the plasma is at zero potential and the spread of the kinetic energy of the ions is as small as possible. The ion optics consist of a series of electromagnets at approximately $10^{-3}$ Torr as maintained by a turbomolecular pump. As there is a large change in pressure between the torch and the ion optics, after passing through the MS interface there is a tendency for electrons to diffuse from the ion beam to result in a positively charged ion beam. If not corrected, heavier ions concentrate towards the centre of the ion beam and repel the lighter ions to the edges; causing heavier ions to have a higher kinetic and to be transmitted preferentially. To mitigate this, voltage on one or more of the ion lenses is used to electrostatically steer the ion beam. As such, the ion optics focus the sample ion beam and steer it slightly off-axis into the mass analyser. In doing so, the optics also prevent particulates, photons and neutral species which cause increased background noise from reaching the mass analyser whilst maintaining the composition of the beam\textsuperscript{143,144}.

The focussed ion beam is then passed through the mass filter, which separates the ions according to their atomic mass to charge ratios. Commonly quadrupole mass filters are used for single-collector ICP-MS, which function through applying an RF field to a pair of rods opposite to a pair of rods which have an applied direct current. For a certain voltage applied to the rods,
Fabrication, dissolution and analytical methodologies

an analyte ion of a certain mass to charge ratio will be magnetically steered into the detector whilst ions of other mass to charge ratios will be ejected from the quadrupole. The voltage is then varied and the process is repeated for another mass to charge ratio until all the desired isotopes have been analysed. As the ions are detected, they are converted to electrical pulses and counted by a multichannel analyser to build up a spectral peak for each isotope of interest. The ability to separate an analyte signal from spectral interferences is defined by resolution (the width of the signal peak at 10 % of its intensity) and abundance sensitivity (the contribution of the tails of neighbouring peaks to the measured signal intensity). The resolution of the quadrupole mass filter can be varied between low, medium and high resolution modes (between 3.0 and 0.3 amu), with higher resolutions having lower sensitivities than lower resolutions. Whilst the same resolution is often used for all analytes, some spectrometers are able to vary the resolution for each isotope throughout the analysis\textsuperscript{143,144}.

Collision mode in ICP-MS uses a gas-filled collision cell to remove spectral interferences from the argon gas\textsuperscript{143}. When a collision cell is used, before the focussed ion beam enters the mass filters the ion beam enters a collision cell filled with He or H\textsubscript{2} gas. A multipole in the cell focusses the ions through an RF field which then collide with the collision gas. Commonly, these collisions convert common interfering species (such as ArO\textsuperscript{+} and ArH\textsuperscript{+}) into noninterfering species. However, in practice these collisions can generate further spectral interferences which are removed through kinetic energy discrimination. Kinetic energy discrimination functions through having a more negative charge on the collision cell than the quadrupole mass filters. Consequently, collisions products created within the cell have a lower kinetic energy which is insufficient to transport them to the mass filters, whilst analyte ions have a higher kinetic energy and are transmitted\textsuperscript{143}.

2.5.4.2. Instrumentation and analysis conditions

Concentration analysis of the diluted filtered leachates took place on a Perkin-Elmer NexION 350D ICP-MS. A Micromist FM05 micro-concentric nebuliser was used operating at 80 µl/min with a baffled quartz cyclonic spray chamber and Ni skimmer and sampler cones. All leachates were analysed for the constituent elements of the Li-Mg-EM samples (\textsuperscript{7}Li, \textsuperscript{11}B, Na, \textsuperscript{24,25,26}Mg, Al, \textsuperscript{29}Si, \textsuperscript{139}La), in addition to \textsuperscript{57}Fe, \textsuperscript{66}Zn, and \textsuperscript{208}Pb to check for contamination. Blanks were analysed first, followed by the 40 °C leachates then the 90 °C leachates. All isotopes lighter than, and including, \textsuperscript{57}Fe were analysed in collision mode using kinetic energy discrimination with a He gas filled collision cell. Standard mode was used for all other elements. Leachates
were analysed at a dilution factor of 5. A set of calibration standards composed of single-element plasma standards of the elements of interest (CPI International, US) were diluted in series using 1% HNO₃ and were analysed at the start of the run and after the blank and 40 °C leachate measurements. Additionally, SPS-SW2 (Spectrapure Standards) and a 10 ng/ml standard (SCP Science) were analysed as secondary standards periodically throughout the analysis to ensure the calibration remained accurate to within 10% of the desired concentration. Drift was measured throughout the run using 100 ng/ml Rh, In and Re internal standards to ensure it was less than 10%. Sensitivity was reported to be 450000 cps/ppb for In and a robustness of 2.8% measured using the CeO/Ce ratio. Raw measured intensities were internally blank corrected then drift corrected and normalised using the internal standards. The calibration standards were used to create linear calibration curves with intercepts of zero using Syngistix 1.1 software, which were then used to calculate concentrations from the raw intensities.

2.5.5. Concentration data treatment
All ICP-MS concentration data underwent the same basic calculations outlined in the PCT-B methodology. Raw concentrations were corrected for the dilution factor used and the volume of leachant lost during the experiments. From these values, an average volume corrected blank concentration, $\bar{C}_i^{Blank}$, was calculated for each element, $i$, for each temperature. Using these average blank concentrations, the significance of the sample concentrations was tested by taking away the average blank concentration for that temperature plus one, three or ten standard deviations from each sample concentration for each element. Samples concentrations greater than the average blank concentration plus three standard deviations were considered significant, and those greater than the average blank concentration plus ten standard deviations were considered suitable measures of glass dissolution. The concentration of each element for each sample, $C_i$, was then corrected for leachant mass loss ($V_f/V_i$) and the average blank concentration for that temperature, $C_i^{Blank}$, to give $C_i^{Sample}$, expressed in g/L (Equation 2-9).

$$C_i^{Sample} = \left( C_i(n) \cdot \frac{V_f}{V_i} \right) - \bar{C}_i^{Blank} \quad \text{Equation 2-9}$$

A SA/V ratio was calculated for each leaching vessel assuming particles were spheres with using Equation 2-10, with: the mass of sample leached, $m$; the density of the glass, $\rho$; the initial volume of leachant used, $V_i$; and a geometric mean spherical particle diameter, $d$, of 112.5 μm.

$$\frac{SA}{V} = \left( \frac{6m}{\pi d^3} \right) \cdot V_i^{-1} \quad \text{Equation 2-10}$$
Corrected concentrations were normalised to the initial SA/V ratio used and the elemental mass fraction of the element $i$ within the pristine glass, $f_i$, using Equation 2-11 to provide normalised releases, $NL_i$ (g/m$^2$). $NL_i$ provide a measure of the extent of glass dissolution and afford accurate comparisons between the leachate concentrations of glass compositions acquired at different SA/V ratios. Additionally, the normalised release rate of element $i$, $NR_i$, may be calculated by dividing the change in the $NL_i$ by change in leaching time.

$$NL_i = \frac{C_{Sample \_i \_SA/V}}{f\_i} \quad \text{Equation 2-11}$$

The estimated fraction of an element $i$ leached from the glass, $LF_i$, was calculated as the ratio of the mass of element $i$ in solution and its’ mass leached in the leaching experiments using Equation 2-12.

$$LF_i = \frac{C_{Sample \_i \_V_i}}{m_{f_i}} \quad \text{Equation 2-12}$$

From the leached fraction of B, an average altered layer thickness, $t$, could be calculated using Equation 2-13. This equation was based on the shrinking core model$^{42,89}$ assuming pristine spherical glass particles (radius, $r_0$, of 56.25 µm) are uniformly altered.

$$t = r_0 \left(1 - \frac{3}{2} \sqrt{1 - LF_B}\right) \quad \text{Equation 2-13}$$

### 2.6. Static batch Li-ISG dissolution

#### 2.6.1. Equipment cleaning, preparations and calibrations

The leaching vessels used in the Li-ISG experiments were the same as those used in the Li-Mg-EM experiments and were cleaned in the same manner (Section 2.5.2). Where PTFE liners and were reused, additional steps were employed to ensure there was no F$^-$ contamination or contamination between glass batches. After rinsing any remaining glass powder out with deionised water, the used liners were soaked in 5 % NaOH at 90 °C for over 16 h before undergoing the same cleaning procedure as the new liners with additional 1 and 16 h soaks in 1 % HNO$_3$. Additionally, used liners underwent pH tests: the liners were filled with deionised water, sealed using a PTFE cap, then heated at 90 °C for 16 h. After cooling to ambient temperature, the pH of the water was measured to ensure it had not fallen below 5.00 (F$^-$ contamination) or risen above 7.00 (contamination from glass species). As a test, triplicate cleaned used leaching liners inside stainless steel vessels were filled deionised water and leached at 90 °C for 7 d. ICP-MS analysis (analysed in the run in Section 2.5.4) demonstrated the blank concentrations from the new and used leaching liners were within error.
The same dry block heaters, pipette (with the addition of a 0.1 to 1.0 ml Eppendorf Research and a 10 to 100 µl Eppendorf Research Plus pipette), balances and pH meters as in the Li-Mg-EM experiments were used (Section 2.5.2). Dry block heater and pipette calibrations took place following the same methodology as in the Li-Mg-EM experiments. Additionally, a 100.0000 ± 0.0002 g OIML (Organisation Internationale de Métrologie Légale) class E2 calibration weight was used to check the calibration of the balances before and after each set of measurements; with the recorded masses being corrected accordingly. The pH meter was calibrated in the same manner as in the Li-Mg-EM experiments, using 7.00 and 10.01 ± 0.01 NIST traceable buffer solutions to measure the sample leachate pH and 4.00 and 7.00 ± 0.01 NIST traceable buffers to measure the pH of the blank leachates.

### 2.6.2. Differences in leaching experimental conditions

As with the Li-Mg-EM compositions, the two batches of the two Li-ISG compositions were leached following the ASTM PCT-B methodology\(^\text{134}\) at 40.0 ± 0.1 °C and 90.0 ± 0.1 °C for 7, 14, 28 and 112 d (± 2 %). Experiments took place using 4.00 ± 0.04 ml of type one deionised water (18.2 MΩ.cm at 25.0 °C) leachant and 0.399 ± 0.001 g of washed and sized (75 to 150 µm) Li-ISG powder per leaching vessel to achieve a SA/V ratio of between 2093 and 2171 m\(^{-1}\) (assuming a spherical particle diameter of 112.5 µm and depending upon the density of the glass batches). The leachant pH was allowed to vary freely throughout the experiments. Each composition for each leaching duration and temperature consisted of samples leached in triplicate with duplicate blanks. Each batch was used for all durations at each temperature. Leaching experiments were started and ended in the same manner as the Li-Mg-EM experiments with some minor improvements. All pipette tips and 15 ml centrifuge tubes used were acid washed (the 4 ml scintillation vials used in the Li-Mg-EM experiments were rinsed with the diluting acid). The OIML class E2 calibration weight was weighed before and after each set of measurements so that more accurate initial SA/V ratios and leachant mass losses after leaching could be calculated. Leachates were filtered in the same manner as in the Li-Mg-EM experiments. Once the pH of the filtered sample leachates had been measured, the pH meter was recalibrated using 4.00 and 7.00 ± 0.01 NIST traceable buffers and the blank leachates were measured as to minimise destabilisation. From the scintillation vials, 0.1 ml aliquots of filtered leachate were diluted 100 times using 9.9 ml 1 % HNO\(_3\) (Teflon double distilled) in 15 ml PP tubes for ICP-MS analysis. Mass loss exceeded 5 % of the initial leachant volume in 9 vessels. These leachates were analysed but only included where the concentrations were similar.
to those from vessels with a mass loss less than 5%. The centrifuge tubes were weighed whilst empty, after adding the sample leachate and after adding the diluant acid to calculate gravimetric dilution factors. Leached glass powders were dried for 16 h at 90 ± 2 °C.

### 2.6.3. Leachate ICP-MS analysis conditions and data treatment

ICP-MS analysis of the Li-ISG leachates took place on the same instrument and setup as analysis of the Li-Mg-EM leachates (Section 2.5.4). Leachates were analysed for the concentrations of common isotopes of all constituent elements of Li-ISG (\(^7\)Li, \(^{11}\)B, Na, Al, \(^{29}\)Si, \(^{43}\)Ca, \(^{90}\)Zr) as well as \(^{56}\)Fe, \(^{60}\)Ni, \(^{66}\)Zn and \(^{208}\)Pb to check for contamination. Blanks were analysed first, followed by the 40 °C and the 90 °C leachates. Standard mode was used to analyse \(^{208}\)Pb, whilst all other isotopes were analysed using kinetic energy discrimination with a He gas filled collision cell. Leachates were analysed at a gravimetric dilution factor of approximately 100. Calibration standards of single-element plasma standards (CPI International, US) diluted in series using 1 % HNO\(_3\) were analysed at the beginning of the run and were externally verified using SPS-SW2 (Spectrapure Standards) at a dilution factor of ten, and a 10 ng/ml standard (SCP Science). A 100 ng/ml Rh, In and Re internal standard was used to ensure drift was less than 10 %. Sensitivity and robustness were the same as in the Li-Mg-EM analysis. Raw intensities were blank and drift corrected then normalised using the internal standards, with the calibration standards used to create linear calibration curves with intercepts of zero using Syngistix 1.1 software. Raw intensities were then converted to concentrations using these curves and were then treated following the methodology outlined in Section 2.5.5.

### 2.7. Static batch MW25 dissolution (70 °C and 80 °C)

#### 2.7.1. Equipment cleaning, preparations and calibrations

The leaching vessel designs, experimental apparatus, cleaning procedures and calibration procedures used in the static batch MW25 dissolution experiments did not differ from those used in the Li-Mg-EM experiments. Where PTFE liners were reused, they were cleaned following the methodology used for the Li-ISG dissolution experiments (Section 2.6.1).

#### 2.7.2. Leaching experimental conditions

The MW25 static batch dissolution experiments at 70.0 ± 0.1 °C and 80.0 ± 0.1 °C took place using between 0.390 and 0.400 g of washed and sized powder (75 to 150 µm) with 4.00 ± 0.08 mL type 1 deionised water (18.2 MΩ.cm at 25.0 °C) leachant per leaching vessel for a SA/V of 1988 ± 45 m\(^{-1}\) (under the assumption particles were spheres with a 112.5 µm diameter). The pH of the leachant was allowed to vary freely and was not buffered. Experiments followed
the PCT-B protocol\textsuperscript{134}. Samples were leached for 0.25, 1, 7, 14 and 28 d (± 2 %). Each leaching duration at each temperature consisted of MW25 leached in triplicate with duplicate blanks. Leaching experiments were started and ended following the same methodology as the Li-Mg-EM experiments (Section 2.5.3), except samples were diluted to a dilution factor of 100. Mass loss exceeded 5 \% of the initial volume in three vessels and these leachates were not analysed.

2.7.3. Leachate ICP-MS analysis conditions

MW25 leachates were analysed for concentrations of common isotopes of the majority of elements of within MW25 (\textsuperscript{7}Li, \textsuperscript{11}B, \textsuperscript{23}Na, \textsuperscript{24}Mg, \textsuperscript{27}Al, \textsuperscript{29}Si, \textsuperscript{31}P, \textsuperscript{43}Ca, \textsuperscript{53}Cr, \textsuperscript{56}Fe, \textsuperscript{60}Ni, \textsuperscript{89}Y, \textsuperscript{90}Zr, \textsuperscript{95}Mo, \textsuperscript{101}Ru, \textsuperscript{125}Te, \textsuperscript{133}Cs, \textsuperscript{137}Ba, \textsuperscript{139}La, \textsuperscript{140}Ce, \textsuperscript{141}Pr and \textsuperscript{143}Nd) and common contaminants (\textsuperscript{66}Zn and \textsuperscript{208}Pb) using the same ICP-MS instrument and setup as for the Li-Mg-EM leachates (Section 2.5.4). Leachates were analysed at a dilution factor of 100. Kinetic energy discrimination with a He gas filled collision cell was used to analyse \textsuperscript{56}Fe and \textsuperscript{125}Te, whilst standard mode was used for all other isotopes. Blanks were first to be analysed, followed by the sample leachates in chronological order starting with the 70 °C 0.25 d leachates. Calibration standards were analysed at the start of the run and consisted of single-element plasma standards (CPI International, US) diluted in series with 1 \% HNO\textsubscript{3}. Calibrations were externally verified using a 10 ng/ml standard (Al, Ba, Cr, Fe, Li, Mg, Na, Ni, P, Pb and Zn, SCP Science) and 10 fold diluted SPS-SW2 (Spectrapure Standards). A 100 ng/ml internal standard containing Rh, In and Re was used to monitor drift throughout the run and ensure it was less than 10 \%. Robustness and sensitivity values were reported to be the same as in the Li-Mg-EM analysis (Section 2.5.4). After blank correcting, drift correcting and normalising the raw intensities using the internal standards, raw intensities were converted to concentrations using linear calibration curves (with intercepts of zero) using Syngistix 1.1 software.

2.7.4. MW25 leachate data treatment

Leachate concentrations were initially dilution factor and blank corrected and normalised following the data treatment methodology outlined in Section 2.5.5 to produce normalised elemental releases. Additionally, an activation energy, $E_a$ (kJmol$^{-1}$), was calculated for each of the mobile elements of MW25 (B, Li, Mo and Na) using the ICP-MS concentrations of the 70 and 80 °C leachates combined with the ICP-OES concentrations of the 40 and 90 °C leachates (see Section 2.8). Firstly, the blank and mass loss corrected leachate concentrations (see Equation 2-9), $C_{\text{Sample}}$, at 6 h of dissolution were divided by 0.25 to obtain dissolution rates at 6 h, $r$ (gL$^{-1}$d$^{-1}$). To visually assess the Arrhenius-type behaviour of these mobile glass species,
Arrhenius plots of the natural log of $r$ against the reciprocal of absolute temperature, $1/T$ (K$^{-1}$), were used. An $E_a$ for each mobile element was obtained through curve fitting (Igor Pro software, Wavemetrics) a plot of $r$ against $1/T$ using Equation 2-14, where $A$ represents the Arrhenius parameter (gL$^{-1}$d$^{-1}$) and $R$ represents the ideal gas constant (8.314 JK$^{-1}$mol$^{-1}$). This equation is used to mathematically describe the Arrhenius-type behaviour of dissolution$^{107}$.

$$r = A \cdot \exp \left( \frac{-E_a}{RT} \right) \quad \text{Equation 2-14}$$

2.8. Static batch sampling MW25 dissolution (40 °C and 90 °C)

2.8.1. Experimental overview

In addition to leachate concentration analysis for the temperature study in Chapter 5, the 40 and 90 °C MW25 leachates also underwent isotopic analysis (see Section 2.12) for the isotopic study in Chapter 7. As a high degree of precision was required to accurately measure subtle changes in the isotopic composition of the leachates with time, rather than individual triplicate leaching vessels which would be removed from the heaters as in the 70 and 80 °C MW25 experiments, it was decided that the same 40 and 90 °C MW25 leachates would be sampled periodically in triplicate in static batch sampling experiments. As such, to preserve the SA/V ratio of the experiments after aliquot sampling, the largest volume of leachant possible (limited by the mass of glass available) was used.

Leaching vessels consisted of 60 ml PFA (Savillex) ‘standard’ jars with ‘fluid transfer closure’ lids (inner diameter of 3.175 mm). This lid design was chosen over the flat ‘standard’ digestion vessel lid design as the ports accommodated direct access to the leachant for aliquot taking using a 5 cm piece of 3.175 mm outer diameter PFA tubing firmly attached to a 200 µl pipette tip, without the need to unseal the leaching vessel entirely for sampling. Whilst not in use, the ports were sealed using a small piece of PFA tubing secured using a ferrule nut.

Between 4.495 and 4.500 g of washed and sized (75 to 150 µm) MW25 powder was leached in 45.0 ± 0.5 ml of type one deionised water (18.2 MΩ.cm at 25 °C) for an initial SA/V of 2012 ± 24 m$^{-1}$ (assuming spherical particle diameter of 112.5 µm) and nominal V/m of 10.0 ml/g. Samples were leached in duplicate at 40.0 ± 0.1 °C and 90.0 ± 0.1 °C with duplicate blanks. Triplicate 100.0 ± 0.8 µl aliquots were taken from each leaching vessel at 0.25, 0.5, 7, 28, 126 and 464 d (± 2 %). The pH of the leachant was unbuffered and allowed to vary freely. As the PFA leaching vessels used were an ‘open system’, atmospheric CO$_2$ and O$_2$ were expected to solubilise into the leachant through the leaching vessel walls and potentially reduce leachant
pH after long dissolution intervals\textsuperscript{134}. As such, a 200 µl aliquot was also taken at each sampling interval for pH analysis. Experiments were designed such that the SA/V of the experiments would remain within 10 % of 2000 m\(^{-1}\) throughout dissolution, but later problems with the pH meter (see Section 2.8.3) meant the 464 d aliquots exceeded a SA/V of 2200 m\(^{-1}\). Mass loss remained within 15 % of the initial leachant volume after 464 d.

2.8.2. Equipment cleaning

Being made of PFA, the leaching vessels and aliquot sampling tubes could be cleaned to a high standard. All cleaning steps took place in a class 100 clean room, with the exception of the used leaching vessel pH and mass loss tests and the initial cleaning steps of the used leaching vessels. Firstly, PFA tubes were cut to 5 cm, with the ends cut flush so that the leachates could be dispensed into sample vials accurately. New PFA tubes were rinsed thrice with deionised water, heated to 90 °C whilst submerged in single distilled concentrated HCl for 48 h, dried at 90 °C, rinsed thrice with deionised water, heated to 90 °C whilst submerged in deionised water for 24 h then dried at 90 °C a final time. Where PFA tubes were reused, they were flushed with deionised water five times (thrice with a pipette and rinsed twice), rinsed with 50 % HNO\(_3\) thrice, heated to 90 °C whilst submerged in 50 % HNO\(_3\) for 48 h, rinsed thrice with deionised water, dried at 90 °C, heated to 90 °C whilst submerged in deionised water for 24 h then dried at 90 °C a final time.

New PFA leaching vessels (jars with lids and ferrule nuts) were rinsed thrice with deionised water, submerged in 50 % aqua regia at 90 °C for 24 h, rinsed thrice with deionised water, and then submerged in deionised water heated to 90 °C for 24 h. This entire procedure was then repeated using 50 % HNO\(_3\) instead of aqua regia before the leaching vessels were rinsed thrice with deionised water and assembled. A piece of acid cleaned PFA tubing held in place using ferrule nuts was used to connect and seal the fluid transfer ports and the empty leaching vessels were submerged fully in deionised water and checked for leaks before being dried at 90 °C.

Used leaching vessels were first cleaned under standard conditions. Vessels were wiped clean of any glass powder, rinsed thrice with deionised water, submerged in 1 % HNO\(_3\) at 90 °C for 1 h, rinsed thrice with deionised water, then filled with 1 % HNO\(_3\) and left to reflux at 90 °C for 14 d (new pieces of PFA tubing were used to seal the vessels, which were discarded after this step). The vessels were then rinsed thrice with deionised water, submerged in 1 % HNO\(_3\) for 24 h at 90 °C twice and then rinsed again. Vessels were transferred to the clean room where
they were filled with 50 % HNO$_3$ and refluxed at 90 °C for 21 d, before being rinsed, filled with deionised water and refluxed at 90 °C for 5 d, then disassembled and submerged in deionised water at 90 °C for 1 h then 16 h. Finally, vessels were reassembled and tested. Vessels were filled with 40 ml deionised water, which had its pH tested, then weighed. After 5 d at 90 °C, the vessels were weighed again to check for mass loss and the pH of the water was measured to ensure there was no significant change. The vessels were rinsed thrice then dried after the tests.

PP vials (0.5 and 1.5 ml) and pipette tips were cleaned by being submerged in 50 % HCl at 60 °C for 24 h, rinsed thrice in deionised water then dried. Care was taken to handle the vials and pipette tips using only plastic tweezers, which did not contact the insides of the vials or pipette tips, the lids of the vials or the ends of the pipette tips. Pipette tips used in aliquot sampling were not cleaned, as the aliquots would only contact the PFA tubing and not the tip.

### 2.8.3. Preparations and calibrations

Grant Instruments QBH2 and QBD2 dry block heaters with Al blocks cut to accommodate the PFA leaching vessels were preheated to either 40.0 ± 0.1 °C or 90.0 ± 0.1 °C 24 h before the experiments. The uniformity and stability of the heating blocks was also checked using an external thermocouple. An Ohaus Pioneer analytical balance and Sartorius MC1 Analytical AC 210s analytical balance were checked before and after each use using a 100.0000 ± 0.0002 g stainless steel OIML class E2 calibration weight. The former balance was used for weighing the leaching vessels and glass powders, whilst the latter balance was used for weighing sample vials and for calculating gravimetric dilution factors. Eppendorf Research Plus 10 to 100 µl and 500 to 5000 µl pipettes and an Eppendorf Research 100 to 1000 µl pipette were calibrated using the same procedure as in the Li-Mg-EM experiments (Section 2.5.2).

A Mettler Toledo F20 FiveEasy pH meter with an InLab Micro Pro-ISM pH electrode was calibrated at the start of each day and again after a few hours if required using buffer solutions which bracketed the analyte solution. Tests demonstrated that an aliquot of 200 µl was sufficient to cover this pH electrode and produce a reliable reading. When analysing the pH of the leachant or the 200 µl blank aliquots, 4.00 and 7.00 ± 0.01 NIST traceable buffer solutions were used to calibrate the pH meter. When analysing the pH of the 200 µl sample aliquots (6 h to 28 d intervals), 7.00 and 10.00 ± 0.01 pH NIST traceable buffer solutions were used. However, the micro pH electrode was not functioning for the 126 and 464 d aliquots, and instead the larger
LE438 pH electrode with the same pH meter was used. This electrode required 1.0 ml of leachate for analysis, and as such this large aliquot volume meant the 464 d experiments slightly exceeded a SA/V of 2200 m⁻¹.

2.8.4. **Beginning the experiments, taking aliquots and ending the experiments**

Experiments were started in a similar fashion to the Li-Mg-EM experiments following the ASTM PCT-B methodology. Sealed PFA leaching vessels (including the piece of PFA tubing used to seal the vessels) were first weighed whilst empty. The desired amount of MW25 powder (4.495 to 4.500 g) was weighed on weighing paper before being transferred into the leaching vessel, which was weighed again. The type one deionised water, aliquots of which had been pH tested prior, was pipetted into the leaching vessels (45.0 ± 0.2 ml), which were then weighed a final time and placed into the pre-heated blocks heaters with the starting time recorded. The 90 °C experiments were started first, followed by the 40 °C experiments an hour later to stagger the experiments.

Before each sampling interval, acid cleaned 1.5 ml vials were weighed whilst empty and after pipetting in 0.9 ml of double distilled 2 % HNO₃. Vials were then centrifuged (5424 microcentrifuge, Eppendorf) at 50 Hz for 3 min. Aliquots were taken from each leaching vessel after 0.25, 0.5, 7, 28, 126 and 464 d (± 2 %) from the beginning of the experiments. At the time of sampling, the ferrule nuts on the leaching vessels were loosened and ports were opened.

For the 100.0 ± 0.8 µl aliquots (for concentration and isotope ratio analyses), a piece of PFA tubing was attached to a 100 µl pipette tip and inserted through one of the ports just under the surface of the leachant. The 0.1 ml aliquot was then aspirated and dispensed directly into the sample vial containing 0.9 ml 2 % HNO₃. This procedure was repeated in triplicate, using a cleaned piece of tubing and new pipette tip for each aliquot. A 200.0 ± 1.6 µl aliquot (1.0 ml for the 126 and 464 d samplings) was taken for pH analysis in the same manner but with a 1 ml pipette tip attached to the tubing instead. The pH of the sample aliquots were measured first then the pH meter was recalibrated using different buffer solutions and the pH of the blanks were measured. After taking the pH aliquot, the fluid transfer ports were sealed fully, and this process was repeated for all leaching vessels. Once all aliquots had been taken, sample vials were mixed for 10 s using a benchtop mixer (FB15013 Topmix, Fisher Scientific) and centrifuged for 3 minutes at 50 Hz. Vials were then inspected to ensure no particles had been aspirated during aliquot taking before they were weighed to calculate a gravimetric dilution.
factor of approximately 10. Prior to analysis, vials were centrifuged and weighed again to ensure sample evaporation was negligible.

After the 28, 126 and 464 d aliquots had been taken, the leaching vessels were briefly removed from the heaters and weighed to ensure leachant mass loss due to evaporation was not excessive (remained within 15% after 464 d). Further, to provide leached samples for analysis, after the 464 d aliquots had been taken the leachant was entirely removed from one leaching vessel at each temperature and the glass powder was dried at 90 ± 2 °C over 16 h. The remaining leaching vessels were left indefinitely.

2.8.5. Leachate ICP-OES analysis conditions and data treatment

Based upon the leachate concentrations from the 70 and 80 °C MW25 static batch experiments, a stock calibration standard was fabricated by diluting a set of single element plasma standards using 2% HNO₃ assuming the leachates would be diluted by a factor of 100. Calibrations standards were produced from this stock through diluting it in series by factors of two, five or ten as required.

Samples at a gravimetric dilution factor of approximately 10 were further diluted by a factor of 10 (50 µl sample and 450 µl 2% HNO₃) to a final dilution factor of 100 for concentration analysis by ICP-OES (5100, Agilent). Blanks were not further diluted. The concentrations of the major constituent elements of MW25 within the leachates (Al, B, Ba, Ca, Cs, Li, Mg, Mo, Na, Si and Te) were measured. Multiple wavelengths were analysed for each element using both axial and radial viewing modes, with the initial exception of B, Ba, Ca and Te which were first analysed in axial mode alone. Calibration standards were analysed at the start of the run to create calibration curves for each element, with concentrations indistinguishable from blank concentrations being excluded from these curves.

To externally verify the accuracy of these calibrations, SPS-SW2 (Spectrapure Standards) at dilution factors of 1, 10 and 50 and undiluted SLRS-6 (CNRC-NRC) were analysed prior to the samples. From the coefficient of determination of each calibration curve and the percent recoveries of the standards, an optimal wavelength and viewing mode were selected for each element. Initially, 8 samples selected from the triplicates leached for 6 h and 28 d were analysed to ensure the sample concentrations fell within the range of the calibration standards. Samples were then analysed in chronological order, starting with the 40 °C 6 h leachates, in sets of five bracketed by acid blank measurements. SPS-SW2 at a dilution factor of 50 was analysed every...
ten samples to ensure there was no drift throughout analysis and demonstrated drift was less than 10% throughout all analyses. The blank leachates were analysed in one set after all samples had been analysed. Raw intensities were internally drift corrected and normalised throughout the run, then were used with the calibration curves to calculate concentrations using ICP Expert software. Whilst Ba and Cs were present in the ICP-OES calibration standards, it was noted the concentrations of Ba and Cs in many of the calibration standards were below their respective ICP-OES detection limits and as such calibration curves could not be plotted for these elements. Leachate concentrations were corrected and normalised following the methodology in Section 2.5.5. The corrected concentrations, $C_{\text{Sample}}$, of mobile elements within MW25 (B, Li, Mo and Na) at 6 h were then used with the $C_{\text{Sample}}$ obtained at 70 and 80 °C to create Arrhenius plots and calculate activation energies following the methodology outlined in Section 2.7.4.

2.9. Static batch sampling $^6\text{Li-Mg-EM}$ dissolution

2.9.1. Experimental overview

In addition to concentration analysis, the $^6\text{Li-Mg-EM}$ leachates would undergo isotopic analyses as part of the proof of concept experiments in Chapter 6 to investigate whether isotopic techniques could be used with the 40 and 90 °C MW25 leachates to elucidate the mechanisms of dissolution (Chapter 7). As a high degree of precision was required, the same static batch sampling methodology as in the 40 and 90 °C MW25 experiments (Section 2.8.1) was employed. As such, the same 60 ml PFA (Savillex) standard jars with fluid transfer closure lids (sealed with a piece of tubing) used in the MW25 experiments were used in the $^6\text{Li-Mg-EM}$ experiments.

An initial SA/V of 2034 ± 28 m$^{-1}$ was targeted (assuming spherical particles of a 112.5 µm diameter) using 4.000 ± 0.020 g of washed and sized $^6\text{Li-Mg-EM}$ powder with 42.5 ± 0.4 ml of type one deionised water (18.2 MΩ.cm at 25 °C). This was 2.5 ml less deionised water and 0.500 g less sample than in the MW25 static batch sampling experiments, but due to the significantly lower density of $^6\text{Li-Mg-EM}$ than MW25 it was necessary to deviate from a nominal V/m ratio of 10.0 ± 0.5 ml/g to achieve an initial SA/V ratio close to 2000 m$^{-1}$. As these were proof of concept experiments which would undergo isotopic analysis before the MW25 leachates, $^6\text{Li-Mg-EM}$ was leached in duplicate with duplicate blank vessels at 90.0 ± 0.1 °C to accelerate dissolution. At intervals of 0.25, 0.5, 7, 28 and 98 d (± 2 %), 100.0 ± 0.8 µl
Aliquots were taken in triplicate from each leaching vessel. However, after the 28 d aliquots had been taken, the leachant was removed from the one set of leaching vessels and replaced with fresh deionised water. After a total dissolution time of 98 d, the leaching experiments were ended. The pH of the deionised water was not buffered and was allowed to vary freely. However, due to the lower volume of leachant used than in the MW25 experiments, it would not have been possible to take aliquots for pH analysis without significantly disturbing the SA/V of the experiments. As such, pH measurements only took place after a total of 98 d and after 28 d in the leaching vessels where the leachant was refreshed. The geometric SA/V remained within 10 % of 2000 m$^{-1}$ throughout dissolution in both leaching vessels. Leachant mass loss remained within 5 % of the initial leachant volume throughout dissolution.

2.9.2. Equipment cleaning, preparations and calibrations
The four 60 ml PFA leaching vessels (standard jars with fluid transfer closure lids) had previously been used to contain dilute leachates (without any glass) as part of another set of experiments. The vessel cleaning procedure was therefore not as rigorous as that used in the MW25 experiments, wherein the vessels were either new or had been used to contain glass powders. Vessels were first cleaned following the same procedure as the PTFE liners (1 h in 1 % HNO$_3$ at 90 °C, deionised water rinse, 16 h in 1 % HNO$_3$ at 90 °C, deionised water rinse, repeat the whole procedure with deionised water instead of HNO$_3$) twice before being submerged in 50 % HCl at 90 °C for 24 h in a class 100 clean room and finally rinsed with deionised water. The leaching vessels were then assembled (including a piece of acid cleaned PFA tubing to seal the fluid transfer ports), filled with approximately 48 ml of deionised water and weighed. The vessels were heated to 90 °C for 24 h, before the vessels were weighed to ensure there was no significant mass loss and the pH of the deionised water was measured to ensure there was no significant change in pH (between 5.0 and 7.0). As a final test, the empty vessels were submerged in deionised water and inspected for any bubbles. Vessels were then rinsed thrice with deionised water, dried and bagged ready for use.

PP vials, pipette tips and PFA tubes were cleaned under class 100 clean room conditions. New PFA tubes which had been cut to 5 cm were cleaned following the same methodology as in the MW25 experiments (48 h in HCl at 90 °C, dried, rinsed thrice with deionised water, 24 h in deionised water 90 °C then finally dried). PP vials and pipette tips were cleaned for 24 h in HCl at 60 °C before being rinsed thrice with deionised water and dried.
The same apparatus and calibration methodologies as in the MW25 40 and 90 °C experiments were used (Section 2.8.4). Grants Instrument dry block heaters (QBH2 and QBD2) with Al blocks were preheated to 90.0 ± 0.1 °C 24 h prior to the experiments. Balances (Ohaus Pioneer analytical balance, Cole-Parmer Symmetry ECII-400 two decimal place balance and Sartorius MC1 Analytical AC 210s balance) were calibrated using the 100.0000 ± 0.0002 g stainless steel OIML class E2 calibration weight. Pipettes were calibrated following the same methodology as in the Li-Mg-EM experiments. A Mettler Toledo LE438 pH electrode with FE20 FiveEasy benchtop pH meter was calibrated using either 4.00 and 7.00 ± 0.01 NIST traceable buffer solutions for deionised water or blank measurements or 7.00 and 10.00 ± 0.01 NIST traceable buffer solutions for sample leachate measurements.

2.9.3. Beginning, refreshing and ending the experiments
Experiments were set up following the ASTM PCT-B methodology in the same manner as the MW25 40 and 90 °C experiments (Section 2.8.4). After weighing the empty leaching vessels, 4.000 ± 0.020 g of washed and sized Li-Mg-EM was weighed onto weighing paper then transferred into a leaching vessel, which was then weighed again. After pH testing the deionised water leachant, 42.5 ± 0.5 ml was added to each leaching vessel, which were then swirled to ensure full coverage of the powders and weighed once more. Vessels were then placed into the pre-heated heaters and the start time of the experiments was recorded.

At periods of 0.25, 0.5, 7, 28 and 98 d (± 2 %), 100.0 ± 0.8 µl aliquots were taken in triplicate from each leaching vessel using a piece of PFA tubing attached to a 100 µl pipette tip following the same methodology as in the MW25 experiments without a 200 µl pH aliquot (Section 2.8.4). The aliquots were dispensed into empty 1.5 ml PP vials and weighed. Once all aliquots were taken, the sampling time was recorded and the aliquots were diluted using 1.0 ml of double distilled 0.1 M HNO₃ and single distilled 0.3 M HF, mixed using a benchtop mixer (Fisher Scientific FB15013 Topmix), ultrasonically shaken for 15 min, inspected for solid precipitates and weighed again.

After the 28 d aliquots had been taken from all the leaching vessels and diluted, all the vessels were removed from heaters briefly and weighed one at a time. One set of leaching vessels (one sample vessel and one blank vessel) was then quickly returned to the heaters and leached for a total of 98 d. The leachants from the other set of leaching vessels was removed using a pipette and the mass of drained leachant was recorded. This leachant then underwent pH analysis in
triplicate. The glass powders were not dried and the leaching vessels were weighed after removing the leachant. Approximately the same volume of fresh deionised water (also pH tested) was then added to the leaching vessels which were then weighed again and returned to the heaters to leach for a further 70 d. After the 98 d aliquots (70 d in the refreshed leachant experiment) had been taken, the leaching vessels were all removed from the heaters and weighed to ensure the leachant mass loss was acceptable (less than 5%). The leachants were then drained and underwent pH analysis in triplicate. The leached glass powders were dried at 90 ± 2 °C for 24 h.

2.9.4. Leachate ICP-MS analysis conditions

The 0.1 ml aliquots diluted with 1.0 ml 0.1 M HNO₃ and 0.3 M HF in 1.5 ml PP vials were centrifuged (50 Hz for 3 minutes) before the samples were transferred to new 1.5 ml vials and centrifuged again. The mass of the empty vials was then recorded so that a gravimetric dilution factor (approximately 11) could be calculated for each aliquot. Using 0.5 ml PP vials, 20 µl of sample was diluted using 480 µl double distilled 0.1 M HNO₃ (volumetric dilution factor of 25), mixed and centrifuged. This procedure was then repeated once more for a total dilution factor of approximately 6250. Finally, 30 µl of sample was diluted using 270 µl double distilled 0.1 M HNO₃ and single distilled 0.3 M HF for a final dilution factor of approximately 62500. Samples were then mixed and centrifuged prior to analysis.

Leachates and blanks were analysed by ICP-MS (Element XR, Thermo Fisher Scientific) for isotopes of the constituent elements of ⁶Li-Mg-EM: ⁶Li, ⁷Li, ¹⁰B, ¹¹B, ²⁵Mg and ¹³⁹La being analysed at low resolution and ⁷Li, ¹¹B, ²³Na, ²⁵Mg, ²⁷Al and ²⁸Si analysed at medium resolution. A set of four multielement calibration standards containing 0.0, 0.5, 5.0 and 50.0 ng/ml B and Li and 0.00, 0.05, 0.50 and 5.00 ng/ml Al, La, Mg, Na and Si were analysed at the beginning and end of the analysis. Samples were analysed in sets of seven, starting with the blank leachates and then in chronological order (shortest duration first). Each set of samples or calibration standards was bracketed by two multielement standard measurements (5.0 ng/ml B and Li and 0.5 ng/ml Al, La, Mg, Na and Si) with each bracketing standard measurements being bracketed by two acid blank (double distilled 0.1 M HNO₃) measurements.

After blank correcting the raw intensities of the samples and standards using the bracketing acid blank measurements, the bracketing multielement standards were used to correct the measurements for instrumental drift and normalise the raw intensities of the leachates. The first
set of multielement calibration standards were then used to create linear calibration curves. All standards were assumed to contain isotopes at natural abundance and all isotopes in the leachates except $^6$Li and $^7$Li were assumed to be present at the same isotopic ratios as in the standards. As such, the counts measured for each non-Li isotope were considered representative of the sum of all isotopes for that element. For example, the counts measured for $^{11}$B in the 5.0 ng/ml standard were considered representative of 5.0 ng/ml B. Separate calibration curves for $^6$Li and $^7$Li were creating by weighting the total Li concentration assuming natural abundance; allowing the concentrations of $^6$Li and $^7$Li in the standards to be distinguished. Data were then treated and normalised elemental releases were calculated following the methodology in Section 2.5.5.

2.10. Post-dissolution analyses

2.10.1. XRD
XRD took place on powders selected from each triplicate for each Li-Mg-EM and Li-ISG composition leached at 40 and 90 °C for 112 d as well as MW25 leached at 40, 70, 80 and 90 °C for 28 d to investigate whether a detectable quantity of crystalline alteration products had formed after dissolution. As the 40 and 90 °C MW25 experiments were ongoing, solid samples at these temperatures were unavailable and instead samples leached in other experiments (under otherwise identical conditions as the 70 and 80 °C experiments described herein) were analysed\textsuperscript{145}. For the MW25 samples, 10 ± 1 mg of leached sample was weighed onto a low background plate. For the Li-Mg-EM and the Li-ISG samples, approximately 100 mg of sample was analysed on a low background plate. Leached samples then underwent the same acquisition methodology as the pristine samples, as given in Section 2.3.4.2.

2.10.2. EDS and SEM
BSE images were acquired and EDS spot analysis took place on one sample from each triplicate for MW25 leached at 70 and 80 °C and each Li-Mg-EM composition leached at 40 and 90 °C for each duration following the same methodology as the BSE imaging and EDS analysis of the pristine glasses outlined in Section 2.3.5.2.

As even a slight roughening of the glass surface after dissolution was of interest when acquiring SE images of the leached samples, samples were not coated prior to SEM imaging. Leached samples of $^6$Li-Mg-EM (refreshed and non-refreshed 98 d total dissolution at 90 °C), each Li-Mg-EM and Li-ISG composition at 40 and 90 °C and MW25 at 70 and 80 °C for each leaching
duration were imaged. Comparing samples leached for similar durations with each other demanded high resolution images were taken. SE images of the leached glasses were acquired under two conditions. Firstly, the same conditions as those used for the pristine glass SE images (Section 2.3.5) were used for the two leached $^6$Li-Mg-EM samples and all 90 °C Li-Mg-EM samples but the 7 d samples. As the features on the other samples were difficult to image under these conditions, SE images of the other leached samples were taken under conditions which had been found to be optimal for the leached samples through testing various conditions. These leached sample SE images were also taken on a FEI QEMSCAN 650F SEM, but images were acquired at high vacuum using a 3.0 kV accelerating voltage, a working distance of 4.0 mm and a spot size of 1.0 with an Everhart-Thornley detector (ETD). Images were acquired at horizontal fields widths ranging from 1.66 to 414 µm, with at least two sets of images acquired per sample.

2.10.3. NMR

2.10.3.1. $^6$Li, $^7$Li, $^{11}$B and $^{23}$Na MAS-NMR
Based upon the difficulties associated with the $^6$Li single-pulse Bloch decay experiments for the pristine Li-Mg-EM samples, post-dissolution $^6$Li MAS-NMR experiments only took place on the $^6$Li-Mg-EM samples which had been leached for a total of 98 d (without refreshing the leachant after 28 d). The same methodology as the pristine $^6$Li experiment was used, as given in Section 2.3.6.2.1, but with 880 mg of sample analysed and 52 Bloch decays accumulated per spectrum. Instead, $^7$Li single-pulse Bloch decay experiments took place on each Li-Mg-EM and Li-ISG composition leached at 40 and 90 °C for 112 d; the methodology of these experiments did not differ from that used for the pristine glasses given in Section 2.3.6.2.2. The longest leaching duration was chosen to assess whether there was a significant difference between the leached and pristine spectra.

As $^{11}$B and $^{23}$Na single-pulse Bloch decay experiments on the Li-Mg-EM compositions leached for 112 d at 90 °C demonstrated significant changes in the spectra occurred after dissolution, experiments took place on all Li-Mg-EM and Li-ISG compositions leached at 40 and 90 °C for all durations to further investigate these effects. Additionally, $^{11}$B experiments also took place on both $^6$Li-Mg-EM leached samples. The methodology of these experiments differed insignificantly from those of the pristine glasses, as given in Sections 2.3.6.2.3 and 2.3.6.2.4 for B and Na respectively. As two well-defined environments were noticeable in the 90 °C leached Li-Mg-EM $^{23}$Na MAS-NMR spectra, spectra were also acquired using a 30.0 s recycle delay and a 0.4 µs pulse length to demonstrate that the conditions used were non-saturating.
2.10.3.2. $^{6}$Li-$^{1}$H CP-NMR

Owing to the absence of protons in measurable quantity from the pristine glass network, $^{6}$Li-$^{1}$H CP-NMR experiments selectively probe Li in the alteration layers and secondary phases. Experiments took place on Li50Na50-Mg-EM and Li29Na71-ISG leached at 40 and 90 °C for 112 d, Li50Na50-Mg-EM leached at 40 and 90 °C for 7 d and $^{6}$Li-Mg-EM leached for 98 d at 90 °C (without refreshing the leachant). Pristine washed and sized Li50Na50-Mg-EM and washed and sized $^{6}$Li-Mg-EM were also analysed to ensure there was no measurable polarisation transferred from ambient proton absorption on to the surface of the glass. For the sake of comparison, additional single-pulse $^{6}$Li Bloch decay experiments also took place on the pristine and leached $^{6}$Li-Mg-EM samples to provide comparisons with the $^{6}$Li-$^{1}$H spectra.

$^{6}$Li-$^{1}$H CP-NMR experiments took place on the Varian Infinity Plus spectrometer operating at Larmor frequencies of 499.72 MHz and 73.54 MHz for $^{1}$H and $^{6}$Li respectively. A 7.5 mm DR MAS probe was used, with samples loaded into 7.5 mm silicon nitride rotors. Whilst 800 to 1200 mg of pristine and leached $^{6}$Li-Mg-EM were available to fill each rotor entirely, PTFE liners had to be placed into the rotors for the Li-Mg-EM and Li-ISG experiments as only 100 to 160 mg of pristine or leached sample was available. Static $^{6}$Li-$^{1}$H spectra were acquired for all samples, with $^{6}$Li-$^{1}$H CP MAS-NMR and $^{6}$Li MAS-NMR spectra also being acquired at a spin speed of approximately 4 kHz for the $^{6}$Li-Mg-EM samples. A $\frac{\pi}{2}$ pulse (8.0 µs) was found for $^{1}$H using RTV silicone and a recycle delay of 3.0 s was used. Powdered LiOH was used to optimise contact time and matching conditions. Spectra were acquired using 75000 to 250000 repetitions and were referenced to $^{6}$Li in 1.0 M $^{6}$LiCl (95.77% $^{6}$Li atoms) in type one deionised water at 0.0 ppm.

2.11. Pristine glass preparation for Li isotopic work

As MW25 would not digest fully using a HNO$_3$-HF mixture, it was decided that alkali fusion would be used to obtain the Li isotopic compositions of pristine $^{6}$Li-Mg-EM and MW25. Standards also underwent alkali fusion to investigate whether measurable isotopic fractionation was taking place. Further, standard addition was used to verify the accuracy and precision of the $^{6}$Li-spiked measurements. HF digests of these pristine glasses then served a confirmatory role, as it was extremely important that the pristine glass isotopic compositions were accurate.

2.11.1. Alkali fusion of pristine powders and standards

A previous study had successfully applied a K$_2$CO$_3$ fusion methodology to obtain the B isotopic
composition of tourmalines without measurable isotopic fractionation\textsuperscript{117}. As such, it was expected that this methodology could be adapted to investigate the Li isotopic compositions of waste glasses. Firstly, 50 mg of sample powder and 250 mg of K\textsubscript{2}CO\textsubscript{3} (Alfa Aesar Puratronic, 99.997 \%, Li below detection limit) were weighed (Ohaus Galaxy 110 analytical balance) into a 90 \% -Pt 10\%-Rh crucible with lid and were mixed well. The crucible was then either heated over a Bunsen burner or in a 950 °C furnace for 15 minutes. Every 5 minutes the crucible was swirled using a pair of tongs to ensure the sample was fully covered by the flux. After 15 minutes of heating, the crucible was cooled to room temperature over 5 minutes, 5 ml deionised water was pipetted into the crucible and the crucible was placed into an ultrasonic bath for 30 minutes. The supernatant was drained into an acid cleaned 15 ml PP tube. This process was repeated two more times for a total of 15 ml of fusion supernatant. After the final supernatant was drained, 5 ml of double distilled concentrated HCl was added to the crucible for 30 minutes, before this was drained and diluted with 10 ml deionised water in a 15 ml PP tube. The crucible was then cleaned in 50 \% HCl at 100 °C for 16 h. The fusion supernatants and residues were centrifuged at 67 Hz for 10 minutes. ICP-OES (5100, Agilent) was used to obtain the concentrations of elements within the fusion supernatants and residues.

\textbf{2.11.1.1. \textsuperscript{6}Li-Mg-EM and MW25}

To test the fusion methodology, a single K\textsubscript{2}CO\textsubscript{3} fusion took place on washed and sized MW25. The fusion supernatant and residue were analysed by ICP-OES at a dilution factor of 10 alongside SPS-SW2 and SLRS-6 at dilution factors of 1, 10 and 50 using the same methodology (see Section 2.8.5) and calibration standards as the 40 and 90 °C MW25 leachates. As with the previous MW25 analyses, many of the calibration standard concentrations were below the detection limits for Ba and Cs. Measured concentrations were corrected for the dilution factors and were converted to concentrations using the calibration curves. Acid blanks showed values which were below detection limits. This test run showed poor recoveries for elements such as Al, Ba, Mg and Si, which were likely present in the white gel phase in the supernatant. The slightly low B recovery (77.6 \%) was consistent with that reported for a basalt fused using this method (76 ± 4\%) without measurable B isotopic fractionation. Similarly, Li displayed a slightly low recovery (84.1 \%), although it was unknown whether this would effect isotopic fractionation.

To ensure the low B and Li recoveries were not a matrix effect, a set of calibration standards for ICP-OES analysis of the MW25 fusions were fabricated by diluting a set of single-element
plasma standards using the supernatant from a blank (no sample powder) fusion; where the 0 µg/ml standard was a blank fusion supernatant rather than acid. The MW25 fusion supernatant and residue were again analysed by ICP-OES following the same methodology as before, but only with SPS-SW2 at dilution factors of 1 and 25 and the samples were diluted by a factor of 25 to ensure they were contained well within the calibration standard concentrations. The B and Li recoveries of this second analysis agreed well with the first analysis and demonstrated this was not a matrix effect. Following the success of this MW25 test run, MW25 was alkali fused an additional four times. Fusion supernatants and residues were then analysed for concentrations using ICP-OES following the same methodology and K₂CO₃ blank bead matrix calibration standards as in the test fusion analysis. Concentrations were calculated for each element from the calibration curves after drift correcting and normalising the raw intensities. Concentrations were then blank corrected using the averages of the blank concentrations for each element measured throughout the run. Sample concentrations were then corrected for the dilution factor used and converted to a mass assuming there was exactly 15 ml of fusion supernatant or residue in total. Four full-procedure fusion replicates also took place on pristine washed and sized ⁶Li-Mg-EM powders following the same fusion procedure as the MW25 fusions. Based upon the MW25 fusion supernatant recoveries and the pristine composition of ⁶Li-Mg-EM, a set of ICP-OES calibration standards for the ⁶Li-Mg-EM supernatants was fabricated using single-element plasma standards and a blank fusion supernatant. ICP-OES analysis took place to obtain the concentrations of the constituent elements of ⁶Li-Mg-EM except La (Al, B, Li, Mg, Na and Si) within the fusion supernatants and residues following the same procedure as the MW25 fusions. Concentrations were then blank and dilution factor corrected.

2.1.1.2. BCR-1, BCR-2 and SGR-1b
To assess whether measurable isotopic fractionation was occurring during alkali fusion, BCR-1 and BCR-2 (United States Geological Survey) powders were alkali fused in duplicate following the same procedure as the sample powders. A set of ICP-OES calibration standards were fabricated based upon the nominal compositions of BCR-1 and BCR-2. Again, single-element plasma standards were diluted using a blank fusion supernatant and the 0.0 µg/ml standard consisted of the blank fusion supernatant. Fusion supernatants and residues were analysed using ICP-OES for elements at concentrations greater than 100 µg/g (except F) in BCR-1 and BCR-
Fabrication, dissolution and analytical methodologies

2 (Li, B, Na, Mg, Al, Si, P, K, Ca, Ti, V, Mn, Fe, Zn, Sr, Mo and Ba). Fusion supernatants and residues were analysed at dilution factors of 1 and 25 respectively alongside SPS-SW2 at dilution factors of 1 and 50. The residue concentrations were corrected for dilution factors before all concentrations were converted to a mass assuming exactly 15 ml of supernatant or residue. Acid blanks had concentrations below detection for all elements, so blank corrections were not necessary.

Although the SPS-SW2 recoveries were within 15% of their nominal compositions for most elements, it was noted the B and Li recoveries were poor and the recoveries of some elements were negligible. As such, the calibration standards were remade with lower concentrations and these negligible elements omitted to ensure this was not a matrix effect. ICP-OES analysis then took place again following the same methodology as the first run using the updated calibration standards but with SPS-SW2 at dilution factors of 25 and 50. However, the B and Li recoveries of the BCR supernatants were still poor (40 to 65%).

As BCR-1 and BCR-2 both contain low Li concentrations (12.9 and 9.44 µg/g respectively), alkali fusions also took place on SGR-1b (United State Geological Survey) which nominally contains 147 µg/g Li\(^{146}\). Firstly, SGR-1b underwent loss on ignition (LOI) through heating the SGR-1b powder in a furnace at 950 °C for over 24 h. To account for the change in the nominal composition of SGR-1b after LOI, a 31.25 % mass loss was assumed (nominal contents of organics within SGR-1b)\(^{146}\). Five full-procedure fusion replicates were acquired for SGR-1b. Based upon the elemental recoveries of the BCR fusion supernatants, a set of ICP-OES calibration standards was fabricated for analysis of the SGR-1b fusion supernatants and residues using single-element plasma standards and a blank fusion supernatant. Elements in SGR-1b at concentrations below 100 µg/g (except B), Zn and Zr were omitted from the standards (Al, B, Ca, Li, Mn, Na, P and Si). ICP-OES analysis of the SGR-1b fusion supernatants and residues took place at dilution factors of 1 and 10 respectively alongside SPS-SW2 at dilution factors of 1 and 10. Raw intensities were converted to concentrations using the calibration curves and were then blank and dilution factor corrected. Assuming there was 15 ml of supernatant or residue, the mass of each element in the supernatant or residue was calculated and divided by the nominal LOI composition of SGR-1b to obtain the recoveries.
2.11.1.3. Standard addition

As the Li isotopic signatures of the $^6$Li-Mg-EM supernatants and leachates significantly differed from that of the L-SVEC standard, standard addition took place through mixing standards with $^6$Li-Mg-EM powder at various fractions to verify the accuracy and precision of the $^6$Li-Mg-EM pristine glass and leachate $^7$Li$^6$Li MC-ICP-MS measurements$^{147}$. Two mixing lines were fabricated, each consisting of four mixes and two end members (Table 2.1): one of $^6$Li-Mg-EM powder mixed with SGR-1b LOI powder (total mass of powder kept constant at 50 mg, variable total Li contents) and one of $^6$Li-Mg-EM powder mixed with a liquid single-element Li plasma standard at a concentration of 9998 µg/ml (constant total Li contents).

Table 2.1.$^6$Li-Mg-EM with SGR-1b and $^4$Li-Mg-EM with single-element Li plasma standard mixing lines with the nominal isotopic signatures of each mixing line standard presented on the $\delta^{12}$Li and $\delta^{28}$Li scales.$^{148,149}$ The Li plasma standard was at a concentration of 9998 µg/ml and the concentration

<table>
<thead>
<tr>
<th>Target mg of glass</th>
<th>Target mg of SGR-1b</th>
<th>Nominal Li from glass (µg)</th>
<th>Nominal Li from SGR-1b (µg)</th>
<th>Nominal total Li (µg)</th>
<th>Fraction of Li from sample</th>
<th>Target $\delta^{12}$Li (%)</th>
<th>Target $\delta^{28}$Li (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.000</td>
<td>0.000</td>
<td>539.266</td>
<td>0.000</td>
<td>539.266</td>
<td>1.00</td>
<td>-916.5</td>
<td>-2483.1</td>
</tr>
<tr>
<td>38.252</td>
<td>11.748</td>
<td>412.555</td>
<td>2.512</td>
<td>415.067</td>
<td>0.99</td>
<td>-910.9</td>
<td>-2468.1</td>
</tr>
<tr>
<td>27.399</td>
<td>22.601</td>
<td>295.511</td>
<td>4.832</td>
<td>300.344</td>
<td>0.98</td>
<td>-901.7</td>
<td>-2446.6</td>
</tr>
<tr>
<td>16.547</td>
<td>33.453</td>
<td>178.468</td>
<td>7.153</td>
<td>185.621</td>
<td>0.96</td>
<td>-881.0</td>
<td>-2387.2</td>
</tr>
<tr>
<td>5.695</td>
<td>44.305</td>
<td>61.424</td>
<td>9.473</td>
<td>70.898</td>
<td>0.87</td>
<td>-793.4</td>
<td>-2150.7</td>
</tr>
<tr>
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<td>50.000</td>
<td>0.000</td>
<td>10.691</td>
<td>10.691</td>
<td>0.00</td>
<td>5.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Weighing took place into the crucible on a calibrated microbalance accurate to ± 0.02 mg (MX5, Mettler Toledo). Powders were mixed with 250 mg K$_2$CO$_3$ in the crucible, alkali fused and leached with deionised water following the same methodology as the glass powders and standards. For the end members (where no mixing was required) samples or standards were weighed on an Ohaus Galaxy 110 analytical balance. For mixtures of $^6$Li-Mg-EM powder and the liquid Li plasma standard, the required mass of $^6$Li-Mg-EM powder was first weighed into the crucible (MX5 Mettler Toledo) followed by 250 mg of K$_2$CO$_3$. After mixing the powders, the required volume of Li plasma standard was pipetted (Eppendorf Research Plus pipette) into
the crucible and heated to approximately 100 °C to dry down the mixture. Once dry, the powders were mixed well and were alkali fused. The Li concentrations of these standard addition fusions were analysed by ICP-OES (5100, Agilent) through a standard addition methodology\textsuperscript{150}: 0, 10 and 20 µl of a 999.8 µg/ml Li plasma standard (0.000, 9.998 and 19.996 µg Li respectively) were added to triplicates of each fusion supernatant, which were then analysed for only Li. The Li concentration (counts/s) measured in the sample was divided by the gradient of Li intensity against mass of added Li to obtain the mass of Li in the sample.

2.11.2. Acid digestion

As acid digestion is routinely used to obtain the Li isotopic compositions of solid samples\textsuperscript{120,124}, SGR-1b powder and pristine washed and sized MW25 and \textsuperscript{6}Li-Mg-EM powders were digested to confirm the accuracy of the Li isotopic compositions obtained through K\textsubscript{2}CO\textsubscript{3} fusion. Three acid cleaned 7 ml PFA (Savillex) vials were filled with 20 ± 1 mg SGR-1b, 15 ± 1 mg MW25 and 15 ± 1 mg \textsuperscript{6}Li-Mg-EM (Galaxy 110 Ohaus analytical balance). Powders were first digested in 0.7 ml single distilled concentrated HF and 0.5 ml double distilled concentrated HNO\textsubscript{3} at 150 °C for over 24 h. In this time, SGR-1b and \textsuperscript{6}Li-Mg-EM were noted to have dissolved completely, whilst some small colourless grains were present in the MW25 digest; these were expected to be spinel phases which contained negligible Li concentrations. The digests were then dried down at 90 °C, taken up in 1 ml double distilled concentrated aqua regia and heated to 150 °C for over 24 h. This step was then repeated twice more using double distilled 6 M HCl rather than aqua regia and the digested samples were left in a 6 M HCl matrix. After these final steps almost all of the MW25 had digested except for a small number of colourless grains.

2.12. Column chromatography and B sublimation

2.12.1. Titrations

Acid needed to be titrated to ensure it was of its target molarity for use on the columns. For the AG MP-50 columns, double distilled 0.7, 1.5 and 10.0 M HCl were calibrated using titrations with certified grade 1.0 M NaOH (Fisher Scientific) and a phenolphthalein indicator. For the AG 50W-X12 columns, single distilled 0.4 and 1.0 M HCL were calibrated using the same indicator but with certified 0.5 and 1.0 M certified grade NaOH respectively. Titrations took place in triplicate through pipetting NaOH in decreasing volumes into 10 ml of acid until the acid changed colour. The volume of added NaOH was recorded and the concentration of the diluted acid was calculated. Where the concentration was not equal to the target concentration to three decimal places, more acid or water was added to the batch as required.
2.12.2. Cleaning

PFA (Savillex) vials (30, 22, 15 and 7 ml) were used for digesting powders, drying down samples to be loaded onto the columns, drying down the Li and Mg cuts from the columns and sublimating leachates for B analysis. Vials which had contained samples which were not isotopically spiked and were going to be used for drying down samples or column elutions were first rinsed thrice with deionised water before being filled one third full with 50 % HNO₃ and heated to 90 °C for 24 h. This procedure was repeated four times in total, with single distilled 50 % HNO₃ being used on the third time and deionised water being used on the final time. Vials for B sublimation were cleaned in a similar manner but by submerging them in 50 % HCl for the first two steps and double distilled concentrated HCl being used for the third step. Where vials had contained isotopically enriched samples, they underwent the same procedure but first underwent an additional concentrated aqua regia step at 110 °C for 24 h, were fully submerged in 50 % HCl at 90 °C for 24 h twice, and then underwent an additional two 50 % HNO₃ steps. For sample digestions or containing the Mg fractions from the X12 columns, vials were filled half full with concentrated aqua regia at 100 °C for 24 h, single distilled concentrated HCl at 100 °C for 24 h and finally deionised water at 100 °C for 24 h before being dried. Pipette tips were cleaned by submerging them in reagent grade 50 % HCl for 24 h, single distilled 50 % HCl for 24 h and finally deionised water for 24 h at 100 °C.

2.12.3. AG MP-50 resin

2.12.3.1. Elution procedure and column calibration

Prior to Li or Mg isotope ratio analysis via MC-ICP-MS, it was necessary to purify the samples into monoelemental solutions to remove any potential mass biases or isobaric interferences which might arise from the sample matrix. Li and Mg were separated from the sample matrices using the macroporous cation exchange resin AG MP-50 (BioRad) in a one-step elution method. This resin afforded excellent separation of Li and Mg from Na for a variety of sample matrices through large differences in their distribution coefficients (ion concentration under equilibrium conditions per unit of mass of resin and per unit of volume of acid), which otherwise would require multiple column steps to separate if microporous gel-type resins were used. It should be noted that increasing the concentrations of elements loaded increases their elutions curve widths, reducing the separation of elements. The AG MP-50 column preparation and elution procedures presented in this section differed insignificantly from those presented in the original study, but any deviations from these procedures for each sample
Fabrication, dissolution and analytical methodologies

type are presented in their respective sections.

A set of twelve 3 ml PFA (Savillex) high aspect ratio (internal diameter of 4 mm and length of 250 mm) ion-exchange columns filled with AG MP-50 resin with 30 ml PFA reservoirs were used. Before each use, the columns were cleaned with at least four alternating pre-washes of at least 15 ml (five column volumes) of 10.0 M HCl and deionised water, ensuring the reservoir was properly rinsed with each wash. This cleaning step not only removed contaminants, but prevented the Na elution curve from building up and tailing into the collected Mg fraction. After pre-washing, the columns were backwashed using a 5 ml pipette tip, a hand-pump system and a PFA vial of deionised water, then the resin was left to settle. This step allowed the resin to expand fully before settling into a homogeneous pore distribution. The columns were then conditioned using 9 ml (three column volumes) of 0.7 M HCl.

Samples were prepared to yield a certain mass of Mg (300 ng for the ⁶Li-Mg-EM leachates) or Li (all other samples) in 200 µl 0.7 M HCl for loading onto the columns (as detailed in their respective sections). Prepared samples were loaded directly onto the resin and then eluted with a 9 ml 0.7 M HCl matrix elution in increments of 0.1, 0.2, 0.2, 0.5 and 8.0 ml as to not disturb the resin bed. A 15 or 30 ml PFA vial was then placed under each column and 13 ml 0.7 M HCl was pipetted into each column to elute Li. After collecting these Li fractions, the waste beakers were returned to under the columns and 19 ml 0.7 M HCl followed by 2 ml 1.5 M HCl were pipetted into each column to elute Na. After the Na elutions had passed, a 15 or 30 ml PFA vial was placed under each column and 13 ml 1.5 M HCl was pipetted into each column to elute Mg. This procedure was then repeated from the beginning until all samples had been passed through the columns. The eluted Li and Mg fractions were then dried down on a hotplate at 80 °C, taken up in 1 ml double distilled concentrated HNO₃, refluxed at 90 °C for 24 h, dried down at 80 °C and taken up in 0.5 or 1.0 ml 2 % HNO₃ for MC-ICP-MS analysis.

As the columns can effect significant isotopic fractionation due to the preferential partitioning of ⁶Li, it was important that the Li was entirely eluted within a single collected fraction. To check whether Li alone was eluting entirely within the correct volume, the columns were calibrated using IAPSO standard seawater; the high Na contents of this seawater (10770 µg/ml) compared to its Li contents (174 ng/ml) allowed for a robust test of the ability of the column to separate Li and Na. IAPSO seawater underwent a 10 fold dilution with 0.7 M HCl such that 200 µl of diluted seawater contained approximately 3.5 ng Li. This diluted seawater was loaded
onto a column then 23 ml 0.7 M HCl (the matrix elution and Li elution) was passed through the column 1 ml at a time, each 1 ml fraction being collected in a 1.5 ml PP vial. These collected fractions were then analysed for Li and Na by ICP-MS (Element XR, Thermo Fisher Scientific). Calibration standards ranged from 10.0 and 0.1 ng/ml Li and Na respectively down to 10.0 and 0.1 pg/ml Li and Na respectively (each calibration standard being an order of magnitude less than the one before it) alongside an acid blank (2 % HNO₃) 0.0 pg/ml standard. The column calibration demonstrated that Li was eluting entirely within the desired volume without significant concentrations of Na (Figure 2.3). Many of the calibration standard Na concentrations were below the detection limit and so the Na results are presented in counts/s alongside a line representing the counts/s measured for the 0.1 ng/ml Na standard.

![Figure 2.3: Concentrations of Li and counts/s of Na measured for the IAPSO standard seawater calibration of the AG MP-50 columns. The dotted line corresponds to the counts/s Na measured in the 0.1 ng/ml Na standard.](image)

### 2.12.3.2. ⁶Li-Mg-EM leachates (Li and Mg)

All ⁶Li-Mg-EM sample leachates underwent column chromatography to obtain both monoelemental Li and Mg fractions. First, using the ⁶Li-Mg-EM leachate concentrations obtained through ICP-MS analysis, the volume of each gravimetrically diluted ⁶Li-Mg-EM leachate required to yield 300 ng Mg were dried down at 80 °C in acid cleaned 15 ml PFA vials. Once dry, 1 ml double distilled concentrated HNO₃ was pipetted into each vial, which were then sealed and refluxed at 90 °C for 24 h. This oxidised any organic material in the samples and converted the Li and Mg to nitrate salts. Samples were again dried down at 80 °C, taken up in 200 µl 0.7 M HCl and then loaded onto the AG MP-50 columns. Li and Mg fractions were eluted from the columns and processed following the procedures given in Section 2.12.3.1, before being taken up in 0.5 ml 2 % HNO₃ for MC-ICP-MS analysis.

### 2.12.3.3. NGM (Li and Mg) and MW25 leachates (Li)

For the MW25 samples, the effects of the REEs, Al, Cr, Cs, Fe, Mo, Na and Ni on the Li and
Mg elutions as well as the largest mass of Li and smallest mass of Mg which could be successfully loaded onto the columns were tested. In particular, the effects of Cs on the Li elutions and Ni on the Mg elutions. A mock MW25 matrix, named the “nuclear glass matrix” (NGM), of the same elemental wt.% proportions as MW25 with Ce representing the REEs (Table 2.2) was fabricated from single-element plasma standards. The Li and Mg contents of NGM came from a 1000 µg/ml Aristar plasma standard and the Cambridge 1 standard respectively. The volumes of NGM required to yield 50, 150, 300 and 700 ng Mg (3, 8, 16 and 38 µl respectively rounded to the nearest µl) were diluted to 200 µl using 0.7 M HCl and then loaded onto the AG MP-50 columns alongside 200 µl 10-fold diluted (0.7 M HCl) IAPSO standard seawater (approximately 3.5 ng Li) in duplicate. The Li and Mg fractions were eluted following the procedure in Section 2.12.3.1 with the addition of three 1.0 ml single distilled 0.5 % HF elutions at the start of the run to elute Al. Further, 1 ml 0.7 N HCl elutions before (included within the 9 ml matrix elution) and after (included within the 19 ml Na elution) the Li fraction were collected in 1.5 ml PP vials as pre- and post-Li cuts to ensure Li was contained entirely within the Li fraction. The Li and Mg fractions were prepared and taken up in 1.0 ml 2 % HNO₃ for MC-ICP-MS analysis. The pre- and post-Li cuts, the Li fractions and the Mg fractions were also analysed for common contaminant concentrations (Na for Li and Al, Cr, Cs, Na and Ni for Mg) on the MC-ICP-MS alongside an acid blank.

Table 2.2: Composition of NGM and masses of elements in the volumes of NGM initially loaded onto the columns.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration in NGM (µg/ml)</th>
<th>Column 1 load (3 µL) (ng)</th>
<th>Column 2 load (8 µL) (ng)</th>
<th>Column 3 load (16 µL) (ng)</th>
<th>Column 4 load (38 µL) (ng)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>16</td>
<td>48</td>
<td>129</td>
<td>257</td>
<td>611</td>
</tr>
<tr>
<td>Ce</td>
<td>6</td>
<td>19</td>
<td>49</td>
<td>99</td>
<td>235</td>
</tr>
<tr>
<td>Cr</td>
<td>3</td>
<td>9</td>
<td>24</td>
<td>48</td>
<td>114</td>
</tr>
<tr>
<td>Cs</td>
<td>8</td>
<td>23</td>
<td>61</td>
<td>122</td>
<td>289</td>
</tr>
<tr>
<td>Fe</td>
<td>15</td>
<td>44</td>
<td>116</td>
<td>232</td>
<td>552</td>
</tr>
<tr>
<td>Li</td>
<td>13</td>
<td>39</td>
<td>104</td>
<td>208</td>
<td>494</td>
</tr>
<tr>
<td>Mg</td>
<td>19</td>
<td>56</td>
<td>149</td>
<td>298</td>
<td>707</td>
</tr>
<tr>
<td>Mo</td>
<td>6</td>
<td>19</td>
<td>51</td>
<td>103</td>
<td>244</td>
</tr>
<tr>
<td>Na</td>
<td>44</td>
<td>132</td>
<td>352</td>
<td>704</td>
<td>1672</td>
</tr>
<tr>
<td>Ni</td>
<td>3</td>
<td>8</td>
<td>21</td>
<td>42</td>
<td>100</td>
</tr>
</tbody>
</table>

In a second test to investigate the effects of these elements on low Li loads, IAPSO standard seawater was loaded onto the columns in triplicate (approximately 3 ng in 150 µl of 0.7 M HCl) alongside 192 µl of 500-fold diluted NGM in 0.7 M HCl (5 ng Li) in triplicate. Li cuts were eluted following the same procedure as the first NGM test but the three 0.5 % HF elutions were omitted and the Mg fractions were not eluted. The Li fractions were prepared for MC-ICP-MS.
analysis in 1.0 ml 2 % HNO₃ in the same manner as before.

For the 40 and 90 °C MW25 leachates, only one sample from each triplicate for each vessel for each duration and temperature was eluted through the columns for a Li fraction. Using the leachate concentrations from ICP-OES analysis, the volumes of gravimetrically diluted MW25 leachates required for 4 ng Li were pipetted into 0.5 ml PP vials and diluted to 200 µl using 0.7 M HCl. For highly concentrated samples, a 100-fold dilution with 0.7 M HCl was first required. The initial 2 % HNO₃ sample matrix was considered negligible. Based on the results of the MC-ICP-MS analyses of the NGM Li fractions (Section 7.2.1), alterations were made to the AG MP-50 elution procedure outlined in Section 2.12.3.1 for the MW25 leachates. Firstly, the Li fraction was increased from 13 to 15 ml 0.7 M HCl to ensure all the Li was collected within a single fraction. To account for this, the volume of the initial matrix elution was decreased from 9 to 7 ml 0.7 M HCl (increments of 0.1, 0.2, 0.2, 0.5 and 5.0 ml followed by a 1.0 ml pre-Li cut). Pre- and post-Li cuts were collected as 1 ml fractions in 1.5 ml PP vials before (as part of the 7 ml matrix elution) and after the 15 ml Li fraction was collected. No Mg fractions were collected. The 0.5 % HF elutions were not necessary for the MW25 leachates due to their negligible Al contents. For each set of six columns, four samples were loaded alongside 200 µl 10-fold diluted IAPSO standard seawater (approximately 3.5 ng Li) in duplicate to ensure the samples were not fractionating in the columns. Li fractions were processed (Section 2.12.3.1) and taken up in 1.0 ml 2 % HNO₃ for MC-ICP-MS analysis.

2.12.3.4. Alkali fusions, standard additions and HF digests (Li)

From their respective ICP-OES analyses, the volume of each MW25 (four), ⁶Li-Mg-EM (four), BCR-1 (two), BCR-2 (two) and SGR-1b (five) alkali fusion supernatant required to yield 4 ng Li was dried down at 80 °C in a 15 ml PFA vial. Due to their high Li contents, the MW25 and ⁶Li-Mg-EM supernatants were first diluted 100-fold with 2 % HNO₃. Once dry, 1 ml double distilled concentrated HNO₃ was pipetted into each vial, the vials were sealed and refluxed at 90 °C for 24 h and the samples were again dried at 80 °C before being taken up in 200 µl 0.7 M HCl. For MW25, ⁶Li-Mg-EM and the two BCR supernatants, four samples were loaded onto the columns at a time alongside two IAPSO standard seawaters. The five SGR-1b samples were loaded onto the columns without a seawater standard. Three 1 ml 0.5 % HF elutions then took place for the SGR-1b samples, but not for any other samples due to the poor Al recoveries in the supernatants. Pre- and post-Li cuts and Li fractions were then eluted following the same methodology as the MW25 leachates (2 ml larger Li fraction and 2 ml smaller matrix elution,
Section 2.12.3.3). Li fractions were prepared in 1.0 ml 2 % HNO₃ for MC-ICP-MS analysis following the same procedure as all other samples (Section 2.12.3.1).

The standard addition fusion supernatants (twelve samples from two mixing lines: ⁶Li-Mg-EM with a 9998 µg/ml Li plasma standard and ⁶Li-Mg-EM with SGR-1b) were prepared for and underwent column chromatography following the same methodology as the other alkali fusion supernatants without accompanying seawater standards. The twelve supernatants were first diluted between 1 and 100 times with 2 % HNO₃ depending on their Li contents before the volume of diluted supernatant required for 4 ng Li was prepared into 200 µl 0.7 M HCl. Samples were loaded onto the columns and three 1 ml 0.5 % HF elutions took place for all six ⁶Li-Mg-EM with SGR-1b supernatants, but not for the ⁶Li-Mg-EM with Li standard samples. Li fractions were prepared and taken up in 1 ml 2 % HNO₃ for MC-ICP-MS analysis.

The HF digests of ⁶Li-Mg-EM, MW25 and SGR-1b (single replicate of each) were present in a 6 M HCl matrix. As these digests had repeatedly been dried down refluxed already, the MW25, ⁶Li-Mg-EM and SGR-1b digests were diluted 1000, 1000 and 10 times respectively in 1.5 ml PP vials with 0.7 M HCl and then centrifuged (50 Hz, 3 minutes). The required volumes of each diluted digest for 4 ng Li (calculated using the masses of sample digested and the nominal compositions of MW25 and SGR-1b and the measured composition of ⁶Li-Mg-EM) were further diluted to 200 µl with 0.7 M HCl. The prepared ⁶Li-Mg-EM and MW25 digests in 0.7 M HCl were loaded onto the AG MP-50 columns in duplicate, each alongside the SGR-1b digest loaded in duplicate and IAPSO standard seawater (3.5 ng Li, diluted with 0.7 M HCl) in duplicate. The Li fractions and pre- and post-Li cuts were then eluted and collected following the same procedure as the alkali fusion supernatants and MW25 leachates, with three 1 ml 0.5 % HF elutions taking place for the SGR-1b digests but not for the MW25 or ⁶Li-Mg-EM digests. Li fractions were then prepared in 1 ml 2 % HNO₃ for MC-ICP-MS analysis.

As an additional test, the prepared samples (4 ng Li in 200 µl 0.7 M HCl) of the SGR-1b digest, SGR-1b fusion supernatant, the pure Li plasma standard (diluted from 9998 µg/ml with 0.7 M HCl as required), the Li plasma standard fusion supernatant and duplicate 10-fold diluted seawaters were loaded on to the columns and the Li fractions were collected following the same methodology as described for the alkali fusion supernatants. The Li fractions were processed using the same methodology as the other samples but were taken up in 200 µl 0.7 M HCl and underwent the same column procedure again. The second Li fractions were taken up in 1.0 ml.
2 % HNO₃ for MC-ICP-MS analysis.

2.12.3.5. **ICP-OES analysis of pre-Li, post-Li and Li cuts**

To assess whether there were contaminants within the Li cuts and ensure Li was entirely contained within the collected fraction for the $^6$Li-Mg-EM, MW25, BCR-1 and BCR-2 alkali fusion supernatant column cuts, these samples were analysed by ICP-OES (5100, Agilent). The pre-Li cuts, post-Li cuts and Li fractions were analysed at dilution factors of 1, 1 and 25 respectively. An alkali fusion supernatant of a known composition (from a previous ICP-OES analysis) for each sample type was diluted to create a series of ad-hoc calibration standards: one supernatant of each $^6$Li-Mg-EM, MW25 and BCR-2 were diluted 8000, 8000 and 2 times respectively with 0.7 M HCl to obtain the first standards, which were then 2-fold diluted twice with 0.7 M HCl to create a set of four standards for analysis (including a 0.7 M HCl acid blank). As this was a rough run to investigate whether there was any measurable contamination, no secondary standards were analysed.

2.12.4. **AG 50W-X12 resin and NGM (Mg)**

In addition to the NGM Mg tests on the AG MP-50 columns, the NGM matrix was passed through microporous gel-type resin AG 50W-X12 columns to test whether this resin would be more suitable to separate Mg from the MW25 leachate sample matrix. A CCS2 standard was loaded in triplicate (approximately 4500 ng Mg) alongside the volumes of NGM required for 750, 1500 and 3500 ng of Mg. Six 10 ml PP BioRad Poly-Prep chromatography columns with 50 ml reservoirs were filled with 1 ml of AG 50W-X12 microporous resin. The columns first underwent four pre-washes of 10 ml single distilled 6.0 M HCl then 10 ml deionised water, before they were conditioned with 10 ml 0.4 M HCl. Samples were dried down at 80 °C in PFA vials, taken up in 200 µl 0.4 M HCl, then loaded onto the columns in two steps of 100 µl followed by a 1.4 ml 0.4 M HCl elution in steps of 200, 200, 500 and 500 µl. For samples containing Al, Ti, Zr, Cr and Fe, 3 ml of 0.5 M HF was then eluted in six 500 µl steps. After which, 50 ml of 0.4 M HCl was eluted through the columns. After this had passed, 30 ml PFA vials were placed under the columns and a 15 ml 1.0 M HCl Mg fraction was eluted and collected. This Mg fraction was then dried down on the hotplate at 80 °C, taken up in 200 µl 0.4 M HCl and then underwent the same column procedure without the HF step. However, this time a 2 ml 6.0 M HCl elution was used to elute and collect Mg in a PFA vial. This final Mg fraction was then dried down at 80 °C and refluxed with 1 ml single distilled aqua regia at 125 °C for 16 h to create Mg salts. After this time, 0.5 ml of concentrated single distilled HNO₃
Fabrication, dissolution and analytical methodologies

was added, the sample was dried down at 80 °C and then taken up in 1.0 ml 2 % HNO₃ for MC-ICP-MS analysis.

2.12.5. B sublimation
B sublimation took place on all ⁶Li-Mg-EM leachates to create monoelemental B solutions for \(^{11}\)B/\(^{10}\)B MC-ICP-MS analysis. Either 30, 15 or 5 µl of gravimetrically diluted leachate was diluted with 100 µl double distilled 0.5 M HCl. The volume of each diluted leachate required to yield 50 ng B was pipetted onto the centre of the lid of a 7 ml PFA vial, which was sealed and placed onto a 99 °C hotplate for over 16 h whilst still inverted. This caused all the B to sublimate into the base (now top) of the 7 ml vial, whilst the matrix elements remained on the lid. After 16 h, the vials were quickly inverted, the lids were removed and 400 µl single distilled 0.5 % HF was pipetted into each vial. New lids were put on the vials to contain the samples.

2.13. MC-ICP-MS
2.13.1. Basic background to MC-ICP-MS
When determining concentrations with a single-detector ICP-MS, the absolute intensity of the ion current is of significant interest. Contrastingly, when determining isotope ratios, absolute intensities are of a lesser importance. The ability for a single-detector ICP-MS to determine isotope ratios is inhibited by uncertainties effected by instabilities in the transmission of the ion beam through the ion optics to the detector and the spread of the kinetic energy of the ions produced in the ICP source. Magnetic sector mass spectrometers use magnetic fields to separate ions along a focal plane to simultaneously measure the ion currents from different isotopes; essentially removing uncertainties from the ion source as all ions would be identically affected by these uncertainties such that they would have a negligible effect on determining isotope ratios. These spectrometers allowed for sufficient mass resolution alongside “flat-topped peak”. This allows for the entire ion image to be captured such that small changes in the positions of the ions in the focal plane do not cause changes in ion current intensities and the isotope ratios.

Variable multi-collector (MC) systems allow for detectors (usually Faraday cup detectors in MC-ICP-MS) to be positioned at a variety of positions across the focal plane with an excellent degree of precision. This allows for an array of isotope systems to be analysed with excellent resolution from interfering polyatomic or molecular ions. Using an ICP source with a variable MC system, however, is made challenging by the large spread of the kinetic energy of the ions from the plasma source. This is overcome using an electrostatic sector lens alongside the
magnetic sector in a double-focussed geometry, where the geometry is designed such that the energy dispersion of the electrostatic and magnetic sectors match to focus both ion energies and angles. For MC-ICP-MS, a Nier-Johnson double-focussing geometry is used, wherein the electrostatic sector lens precedes the magnetic sector\textsuperscript{144}.

In this arrangement, the ion beam from the plasma passes through the ion optics before entering the mass filters as described in Section 2.5.4.1. Two mass filters are then used: an electrostatic analyser (ESA, electrostatic sector) and a magnetic field (magnetic sector). The ion beam is first accelerated in the ion optics through an entrance slit into the ESA. The ESA is dispersive only with respect to energy (separates ions based on their kinetic energy) whilst focussing them into the magnetic sector. As such, the ESA and an intermediate slit between the electrostatic and magnetic sectors act as an energy filter for the magnetic field. The ion beam then passes through the magnetic field of the magnetic sector, which is dispersive with respect to both energy and mass. That is, in the magnetic sector, ions are separated by their mass to charge ratio as well as their kinetic energy along a focal plane. The dispersion of one sector is entirely corrected by the other such that ions of the same mass to charge ratio with differences in both kinetic energy and direction are focussed to one point. The magnetic sector focuses the separated ions into the zoom lenses and subsequently into the array of detectors, where the ion current of each isotope is simultaneously measured. This geometry affords excellent resolution of analyte ions from polyatomic or molecular interferences through combined energy filtering and mass separation\textsuperscript{143,144}.

The double-focussing geometry allows for the “flat-topped” peaks of the mass analyser to be retained despite using an ICP source. This spatial peak resolution is crucial to remove spectral interferences in high resolution measurements. This is accomplished through adjusting the width of the entrance slit such that there is an “interference-free space” between the focal plane and ion beams. The width of the slit is such that the detector opening is narrower than the separation between adjacent ion beams so that the peaks can be resolved. Instrumental mass bias effects during isotope ratio analysis, where the heavier isotope is preferentially transmitted due to space-charge effects and the expansion of ions in the skimmer and sampler cones respectively, are particularly important for lighter isotopes and can result in measured ratios deviating from their ‘true’ value by up to 25 % for Li. Further, sample matrix effects can also result in significant compositionally dependent mass bias effects\textsuperscript{144}. These effects are overcome
through purifying the sample into a monoelemental solution to match the matrix of a calibrating standard solution and using a concentration-matched sample-standard bracketing (SSB) methodology, wherein the sample isotope ratios are determined with respect to those of bracketing standard measurements\(^ {114,133,152}\).

### 2.13.2. Instrumentation and data treatment

Isotope ratio analysis (B, Li and Mg) of the prepared monoelemental solutions took place on a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific) in-house, using SSB to correct for mass bias effects and instrumental drift with peak centring during each standard measurement\(^ {114,133,152}\). A wash then a blank background measurement (2 % HNO\(_3\) for Li and Mg, 0.5 % HF for B) took place before and after each sample or standard measurement. Sample and standard isotopic measurements were first blank corrected using the average of the bracketing blank measurements. Blank corrected sample isotope ratios, \(R_{\text{Sample}}\) (heavier isotope, \(A\), to lighter isotope for that element, \(X\)), were converted to the δ scale (‰) using the average of the two blank corrected bracketing standard isotope ratios, \(R_{\text{Standard}}\), with Equation 2-15.

\[
\delta^{A}X_{\text{Sample}} = \left( \frac{R_{\text{Sample}}}{\frac{1}{2}(R_{\text{Standard}\,1} + R_{\text{Standard}\,2})} - 1 \right) \times 1000 \quad \text{Equation 2-15}
\]

It should be noted that the δ scale is not linear and as such would not yield linear mixing lines when comparing the isotopic signatures of significantly spiked and natural abundance samples\(^ {148}\). Instead, the δ’ scale may be used, which employs the natural log of the sample-standard ratio, as defined in Equation 2-16\(^ {149}\).

\[
\delta'^{A}X_{\text{Sample}} = \ln \left( \frac{R_{\text{Sample}}}{\frac{1}{2}(R_{\text{Standard}\,1} + R_{\text{Standard}\,2})} \right) \times 1000 \quad \text{Equation 2-16}
\]

Where samples were measured in duplicate or triplicate (Li or Mg), an average \(\delta^{A}X_{\text{Sample}}\) was calculated for each sample as the average of the sample measurements and one or two interpolated \(\delta^{A}X_{\text{Sample}}\) values calculated using a standard measurement taken between the two sample measurements and the average of its two bracketing sample measurements. In this case, errors (2σ) were calculated as twice the standard deviation of these sample and interpolated \(\delta^{A}X_{\text{Sample}}\) values. For all B MC-ICP-MS and some Li and Mg MC-ICP-MS samples, each prepared monoelemental solution was only measured once and so errors (2σ) were calculated using the RSD values of the sample and its bracketing standards with Equation 2-17.
\[ 2\sigma = 2\sqrt{(1000RSD_{\text{Sample}})^2 + \left(\frac{1000RSD_{\text{standard} 1} + 1000RSD_{\text{standard} 2}}{2}\right)^2} \]  

Equation 2-17

2.13.3. \(^{7}\text{Li}/^{6}\text{Li} \text{ MC-ICP-MS}

The prepared \(\text{Li}\) fractions of the \(^{6}\text{Li}\)-Mg-EM leachates were diluted to a concentration of 9 ng/ml in 1000 \(\mu\text{l}\) of 2 % HNO\(_3\) in 2 ml ICP vials. \(^{7}\text{Li}/^{6}\text{Li}\) analysis took place at low resolution with \(10^{11}\ \Omega\) amplifiers using L4 and H4 Faraday cups for \(^{6}\text{Li}\) and \(^{7}\text{Li}\) respectively. Samples were introduced using a quartz Apex-IR (ESI, US) sample introduction system with 140 °C spray chamber with 2 °C Peltier cooling coil. A Savillex PFA C-flow self-aspirating nebuliser at 100 \(\mu\text{l}/\text{min}\), a 1.8 mm Pt injector and Ni JET type and X type sampler and skimmer cones respectively were used. An RF power of 1200 W was used with the guard electrode on. Each leachate was measured in duplicate, with some leachates reanalysed at later times throughout the analysis to ensure the measurements remained reproducible. Measurements consisted of one block of 30 cycles with an integration time of 8.4 s and were taken with respect to and bracketed by NIST SRM 8545 L-SVEC\(^{132}\) at a concentration of 9 ng/ml using a SSB methodology\(^{114,133,152}\). After each standard or sample measurement, a wash then a 2 % HNO\(_3\) blank background measurement took place. \(\text{Li}7\)-N at a concentration of 9 ng/ml was analysed as a secondary standard at the beginning of each set of nine samples\(^{156}\). A \(\delta\)^{7}\text{Li} was calculated for each sample as the average of the duplicate sample measurements and an interpolated sample measurement, which could then be converted back to a \(^{7}\text{Li}/^{6}\text{Li}\) ratio assuming a \(^{7}\text{Li}/^{6}\text{Li}\) ratio of 12.330 for the L-SVEC standard\(^{132,133}\).

The \(\text{Li}\) fractions of the other samples were analysed under the same conditions as the \(^{6}\text{Li}\)-Mg-EM leachates with some minor alterations. Firstly, the \(\text{Li}\) fractions were analysed at lower concentrations so that the \(10^{13}\ \Omega\) amplifiers could be used. The low electronic noise of these amplifiers afforded significantly improved signal to noise ratios for the samples and a high degree of precision on the measured \(^{7}\text{Li}/^{6}\text{Li}\) ratios\(^{152}\). The MW25 leachate \(\text{Li}\) fractions were analysed in triplicate at 2.5 ng/ml for the 6 h to 126 d leachates and 1.0 ng/ml for the 464 d leachates. The \(\text{Li}\) fractions of the four MW25, four \(^{6}\text{Li}\)-Mg-EM, two BCR-1, two BCR-2 and twelve standard addition alkali fusions (mixing lines) were analysed in triplicate at either 0.7 or 2.5 ng/ml (former for \(^{6}\text{Li}\)-Mg-EM, latter for other fusions). The \(\text{Li}\) fractions of the five SGR-1b alkali fusion were analysed in duplicate at a \(\text{Li}\) concentration of 2.5 ng/ml. The HF digest \(\text{Li}\) fractions (one of each \(^{6}\text{Li}\)-Mg-EM, MW25 and SGR-1b digest run through the columns in duplicate, duplicate and quadruplicate respectively) were analysed in duplicate at 0.56 ng/ml.
The Li fractions of the NGM standards loaded at various Li loads were analysed in duplicate at 0.45 ng/ml and the NGM standards loaded as 5 ng Li were analysed in triplicate at 2.5 ng/ml. As the samples run through the columns twice were a test, they were analysed only once at a concentration of 2.5 ng/ml. In addition to Li7-N, Li6-N was also analysed throughout each analysis to assess external reproducibility. The concentrations of L-SVEC, Li7-N and Li6-N used in each analysis were adjusted to match 7Li concentration as the samples. A 5 µg/ml Ca wash took place after each sample or standard measurement and before each blank measurement to stop the Li blank background concentrations increasing during the analysis.

2.13.4. 11B/10B MC-ICP-MS
The sublimated 6Li-Mg-EM leachate B fractions (50 ng B in 0.5 % HF) were diluted to 10 ng/ml in 600 µl using single distilled 0.5 % HF in 2 ml ICP vials. Samples were analysed using a Savillex PFA C-flow self-aspirating nebuliser at 50µl/min, Savillex PFA single-pass Scott-type spray chamber, 1.8 mm Pt injector and Pt JET type and X type sampler and skimmer cones respectively. The guard electrode was on and an RF power of 1350 W was used. 11B/10B analysis took place at low resolution using L3 and H3 Faraday cups for 10B and 11B respectively with 10^13 Ω amplifiers. Samples were measured once with respect to NIST SRM 951 at 10 ng/ml using a SSB methodology, with each measurement bracketed by a wash and 0.5 % HF blank measurement. Measurements consisted of one block of 30 cycles with an integration time of 8.4 s. ERM-AE121 at 10 ng/ml was analysed as a secondary standard before and after each set of five sample measurements. Calculated δ11B values could be converted back to a 11B/10B ratio assuming a 11B/10B ratio of 4.0436 for NIST SRM 951.

2.13.5. Mg isotope MC-ICP-MS
Mg fractions of the 6Li-Mg-EM leachates from the AG MP-50 columns and the NGM from both AG MP-50 and AG 50W-X12 columns were diluted to 250 and 200 ng/ml respectively in 500 µl of 2 % HNO3; where the leachates were too dilute, samples were not analysed. A Savillex PFA C-flow self-aspirating nebuliser at 50 µl/min, single-pass Scott-type PFA spray chamber, 1.8 mm Pt injector, Pt Jet type sample cone, and Pt X type skimmer cone were used. An RF power of 1300 or 1200 W was used for the 6Li-Mg-EM leachates and NGM standards respectively and the guard electrode was on. The ratios of 24Mg, 25Mg and 26Mg were measured using the L1, C and H1 Faraday cups respectively in wet plasma conditions at medium resolution with 10^11 Ω amplifiers. Fractions from the AG MP-50 and AG 50W-X12 columns were measured in duplicate consisting of one block of 25 cycles and triplicate consisting of one
Fabrication, dissolution and analytical methodologies

A block of 36 cycles (30 cycles for bracketing standard measurements) respectively, both with an integration time of 8.4 s. Samples were measured with respect to DSM-3 at 250 and 200 ng/ml for the $^6$Li-Mg-EM and NGM samples respectively using a SSB methodology\(^{155}\). Cambridge 1 was analysed as a secondary standard at 250 ng/ml before and after each set of five $^6$Li-Mg-EM leachates and at 200 ng/ml at the start of the run for the NGM samples\(^{155}\). Average $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ (both relative to $^{24}\text{Mg}$) were then calculated for each sample.

2.13.6. $^{11}\text{B}/^{10}\text{B}$ LA-MC-ICP-MS

Pristine, polished (diamond pastes down to 3 µm) $^6$Li-Mg-EM and MW25 pieces mounted in two-part epoxy resin were sent to the University of Western Australia as part of a collaboration to undergo $^{11}\text{B}/^{10}\text{B}$ LA-MC-ICP-MS. Laser ablation took place using a Coherent COMPexPro 110 Excimer laser ablation system with 193 nm ArF laser and large 2-volume sample cell connected to a Neptune Plus (Thermo Fisher Scientific) MC-ICP-MS. Spot analysis took place by ablating four sets of three 30 by 30 µm squares from different locations on the three pieces of $^6$Li-Mg-EM and two sets of ten 30 by 30 µm squares from different locations on the two pieces of MW25. Squares were ablated at a rate of 5 Hz and a fluence of 3 Jcm\(^{-2}\) with 10 pre-ablation pulses to remove surface contamination for a run time of approximately 41 s per square. For the NIST 610 standard, 70 by 70 µm squares were ablated from different locations and analysed only for their relative ratios with a run time of approximately 120 s per square. Measurements took place at low resolution using $10^{11}$ Ω amplifiers with the L4 and H4 Faraday cups for $^{10}\text{B}$ and $^{11}\text{B}$ respectively. $^{11}\text{B}/^{10}\text{B}$ ratios were acquired with respect to NIST 610\(^{159,160}\) using a SSB technique\(^{161}\). Measurements were blank corrected using bracketing gas blank background concentrations. Each corrected sample $^{11}\text{B}/^{10}\text{B}$ ratio was converted to a $\delta^{11}\text{B}$ value using the average bracketing NIST 610 standard measurements, which could be converted back to a $^{11}\text{B}/^{10}\text{B}$ ratio assuming a $^{11}\text{B}/^{10}\text{B}$ ratio of 4.049 for the NIST SRM 610 standard\(^{160}\).
3. Impacts of lithium on analogues of a Magnox waste glass.

The majority of the work presented in this chapter has been published in the Journal of Non-Crystalline Solids\textsuperscript{162}. The text has been modified for use in this dissertation.

3.1. Introduction to the Li-Mg-EM compositions

The six-component simplified analogue of MW25, Mg-EM (Table 3.1), was formulated such that the molar ratios of Al, B, Mg, Na and Si in Mg-EM and MW25 would be the same\textsuperscript{46,89}, where La in Mg-EM represented the REEs of MW25 on a charge-for-charge basis. Structural investigations and dissolution experiments demonstrated Mg-EM was an excellent analogue of MW25\textsuperscript{46,89}, despite Li being absent from the Mg-EM composition.

Li has been shown to leach from the French complex simulant waste glass, SON68, with a smooth interdiffusion profile which precedes the sharper dissolution fronts of alkalis which preferentially modify the B network, such as Na\textsuperscript{38}. It is therefore expected that, partially also owing to Li’s small ionic radius and hypothetical easier diffusion out of the hydrated glass structure, that the dissolution behaviour of Li differs from other alkali metals\textsuperscript{37,38}. Further, the presence of Li in the glass composition at an equal proportion to Na is expected to affect wasteform aqueous durability in ways which could be difficult to replicate in a single alkali-metal composition\textsuperscript{16}; optimising many transport related properties of the glass by affecting the connectivity of alkali ion channels. Therefore, owing to Li’s seemingly unique dissolution behaviour, Li’s potentially important role within the glass and the potential for a Li-Na mixed alkali effect, it was concluded that a simplified analogue of a Li-containing complex nuclear waste glass should also contain Li as to better replicate its’ aqueous dissolution mechanisms.

As discussed in Chapter 1, in many vitrification campaigns a target Magnox waste loading of 25wt.% was used\textsuperscript{8,15,163}. As the final Li contents of the vitrified wasteform is split equally during vitrification between LiNO\textsubscript{3} added to the calciner and the MW base glass frit\textsuperscript{8,11,20}, this resulted in some vitrified products containing excess Li concentrations\textsuperscript{16,19}. A previous study demonstrated that the addition of Li to MW25 had a significant negative impact on aqueous durability\textsuperscript{16}. However, in this study Li was added to MW25, which convoluted the effects of Li on aqueous durability through increasing the total alkali metal concentration and decreasing the concentrations of elements beneficial to aqueous durability (such as Al and Si) within the pristine glass. As simulant MW25 pours took place on a full-scale inactive replica of the vitrification process\textsuperscript{8,18}, Li could not simply be substituted for another element in MW25 during
In the work presented in this chapter, two Li-containing seven-component analogues of MW25 were fabricated and leached in deionised water. To isolate the effects of Li on aqueous durability, rather than being added to the glass composition Li was instead substituted in place of Na on an atom for atom basis. Additionally, experiments took place at both 40 and 90 °C to investigate whether these effects occurred consistently at both a theoretical GDF temperature and an accelerated dissolution temperature respectively.

A Mg-EM composition in which half the elemental molar Na had been replaced with Li to yield a molar Li:Na ratio of 1.00, referred to as Li50Na50-Mg-EM (Table 3.1), was fabricated and leached with the aim of providing a Li-containing simplified analogue to represent the structure and dissolution behaviour of MW25. Mg-EM was chosen as the starting composition as it contained elemental ratios based upon MW25 and by varying only the Li:Na ratio, the total alkali metal to elemental ratios and other elemental ratios of Li50Na50-Mg-EM remained equal to those of Mg-EM. As such, differences in dissolution behaviour between Li50Na50-Mg-EM and Mg-EM could only be attributed to the presence of Li. An equimolar Li:Na ratio was chosen not only to optimise transport-related glass properties in Mg-EM, but also to replicate the Li:Na ratio of MW25 (1.01). In addition to Li50Na50-Mg-EM, an analogue of Mg-EM with a Li:Na ratio of 1.50, referred to as Li60Na40-Mg-EM (Table 3.1), was fabricated and leached with the aim of investigating the effects of an excess Li concentration on MW25. Again, differences in glass structure and dissolution behaviour between Li60Na40- and Li50Na50-Mg-EM could only be attributed to Li and deviating from an equimolar Li:Na ratio; providing a better understanding of Li’s impact on aqueous durability and Li’s role within the analogues, which could then be extended to MW25. Two batches of each Li-Mg-EM composition were fabricated as to produce enough glass for the experiments.

Table 3.1: Nominal cation atomic percent (at.%) compositions of Li50Na50-Mg-EM and Li60Na40-Mg-EM compared with Mg-EM.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mg-EM</th>
<th>Li50Na50</th>
<th>Li60Na40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>4.87</td>
<td>4.87</td>
<td>4.87</td>
</tr>
<tr>
<td>B</td>
<td>27.58</td>
<td>27.58</td>
<td>27.58</td>
</tr>
<tr>
<td>La</td>
<td>1.72</td>
<td>1.72</td>
<td>1.72</td>
</tr>
<tr>
<td>Li</td>
<td>0.00</td>
<td>7.69</td>
<td>9.23</td>
</tr>
<tr>
<td>Mg</td>
<td>6.54</td>
<td>6.54</td>
<td>6.54</td>
</tr>
<tr>
<td>Na</td>
<td>15.38</td>
<td>7.69</td>
<td>6.15</td>
</tr>
<tr>
<td>Si</td>
<td>43.91</td>
<td>43.91</td>
<td>43.91</td>
</tr>
</tbody>
</table>
Impacts of lithium on analogues of a Magnox waste glass.

3.2. Pristine Li-Mg-EM characterisation

3.2.1. The formation of cristobalite in Li-Mg-EM

3.2.1.1. XRD

After the first pour of each Li-Mg-EM batch, it was noted in each batch was a small opaque white crystallite within an optically clear glass matrix. However, after the second pour and annealing of each batch it was noted all batches appeared optically clear and vitreous. In order to ensure that the four fabricated Li-Mg-EM batches were amorphous, XRD analysis took place on the glass fines (<75 µm) which had been decontaminated of magnetic particles. The spectra of all four batches exhibited the main characteristic peak of synthetic α-cristobalite at approximately 22.3 ° (2θ) (ICDD card [082-1408]) (Figure 3.1a). As such, washed and sized fractions (75 to 150 µm) of each batch were subsequently analysed by XRD alongside some crushed and sieved ISG (supplied by Savannah River National Laboratory, US). All washed and sized batches except Li50Na50-Mg-EM-1, which had the most crystalline fines, were shown to be amorphous (Figure 3.1b). However, the crystallinity of Li50Na50-Mg-EM-1 was less than that found in ISG and reanalysing a different Li50Na50-Mg-EM-1 washed and sized sample demonstrated it was amorphous. As it was the washed and sized fraction that would be leached, the crystallinity in the fines was not considered to significantly impact the results of the dissolution experiments and the crystallinity of Li50Na50-Mg-EM-1 was considered negligible.

Figure 3.1: XRD spectra of the fines of the four Li-Mg-EM batches (a) and the washed and sized fractions of the four Li-Mg-EM batches presented alongside crushed International Simple Glass (background corrected) (b). “C” corresponds to the characteristic peaks of synthetic α-cristobalite (ICDD card [082-1408]). The number suffix on the sample name denotes the batch number. Analysis in (a) took place on a low-background plate with weighed fines, analysis in (b) did not.

3.2.1.2. $^{29}$Si MAS-NMR

$^{29}$Si MAS-NMR experiments took place to attempt to quantify the crystallinity of the fines of Li50Na50-Mg-EM-1 and Li60Na40-Mg-EM-1, as well as compare the degree of polymerisation of the Si network of the two analogue compositions. Firstly, spectra were acquired for the fines of a Li-Na borosilicate MW base glass frit with and without the addition
of 1 wt.% powdered cristobalite (fabricated by heating SiO$_2$ powder to 1470 °C for over 24 h$^{164-166}$); where the MW base glass fines had been shown to be amorphous through XRD. In addition to the amorphous curve representing the Si environments of the glass, a peak was clearly visible at approximately -109 ppm in the 1 wt.% mixture spectrum (Figure 3.2a) which represents cristobalite$^{164}$. As it was shown using the MW base glass that 1 wt.% cristobalite could be detected through $^{29}$Si MAS-NMR, the absence of a cristobalite peak from the Li-Mg-EM spectra (Figure 3.2b) suggested there was less than 1 wt.% cristobalite in the fines; supporting the conclusion that any crystallinity in the washed and sized fraction of Li50Na50-Mg-EM-1 was negligible. However, it was noted the Li-Mg-EM spectra were noisy and it remains possible that the 1 wt.% cristobalite peak was smaller than the noise.

Figure 3.2: $^{29}$Si MAS-NMR spectra of: the full-Li MW base glass fines (Cyan) and the full-Li MW base glass fines mixed with 1 wt.% cristobalite (Magenta) (a); Li50Na50-Mg-EM-1 fines (Cyan) and Li60Na40-Mg-EM-1 fines (Magenta) (b). Spectra were normalised to the same intensity.

A more negative chemical shift in the $^{29}$Si spectra of alkali silicate glasses corresponds to a higher degree of polymerisation (higher n for Q$^n$) of the Si network$^{58,167-169}$. However, in alkali borosilicates this effect is convoluted by the presence of IVB units as second-neighbours to Si resulting in a more positive chemical shift. This effect stems from Si(Q$^4$) species with two IVB units as second nearest neighbours having a similar charge distribution to Si(Q$^3$) species$^{170}$, with contributions at approximately -100 ppm consisting of Si(Q$^4$) and Si(Q$^4$)-III-B units whilst the contributions at approximately -90 ppm consist of Si(Q$^3$) and Si(Q$^4$)-IVB units$^{168,170}$. Notably, the MW base glass spectrum appeared symmetrical around -100 ppm, whilst the asymmetrical Li-Mg-EM spectra peaked at a more negative chemical shift of approximately -105 ppm. When interpreting these shifts it should be considered that the MW base glass and Li-Mg-EM compositions have similar nominal Si:B ratios (1.63 and 1.59 respectively) and measured IVB concentrations within error of one another (see Section 3.4.2.3). Therefore, this suggests the Si networks of the Li-Mg-EM compositions indeed have a higher degree of polymerisation (fewer lower n for Q$^n$ species) than the MW base glass. The similarity of the Li-
Impacts of lithium on analogues of a Magnox waste glass.

3.2.1.3. EDS
The presence of cristobalite in the glass fines but not in the washed and sized fractions suggested that cristobalite was easier to crush in the mortar and pestle than the amorphous phase. As such, it was possible that there could be a slight deficiency of Si in the washed and sized fraction and an enrichment in the fines. Qualitative EDS analysis therefore took place to compare the Si contents of the fines and the washed and sized fractions of all Li-Mg-EM batches through comparing their Si:Elemental ratios. For comparison, the fines and washed and sized fractions of both MW base glass compositions were also analysed. This analysis demonstrated no measurable Si enrichment took place in the fines, likely due to the low crystallinity of the fines as shown by the $^{29}$Si MAS-NMR spectra. This conclusion was later supported through the compositions obtained from EPMA and from acid digestion then ICP-OES analysis being in good agreement (see Section 3.2.3).

3.2.1.4. Investigating and preventing cristobalite formation
Six tests took place to find the source of the cristobalite and ensure future glass pours were amorphous, with the resulting powders analysed by XRD to compare the amounts of resulting cristobalite. As devitrification was not reported to have occurred whilst fabricating Mg-EM, it was expected either the presence of Li in the glass composition, the precursors used or the preparation of the precursors was promoting the formation of cristobalite; with a likely cause being moisture adsorbed onto the surface of the 1 µm particle size SiO$_2$ powder precursor potentially accelerating crystallisation. Test one consisted of remelting some full-Li MW base glass frit using the same heating procedure as the Li-Mg-EM glasses to confirm the procedure itself was not responsible for cristobalite formation. Test two took place on the fines of Li$_6$Na$_{40}$-Mg-EM-1 to see if changing the heating procedure (heating at 5 °C/min to 650 °C, dwelling for 2.5 h, heating to 1300 °C and then water quenching) could remove the already-formed cristobalite from the glass, but demonstrated it could not.

The results from Test one confirmed the problem lied in the precursors used for the experiments and their preparation. After demonstrating the 1 µm SiO$_2$ precursor used in the fabrication of all compositions was amorphous, Test three involved drying the SiO$_2$ precursor powder at 120 °C for 2 h before undergoing the same heating procedure as in Test two. For comparison, Test four involved heating the same SiO$_2$ precursor using the same heating procedure as the Li-
Impacts of lithium on analogues of a Magnox waste glass.

Mg-EM glasses without any prior drying and Test five used the same methodology as Test four but with a different SiO₂ precursor of a larger particle size. Finally, Test six involved the same methodology as Test three, but with a higher drying temperature of 250 °C. The results of these tests are summarised in Figure 3.3. These XRD spectra demonstrated that the cristobalite formed due to a combination of both the drying and glass pouring procedures, rather than strictly depending upon the particle size of SiO₂ used. Whilst drying at 120 °C and water quenching the glass once it reached 1300 °C rather than pouring it at 1500 °C significantly reduced the amount of cristobalite formed (Test three compared to Test four), further increasing the drying temperature to 250 °C almost entirely prevented the formation of cristobalite (Test six compared to Test three). Therefore, when making the Li-ISG batches a higher precursor drying temperature was employed and the glass was water quenched rather than poured.

![XRD spectra](image)

Figure 3.3: XRD spectra of the resulting powders from cristobalite tests three to six. “C” corresponds to the characteristic peaks of synthetic α-cristobalite (ICDD card [082-1408]).

### 3.2.2. Geometric analyses

#### 3.2.2.1. Laser diffraction analysis

The median particle sizes of all Li-Mg-EM batches appeared internally consistent (Table 3.2). Whilst being higher than the geometric mean of 112.5 μm, this is likely due to the presence of needle-like particles passing through the 150 μm sieve and demonstrated the sieving and washing procedures worked as intended. Particle size distributions appeared uniform.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Li₅₀Na₅₀-Mg-EM-1</th>
<th>Li₅₀Na₅₀-Mg-EM-2</th>
<th>Li₆₀Na₄₀-Mg-EM-1</th>
<th>Li₆₀Na₄₀-Mg-EM-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median</td>
<td>129.1</td>
<td>132.1</td>
<td>134.7</td>
<td>140.1</td>
</tr>
<tr>
<td>D[v, 0.9]</td>
<td>202.1</td>
<td>216.9</td>
<td>206.3</td>
<td>225.3</td>
</tr>
<tr>
<td>D[v, 0.1]</td>
<td>76.9</td>
<td>73.1</td>
<td>79.7</td>
<td>86.4</td>
</tr>
</tbody>
</table>

Table 3.2: Measured particle size distributions of the four Li-Mg-EM batches.
3.2.2.2. BET analysis

The BET surface areas varied considerably between batches and a positive BET surface area could not be calculated for Li60Na40-Mg-EM-1 (Table 3.3). As the particle sizes for the batches appeared consistent and they were prepared in the exact same manner, this was attributed to the low surface areas of all the Li-Mg-EM batches. Using a larger sample mass with Kr adsorption rather than N2 potentially could have improved the results, but the amount of washed and sized sample available was severely limited and a Kr pressure regulator was not available at the time of analysis.

Table 3.3: Measured BET surface areas of the four Li-Mg-EM batches with their linear correlation coefficients.

<table>
<thead>
<tr>
<th>Li50Na50-Mg-EM</th>
<th>Li60Na40-Mg-EM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch 1</td>
<td>Batch 2</td>
</tr>
<tr>
<td>BET surface area</td>
<td>0.025 ± 0.002 m²/g</td>
</tr>
<tr>
<td>Correlation Coefficient</td>
<td>0.980</td>
</tr>
</tbody>
</table>

The BET surface areas were similar to the geometric mean surface area of 0.021 m²/g (assuming a spherical particle with a diameter of 112.5 µm and glass density of 2.50 g/cm³) and were an order of magnitude lower than those reported for Mg-EM (also prepared at a 75 to 150 µm size fraction) at 0.21 m²/g.89 This discrepancy between Mg-EM and Li-Mg-EM could be attributed to Mg-EM being washed using a combination of deionised water and absolute ethanol, whilst the Li-Mg-EM glasses were washed using only absolute ethanol; demonstrating that washing the glass powders in water results in significant roughening of the glass surface prior to the dissolution experiments and as such should be avoided.

3.2.2.3. Density characterisation

Densities were highly consistent across all batches, with an average density of 2.52 g/cm³ observed for both Li50Na50-Mg-EM and Li60Na40-Mg-EM (Table 3.4). The minor discrepancy between the two batches of Li60Na40-Mg-EM was considered to be negligible. The densities showed no measurable change with variations in the Li:Na ratio, with all densities except Li60Na40-Mg-EM-1 being within error of Mg-EM at 2.49 ± 0.01 g/cm³.

Table 3.4: Measured densities of the Li-Mg-EM batches. Errors are given to 1σ calculated from the triplicate measurements.

<table>
<thead>
<tr>
<th>Li50Na50-Mg-EM-1</th>
<th>Li50Na50-Mg-EM-2</th>
<th>Li60Na40-Mg-EM-1</th>
<th>Li60Na40-Mg-EM-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>2.51 ± 0.01</td>
<td>2.52 ± 0.09</td>
<td>2.54 ± 0.02</td>
</tr>
</tbody>
</table>
3.2.2.4. **SEM of prepared glass powders**

No fines were visible in the SE images of pristine washed and sized Li50Na50-Mg-EM-1 and Li60Na40-Mg-EM-1 or the BSE images of the pristine washed and sized batches (see Section 3.4.1), confirming effectiveness of the washing methodology.

3.2.3. **Pristine glass compositions**

To ensure the Li-Mg-EM batches were close to their nominal compositions, the compositions of the pristine glasses were obtained through a combination of EPMA, LA-ICP-MS and acid digestion then ICP-OES (Table 3.5). Errors during the weighing of the precursors, spillages during mixing or the volatilisation of elements during heating might have resulted in deviations from these targets. Therefore, a measured composition was required to ensure leaching the glasses would have the intended effect and so that the leachate concentrations could be normalised accurately. The technique chosen to represent each oxide was based upon the percent recoveries (measured composition divided by nominal composition). EPMA reported excellent recoveries for all oxides except Al2O3 and Na2O, but B2O3 and Li2O could not be measured due to their low atomic masses. The consistently low recoveries reported for Na2O may be attributed to the known volatility of Na in the electron beam\(^{89}\), whilst the recoveries of Al2O3 seem to be consistently high. Despite the LA-ICP-MS results being normalised to the EPMA SiO2 concentrations as an internal standard, the reported recoveries for B2O3, Li2O and Na2O were poor and the errors on all measurements frequently exceeded an RSD of 10 %. As such, LA-ICP-MS measurements were not used in the final compositions. Instead, the concentrations of Al2O3, B2O3, Li2O and Na2O measured using ICP-OES displayed significantly improved recoveries. The ICP-OES measurements were not normalised to the EPMA SiO2 concentrations.
Impacts of lithium on analogues of a Magnox waste glass.

Table 3.5: Table of the nominal and measured oxide wt.% compositions of the four Li-Mg-EM batches. EPMA errors are reported as 1σ calculated from the 36 points analysed and ICP-OES errors are conservatively reported as 5% of the measured value as all values reported RSD less than 5%.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Oxide</th>
<th>Nominal oxide wt.%</th>
<th>Measured oxide wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li50Na50</td>
<td>Li50Na50</td>
<td>Li50Na50</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Al₂O₃</td>
<td>5.24</td>
<td>5.26</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>B₂O₃</td>
<td>20.24</td>
<td>20.34</td>
</tr>
<tr>
<td>EPMA</td>
<td>La₂O₃</td>
<td>5.91</td>
<td>5.94</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Li₂O</td>
<td>2.42</td>
<td>2.92</td>
</tr>
<tr>
<td>EPMA</td>
<td>MgO</td>
<td>5.56</td>
<td>5.59</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Na₂O</td>
<td>5.02</td>
<td>4.04</td>
</tr>
<tr>
<td>EPMA</td>
<td>SiO₂</td>
<td>55.61</td>
<td>55.91</td>
</tr>
</tbody>
</table>

All oxide concentrations in the final compositions were within 7.5% of their respective target concentrations, with the exception of Li₂O for Li50Na50-Mg-EM-1 which was 15.0%. However, this lower Li concentration is compensated by the lower Na and B concentrations of this batch; resulting in the two batches of Li50Na50-Mg-EM having internally consistent Li:Na and B:Li+Na ratios. Therefore, the fabricated batches were considered to be representative of their respective target compositions. The small errors associated with the EPMA results (RSD less than 10% for all oxides except La and Mg for Li60Na40-Mg-EM-1), which took place in random spots across the glass, suggests the fabricated batches were homogeneous.

3.3. Li-Mg-EM leachate concentrations and pH

Following the dissolution of the Li-Mg-EM compositions in deionised water (SA/V of 2000 m⁻¹) at 40 and 90 °C for between 7 and 112 d (Section 2.5), leachates were analysed for the concentrations of the constituent elements of the Li-Mg-EM compositions and common contaminants (Fe, Pb and Zn) using ICP-MS. The data was then treated following the calculations in Section 2.5.5. All glass constituents measured within the leachates were well above detection limits and significant from the blank concentrations (greater than three standard deviations plus the average blank concentration for that element), except La at 40 and 90 °C and Al at 40 °C which observed concentrations not significant from the blanks (blanks were greater than 10% of the sample concentrations for Al and La). Average blank concentrations for glass constituents were reported to be less than 0.050 μg/ml for all elements except Na and Si, which reported average blanks less than 0.500 μg/ml. RSD values for the triplicate sample measurements were less than 7.5% for all elements except Al and La, which were less than 20%. Concentrations of Fe and Pb in both the samples and blanks were less than 0.075 and 0.003
Impacts of lithium on analogues of a Magnox waste glass.

µg/ml respectively, with the exception of one outlying vessel. Zn concentrations were below 0.030 µg/ml in all blanks, but appeared to increase in the samples with leaching time up to 0.160 µg/ml; potentially suggesting a small quantity of Zn was present as a contaminant in one of the precursor oxides.

The normalised releases of the mobile glass species (B, Li and Na) and Si from Li-Mg-EM are displayed in Figure 3.4. For comparison, the normalised releases of Mg-EM at 90 °C\textsuperscript{46,89} and MW25 at 40 and 90 °C (taken from Chapter 5) are also given, which had been leached under similar conditions to the Li-Mg-EM experiments (with Mg-EM leached at a SA/V of 1200 m\textsuperscript{-1} rather than 2000 m\textsuperscript{-1}).

![Figure 3.4: Normalised releases of B, Li, Na and Si measured in the Li-Mg-EM leachates using ICP-MS. For comparison, the normalised releases measured in the Mg-EM leachates at 90 °C\textsuperscript{46,89} and MW25 at both 40 °C and 90 °C (from Chapter 5) are also given. Errors are given to 1σ calculated from the triplicate sample measurements, with the exception of the Mg-EM releases which have been assigned a conservative 10 % error due to absence of available triplicate data from the original study.](image-url)
Commonly, B is used to measure the extent of glass alteration as it is not expected to be retained in the alteration layers or incorporated into any secondary phases in significant quantities\(^5\) from comparing the normalised B releases of Mg-EM with Li50Na50-Mg-EM and Li60Na40-Mg-EM at 90 °C (Figure 3.4a), it is evident that substituting Li for Na had a significant negative impact on the aqueous durability of the glass. However, a comparison of the normalised B releases of the two Li-Mg-EM compositions leached at both 40 and 90 °C demonstrates that despite having an initially enhanced rate of alteration at a higher Li:Na ratio, further increasing the Li:Na ratio had no measurable impact on the residual rate of alteration. That is, the substitution of Li into Mg-EM at an equimolar Li:Na ratio had a significant negative long-term impact on aqueous durability, but the further substitution of Li for Na to an excessively high Li:Na ratio had no measurable long-term effect. The normalised B releases of Li50Na50-Mg-EM and Li60Na40-Mg-EM converged faster at 90 °C than at 40 °C, presumably due to the significantly lower rate of dissolution and longer time taken to reach the residual rate regime at 40 °C. As the total alkali metal contents of the Li-Mg-EM compositions were equal to those within Mg-EM, this negative effect on aqueous durability was attributed solely to changes in the Li:Na ratio. Interestingly, despite the Li-Mg-EM normalised B releases being higher than those of MW25 at 90 °C, the releases of all three compositions converged to the same residual rate of dissolution from 28 d onwards. However, at 40 °C the Li-Mg-EM normalised B releases remained significantly higher than those of MW25. Similarly, upon increasing the Li:Na ratio, the same trends were observed in the normalised Li releases of Li-Mg-EM as in the B releases at both 40 °C and 90 °C; with the exception of at 112 d at 90 °C where the normalised Li releases of Li60Na40-Mg-EM were insignificantly higher than those of Li50Na50-Mg-EM (Figure 3.4b).

Changing the Li:Na ratio had a notably more modest impact on the normalised Na releases (Figure 3.4c): at 40 °C the normalised Na releases of the Li-Mg-EM compositions remained within error of one another except at 14 d (although this difference is considered negligible), whereas at 90 °C the Na releases of Li50Na50-Mg-EM and Mg-EM remained within error throughout dissolution whilst the Na releases of Li60Na40-Mg-EM were higher than those of Mg-EM at 7 d. Although the normalised Na releases of Li60Na40-Mg-EM at 7 and 14 d at 90 °C were higher than those of Li50Na50-Mg-EM, at 14 d the normalised Na releases of both Li-Mg-EM compositions were within error of those of Mg-EM and as such this the difference
Impacts of lithium on analogues of a Magnox waste glass.

was considered negligible. After 7 d of dissolution at 90 °C, the normalised Si releases of the two Li-Mg-EM compositions converged to remain equal throughout dissolution; also converging with the Si releases of Mg-EM after 112 d of dissolution, although the Si releases of Mg-EM decreased with time (Figure 3.4d). At 40 °C, the normalised Si releases of the two Li-Mg-EM compositions followed an opposite, decreasing trend with time whilst the Si releases of Li50Na50-Mg-EM remained consistently higher than those of Li60Na40-Mg-EM throughout dissolution. The normalised Si releases suggest that Si reached an apparent steady-state concentration after 14 d at 90 °C and 7 d at 40 °C.

The normalised Mg releases of the Li-Mg-EM compositions were significantly higher at 40 °C than at 90 °C, with releases which converged after 28 d at 40 °C and remained equal throughout dissolution at 90 °C (Figure 3.5). The decreasing releases at 40 °C demonstrated Mg was precipitating out of solution faster than it was being leached from the glass, with the low 90 °C concentrations being attributable to Mg precipitating faster at higher temperatures. Similarly, low Mg releases were observed for Mg-EM at 90 °C which also decreased with time\textsuperscript{46,89}. Interestingly, this appears to be opposite to MW25, where the normalised Mg releases at 90 °C were higher than at 40 °C. The low concentrations of Al and La in the leachates meant their respective normalised releases had large errors and no significant trends could be observed.

The average pH of the leachates were higher at 40 °C than at 90 °C (Figure 3.6), with the pH of the leachates at 90 °C being lower than expected. Further, the pH of the leachates of each Li-Mg-EM composition remained equal throughout dissolution, with the exception of the 112 d
leachates at 40 °C. However, this difference was considered negligible as it was just 0.06 pH units.

Figure 3.6: pH of the Li-Mg-EM leachates. Errors are reported to 1σ calculated from the triplicate measurements.

3.4. Characterisation of the glass structures and effects of dissolution

3.4.1. SEM and EDS

High-resolution SE images were taken of each Li-Mg-EM composition leached for each interval at each temperature to investigate in detail the alteration of the glass surface and how this may be affected by composition. EDS analysis then took place on the same samples to obtain the composition of any secondary phase precipitates and investigate how the composition of the glass surface evolved throughout dissolution.

SE images of the Li-Mg-EM compositions leached at 90 °C showed a macroporous layer formed after just 7 d of dissolution (Figure 3.7), which wholly covered all of the leached glass particles. As dissolution progressed, this layer appeared to mature in terms of pore size and pore depth. There appeared to be no difference in the appearance of this layer or the kinetics of its formation between the two Li-Mg-EM compositions, with the pores at each leaching interval appearing to be of a similar size and depth for each composition.

After 112 d of dissolution at 90 °C the pores and features of this macroporous surface layer were visible at lower magnifications, which also revealed large clusters of precipitates and minor cracks in the glass surface had formed (Figure 3.8a and b). Further, delamination of the surface layer was clearly visible in some samples, which revealed a rough layer of altered glass beneath it (Figure 3.8c and d). This suggested that rather than being a relict depleted gel layer, this macroporous surface layer was a secondary phase precipitate which covered the depleted gel layer.
Impacts of lithium on analogues of a Magnox waste glass.

Figure 3.7: Secondary electron SEM images of Li50Na50-Mg-EM (top row) and Li60Na40-Mg-EM (bottom row) leached at 90 °C for: pristine (a and f), 7 d (b and g), 14 d (c and h), 28 d (d and i) and 112 d (e and j).

Figure 3.8: Secondary electron SEM images of Li50Na50-Mg-EM (a) and Li60Na40-Mg-EM (b and c) leached for 112 d at 90 °C, and Li60Na40-Mg-EM leached for 14 d at 90 °C (d).
Impacts of lithium on analogues of a Magnox waste glass.

BSE images of the 112 d 90 °C altered Li-Mg-EM compositions at low magnification provided further evidence for large clusters of precipitates and cracks forming on the glass surface after dissolution (Figure 3.9b and c). Additionally, whilst all of the glass particles appeared highly altered and wholly covered in a macroporous layer, some particles appeared to be significantly more altered such that the entire particle was visibly deformed (for example, spot 2 and spot 3 in Figure 3.9b and c respectively).

The EDS spectra of both Li-Mg-EM compositions after dissolution demonstrated the altered glass surface was significantly depleted in all glass species, especially B and Na, with the exception of Mg, which was enriched in some particles (Figure 3.10). The level of Mg enrichment, the depletion of elements and the elemental ratios appeared to vary between glass particles of the same sample, showing some particles leached selectively rather than a uniform alteration layer being formed across the surface of all samples. For example, the highly altered particle at spot 3 in Figure 3.9c displayed a higher Mg contents than its notably less altered ‘shell’ surrounding it at spot 4, but both particles had similar Al, Na and Si contents. Due to this variation between particles of the same sample, differences between the EDS spectra of the two Li-Mg-EM compositions could not be observed and accurate estimations of the Mg contents of the glass surface at each leaching interval could not be made; again, presumably due to the alteration layer not having a uniform thickness across each leached glass particle.

Figure 3.9: Backscattered electron SEM images of pristine Li50Na50-Mg-EM (a), and Li50Na50-Mg-EM and Li60Na40-Mg-EM leached for 112 d at 90 °C (b and c respectively). Numbered labels on the images correspond to spot numbers for EDS analysis (see Figure 3.10 for spectra).
Impacts of lithium on analogues of a Magnox waste glass.

Figure 3.10: EDS spectra of 112 d 90 °C leached Li50Na50-Mg-EM (a) and Li60Na40-Mg-EM (b). The pristine glass spectrum corresponds to spot 1 in Figure 3.9(a), whilst the spot numbers in (a) and (b) correspond to the numbers given in Figure 3.9(b) and (c) respectively.

With this in mind, it was clear that the macroporous surface layer (such as spot 1 and spot 2 in Figure 3.9b and c respectively) was a magnesium silicate which was highly depleted in B and Na. Interestingly, this layer also appeared to be depleted in Al and La, despite these elements having a low solubility within the leachates. Analysis of the clusters of precipitates which formed upon the glass surface (such as spot 4 and spot 1 in Figure 3.9b and c respectively) revealed these were also highly enriched in Mg, implying they were of a similar, if not the same, composition to the macroporous surface layer and that these precipitate clusters grew out of the macroporous layer.

SE images of the Li-Mg-EM compositions leached at 40 °C showed that despite altering significantly slower at 40 °C than at 90 °C, even after just 7 d at 40 °C the glass surface became significantly rougher and it appeared the macroporous layer began forming across all leached glass particles (Figure 3.11). Whilst the macroporous layer matured at a significantly lower rate at 40 °C, as reflected by the lower rate of alteration (Section 3.3), precipitates began to sparsely
form on the glass surfaces after 112 d (Figure 3.11e and j). As with the 90 °C images, no differences could be observed between the two Li-Mg-EM compositions.

![Image](image1)

**Figure 3.11**: Secondary electron SEM images of Li50Na50-Mg-EM (top row) and Li60Na40-Mg-EM (bottom row) leached at 40 °C for: pristine (a and f), 7 d (b and g), 14 d (c and h), 28 d (d and i) and 112 d (e and j).

Unlike the surfaces of the 90 °C leached Li-Mg-EM samples, no delamination of the macroporous layer was visible at 40 °C; presumably as the layer which developed after 112 d at 40 °C was too thin for delamination to occur. Interestingly, the precipitates at 40 °C did not appear to cluster significantly, but rather spread across the surface of the leached glass and appeared more distinct from the macroporous layer (Figure 3.12). Additionally, no cracks in the glass were observed in these low magnification SE images or in the BSE images acquired prior to EDS analysis (Figure 3.13).

![Image](image2)

**Figure 3.12**: Secondary electron SEM images of Li50Na50-Mg-EM (a) and Li60Na40-Mg-EM (b) leached for 112 d at 40 °C.
Impacts of lithium on analogues of a Magnox waste glass.

EDS analysis of the 40 °C leached samples displayed their surfaces were depleted in all elements, including Mg. This is thought to be due to the rate of Mg precipitation being significantly lower at 40 °C than at 90 °C, with the composition of the precipitates being the same at both temperatures. This view is consistent with the larger concentrations of Mg in the leachates at 40 °C than at 90 °C (Figure 3.5).

Figure 3.13: Backscattered electron SEM images of Li50Na50-Mg-EM (a) and Li60Na40-Mg-EM (b) leached for 112 d at 40 °C. Numbered labels on the images correspond to spot numbers for EDS analysis (see Figure 3.14 for the spectra).

Figure 3.14: EDS spectra of 112 d 40 °C leached Li50Na50-Mg-EM (a) and Li60Na40-Mg-EM (b). The pristine glass spectrum corresponds to spot 1 in Figure 3.9(a), whilst the spot numbers in (a) and (b) correspond to the numbers given in Figure 3.13(a) and (b) respectively.
3.4.2. NMR

3.4.2.1. $^6$Li and $^7$Li MAS-NMR

The low natural abundance of $^6$Li and its high T1 relaxation times for the Li-Mg-EM compositions made $^6$Li MAS-NMR experiments challenging. Instead, only the results of $^7$Li MAS-NMR experiments on the fines of each Li-Mg-EM batch and each Li-Mg-EM composition leached at 40 and 90 °C for 112 d will be presented.

Attempts to characterise any changes in the role of Li in Li-Mg-EM through $^7$Li MAS-NMR experiments showed no significant difference in chemical shift or peak shape between any of the Li50Na50-Mg-EM and Li60Na40-Mg-EM batches (Figure 3.15a). Similarly, no changes in chemical shift or peak shape were observed in either composition after dissolution at either 40 or 90 °C (Figure 3.15b and c). This demonstrated that the structural role of Li within Li-Mg-EM does not change with the Li:Na ratio and implies that the preferential leaching of Li from a particular environment within the glass does not take place, regardless of the Li:Na ratio.

![Figure 3.15: $^7$Li MAS-NMR spectra of fines of the four Li-Mg-EM batches (a), Li50Na50-Mg-EM leached at 40 and 90 °C for 112 d (b) and Li60Na40-Mg-EM leached at 40 and 90 °C for 112 d (c). Spectra have been normalised to the same peak intensities. Colours correspond to: (a) Li50Na50 batch 1 (Black), batch 2 (Blue), Li60Na40 batch 1 (Orange) and batch 2 (Red); (b) Li50Na50 batch 1 (Black), batch 2 (Blue), 112 d 40 °C leached (Orange) and 112 d 90 °C leached (Red); and (c) Li60Na40 batch 1 (Black), batch 2 (Blue), 112 d 40 °C leached (Orange) and 112 d 90 °C leached (Red).](image)

3.4.2.2. Static $^6$Li-$^1$H CP-NMR

Static $^6$Li-$^1$H CP-NMR experiments took place on Li50Na50-Mg-EM leached at 40 and 90 °C for 7 and 112 d and, following the discovery of a signal in some samples, washed and sized pristine Li50Na50-Mg-EM to ensure the polarisation did not originate from ambient proton adsorption (Figure 3.16).
Impacts of lithium on analogues of a Magnox waste glass.

Figure 3.16: Static $^6$Li-$^1$H CP-NMR spectra of Li50Na50-Mg-EM leached at 40 °C (a) and 90 °C (b). Lines correspond to the washed and sized pristine glass (Magenta), the 7 d leached glass (Cyan) and the 112 d leached glass (Gold). Spectra intensities were normalised using the mass of sample analysed and the number of repetitions acquired.

Whilst no measurable polarisation was observed after 7 d at 40 °C, a small peak was observed after 112 d at 40 °C (Figure 3.16a). Further, analysis of the pristine washed and sized glass demonstrated no measurable polarisation was originating from ambient proton adsorption. Therefore, this signal was caused by Li within alteration products. Whilst small, this signal demonstrated that a Li-bearing phase was precipitating at 40 °C, despite a significantly slower rate of dissolution and Mg precipitation compared with at 90 °C. Contrastingly, a well-defined peak was clearly visible in the 7 d 90 °C leached sample, which appeared to increase only slightly in intensity after 112 d of dissolution (Figure 3.16b). This demonstrates that at 90 °C a significant amount of Li is being incorporated into alteration products after just 7 d and the precipitation of a Li-bearing phase continues between 7 and 112 d. Further, it appears at 90 °C the majority of the Li-bearing precipitates form before 7 d of dissolution and the rate of Li precipitation between 7 and 112 d is significantly abated; as is consistent with dissolution going through the rate drop regime and being well within the residual rate regime after this time. The poor signal-to-noise ratios of the spectra meant quantification of the masses of Li in the alteration products was not possible.
3.4.2.3. $^{11}$B MAS-NMR

$^{11}$B MAS-NMR experiments initially took place on all washed and sized Li-Mg-EM batches to probe whether the coordination of the B network changed with the Li:Na ratio. Subsequent experiments took place on one sample from each composition leached for each duration at each temperature to investigate whether selective dissolution of $^{III}$B units or $^{IV}$B units occurred. As the electric field gradients of $^{III}$B and $^{IV}$B units differ, $^{11}$B MAS-NMR spectra of borosilicate glasses consist of a narrow Gaussian $^{IV}$B peak centred at 0 ppm and a broad $^{III}$B doublet centred at approximately 12 ppm; this doublet in turn consists of ring and non-ring $^{III}$B contributions at approximately 11 and 17 ppm respectively. This technique affords quantitative comparisons of the number of $^{III}$B relative to $^{IV}$B units as the area under each peak is proportional to the number of B atoms in that environment. The reported spectra herein were normalised to the intensity of their $^{IV}$B peaks so that changes in the proportions of $^{III}$B to $^{IV}$B units would be visible through changes in the sizes of the $^{III}$B doublets.

Comparisons of the spectra of the four pristine washed and sized Li-Mg-EM batches with Mg-EM (spectrum taken from another study for comparison) showed no significant change in the proportion of $^{III}$B to $^{IV}$B units with a changing Li:Na ratio (Figure 3.17). Small discrepancies observed in the intensities of the $^{III}$B doublets may be attributed to minor variations in the total alkali metal to B ratios of the glass batches, and as such are considered negligible.

![Figure 3.17: $^{11}$B MAS-NMR spectra of washed and sized pristine: Li50Na50-Mg-EM-1 (Blue), Li50Na50-Mg-EM-2 (Green), Li60Na40-Mg-EM-1 (Orange), Li60Na40-Mg-EM-2 (Red) and Mg-EM (Black; taken from another study for comparison). Some spectra were shifted to correct for referencing errors (Li50Na50-Mg-EM-1 +0.2 ppm, Li50Na50-Mg-EM-2 -0.1 ppm, and Mg-EM -0.2 ppm). Spectra were normalised to the intensity of the $^{IV}$B peak as to compare changes in the proportion of $^{III}$B to $^{IV}$B units through the $^{III}$B doublet.](image-url)
Impacts of lithium on analogues of a Magnox waste glass.

Similarly, in all Li50Na50-Mg-EM and Li60Na40-Mg-EM samples leached at 40 °C, there was no visible change in the proportion of \( ^{\text{III}}\text{B} \) to \( ^{\text{IV}}\text{B} \) units (Figure 3.18a and c). Contrastingly, after 112 d of leaching at 90 °C, a significant decrease in the proportion of \( ^{\text{III}}\text{B} \) to \( ^{\text{IV}}\text{B} \) units was observed for both compositions (Figure 3.18b and d). To quantify this observed change in the \( ^{\text{III}}\text{B}/^{\text{IV}}\text{B} \) ratio, spectra were quantified through curve fitting the \( ^{\text{III}}\text{B} \) doublet (both ring and non-ring structures) and the \( ^{\text{IV}}\text{B} \) peak using DMFIT software. Quantification was made difficult by the significant overlap of the \( ^{\text{III}}\text{B} \) peaks and the \( ^{\text{IV}}\text{B} \) peak, but it should also be noted that the first-order satellite transition sidebands fall under the \( ^{\text{IV}}\text{B} \) peak due to the low electric field gradient of \( ^{\text{IV}}\text{B} \) units. Therefore, these sidebands must be considered during quantification.

Figure 3.18: \(^{11}\text{B} \) MAS-NMR spectra of Li50Na50-Mg-EM leached at 40 °C (a) Li50Na50-Mg-EM leached at 90 °C (b), Li60Na40-Mg-EM leached at 40 °C (c) and Li60Na40-Mg-EM leached at 90 °C (d). Lines correspond to: the first washed and sized pristine glass batch (Black), the second washed and sized batch (Blue), leached for 7 d (Green), leached for 14 d (Yellow), leached for 28 d (Orange), and leached for 112 d (Red). Spectra were normalised to the \( ^{\text{IV}}\text{B} \) peak as to compare changes in the proportion of \( ^{\text{III}}\text{B} \) to \( ^{\text{IV}}\text{B} \) units through the \( ^{\text{III}}\text{B} \) peak. Spectra were shifted to correct for referencing errors (Li50Na50-Mg-EM-2 -0.3 ppm in (a) and Li50Na50-Mg-EM-1 +0.3 ppm in (b)).
Impacts of lithium on analogues of a Magnox waste glass.

Spectra were quantified by fitting the Gaussian $^{11}B$ peak, the $^{13}B$ quadrupole doublet and a first-order spinning sideband manifold based upon the profile of the observed sidebands. Non-ring and ring $^{13}B$ peaks were fitted separately using peaks which coincided with the quadrupole coupling constants and chemical shifts reported in the literature for non-ring and ring resonances$^{32,174}$. As the $^{11}B$ peak appeared asymmetrical rather than Gaussian, this peak could not be satisfactorily fit in the Li-Mg-EM spectra using a single Gaussian or Voigt peak (example in Figure 3.19a). This was also the case for Mg-EM (spectrum taken from another study$^{46}$, but curve fitted here). This asymmetry likely arises due to asymmetric distribution resonances from $^{11}B$ sites in the glass and was considered by adding a second Voigt peak under the $^{11}B$ peak (example in Figure 3.19b). Note, this additional $^{11}B$ peak was fitted to account for the observed asymmetry and was not assigned an additional interpretation; both peaks simply represented $^{11}B$ species and the area of the two $^{11}B$ peaks were merely added when calculating the relative proportions of $^{13}B$ and $^{11}B$ units.

![Figure 3.19: Quantification of the washed and sized Li50Na50-Mg-EM $^{11}B$ MAS-NMR spectrum using one $^{11}B$ peak (a) and two $^{11}B$ peaks (b). Lines correspond to: the original spectrum (Blue), the fit (Red), the residual (Grey). The two Voigt peaks used to fit the $^{11}B$ peak are given in magenta and red, with the $^{13}B$ doublet fit using the grey and cyan peaks. The small green peaks are from the quadrupole first-order spinning sideband manifold.](image-url)
The relative areas of the fitted peaks provide a measure of the fractions of $^{\text{III}}$B and $^{\text{IV}}$B units within the glass, affording quantification of how the B network is affected by changes in the Li:Na ratio and evolves throughout dissolution. Table 3.6 shows the fractions of $^{\text{III}}$B and $^{\text{IV}}$B units in the pristine, 7 d and 112 d leached samples estimated from curve fitting alongside their respective calculated $^{\text{III}}$B/$^{\text{IV}}$B ratios and the difference in the fraction of $^{\text{III}}$B between the leached and pristine samples. The analysed molar concentrations of B, Li and Na within the pristine glasses (calculated from Table 3.5) as well as the results from fitting the pristine Mg-EM spectrum$^{46}$ using two peaks to fit the $^{\text{IV}}$B peak are also given for comparison.

Table 3.6: Measured elemental molar percentages of Li, Na and B in the pristine Li-Mg-EM samples (calculated from Table 3.5) alongside the fractions of $^{\text{III}}$B and $^{\text{IV}}$B estimated from quantifying the pristine, 7 d leached and 112 d leached (40 and 90 °C) $^{\text{II}}$B NMR spectra. For the sake of comparison, values for Mg-EM are given (concentrations and spectrum taken from another study whilst the spectrum was quantified here using two $^{\text{IV}}$B peaks.) Errors given on the concentrations are conservatively reported as 5% of the measured value as all values reported RSD less than 5%, with the errors on the [B]/[Total alkali], [III]B and [IV]B propagated from these values.

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<th>Li60Na40-Mg-EM</th>
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<tr>
<td></td>
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<td>40 °C Leached</td>
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<tr>
<td></td>
<td>Pristine</td>
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<tr>
<td>Mg-EM$^1$</td>
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<td>Li50Na50-2</td>
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<tr>
<td>[Li] (at.%)</td>
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<td>[Na] (at.%</td>
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<tr>
<td>[B] (at.%</td>
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<td>27.2 ± 1.4</td>
</tr>
<tr>
<td>[B]/[Total alkali]</td>
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<tr>
<td>[III]B (%)</td>
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</tr>
<tr>
<td>[IV]B (%)</td>
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</tr>
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<td>17.3 ± 0.9</td>
</tr>
<tr>
<td>[IV]B (at.%)</td>
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<tr>
<td>[III]B/$^{\text{IV}}$B</td>
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<td>1.74</td>
</tr>
<tr>
<td>Change in [III]B from pristine (% points)</td>
<td>-</td>
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Impacts of lithium on analogues of a Magnox waste glass.

differ from those quantified from curve fitting the spectra (Table 3.6). In this instance, visual comparisons of the spectra and the quantified changes in the $^{\text{III}}$B/$^{\text{IV}}$B ratio after dissolution appeared to be in good agreement.

The quantified small variations in the fractions of $^{\text{III}}$B units in the pristine Li-Mg-EM batches may be attributed to small differences in their respective total alkali metal to B ratios. As the errors associated with the measurements of the pristine glass compositions were large, the exact cause of these subtle discrepancies could not be further investigated. For the sake of comparison, the curve fitting results of the Mg-EM spectrum is also given in Table 3.6; these values were in good agreement with those reported from curve fitting in the original study\textsuperscript{46}.

The negligible variations in the $^{\text{III}}$B fractions of the pristine Li-Mg-EM batches suggests that the discrepancy in the fraction of $^{\text{III}}$B observed between Li-Mg-EM and Mg-EM can also be explained by differences in the alkali metal to B ratios of Mg-EM and Li-Mg-EM. That is, if these changes were brought about by a variation in the Li:Na ratio, a similar effect between Li$_{50}$Na$_{50}$-Mg-EM and Li$_{60}$Na$_{40}$-Mg-EM should be observed as well. Therefore, these consistent fractions of $^{\text{III}}$B units in the pristine glasses demonstrates the number of $^{\text{IV}}$B units, and by extension the number of species charge compensating the B network, changes negligibly across the wide range of Li:Na ratios probed (0.0, 1.0 and 1.5).

As is consistent with visual comparisons of the spectra (Figure 3.18), curve fitting confirmed there was a significant drop in the proportion of $^{\text{III}}$B to $^{\text{IV}}$B units in both Li-Mg-EM compositions after 112 d of leaching at 90 °C (Table 3.6). Interestingly, whilst the majority of this drop appears to occur after just 7 d in Li$_{50}$Na$_{50}$-Mg-EM (-1.7% $^{\text{III}}$B units), there was a negligible change for Li$_{60}$Na$_{40}$-Mg-EM after 7 d (-0.1% $^{\text{III}}$B units). It should be noted that the errors associated with the differences calculated between the leached and pristine sample fits would be less than those associated with comparing the fits of the pristine glass batches, as the B to total alkali metal ratio of the pristine glass does not vary when comparing leached and pristine samples. Therefore, this demonstrates that at long duration at 90 °C there is preferential leaching of $^{\text{III}}$B units from both Li-Mg-EM compositions. After 7 d at 40 °C, both Li-Mg-EM compositions observed a slight increase in the fraction of $^{\text{III}}$B. Similarly, after 112 d at 40 °C there was no further change in the fraction of $^{\text{III}}$B for Li$_{60}$Na$_{40}$-Mg-EM, whereas for Li$_{50}$Na$_{50}$-Mg-EM there was a slight drop in the fraction of $^{\text{III}}$B. However, the magnitude of these changes at 40 °C are considered negligible as they likely fall within the error of the fits.
3.4.2.4. $^{23}$Na MAS-NMR

$^{23}$Na MAS-NMR experiments took place on all washed and sized Li-Mg-EM batches, washed and sized Mg-EM and one sample from each Li-Mg-EM composition leached for each duration at each temperature to compare how the structural role of Na changed with the Li:Na ratio and investigate how Na was leached from the glass. The spectra of the four pristine Li-Mg-EM batches appeared identical (Figure 3.20). Whilst a small shift (approximately +1.5 ppm) was observed for Mg-EM relative to the Li-Mg-EM batches, this shift is considered negligible in terms of structural change; a conclusion which is supported by the similarity of the Li-Mg-EM spectra displaying no change in chemical shift or peak shape with a changing Li:Na ratio.

![Figure 3.20: $^{23}$Na MAS-NMR spectra of the pristine washed and sized Li-Mg-EM batches: Li50Na50-Mg-EM-1 (Blue), Li50Na50-Mg-EM-2 (Green), Li60Na40-Mg-EM-1 (Orange) and Li60Na40-Mg-EM-2 (Red) alongside Mg-EM (Black). Spectra were normalised to the same intensity.](image)

No change in the spectra were visible after dissolution of either composition at 40 °C for all durations probed (Figure 3.21a and c). However, a well-defined peak was clearly visible at approximately -7.3 ppm in the spectra of both compositions leached at 90 °C from 7 d onwards, with an intensity which increased with dissolution time (Figure 3.21b and d). The nutation behaviour of this peak suggested it had a very small or zero electric field gradient and as such corresponded to a cubic Na site, implying it was a Na-bearing alteration product.

To quantify the amount of Na in each site, curve fitting of the $^{23}$Na spectra took place using Igor Pro software (Wavemetrics). Firstly, the pristine Li50Na50-Mg-EM spectrum was fit using two peaks (one exponentially modified Gaussian distribution and one Lorentz distribution); these lines were not assigned separate meanings but rather were used to obtain a good fit of the quadrupolar Na line shape. Leached spectra were then fit using an additional Lorentz peak (example given in Figure 3.22), with the position and width of two of the lines kept the same as in the pristine glass curve fitting. To quantify the spectra, the area under the peak at
approximately -7.3 ppm was multiplied by 0.4 and the amount of Na in each site was calculated from the quantified pristine glass spectrum and measured composition\textsuperscript{139}. Assuming the B releases provided a measure of the fraction of glass altered, an estimated Na concentration in solution was calculated from this fraction of glass altered and the mass of Na in precipitates at each leaching interval at 40 and 90 °C was estimated from the difference between the estimated and measured concentrations (Table 3.7).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3_21.png}
\caption{\textsuperscript{23}Na MAS-NMR spectra of pristine and leached 40 °C leached Li50Na50-Mg-EM (a), 90 °C leached Li50Na50-Mg-EM (b), 40 °C leached Li60Na40-Mg-EM (c) and 90 °C leached Li60Na40-Mg-EM (d). Coloured lines represent: pristine batch 1 (Black), pristine batch 2 (Blue), 7 d leached (Green), 14 d leached (Yellow), 28 d leached (Orange) and 112 d leached (Red). Spectra were normalised to the intensity of the main peak (approximately -20 ppm).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3_22.png}
\caption{Example of a \textsuperscript{23}Na MAS-NMR spectrum (90 °C 112 d leached Li50Na50-Mg-EM) fit using three peaks in the Igor Pro software. The top line represents the fit residual, in the middle the red line represents the spectrum and the blue line represents the fit, and the bottom numbered peaks represent the fitted peaks.}
\end{figure}
Table 3.7: Table comparing the percentage B released from the glass, the concentrations of Na in solution estimated from this B fraction released, the measured concentrations of Na in solution, the difference between the estimated and measured concentrations presented in mg/l and mg and the quantification of the leached and pristine $^{23}$Na MAS-NMR spectra (Figure 3.21). Errors are given to 1σ propagated from the triplicate concentration measurements, pristine glass compositions, glass masses and leachant volumes used.

<table>
<thead>
<tr>
<th>Leaching time at 40 °C</th>
<th>7 d</th>
<th>14 d</th>
<th>28 d</th>
<th>112 d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li50Na50-Mg-EM</td>
<td>% glass altered (From B releases)</td>
<td>1.54 ± 0.10%</td>
<td>2.13 ± 0.16%</td>
<td>3.15 ± 0.40%</td>
</tr>
<tr>
<td></td>
<td>Estimated [Na] in solution (mg/l)</td>
<td>56.0 ± 5.8</td>
<td>77.9 ± 8.8</td>
<td>108.3 ± 17.8</td>
</tr>
<tr>
<td></td>
<td>[Na in solution] (mg/l)</td>
<td>62.3 ± 5.3</td>
<td>80.1 ± 3.9</td>
<td>107.0 ± 3.2</td>
</tr>
<tr>
<td></td>
<td>Difference (mg/l)</td>
<td>6.3 ± 11.0</td>
<td>2.3 ± 12.7</td>
<td>-1.3 ± 20.9</td>
</tr>
<tr>
<td></td>
<td>Estimated precipitated (mg)</td>
<td>-0.03 ± 0.04</td>
<td>-0.01 ± 0.05</td>
<td>0.01 ± 0.08</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Leaching time at 40 °C</th>
<th>7 d</th>
<th>14 d</th>
<th>28 d</th>
<th>112 d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li50Na50-Mg-EM</td>
<td>% glass altered (From B releases)</td>
<td>1.98 ± 0.20%</td>
<td>2.83 ± 0.25%</td>
<td>3.85 ± 0.45%</td>
</tr>
<tr>
<td></td>
<td>Estimated [Na] in solution (mg/l)</td>
<td>58.0 ± 7.9</td>
<td>82.8 ± 10.4</td>
<td>112.6 ± 17.2</td>
</tr>
<tr>
<td></td>
<td>[Na in solution] (mg/l)</td>
<td>54.1 ± 2.1</td>
<td>71.3 ± 1.6</td>
<td>93.6 ± 6.9</td>
</tr>
<tr>
<td></td>
<td>Difference (mg/l)</td>
<td>-3.9 ± 10.1</td>
<td>-11.5 ± 12.7</td>
<td>-19.0 ± 24.1</td>
</tr>
<tr>
<td></td>
<td>Estimated precipitated (mg)</td>
<td>0.02 ± 0.04</td>
<td>0.05 ± 0.05</td>
<td>0.08 ± 0.10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Leaching time at 90 °C</th>
<th>7 d</th>
<th>14 d</th>
<th>28 d</th>
<th>112 d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li50Na50-Mg-EM</td>
<td>% glass altered (From B releases)</td>
<td>15.11 ± 1.81%</td>
<td>19.14 ± 1.49%</td>
<td>24.80 ± 6.21%</td>
</tr>
<tr>
<td></td>
<td>Estimated [Na] in solution (mg/l)</td>
<td>545.5 ± 85.4</td>
<td>691.6 ± 80.3</td>
<td>854.1 ± 240.3</td>
</tr>
<tr>
<td></td>
<td>[Na in solution] (mg/l)</td>
<td>391.0 ± 21.2</td>
<td>467.7 ± 12.9</td>
<td>554.7 ± 96.3</td>
</tr>
<tr>
<td></td>
<td>Difference (mg/l)</td>
<td>-154.5 ± 106.6</td>
<td>-223.9 ± 93.2</td>
<td>-299.4 ± 336.6</td>
</tr>
<tr>
<td></td>
<td>Estimated precipitated (mg)</td>
<td>0.62 ± 0.42</td>
<td>0.90 ± 0.37</td>
<td>1.19 ± 1.34</td>
</tr>
<tr>
<td></td>
<td>% cubic Na from NMR</td>
<td>3.9 ± 0.3%</td>
<td>5.3 ± 0.3%</td>
<td>7.8 ± 0.4%</td>
</tr>
<tr>
<td></td>
<td>Measured [Cubic Na] (mg)</td>
<td>0.46 ± 0.10</td>
<td>0.51 ± 0.09</td>
<td>0.71 ± 0.13</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Leaching time at 90 °C</th>
<th>7 d</th>
<th>14 d</th>
<th>28 d</th>
<th>112 d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li60Na40-Mg-EM</td>
<td>% glass altered (From B releases)</td>
<td>21.14 ± 1.89%</td>
<td>24.78 ± 2.64%</td>
<td>22.87 ± 2.75%</td>
</tr>
<tr>
<td></td>
<td>Estimated [Na] in solution (mg/l)</td>
<td>616.4 ± 78.6</td>
<td>722.4 ± 103.9</td>
<td>670.9 ± 105.2</td>
</tr>
<tr>
<td></td>
<td>[Na in solution] (mg/l)</td>
<td>367.1 ± 9.5</td>
<td>420.8 ± 25.0</td>
<td>389.6 ± 15.2</td>
</tr>
<tr>
<td></td>
<td>Difference (mg/l)</td>
<td>-249.3 ± 88.1</td>
<td>-301.7 ± 128.9</td>
<td>-281.3 ± 120.4</td>
</tr>
<tr>
<td></td>
<td>Estimated precipitated (mg)</td>
<td>0.99 ± 0.35</td>
<td>1.21 ± 0.52</td>
<td>1.13 ± 0.48</td>
</tr>
<tr>
<td></td>
<td>% cubic Na from NMR</td>
<td>3.1 ± 0.3%</td>
<td>5.9 ± 0.3%</td>
<td>6.0 ± 0.4%</td>
</tr>
<tr>
<td></td>
<td>Measured [Cubic Na] (mg)</td>
<td>0.35 ± 0.08</td>
<td>0.59 ± 0.11</td>
<td>0.53 ± 0.10</td>
</tr>
</tbody>
</table>

Whilst such an assumption about the release of Na ignores differences in the mechanisms by which B and Na are expected to leach from glasses, the estimated masses of Na in precipitates...
for the Li-Mg-EM compositions at 90 °C were either within error or greater than those measured from curve fitting the $^{23}$Na spectra; thereby agreeing with the view that significant masses of Na were being incorporated into alteration products$^{40}$.

For the compositions leached at 40 °C, the estimated masses of precipitated Na were all within error of zero (Table 3.7). That is, the extent of dissolution for both compositions leached at 40 °C appeared to be insufficient for significant masses of Na to precipitate and a second Na peak to be visible. This is highlighted well by this peak being a small bump for Li60Na40-Mg-EM leached at 90 °C for 7 d with 21.14 ± 1.89 % of the B released, whereas at 40 °C after 112 d only 7.28 ± 1.16 % of the B was released and no second peak was visible.

3.4.3. XRD

XRD analysis took place on each Li-Mg-EM composition leached at 40 and 90 °C for 112 d to investigate whether crystalline alteration products had formed on the glass surfaces after dissolution (Figure 3.23). Analysis revealed no detectable crystalline secondary phases on any of the leached glasses, but the main characteristic peak of cristobalite was visible in the 90 °C leached samples. This peak originated from the pristine glass and reanalysing these samples demonstrated they were amorphous. Whilst significant masses of secondary phases formed during the dissolution of the Li-Mg-EM compositions at 90 °C (as evidenced by Sections 3.4.1 and 3.4.2), no crystalline phases were detected during XRD analysis. Based upon observations in the literature of crystalline secondary phases forming on various glass compositions after significantly longer dissolution times$^{38,40,41,49}$, this suggests that the timespans probed were insufficient for crystalline secondary phases to form in detectable masses and the secondary phases formed were in a proto-crystalline phase$^{175}$. Such proto-crystalline secondary phases would develop into a crystalline phase as dissolution progressed, fuelling further dissolution of the glass as they precipitate; potentially leading to a resumption of the initial dissolution rate during the residual rate regime$^{47,176,177}$. Further, as the entire glass particle underwent analysis and secondary phases would only be present in the alteration layers, it is likely a larger fraction of the glass needs to be altered and larger masses of crystalline secondary phases would need to be precipitated before they could be detected through XRD analysis.
Impacts of lithium on analogues of a Magnox waste glass.

3.5. Discussion

3.5.1. Pristine glass structures

Studies of Li-Na and Li-K borosilicate systems using $^{17}$O MAS-NMR have reported that instead of being randomly mixed, high field strength network modifying cations (Li) associate preferentially with non-bridging oxygen (NBO) in the Si network compared with those of lower field strengths (Na or K)$^{32,174}$. Combined with observations of a larger number of Si-NBOs in Li, Li-Na or Li-K borosilicates compared with Na, K or Na-K borosilicates$^{25,32}$, Li was suggested to preferentially modify the Si network over Na. Similar chemical shifts for a Li-Na borosilicate and a Na borosilicate were observed in $^{11}$B MAS-NMR for both IVB and IIIB ring peaks, demonstrating Na preferentially charge compensates the B network over Li$^{32}$. It was suggested these preferences effected nanoscale heterogeneity in Li-Na borosilicates, with Li-Si-rich domains present in a Na-rich borosilicate host matrix$^{32}$. Elemental profiles of leached glass provide further evidence for Na preferentially compensating the B network over Li, which display similarly sharp dissolution profiles for Na and B behind a significantly wider Li interdiffusion layer$^{38}$. This difference in dissolution behaviour between Li and Na was attributed to Na being more strongly bonded to the B network in its’ charge compensation role than Li to the Si network in its’ NBO role$^{38}$.

The near-identical proportions of IIIB to IVB units of the pristine Li-Mg-EM batches and Mg-EM shows that varying the Li:Na ratio had no measurable impact on the coordination of the B network. This conclusion is based not only upon the visual similarity of the spectra (Figure 3.17) but also the estimated concentrations of IIIB and IVB for these batches being within error of one another (Table 3.6). Additionally, the similar shapes of the IIIB doublets across all Li-
Impacts of lithium on analogues of a Magnox waste glass.

Mg-EM batches and Mg-EM suggests the proportion of ring to non-ring $^{III}$B units does not vary with the Li:Na ratio.

Based upon the preference of Li to modify the Si network\textsuperscript{32}, Li is not expected to compete with Na to charge compensate $^{IV}$B units\textsuperscript{178}. Consequently, although the concentration of Na in Li60Na40-Mg-EM was approximately 2.5 times less than that of Mg-EM, the majority of $^{IV}$B in Li50Na50-Mg-EM and Li60Na40-Mg-EM was expected to still be charge compensated by Na. This is consistent with the $^{23}$Na MAS-NMR spectra of the pristine Li-Mg-EM batches and Mg-EM displaying negligible changes in peak position or shape as the Li:Na ratio was varied (Figure 3.20), which suggests there was no change in the role of Na within the pristine glass as the Li:Na was increased. Further, a lack of change in the role of Na would contribute to the $^{11}$B MAS-NMR spectra of the pristine glasses being nearly identical across all compositions studied (Figure 3.17).

It should be noted that both Li50Na50-Mg-EM and Li60Na40-Mg-EM contained lower concentrations of Na than $^{IV}$B (Table 3.6). Therefore, when the concentration of Na was less than that of $^{IV}$B, as the proportion of $^{III}$B to $^{IV}$B units remained constant across all batches another cation must be charge compensating the $^{IV}$B units in place of Na; else there would be a reduction in the fraction of $^{IV}$B units. As such, it is expected that at higher Li:Na ratios a significant amount of Li compensates the B network in place of the removed Na. However, the preference of Li to continue modifying the Si network at all Li:Na ratios probed may be reflected in the similarity of the $^{7}$Li MAS-NMR spectra of the Li-Mg-EM batches (Figure 3.15); although this result may be questionable due to the small range of chemical shifts associated with $^{7}$Li spectra potentially meaning any subtle differences between analogues would be immeasurably small. Additionally, it should be considered that whilst Li preferentially modifies the Si network, a small fraction of Li may also charge compensate $^{IV}$B units at lower Li:Na ratios. Some Mg and La may also charge compensate the B network once there is insufficient Na. However, alkaline earths (in this case Mg) are expected to compensate $^{IV}$Al over $^{IV}$B units preferentially to alkali metals\textsuperscript{174,179}, suggesting Mg maintains its role compensating Al throughout the glass network as the Li:Na ratio is varied.

### 3.5.2. Lithium promoting glass dissolution

Using the normalised B releases to measure of the extent of glass alteration\textsuperscript{37,50}, through comparing the releases of Li50Na50-Mg-EM and Li60Na40-Mg-EM with Mg-EM at 90 °C
Impacts of lithium on analogues of a Magnox waste glass.

(Figure 3.4a) it is evident that substituting Li for Na had a significant detrimental impact on wasteform aqueous durability; with the normalised B releases of the two Li-Mg-EM compositions being higher than the Mg-EM glass (Li-free) by a factor approaching two at long dissolution times. Similarly, from comparing the normalised B releases of the two Li-Mg-EM compositions at both 40 and 90 °C (Figure 3.4), it is clear that increasing the Li:Na ratio had a detrimental effect on aqueous durability during the initial dissolution regimes but had no effect on the residual rate of alteration. Interestingly, the same effect was also visible in the normalised Li releases at both temperatures, with only a minor discrepancy between the two compositions at 112 d at 90 °C (Figure 3.4b). However, this effect was only partially observed in the normalised Na releases at 90 °C and was not observed in the normalised Na releases at 40 °C (Figure 3.4c) or the normalised Si releases at either temperature (Figure 3.4d). The 90 °C normalised Mg releases displayed no significant change with the Li:Na ratio: the Li-Mg-EM compositions were within error of each other throughout dissolution and were within error of the Mg-EM Mg releases at 7 and 112 d, with the Mg releases of the Li-Mg-EM compositions decreasing at a faster rate to this 112 d value (Figure 3.5). Similar to B and Li at 40 °C, Li60Na40-Mg-EM observed initially higher normalised Mg releases than Li50Na50-Mg-EM but the releases became equal from 28 d onwards.

Quantification of the spectra of the pristine, 7 d leached and 112 d leached samples leached at 40 °C displayed no significant evolution in the proportion of III B to IV B units (Table 3.6). Further, there was no visible change in the proportion of ring to non-ring III B units (Figure 3.18). However, a significant drop in the proportion of III B to IV B units was observed after 112 d at 90 °C in both Li-Mg-EM compositions, demonstrating that at 90 °C preferential dissolution of III B units was taking place. It was hypothesised that similar incongruent dissolution of the B network also took place at 40 °C but the extent of glass alteration was too small for this to be observable. This effect could not simply be caused by III B units having lower aqueous durability than IV B units, as the B network of Mg-EM was shown to leach congruently after 112 d at 90 °C. Consequently, it was shown that substituting Li for Na promoted the dissolution of III B units.

As previously discussed, Na in its’ charge compensation role was expected to be more strongly bonded than Li in its’ network modifying role. In this view, it was hypothesised that the incongruent leaching of III B units and the long-term decrease in chemical durability associated
with the Li-Mg-EM analogues compared with Mg-EM arose due to a combination of Li’s preference to modify the Si network and network modifying Li leaching readily. Due to Li preferentially modifying the Si network, the Si network of the Li-Mg-EM compositions is more depolymerised and has a higher number of NBOs than that of Mg-EM. As water ingresses into the glass, this lower degree of connectivity might have resulted in the Li-modified Si network presenting less of a barrier to the inward diffusion of water species; in turn resulting in more rapid hydration of the glass network in a composition containing Li. Further, as Li leaches more easily from its’ modifying role than Na from its’ compensating role, in the Li-Mg-EM compositions a nanoscale region denuded of alkalis with a more open depolymerised Si character was formed at a faster rate, which also resulted in further and faster interdiffusion into the glass. Despite the preference of Na to charge compensate $^{IV}_B$ units, the higher concentration of Na than $^{IV}_B$ units in Mg-EM (Table 3.6) suggests that some Na might have modified the Si network. Further, it was expected that a small amount of Na also modified the Si network in the Li-Mg-EM compositions. As such, it was hypothesised that a preferential exchange of protonated water species for Li over Na combined with the smaller ionic radius of Li compared with Na resulted in Li leaching out earlier than Na to provide a more open glass structure and presenting less of a barrier to the hydration of the glass respectively compared with Mg-EM. In addition to the previously discussed effects of depolymerisation and cation preferences, it was expected that Li modifying the Si network facilitated faster hydration of the glass than if just Na was modifying it. As the bonds of the Si network require a high amount of energy to break, the higher degree of depolymerisation and rate of glass hydration effected by Li had no measurable impact on the rate of Si network dissolution. As the energy required to hydrolyse the B network bonds is low, these effects resulted in an increased rate of B network dissolution in the Li-containing analogues (Figure 3.4a). The preference of Na to compensate the B network meant it remained largely unaffected by the effects of Li on the Si network, as shown by the Na releases of Li50Na50-Mg-EM and Mg-EM being within error of one another throughout dissolution (Figure 3.4c). That is, whilst the faster hydration of the glass resulted in enhanced dissolution of the B network, charge compensating Na appeared unaffected. Consequently, these effects caused the $^{III}_B$ units to leach at a faster rate whilst the Na compensated $^{IV}_B$ units appeared to
Impacts of lithium on analogues of a Magnox waste glass.

remained unaffected, resulting in incongruent dissolution of \( \text{III}_B \) and \( \text{IV}_B \) units which became more visible as dissolution progressed.

Comparing the normalised B and Li releases (Figure 3.4a and b) of the Li-Mg-EM compositions at both temperatures, it could be expected that the initially increased rate of glass dissolution associated with Li60Na40-Mg-EM arose from its higher Li contents enhancing the previously discussed effects. Note that these differences in dissolution behaviour might also have been influenced by a high concentration of Li in Li60Na40-Mg-EM compensating the B network in lieu of Na. The comparable residual release rates of all species from the two Li-Mg-EM compositions at both temperatures suggests that despite Li60Na40-Mg-EM observing an enhanced initial dissolution rate effected by a higher Li:Na ratio, a similar passivating altered layer structure formed in the later stages of dissolution regardless of composition. After such a layer formed, any hydration effects became significantly less relevant. Therefore, raising the Li:Na ratio from 1.0 to 1.5 was concluded to have no impact on the long-term aqueous durability of the glass.

After 7 d at 90 °C, the B network of Li50Na50-Mg-EM leached incongruently whilst that of Li60Na40-Mg-EM did not (Table 3.6). However, the aqueous durability of Li60Na40-Mg-EM was lower than Li50Na50-Mg-EM during this time (Figure 3.4). It should also be noted that at this time the normalised Na releases of Li60Na40 were greater than those of Li50Na50, which was within error of those of Mg-EM (Figure 3.4c). As there was less Na than \( \text{IV}_B \), a significant fraction of Li likely compensated the \( \text{IV}_B \) units in place of Na in Li60Na40-Mg-EM. The Li-compensated, and neighbouring Na-compensated, \( \text{IV}_B \) units would be subject to the previously discussed effects and so more Na and \( \text{IV}_B \) units in Li60Na40-Mg-EM were affected by these Li effects compared with Li50Na50-Mg-EM; resulting in higher \( \text{IV}_B \) releases, virtually congruent dissolution of the B network, and a small increase in the Na releases at 7 d for Li60Na40-Mg-EM. As the majority of the \( \text{IV}_B \) remained compensated by Na, these differences appeared to become more negligible over time such that the Na releases of Li50Na50-Mg-EM and Li60Na40-Mg-EM remained within error of one another after 14 d and similar magnitudes of incongruent B network dissolution were clearly visible after 112 d in both Li-Mg-EM compositions. At 40 °C, the absence of such incongruence or Na behaviour was attributed to the magnitude of alteration being too low.

The negligible difference between the normalised Si releases of the Li-Mg-EM compositions
Impacts of lithium on analogues of a Magnox waste glass.

at 7 d at 90 °C and the consistently higher Si releases of Li50Na50-Mg-EM at 40 °C throughout dissolution coincided with Si reaching an apparent solubility limit in solution after 7 d at 40 °C and 14 d at 90 °C. The longer time taken to reach saturation at 90 °C may be attributed a higher apparent Si solubility limit than at 40 °C, as also influenced by the higher in-situ pH at higher temperatures. As such, the apparent Si solubility limits for the Li-Mg-EM compositions were comparable at 40 °C and within error at 90 °C. At this steady state Si concentration, the rates of Si dissolution and precipitation remain equal and any subtle differences between the rates of Si network dissolution would therefore not be reflected in the normalised releases. Consequently, the Si releases cannot provide detailed information regarding the associated changes in the kinetics of dissolution of the Si network for such subtle compositional changes.

3.5.3. Precipitates reducing aqueous durability

In the literature, Na has been shown to precipitate as a crystalline sodium silicate hydrate phase on a Na borosilicate after 13.6 years of dissolution at 90 °C in deionised water. Whilst XRD detected no crystalline phases in the 40 and 90 °C leached Li-Mg-EM compositions (Figure 3.23), 23Na MAS-NMR, 6Li-1H CP-NMR and SEM showed a significant amount of amorphous alteration products formed after 7 d at both 40 and 90 °C for both Li-Mg-EM compositions. The second peak in the 23Na MAS-NMR spectra of the 90 °C leached Li-Mg-EM samples (Figure 3.21b and d) shows significant amounts of a Na-bearing phase precipitated from solution. As the quantified mass of precipitated Na was less than or within error of the estimated mass of precipitated Na as calculated from the fraction of glass altered (Table 3.7), this peak was associated with a Na-bearing phase. Consistent with the literature, the chemical shift of this peak (centred at approximately -7.3 ppm) was similar to those reported for sodium silicate hydrates. The symmetry of this peak compared to those in the literature was attributed to the precipitate lacking the well-defined sites of a crystalline sodium silicate hydrate.

The presence of precipitated sodium silicate hydrate in a Na borosilicate system implies that this phase should eventually be observable in all Na-bearing borosilicate glasses. However, this peak was absent from the 40 °C leached spectra (Figure 3.21a and c) and estimated masses of Na in precipitated phases for these samples were all within error of zero (Table 3.7). It was expected that a Na-bearing phase also precipitates on the Li-Mg-EM glasses at 40 °C but these phases are only observable after a significant fraction of the glass has been altered. The larger mass of precipitated Na for Li50Na50-Mg-EM than Li60Na40-Mg-EM was attributed to Li50Na50-Mg-EM containing and releasing more Na into solution (Table 3.7).
sodium silicate hydrate precipitation on aqueous durability is questionable as Li50Na50-Mg-EM reported higher masses of precipitated Na but initially lower normalised releases for Li, B and Na than Li60Na40-Mg-EM, although this effect is convoluted by the negative effect of Li on aqueous durability.

Despite displaying estimated masses of precipitated Na within error of zero, the 40 °C leached samples showed a magnesium silicate layer formed after just 7 d (Figure 3.11) which appeared to mature in terms of thickness and pore size with time and temperature (Figure 3.7). EDS analysis of the 40 °C leached surfaces showed these were depleted in Mg compared with the 90 °C leached surfaces (Figure 3.14 and Figure 3.10 respectively), as is consistent with observations of a thinner, less developed magnesium silicate layer at this lower temperature. This faster rate of precipitation at 90 °C was also reflected in the normalised Mg releases (Figure 3.5) at 90 °C being lower than at 40 °C releases and negligible at longer durations. Delamination of this layer suggested it was a secondary phase precipitate rather than a relict glass structure (Figure 3.8c and d). This layer is expected to be an amorphous, or proto-crystalline, precursor to a smectite clay mineral47,49. As is consistent with observations in the literature of poorer aqueous durability when Mg is present in the glass or leachant composition49,102, this layer is expected to consume significant amounts of Si from solution as it forms to fuel further hydrolysis of the glass or passivating alteration layer to accelerate dissolution. This is a crucial dissolution process which is also expected to control the residual rate of alteration alongside interdiffusion reactions across the passivating alteration layer, resulting in poorer aqueous durability throughout dissolution for Mg-containing glasses47,48,50. Consequently, the aqueous durability of Li and Mg-containing borosilicates appears to be poor due to a cycle of Li promoting more rapid interdiffusion reactions and the precipitation of a magnesium silicate promoting dissolution of this hydrated glass.

Similarly, a Li-bearing phase formed after 112 and 7 d at 40 and 90 °C respectively in Li50Na50-Mg-EM (Figure 3.16). This is consistent with significant amounts of Li being incorporated into alteration products during the dissolution of Mg-rich basaltic glasses48, but the low signal to noise ratio associated with the 6Li-1H CP-NMR spectra (Figure 3.16) made quantification impossible. As with Na (Table 3.7), the majority of the Li-bearing phase appeared to precipitate at 90 °C before 7 d of dissolution but precipitation continued between 7 and 112 d. Further, the consistently lower normalised releases of Li than B throughout
dissolution combined with observations of the magnesium silicate layer beginning to form after just 7 d at 40 °C (Figure 3.11) suggests a Li-bearing phase was also precipitating at 40 °C after 7 d but the mass was too low to be detected. This view is also consistent with detectable masses of a Li-bearing phase after 112 d at 40 °C accompanying a more developed magnesium silicate layer and a larger number of sparse precipitates (Figure 3.11); with the Li-bearing phase precipitating significantly faster at 90 than at 40 °C, as was suggested by SEM of the magnesium silicate layer. The observation of measurable masses of Li in a precipitated phase after 112 d at 40 °C but no detectable Na-bearing precipitates suggests this phase precipitates somewhat independently of Na and that the precipitation of the magnesium silicate layer results in Li being incorporated into the alteration products; either through small quantities of Li substituting for Mg in the precursor clay due to their similar ionic radii or the precursor clay itself containing a significant fraction of Li such as in a Hectorite.49

3.5.4. Suitability as an analogue
Using the normalised B releases to assess the suitability of the analogues as representations of MW25, Li50Na50-Mg-EM was shown to be an excellent analogue of MW25 during the later dissolution regimes (Figure 3.4a); with normalised B releases within error of MW25’s from 28 d onwards (112 d Li50Na50 being within error of the 126 d MW25 measurement). The 7 d 90 °C MW25 B releases were noted to be between those of Li50Na50 and Mg-EM. Despite an intermediate Li:Na ratio of 1.00 having been shown to have poorer aqueous durability than a Li-free composition (Mg-EM), the dissolution behaviour of Li50Na50-Mg-EM better matched that of MW25 than Mg-EM during the later dissolution regimes. However, at 40 °C the releases of all elements from MW25 except Si were significantly lower than from both Li-Mg-EM compositions, although the reasons for this difference in behaviour remain unclear. It is expected that having Li in the glass composition significantly affects the mechanical and structural properties of the glass, including aqueous durability95,181, in ways which would be difficult to represent in a Li-free composition. Further, in elemental profiles of leached glass cross-sections, Li was seen to leach in a wide interdiffusion profile preceding the Na ion-exchange front and B hydrolysis front38. This is consistent with the changes in dissolution behaviour accompanying a change in the Li:Na ratio observed here, which were expected to have arisen partly due to the preferential release of Li over Na during the initial interdiffusion stage of glass dissolution. Consequently, representing Li in the simplified analogue composition was thought to better replicate the dissolution processes of MW25.
3.6. Summary

It was shown that for both pristine Li-Mg-EM analogues that the ratio of $^{III}$B to $^{IV}$B units remained constant across all Li:Na ratios studied. The absence of a change was consistent with the view that Na acts preferentially as a network modifier to the B network, with Li instead preferentially charge compensating the Si network. Further, the constant $^{III}$B/$^{IV}$B ratio demonstrated that the number of species acting as charge compensators to the B network remained constant with the Li:Na ratio. As such, the lower concentrations of Na than $^{IV}$B units in the Li-Mg-EM analogues suggested that Li fulfilled the role of Na in compensating the B network as the Li:Na ratio was increased.

At 90 °C and longer leaching durations, it was shown that $^{III}$B units leached more readily than $^{IV}$B units for the Li-Mg-EM analogues. As this effect was not observed for Mg-EM, it was attributed to the presence of Li in Li-Mg-EM enhancing hydration, and subsequently dissolution, of the glass network whilst the Na-compensated $^{IV}$B units were less affected. Incongruent dissolution of the B network was expected for the Li-Mg-EM analogues leached at 40 °C but the extent of dissolution of the B network might not have been sufficient enough to observe it.

Initially faster glass alteration (B releases) was observed for the Li-Mg-EM analogues relative to Mg-EM at 90 °C but the Na releases appeared unaffected; as was consistent with the view of Li promoting glass hydration and dissolution through leaching more readily from its Si network modifying role than charge compensating Na to leave Na-compensated $^{IV}$B units less affected. Further, Li60Na40-Mg-EM had higher initial Li, B and Na releases than Li50Na50-Mg-EM, as was also attributable to the excess Li-contents enhancing the Li hydration effects. Whilst the Li-Mg-EM analogues observed consistently poorer aqueous durability than Mg-EM throughout dissolution at 90 °C, the releases of all species from the Li-Mg-EM analogues at longer durations at 40 and 90 °C were within error of one another. This was attributed to a passivating alteration layer structure forming which rendered the effects of excess Li contents less relevant. Na-bearing and Li-bearing secondary phases were also shown to precipitate during the dissolution of the Li-Mg-EM analogues at 90 °C, which were attributed to a sodium silicate hydrate and Li either substituting for Mg or being incorporated directly into a phase respectively. Whilst a Li-bearing phase was observed at long-duration at 40 °C, a Na-bearing phase was not.
4. Relating Magnox and international waste glasses

A significant portion of the work presented in this chapter has been accepted for publication in the Journal of Non-Crystalline Solids. The text has been altered as required for use herein.

4.1. Introduction to the Li-ISG compositions

The French R7T7-type complex simulant waste glass SON68 has undergone numerous dissolution experiments under a variety of different temperatures, leachant compositions, leachant pH and SA/V ratios in experiments spanning up to three decades\textsuperscript{38–44,49,50,57,61,81,182}. Similarly, the six-component borosilicate glass ISG (Table 4.1) has undergone a significant number of structural studies and sophisticated dissolution experiments\textsuperscript{4,40,58,59,63,73,74,80,183}. Initially, a batch of ISG (originally named CJ 4) was fabricated as part of a study aiming to investigate the effects of various elements on wasteform aqueous durability\textsuperscript{40}. Later, the production of a 50 kg batch of ISG was commissioned and ISG was put forward as a common benchmark composition for researchers to study internationally\textsuperscript{4}. In fabricating ISG, its nominal elemental molar ratios were identical to those in SON68, with the exceptions of the REE and paramagnetic elements of SON68 which were omitted and Li which was instead replaced entirely by Na\textsuperscript{40}. As such, ISG may be considered a Li-free simplified analogue of SON68.

Both complex and analogue UK simulant Magnox waste glasses have been shown to be significantly less durable than their French equivalents\textsuperscript{20,49,104–106,110}. This may be attributed to significant differences in pristine glass, and subsequently secondary phase precipitate, composition: MW25 nominally contains 4.5 wt.% MgO but no CaO, whilst SON68 nominally contains 4.1 wt.% CaO but no MgO\textsuperscript{15,37}. Rather than being caused by differences in pristine glass structure between glasses containing Ca or Mg, this long-term drop in aqueous durability associated with Mg-containing glasses has been attributed in the literature to the formation of Mg-bearing secondary phases\textsuperscript{43,46,47,49}. In the previous chapter, the effects of substituting Li for Na in the simplified analogue of MW25, Mg-EM, was investigated. Batches of Li-Mg-EM were fabricated at an intermediate Li:Na ratio aimed at representing MW25 (Li:Na ratio of 1.0, Li\textsubscript{50}Na\textsubscript{50}-Mg-EM) and a high Li:Na ratio aimed at representing MW25 with excess Li contents (Li:Na ratio of 1.5, Li\textsubscript{60}Na\textsubscript{40}-Mg-EM). Whilst Li was shown to have a negative impact on aqueous durability under the test conditions used, increasing the Li:Na ratio further was shown to have no measurable effect on the residual rate of alteration. Further, at longer durations at 90 °C, \textsuperscript{11}B species were shown to
leach more readily than IVB species from both Li-Mg-EM compositions.

In this chapter, Li was substituted for Na in ISG to produce two seven-component simplified analogues of SON68 (Li-ISG) which were leached under the same conditions as the Li-Mg-EM glasses. As with MW25, analogues had to be used as it was not possible to vary the Li:Na ratio of SON68 to mechanistically investigate the effects of Li. Whilst batches of Li-Mg-EM were fabricated at molar Li:Na ratios of 1.0 and 1.5 based upon MW25 (Li:Na ratio of 1.01) and MW25 with excess Li contents respectively, SON68 nominally contains a Li:Na ratio of 0.40\textsuperscript{15,37}. As such, batches of Li-ISG were fabricated at Li:Na ratios of 0.4 and 0.9 (Li29Na71-ISG and Li47Na53-ISG respectively) with the aims of providing a Li-containing simplified analogue of SON68 and investigating the effects of excess Li contents on the aqueous durability of SON68 respectively. The total alkali metal to elemental molar ratios and other molar ratios of Li-ISG remained equal to those in ISG (Table 4.1) and, by extension, SON68. Therefore, differences in pristine glass structure and dissolution behaviour between ISG and the Li-ISG analogues could only be attributed to the presence of Li in the glass composition and changes in the Li:Na ratio. Ultimately, through mechanistic studies of the effects of Li on the simplified analogues of MW25 and SON68, this work aimed to: form a relationship between the simplified analogues and the complex glasses they aimed to represent, compare the effects of Li on these simplified analogues, extend these conclusions to their respective complex waste glasses and reconcile differences in dissolution behaviour between the two analogue types with glass structure and composition.

Table 4.1: Nominal cation atomic percent (at.%) compositions of Li29Na71-ISG and Li47Na53-ISG compared with ISG\textsuperscript{40}. For comparison, the nominal at.% compositions of Mg-EM\textsuperscript{46,89} and the Li-Mg-EM compositions (Table 3.1) are shown.

<table>
<thead>
<tr>
<th>Element</th>
<th>ISG</th>
<th>Li29Na71</th>
<th>Li47Na53</th>
<th>Mg-EM</th>
<th>Li50Na50</th>
<th>Li60Na40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>5.80</td>
<td>5.80</td>
<td>5.80</td>
<td>4.87</td>
<td>4.87</td>
<td>4.87</td>
</tr>
<tr>
<td>B</td>
<td>24.11</td>
<td>24.11</td>
<td>24.11</td>
<td>27.58</td>
<td>27.58</td>
<td>27.58</td>
</tr>
<tr>
<td>Ca</td>
<td>4.32</td>
<td>4.32</td>
<td>4.32</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>La</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>1.72</td>
<td>1.72</td>
<td>1.72</td>
</tr>
<tr>
<td>Li</td>
<td>0.00</td>
<td>5.46</td>
<td>9.05</td>
<td>0.00</td>
<td>7.69</td>
<td>9.23</td>
</tr>
<tr>
<td>Mg</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>6.54</td>
<td>6.54</td>
<td>6.54</td>
</tr>
<tr>
<td>Na</td>
<td>19.10</td>
<td>13.64</td>
<td>10.05</td>
<td>15.38</td>
<td>7.69</td>
<td>6.15</td>
</tr>
<tr>
<td>Si</td>
<td>45.37</td>
<td>45.37</td>
<td>45.37</td>
<td>43.91</td>
<td>43.91</td>
<td>43.91</td>
</tr>
<tr>
<td>Zr</td>
<td>1.30</td>
<td>1.30</td>
<td>1.30</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
4.2. Fabricating amorphous Li-ISG and XRD

An initial test pour of Li29Na71-ISG following an adaptation of the ISG methodology (Section 2.2.1.2) yielded an optically clear glass matrix rife with opaque patches of crystallites. XRD analysis of this powdered glass revealed it was highly crystalline and contained a muscovite (Figure 4.1a). Subsequently, the Li-ISG batches were fabricated following an adaptation of the Li-Mg-EM fabrication procedure (Section 2.2.1.2), which produced glasses which appeared vitreous and were optically clear. XRD analysis of these Li-ISG batches demonstrated they were amorphous (Figure 4.1b).

![Figure 4.1: X-ray diffractograms from the test run of the Li29Na71-ISG pour (a) and the fabricated Li-ISG batches (b). The colours in (a) correspond to the characteristic peaks of different muscovites (ICDD numbers: Red [046-1409], Blue [002-1019], Green [001-1098]). A low-background sample holder was used.](image)

4.3. Pristine Li-ISG characterisation

4.3.1. Geometric analyses

4.3.1.1. Laser diffraction analysis

The particle size distribution of a washed and sized full-Li MW base glass was initially acquired during laser diffraction analysis of the Li-Mg-EM batches (Section 3.2.2.1). This powder was then reanalysed during the Li-ISG analysis as an ad-hoc ‘in-house standard’. It was noted during the Li-ISG analysis that the median particle sizes were significantly higher than those of the Li-Mg-EM powders (frequently exceeding 150 µm), but the full-Li MW base glass median particle size was also significantly higher (Table 4.2). As such, the Li-ISG particle size distributions were corrected by shifting the median particle size of each distribution by the difference between the two MW base glass median particle sizes. The median particle size was highly consistent across all Li-ISG batches, with all values being within 2 µm of one another (Table 4.2). Distributions appeared uniform. Whilst these median particle sizes appeared higher than those of the Li-Mg-EM batches, this was considered negligible and again attributed to needle-like particles passing through the 150 µm sieve; demonstrating the sieving procedure worked as intended and produced consistent particle size distributions.

113
Table 4.2: Measured particle size distributions of the four Li-ISG batches compared with the distributions acquired for the full-Li MW base glass during this run and previously in the Li-Mg-EM run (Table 3.2).

<table>
<thead>
<tr>
<th></th>
<th>Full-Li MW base glass</th>
<th>Li29Na71-ISG</th>
<th>Li47Na53-ISG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li-Mg-EM run</td>
<td>Batch 1</td>
<td>Batch 2</td>
</tr>
<tr>
<td>Median</td>
<td>124.59</td>
<td>144.32</td>
<td>145.50</td>
</tr>
<tr>
<td>D[v, 0.9]</td>
<td>199.44</td>
<td>222.95</td>
<td>224.20</td>
</tr>
<tr>
<td>D[v, 0.1]</td>
<td>76.84</td>
<td>94.06</td>
<td>90.94</td>
</tr>
</tbody>
</table>

4.3.1.2. BET analysis

Based upon the inconsistent results of the Li-Mg-EM BET analyses, analysis took place solely on Li29Na71-ISG-1 and yielded a BET surface area of 0.416 ± 0.024 m²/g with a linear correlation coefficient of 0.988. This value was significantly higher than the geometric mean surface area (0.021 m²/g), any of the Li-Mg-EM batch surface areas (Table 3.3) and the surface area reported for Mg-EM (0.21 m²/g) which had been washed using both deionised water and ethanol. As the Li-ISG batches were subjected to the same washing methodology as the Li-Mg-EM batches, it seemed unlikely the surface area of the Li-ISG batches would be a factor of approximately 20 higher than the Li-Mg-EM batches. As such, this Li-ISG BET surface area measurement was considered erroneous and further BET measurements did not take place.

4.3.1.3. Density measurements

The densities of the Li-ISG batches appeared consistent (Table 4.3), yielding average densities of 2.50 ± 0.04 g/cm³ and 2.48 ± 0.01 g/cm³ for Li29Na71-ISG and Li47Na53-ISG respectively. Whilst the batches of Li47Na53-ISG had a lower density than Li29Na71-ISG-2, this difference was considered negligible as there was no difference in density between these batches and Li29Na71-ISG-1. Further, all Li-ISG batches had densities within error of ISG. As such, densities did not appear to change with the Li:Na ratio. These densities also appeared consistent with those of Mg-EM (2.49 ± 0.01 g/cm³) and the Li-Mg-EM batches (Table 3.4, 2.52 g/cm³).

Table 4.3: Measured densities of the Li-ISG batches with errors given to 1σ as calculated from the triplicate measurements. For comparison, the density of ISG is displayed. An error of ±0.01 g/cm³ was assigned to ISG due to the absence of a reported error in the literature.

<table>
<thead>
<tr>
<th></th>
<th>Li29Na71-ISG</th>
<th>Li29Na71-ISG</th>
<th>Li47Na53-ISG</th>
<th>Li47Na53-ISG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Batch 1</td>
<td>Batch 2</td>
<td>Batch 1</td>
<td>Batch 2</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.50 ± 0.06</td>
<td>2.51 ± 0.01</td>
<td>2.48 ± 0.01</td>
<td>2.48 ± 0.01</td>
</tr>
</tbody>
</table>

4.3.2. Compositional analyses and final compositions

Characterisation of the Li-ISG compositions took place to ensure all fabricated batches were close their respective nominal compositions. SiO₂ concentrations were obtained using EPMA,
whilst the concentrations of all other oxides were obtained through acid digestion then ICP-OES (Table 4.4). The analytical technique selected to represent each oxide was chosen based upon the percent recoveries measured for that concentration. All representative concentrations reported excellent recoveries, with concentrations within 10 % of their respective targets for all oxides except Li₂O for Li₂9Na71-ISG-2 and Li₄7Na53-ISG-2 which had recoveries within 12.5 %. As such, the fabricated compositions were considered to be within acceptable error of their respective nominal compositions. EPMA reported recoveries for CaO and Na₂O which frequently exceeded 5 % and recoveries for Al₂O₃ and ZrO₂ which frequently exceeded 10 %; with the recoveries of Na₂O being underestimated (again, likely due to the volatility of Na in the electron beam) and the recoveries of Al₂O₃, CaO and ZrO₂ being overestimated. As such, only the concentrations of SiO₂ measured using EPMA were selected. ICP-OES yielded significantly improved recoveries for Al₂O₃ and ZrO₂, and as such was used to obtain the concentrations of all oxides except SiO₂. The RSD for all concentrations from EPMA were less than 3.5 % for all oxides and therefore evidence the compositional homogeneity of the Li-ISG batches.

Table 4.4: The measured oxide wt.% compositions of the two batches of each Li-ISG composition given alongside their respective nominal compositions and the technique used to measure that oxide. Errors on the EPMA SiO₂ measurements are given to 1σ as calculated from the 40 points analysed. ICP-OES errors are conservatively reported as 5 % of the measured value, as all values reported RSD less than 5 %.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Oxide</th>
<th>Li₂9Na71 Batch 1</th>
<th>Li₂9Na71 Batch 2</th>
<th>Li₄7Na53 Batch 1</th>
<th>Li₄7Na53 Batch 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP-OES</td>
<td>Al₂O₃</td>
<td>6.21</td>
<td>6.28</td>
<td>6.41 ± 0.13</td>
<td>6.37 ± 0.13</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>B₂O₃</td>
<td>17.60</td>
<td>17.82</td>
<td>16.84 ± 0.34</td>
<td>16.58 ± 0.33</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>CaO</td>
<td>5.09</td>
<td>5.15</td>
<td>5.01 ± 0.10</td>
<td>4.84 ± 0.10</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Li₂O</td>
<td>1.71</td>
<td>2.87</td>
<td>1.61 ± 0.03</td>
<td>1.50 ± 0.03</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Na₂O</td>
<td>8.87</td>
<td>6.61</td>
<td>8.63 ± 0.17</td>
<td>8.29 ± 0.17</td>
</tr>
<tr>
<td>EPMA</td>
<td>SiO₂</td>
<td>57.17</td>
<td>57.87</td>
<td>58.48 ± 0.45</td>
<td>58.9 ± 0.45</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>ZrO₂</td>
<td>3.36</td>
<td>3.40</td>
<td>3.17 ± 0.06</td>
<td>3.15 ± 0.06</td>
</tr>
</tbody>
</table>

4.4. Li-ISG leachate compositions and pH

After leaching the Li-ISG powders (75 to 150 µm) under the same conditions as the Li-Mg-EM compositions (unbuffered deionised water leachant at a SA/V of 2000 m⁻¹, leached at 40 and 90 °C for 7, 14, 28 and 112 d, see Section 2.6), diluted leachates underwent ICP-MS analysis. The measured concentrations of the constituent elements of Li-ISG and common contaminants
(Fe, Ni, Pb and Zn) were then treated using the equations given in Section 2.5.5. With the exceptions of Ca at both temperatures and Al at 40 °C, which had blank concentrations greater than 10 % of their respective sample concentrations, all glass species within the leachates were well above detection limits and greater than the average blank concentration plus three standard deviations. Average blank concentrations were reported to be below detection limits for B, Li, Si and Zr, less than 0.07 µg/ml for Al and Na, and less than 1.25 µg/ml for Ca. Triplicate sample RSD values of less than 10 % were observed for all but two triplicates for Li, B, Na and Si, with RSD values frequently exceeding 10 % for Al, Ca and Zr. Concentrations of Fe and Pb were less than 0.0500 and 0.0002 µg/ml respectively in the samples and blanks, whilst concentrations of Ni and Zn were both less than 0.2000 µg/ml. Unlike the Li-Mg-EM experiments, the concentration of Zn in the sample leachates did not appear to increase with dissolution time.

The normalised releases of mobile glass species (Li, B and Na) and Si for the Li-ISG compositions are plotted in Figure 4.2 alongside the normalised releases for ISG and SON68 which have been taken from another study for comparison40; these glasses had been leached in initially pure deionised water at 90 °C with average geometric SA/V ratios of approximately 3000 m⁻¹ (reported as 8000 m⁻¹ in the original study as measured specific surface areas were used rather than geometric mean particle sizes of 70 µm) at regular intervals between 1 d and 13.9 years. Using B as a tracer for glass dissolution, as B is not expected to be incorporated into any secondary phases in significant quantities50, it was evident that whilst both Li-ISG batches demonstrated poorer aqueous durability than ISG and SON68 (except at 14 d for Li29Na71-ISG and 7 to 28 d for Li47Na53-ISG) at 90 °C (Figure 4.2a), Li29Na71-ISG displayed higher B releases than Li47Na53-ISG at all times at 40 °C and all times except 14 d at 90 °C. However, this discrepancy at 90 °C may be attributed to the large error associated with the Li47Na53-ISG releases at 14 d. The residual rates of B release from Li29Na71-ISG at both temperatures appeared subtly larger than those of Li47Na53-ISG, with the difference between the residual rate of B release of the two compositions appearing to be larger at 90 °C than at 40 °C. Further, the residual rates of B release at 90 °C appeared subtly larger for both Li-ISG compositions than those of ISG and SON68. This demonstrated that whilst the substitution of Li for Na into ISG had a significant negative impact on aqueous durability, the further substitution of more Li for Na towards an equimolar ratio not only improved initial
Relating Magnox and international waste glasses

aqueous durability but also had a subtle positive effect on long-term aqueous durability as measured through the residual rates of B release.

![Figure 4.2: Normalised elemental releases of B (a), Li (b), Na (c) and Si (d) for the Li-ISG compositions. For comparison, the normalised releases for ISG and SON68 at 90 °C taken from another study are displayed. Errors are given to 1σ for the Li-ISG batches, as calculated from the triplicate values. ISG and SON68 were assigned an error of 10 % due to the absence of reported errors on each measurement.](image)

Whilst Li29Na71-ISG displayed higher normalised Li releases than Li47Na53-ISG at 40 °C (Figure 4.2b), the difference in releases between the two compositions remained approximately
constant and was considered negligible. This is consistent with the 90 °C normalised Li releases, where Li29Na71-ISG observed a negligibly higher initial Li release at 7 d but the Li releases of the Li-ISG compositions later converged. As such, the release rate of Li was shown to be unaffected by changes in the Li:Na ratio. Interestingly, the residual Li release rates from the Li-ISG compositions appeared significantly higher than that of SON68 at 90 °C.

A similar effect to B was observed in the normalised Na releases at 90 °C (Figure 4.2c), with the releases of Li29Na71-ISG consistently exceeding those of Li47Na53-ISG except at 14 d. Again, the residual rates of Na release of the two Li-ISG compositions appeared subtly different at both temperatures, with a lower residual rate of Na release for Li47Na53-ISG which resembled that of SON68 at 90 °C. Further, the normalised Na releases of Li29Na71-ISG and Li47Na53-ISG at 90 °C were within error of those of SON68 until 112 d and throughout dissolution respectively. However, despite ISG observing similar initial Na releases to both Li-ISG compositions, the residual rate of Na release from ISG at 90 °C was significantly higher than both Li-ISG compositions and SON68. As was consistent with the B releases, further substituting more Li for Na towards an equimolar ratio appeared to improve aqueous durability. However, the lower residual Na release rates of both Li-ISG compositions and SON68 than ISG suggested having Li in the pristine glass composition limited the release of Na from the glass. The 40 °C Na releases from the Li-ISG compositions were initially equal but the Na releases from Li29Na71-ISG remained higher after 14 d, with a subtly larger residual rate of Na releases for Li29Na71-ISG.

The normalised Si releases of the Li-ISG compositions (Figure 4.2d) remained equal throughout dissolution at 90 °C and the normalised Si releases of Li29Na71-ISG at 40 °C remained negligibly higher until 112 d. The apparent solubility limit of Si was achieved in solution after 7 d at 90 °C and 28 d at 40 °C for both Li-ISG compositions. Further, the 90 °C normalised Si releases of the Li-ISG compositions were noted to be similar to those of ISG and marginally lower than those of SON68; suggesting there was no change in the steady state apparent Si solubility limit with the Li:Na ratio.

The high RSD values and low concentrations in solution associated with Al, Ca and Zr meant meaningful trends could not be observed for these elements. Notably, similar normalised releases were observed at 40 and 90 °C for these elements, likely arising from their low solubility in solution.
It was noted the normalised elemental releases of all mobile glass species (B, Li and Na) from the Li-ISG compositions were an order of magnitude lower than those of the Li-Mg-EM compositions. This is highlighted by less than 2.5 % of the B being released from the Li-ISG compositions after 112 d at 90 °C, whilst over 25 % of the B was released from both Li-Mg-EM compositions at this time and temperature (Table 4.5). However, whilst B had the highest normalised releases of any element from both Li-Mg-EM compositions at all durations at both temperatures (except 7 and 14 d at 40 °C where Na had higher normalised releases), Li had the highest normalised releases at 90 °C for both Li-ISG compositions and observed similar normalised releases to B at 40 °C. Notably, the normalised Si releases of the Li-Mg-EM and Li-ISG compositions were similar at both temperatures (Figure 3.4d and Figure 4.2d respectively), suggesting this apparent Si solubility limit was negligibly affected by the differences in composition between the two analogue types and changes in the Li:Na ratio.

Table 4.5: Estimated percentage of B leached from each Li-ISG and Li-Mg-EM composition for each leaching duration at each temperature. Values were calculated from the pristine glass compositions (Table 3.5 and Table 4.4), the masses of glass, the concentrations of B in solution and the volumes of leachant. Values are reported as the average percentage of B released for each triplicate, with errors given to 1σ.

<table>
<thead>
<tr>
<th>% B released from the glass</th>
<th>Leaching time</th>
<th>7 d</th>
<th>14 d</th>
<th>28 d</th>
<th>112 d</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li50Na50</td>
<td>1.54 ± 0.10%</td>
<td>2.13 ± 0.16%</td>
<td>3.15 ± 0.40%</td>
<td>7.67 ± 0.84%</td>
<td></td>
</tr>
<tr>
<td>-Mg-EM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li60Na40</td>
<td>1.98 ± 0.20%</td>
<td>2.83 ± 0.25%</td>
<td>3.85 ± 0.45%</td>
<td>7.28 ± 1.16%</td>
<td></td>
</tr>
<tr>
<td>-Mg-EM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li29Na71</td>
<td>0.25 ± 0.03%</td>
<td>0.46 ± 0.05%</td>
<td>0.65 ± 0.06%</td>
<td>0.87 ± 0.09%</td>
<td></td>
</tr>
<tr>
<td>-ISG</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li47Na53</td>
<td>0.19 ± 0.02%</td>
<td>0.33 ± 0.04%</td>
<td>0.54 ± 0.03%</td>
<td>0.69 ± 0.08%</td>
<td></td>
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<tr>
<td>-ISG</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>90 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li50Na50</td>
<td>15.11 ± 1.81%</td>
<td>19.14 ± 1.49%</td>
<td>24.80 ± 6.21%</td>
<td>26.11 ± 4.44%</td>
<td></td>
</tr>
<tr>
<td>-Mg-EM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li60Na40</td>
<td>21.14 ± 1.89%</td>
<td>24.78 ± 2.64%</td>
<td>22.87 ± 2.75%</td>
<td>26.25 ± 2.08%</td>
<td></td>
</tr>
<tr>
<td>-Mg-EM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li29Na71</td>
<td>1.28 ± 0.08%</td>
<td>1.38 ± 0.29%</td>
<td>1.60 ± 0.15%</td>
<td>2.10 ± 0.19%</td>
<td></td>
</tr>
<tr>
<td>-ISG</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li47Na53</td>
<td>1.14 ± 0.11%</td>
<td>1.21 ± 0.11%</td>
<td>1.36 ± 0.11%</td>
<td>1.79 ± 0.08%</td>
<td></td>
</tr>
<tr>
<td>-ISG</td>
<td></td>
<td></td>
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</tbody>
</table>

The pH of the leachates of each Li-ISG composition at each temperature remained within error of one another throughout dissolution, with the leachant pH at 90 °C being initially higher than the leachant pH at 40 °C (Figure 4.3). Despite the pH appearing to increase at a similar rate at both temperatures, the pH at both temperatures converged to within error of one another after 112 d.
Figure 4.3: Measured pH of the Li-ISG leachates. Errors are given to 1σ calculated from the triplicate measurements.

4.5. Characterisation of pristine and leached glass structures

4.5.1. SEM

SE images were acquired for each Li-ISG composition leached at each temperature for each interval with the aim of investigating the evolution of the glass surface with dissolution time and temperature and how this may be affected by glass composition. EDS analysis did not take place on any of the Li-ISG samples due to the absence of any large precipitate clusters or significant changes to the glass surface after dissolution.

High resolution SE images of the Li-ISG surfaces after dissolution at 90 °C displayed minimal evidence of surface alteration (Figure 4.4), especially in contrast to the well-developed macroporous layer formed after 7 d at 90 °C on the Li-Mg-EM compositions (Figure 3.7). Whilst some roughening of the surface was visible after 7 d at 90 °C in the Li-ISG samples, even after 112 d there appeared to be no further change to the surface topography. The absence of the macroporous layer from the surface of the Li-ISG compositions may simply be attributed to this layer being a magnesium silicate and Mg being absent from the Li-ISG compositions. Whilst some precipitates appeared to be present at longer durations (for example, Figure 4.4g and h), these were sparsely populated and all appeared smaller than 400 nm. There appeared to be no significant differences between the leached surfaces of the two Li-ISG compositions.
No alteration of the Li-ISG surfaces was visible after dissolution at 40 °C and the surface topography did not appear to evolve with dissolution time (Figure 4.5), despite the fraction of glass altered estimated from the B releases increasing by a factor of approximately three between 7 and 112 d at 40 °C (Table 4.5). Additionally, at 40 °C there were no visible precipitates. The absence of surface alteration and precipitates at 40 °C may be attributed to the low fraction of glass altered (estimated 0.87 ± 0.09 % after 112 d at 40 °C for Li29Na71-ISG). That is, only a slight roughening of the glass surface with a small number of sparse precipitates were visible at 90 °C, but the fraction of glass altered at 40 °C was an order of magnitude lower than at 90 °C (Table 4.5); suggesting significantly longer dissolution times would be required at 40 °C to observe any surface changes.

At lower magnifications, the roughening of the glass surface and precipitates after 112 d at 90 °C were not visible and the glass particles appeared pristine (Figure 4.6a and b). As such, at this magnification the particles leached for 112 d appeared identical at 40 and 90 °C (Figure 4.6); highlighting the exceptionally low magnitude of glass alteration compared with the Li-Mg-EM samples, where the pores of the macroporous layer and precipitates were visible even at low magnifications (Figure 3.8). The large bumps observed on the surfaces of all glass particles may be attributed to fractures during crushing.
Figure 4.5: Secondary electron SEM images of Li$_{29}$Na$_{71}$-ISG (top row) and Li$_{47}$Na$_{53}$-ISG (bottom row) leached at 40 °C for: 7 d (a and e), 14 d (b and f), 28 d (c and g) and 112 d (d and h).

Figure 4.6: Secondary electron SEM images of Li$_{29}$Na$_{71}$-ISG leached for 112 d at 90 °C (a) and 40 °C (c), and Li$_{47}$Na$_{53}$-ISG leached for 112 d at 90 °C (b) and 40 °C (d).
4.5.2. NMR

4.5.2.1. $^7$Li MAS-NMR

$^7$Li MAS-NMR experiments took place on the fines of the four pristine Li-ISG batches and one sample of each composition leached at each temperature for 112 d to investigate how the structural role of Li in Li-ISG was affected by composition and whether preferential leaching of Li from a certain environment took place respectively. $^6$Li MAS-NMR experiments did not take place due to the long relaxation times and low natural abundance rendering analysis of the samples challenging. Notably, the linewidth of the $^7$Li MAS-NMR spectra of the pristine Li$_{47}$Na$_{53}$-ISG batches was larger than that of the Li$_{29}$Na$_{71}$-ISG batches (Figure 4.7). Whilst this is consistent with the literature observation that increasing the Li:Na ratio in a series of Li-Na silicate glasses resulted in an increase in the linewidth of $^7$Li spectra$^{184}$, it should be noted the linewidth and chemical shift of the $^7$Li spectra of the two pristine Li-Mg-EM compositions appeared identical (Figure 3.15a). This is suggestive of some degree of clustering in the alkali metals taking place in the Li-Mg-EM compositions, whilst there is a mixing of the alkalis when the Li:Na ratio is increased in the Li-ISG compositions$^{184}$. As was consistent with the Li-Mg-EM $^7$Li MAS-NMR spectra (Figure 3.15b and c), no significant change in the spectra were observed for either Li-ISG composition after dissolution (Figure 4.8).

Figure 4.7: $^7$Li MAS-NMR spectra of the four pristine Li-ISG batches: Li$_{29}$Na$_{71}$-ISG-1 (Blue), Li$_{29}$Na$_{71}$-ISG-2 (Red), Li$_{47}$Na$_{53}$-ISG-1 (Magenta) and Li$_{47}$Na$_{53}$-ISG-2 (Black).
To investigate whether Li was being incorporated into alteration products in measurable masses, static $^6\text{Li}$-$^1\text{H}$ CP-NMR experiments took place on Li$_{29}$Na$_{71}$-ISG leached for 112 d at 40 and 90 °C. As suggested by the sparse nature of the precipitates imaged on the 90 °C leached Li-ISG samples (Figure 4.4) and the low estimated fraction of Li$_{29}$Na$_{71}$-ISG altered at both temperatures (Table 4.5), no signal was visible in the 112 d leached Li-ISG $^6\text{Li}$-$^1\text{H}$ CP-NMR spectra at either temperature (Figure 4.9). The absence of Li from the Li-ISG alteration products may be attributable to the absence of the magnesium silicate layer promoting the precipitation of Li (see Section 3.5.3). Further, it should be noted that the intensity of the $^6\text{Li}$-$^1\text{H}$ CP-NMR signal for the 112 d 40 °C leached Li$_{50}$Na$_{50}$-Mg-EM spectrum was low (Figure 3.16a) with 7.67 ± 0.84 % of the glass altered, whilst only 2.10 ± 0.19 % of Li$_{29}$Na$_{71}$-ISG was altered after 112 d at 90 °C (Table 4.5).

Figure 4.9: Static $^6\text{Li}$-$^1\text{H}$ CP-NMR spectra of Li$_{29}$Na$_{71}$-ISG leached for 112 d at 40 °C (Magenta) and 90 °C (Cyan). Intensities were corrected for the mass of sample analysed and the number of repetitions acquired.
4.5.2.3. $^{11}\text{B MAS-NMR}$

As with the Li-Mg-EM compositions, $^{11}\text{B MAS-NMR}$ experiments took place on all washed and sized Li-ISG batches as well as one sample from each composition leached for each duration at each temperature to investigate the coordination of the pristine B network and how the proportion of $\text{III}_\text{B}$ to $\text{IV}_\text{B}$ units evolved throughout dissolution respectively. An additional $^{11}\text{B}$ experiment also took place on pristine ISG powder (supplied by Savannah River National Laboratory, USA). As discussed in Section 3.4.2.3, the different electric field gradients of $\text{IV}_\text{B}$ and $\text{III}_\text{B}$ species result in a narrow Gaussian $\text{IV}_\text{B}$ peak (0 ppm) being well resolved from a $\text{III}_\text{B}$ doublet consisting of non-ring (17 ppm) and ring (11 ppm) contributions. The area under each peak is directly proportional to the number of atoms in that environment and therefore allows for quantification of the proportion of $\text{III}_\text{B}$ to $\text{IV}_\text{B}$ units. Spectra were normalised to the intensity of their $\text{IV}_\text{B}$ peak so that changes in the pristine coordination of the B network with the Li:Na ratio or incongruent dissolution of B species would be visible through the shape and size of the $\text{III}_\text{B}$ doublets.

Consistent with the pristine Li-Mg-EM $^{11}\text{B}$ spectra (Figure 3.17), no significant change in the proportion of $\text{III}_\text{B}$ to $\text{IV}_\text{B}$ units was observed in the Li-ISG pristine $^{11}\text{B}$ spectra with a changing Li:Na ratio (Figure 4.10a). The lower proportion of $\text{III}_\text{B}$ to $\text{IV}_\text{B}$ associated with Li29Na71-ISG-1 (Blue line, Figure 4.10a) was attributed to the B to total alkali metal ratio deviating slightly between batches and was considered negligible. Similarly, the ISG spectrum was noted to be wider than the Li-ISG spectra (Figure 4.10a), which may also be attributable to differences in thermal history. The $\text{III}_\text{B}/\text{IV}_\text{B}$ ratio of the Li-ISG compositions was significantly lower than that of the Li-Mg-EM compositions (Figure 4.10b). This was likely caused by the lower B to total alkali metal ratios of the Li-ISG compositions (Table 4.1) but is also consistent with the $\text{III}_\text{B}/\text{IV}_\text{B}$ ratio increasing when Mg is substituted for Ca due to the higher ionic field strength of Mg.
Figure 4.10: $^{11}$B MAS-NMR spectra of the four pristine Li-ISG batches with ISG (a) and the two Li-ISG compositions compared with the two Li-Mg-EM compositions (b). Coloured lines in (a) correspond to: Li29Na71-ISG-1 (Blue), Li29Na71-ISG-2 (Green), Li47Na53-ISG-1 (Orange), Li47Na53-ISG-2 (Red) and ISG (Black). Coloured lines in (b) correspond to: Li29Na71-ISG-1 (Orange), Li47Na53-ISG-1 (Blue), Li50Na50-Mg-EM-1 (Green) and Li60Na40-Mg-EM-1 (Red). The Li60Na40-Mg-EM spectrum was shifted +0.1 ppm to correct for referencing error. Spectra were normalised to their $^{11}$B peaks.

The $^{11}$B spectra of both Li-ISG compositions displayed no change in the $^{\text{III}}$B/$^{\text{IV}}$B ratio with dissolution time at both 40 and 90 °C (Figure 4.11). This is consistent with the 40 °C leached Li-Mg-EM $^{11}$B spectra, which demonstrated no change in the $^{\text{III}}$B/$^{\text{IV}}$B ratio after leaching, but is not consistent with the 90 °C Li-Mg-EM $^{11}$B spectra, which displayed a significant decrease in the $^{\text{III}}$B/$^{\text{IV}}$B ratio after 112 d. To quantify the $^{\text{III}}$B/$^{\text{IV}}$B ratio of the pristine, 7 d and 112 d spectra of each composition at each temperature, curve fitting took place using DMFIT software. Curve fitting took place by fitting the Gaussian $^{\text{IV}}$B peak, the $^{\text{III}}$B quadrupole doublet and a first-order SSB manifold based upon the observed sidebands.

Firstly, as the low electric field gradient of the $^{\text{IV}}$B units results in the first-order satellite transition sidebands falling under the $^{\text{IV}}$B peak, these sidebands were fitted based upon the profile of the observed sidebands using a first-order spinning sideband manifold. As with the Li-Mg-EM spectra (Section 3.4.2.3), due to the asymmetry of the $^{\text{IV}}$B peak, a satisfactory fit could not be achieved for the Li-ISG spectra using a single Voigt peak (as in Figure 3.19a). As such, when curve fitting the Li-ISG and ISG spectra, two Gaussian peaks were used to fit the $^{\text{IV}}$B peaks (example fit in Figure 4.12); with the area under each of these peaks simply being added when calculating the $^{\text{III}}$B/$^{\text{IV}}$B ratios without any additional interpretation. Non-ring and ring $^{\text{III}}$B species were then fitted separately using peaks of quadrupole coupling constants which have been reported for their respective resonances.
Figure 4.11: $^{11}$B MAS-NMR spectra of Li29Na71-ISG leached at 40 °C (a), Li47Na53-ISG leached at 40 °C (b), Li29Na71-ISG leached at 90 °C (c) and Li47Na53-ISG leached at 90 °C (d). Coloured lines correspond to: pristine glass (Black), 7 d leached (Blue), 14 d leached (Green), 28 d leached (Orange) and 112 d leached (Red). Spectra were normalised to their $^{11}$B peaks.

Figure 4.12: Example of curve fitting the Li-ISG $^{11}$B MAS-NMR spectra as demonstrated using Li29Na71-ISG leached at 40 °C for 112 d. Coloured lines correspond to: the original spectrum (Blue), the fit (Red), the residual of the fit (Grey), the two Gaussian peaks used to fit the $^{11}$B peak (Magenta and Red), the peaks used to fit the $^{10}$B ring and non-ring peaks (Cyan and Grey respectively) and the first order spinning sideband manifold (Green). The baseline is given by the horizontal red line.
Curve fitting provided a measure of the $^{3}$$^\text{B}/^{4}$$^\text{B}$ ratios of the samples, affording comparisons between the pristine and leached spectra. Quantification of the pristine spectra confirmed the four pristine Li-ISG batches had $^{3}$$^\text{B}$ and $^{4}$$^\text{B}$ molar fractions within error of one another (Table 4.6) and minor discrepancies may be attributed to the B to alkali metal ratio varying between glass batches. Quantification of the ISG spectrum showed ISG contained a lower $^{3}$$^\text{B}/^{4}$$^\text{B}$ ratio than the Li-ISG compositions (Table 4.6). However, if this effect was solely caused by the substitution of Li for Na, a similar effect would be expected to be visible between the two Li-ISG compositions as well.

**Table 4.6: Measured elemental molar percentages of Li, Na and B in the pristine Li-ISG samples (calculated from Table 4.4) alongside the fractions of $^{3}$$^\text{B}$ and $^{4}$$^\text{B}$ estimated from quantifying the pristine, 7 d leached and 112 d leached (40 and 90 °C) $^{11}$$^\text{B}$ NMR spectra. For the sake of comparison, the nominal composition of ISG and the results of the curve fitting are given. Errors given on the concentrations are conservatively reported as 5% of the measured value as all values reported RSD less than 5%, with the errors on the $\text{[B]/[Total alkali]}$, $^{3}$$^\text{B}$ and $^{4}$$^\text{B}$ propagated from these values.**

<table>
<thead>
<tr>
<th></th>
<th>Li29Na71-Li-ISG</th>
<th>Li47Na53-Li-ISG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pristine</td>
<td>40 °C Leached</td>
</tr>
<tr>
<td>ISG</td>
<td>Li29Na71-1</td>
<td>Li29Na71-2</td>
</tr>
<tr>
<td>[Li] (at. %)</td>
<td>-</td>
<td>5.2 ± 0.3</td>
</tr>
<tr>
<td>[Na] (at. %)</td>
<td>19.1</td>
<td>13.4 ± 0.7</td>
</tr>
<tr>
<td>[B] (at. %)</td>
<td>24.1</td>
<td>23.2 ± 1.2</td>
</tr>
<tr>
<td>[B]/[Total alkali]</td>
<td>1.26</td>
<td>1.25 ± 0.09</td>
</tr>
<tr>
<td>$^{11}$$^\text{B}$ (%)</td>
<td>46.9</td>
<td>49.7</td>
</tr>
<tr>
<td>$^{3}$$^\text{B}$ (%)</td>
<td>53.1</td>
<td>50.3</td>
</tr>
<tr>
<td>$^{11}$$^\text{B}$ (at. %)</td>
<td>11.3</td>
<td>11.5 ± 0.6</td>
</tr>
<tr>
<td>$^{3}$$^\text{B}$ (at. %)</td>
<td>12.8</td>
<td>11.7 ± 0.6</td>
</tr>
<tr>
<td>$^{3}$$^\text{B}/^{11}$$^\text{B}$</td>
<td>0.88</td>
<td>0.99</td>
</tr>
<tr>
<td>Change in $^{11}$$^\text{B}$ from pristine (% points)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Quantification of the 90 °C leached spectra agreed with the observation that the B network of both Li-ISG compositions leached congruently, displaying less than a 0.7 percentage point decrease in the fraction of $^{3}$$^\text{B}$ units after leaching which was considered to be within error of the fits (Table 4.6). However, quantification of the 40 °C leached spectra displayed a 1.4 percentage point increase in the fraction of $^{3}$$^\text{B}$ units after 7 d for both compositions (Table 4.6). It was possible the visual similarity of these spectra arose due to variations in the intensity and positions of the first-order satellite transition sidebands between samples, which would not be visible when overlaying the spectra normalised to their $^{11}$$^\text{B}$ peaks. However, as this increase
was small, was not visible in the 112 d samples and was not at all visible in the spectra (Figure 4.11a and b), this difference was also considered negligible and within the error of the fits.

### 4.5.2.4. $^{23}$Na MAS-NMR

To investigate how the structural role of Na varied with composition and whether sodium silicate hydrate precipitation was taking place in the Li-ISG samples, $^{23}$Na MAS-NMR experiments took place on all four washed and sized Li-ISG batches, pristine ISG and one sample from each composition leached for each duration at each temperature. As was consistent with the Li-Mg-EM batches, spectra of the four pristine Li-ISG batches appeared near-identical and displayed no change in the environment of Na with the Li:Na ratio (Figure 4.13a). Notably, a small shift (approximately +1.5 ppm) was observed for ISG relative to Li-ISG, which was consistent with the shift of approximately +1.5 ppm observed for Mg-EM relative to Li-Mg-EM (Figure 3.20). Again, the similarity of the spectra of both Li-ISG compositions suggests this shift was negligible in terms of structural change. This is further substantiated by the spectra of both Li-ISG and both Li-Mg-EM compositions appearing near-identical despite covering a range of Li:Na ratios across two significantly different compositions (Figure 4.13b). The similarity of the Li-Mg-EM and Li-ISG spectra suggests Na fulfils the same role in the same environment in both analogue types, regardless of changes in the Li:Na ratio and composition.

![Figure 4.13: $^{23}$Na MAS-NMR spectra of pristine ISG and the pristine Li-ISG batches (a) and the two Li-ISG compositions compared with the two Li-Mg-EM compositions (b). Coloured lines in (a) correspond to: ISG (Black), Li29Na71-ISG-1 (Blue), Li29Na71-ISG-2 (Green), Li47Na53-ISG-1 (Orange) and Li47Na53-ISG-2 (Red). Coloured lines in (b) correspond to: Li29Na71-ISG-1 (Orange), Li47Na53-ISG-1 (Blue), Li50Na50-Mg-EM-1 (Green) and Li60Na40-Mg-EM-1 (Red). Spectra were normalised to the same intensity.](image)

For both Li-ISG compositions, there were no visible changes in the $^{23}$Na spectra after dissolution at either 40 or 90 °C (Figure 4.14). Whilst this was consistent with the 40 °C Li-
Mg-EM spectra in displaying no change (Figure 3.21a and c), at 90 °C a second peak was visible in the Li-Mg-EM spectra at approximately -7.3 ppm (Figure 3.21b and d) which was attributed to a sodium silicate hydrate secondary phase precipitating on the surface of the glass.

Under the assumption that the concentration of B in solution can be used to calculated the fraction of glass altered, an estimated Na concentration in solution can be calculated assuming Na is released congruently with B. The difference between the estimated and measured Na concentrations can be used with the known leachant volumes to provide an estimated concentration of Na in precipitates (Table 4.7).

**Figure 4.14:** $^{23}$Na MAS-NMR spectra of Li29Na71-ISG leached at 40 °C (a) and 90 °C (b), and Li47Na53-ISG leached at 40 °C (c) and 90 °C (d). Coloured lines represent: pristine glass (Black), 7 d leached (Blue), 14 d leached (Green), 28 d leached (Orange) and 112 d leached (Red). Spectra were normalised to the same intensity.

Notably, at 40 °C the Na releases frequently exceeded the B releases, resulting in negative estimated masses of Na precipitates (Table 4.7). At 90 °C, the estimated masses of Na precipitates were often within error of zero or at masses which were likely too small for detection by NMR and were considered negligible (Table 4.7). As such, Na was shown not to precipitate in measurable quantities on the Li-ISG compositions at either temperature. It was
expected the extent of dissolution was merely insufficient in these samples for measurable masses of Na precipitation to take place; as demonstrated by only 2.10 ± 0.19% of the B being released from Li29Na71-ISG after 112 d at 90 °C, but the precipitated Na peak being a small bump in the spectra of Li60Na40-Mg-EM leached for 7 d at 90 °C with 21.14 ± 1.89% of the B released.

Table 4.7: Table comparing the percentage of B released from the glass, the concentration of Na in solution estimated from the fraction of B released, the measured concentration of Na in solution and the difference between the measured and estimated Na concentrations presented in mg/l and mg. Errors were propagated from the triplicate leachate concentrations, the pristine glass compositions, and the masses of glass and volumes of leachant used in the experiments.

<table>
<thead>
<tr>
<th>Leaching time at 40 °C</th>
<th>7 d</th>
<th>14 d</th>
<th>28 d</th>
<th>112 d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li29Na71-Li-ISG</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% glass altered (From B releases)</td>
<td>0.25 ± 0.03%</td>
<td>0.46 ± 0.05%</td>
<td>0.65 ± 0.06%</td>
<td>0.87 ± 0.09%</td>
</tr>
<tr>
<td>Estimated [Na] in solution (mg/L)</td>
<td>15.9 ± 2.6</td>
<td>29.2 ± 4.1</td>
<td>41.7 ± 5.6</td>
<td>55.1 ± 7.9</td>
</tr>
<tr>
<td>[Na in solution] (mg/L)</td>
<td>23.3 ± 1.4</td>
<td>34.1 ± 3.0</td>
<td>43.6 ± 0.7</td>
<td>53.7 ± 0.6</td>
</tr>
<tr>
<td>Difference (mg/l)</td>
<td>7.4 ± 4.0</td>
<td>4.9 ± 7.1</td>
<td>1.9 ± 6.3</td>
<td>-1.4 ± 8.5</td>
</tr>
<tr>
<td>Estimated precipitated (mg)</td>
<td>-0.03 ± 0.02</td>
<td>-0.02 ± 0.03</td>
<td>-0.01 ± 0.02</td>
<td>0.01 ± 0.03</td>
</tr>
<tr>
<td>Li47Na53-Li-ISG</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% glass altered (From B releases)</td>
<td>0.19 ± 0.02%</td>
<td>0.33 ± 0.04%</td>
<td>0.54 ± 0.03%</td>
<td>0.69 ± 0.08%</td>
</tr>
<tr>
<td>Estimated [Na] in solution (mg/L)</td>
<td>9.3 ± 1.4</td>
<td>16.0 ± 2.4</td>
<td>26.8 ± 2.4</td>
<td>33.7 ± 4.9</td>
</tr>
<tr>
<td>[Na in solution] (mg/L)</td>
<td>16.0 ± 1.4</td>
<td>21.1 ± 0.3</td>
<td>28.4 ± 0.8</td>
<td>36.0 ± 0.4</td>
</tr>
<tr>
<td>Difference (mg/l)</td>
<td>6.7 ± 2.8</td>
<td>5.1 ± 2.7</td>
<td>1.6 ± 3.2</td>
<td>2.3 ± 5.3</td>
</tr>
<tr>
<td>Estimated precipitated (mg)</td>
<td>-0.03 ± 0.01</td>
<td>-0.02 ± 0.01</td>
<td>-0.01 ± 0.01</td>
<td>-0.01 ± 0.02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Leaching time at 90 °C</th>
<th>7 d</th>
<th>14 d</th>
<th>28 d</th>
<th>112 d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li29Na71-Li-ISG</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% glass altered (From B releases)</td>
<td>1.28 ± 0.08%</td>
<td>1.38 ± 0.29%</td>
<td>1.60 ± 0.15%</td>
<td>2.10 ± 0.19%</td>
</tr>
<tr>
<td>Estimated [Na] in solution (mg/L)</td>
<td>78.5 ± 8.0</td>
<td>84.3 ± 20.3</td>
<td>98.8 ± 12.9</td>
<td>128.4 ± 16.6</td>
</tr>
<tr>
<td>[Na in solution] (mg/L)</td>
<td>67.2 ± 0.1</td>
<td>73.6 ± 11.6</td>
<td>76.0 ± 1.0</td>
<td>99.6 ± 0.6</td>
</tr>
<tr>
<td>Difference (mg/l)</td>
<td>-11.3 ± 8.1</td>
<td>-10.7 ± 31.9</td>
<td>-22.8 ± 13.9</td>
<td>-28.8 ± 17.2</td>
</tr>
<tr>
<td>Estimated precipitated (mg)</td>
<td>0.05 ± 0.03</td>
<td>0.04 ± 0.13</td>
<td>0.09 ± 0.05</td>
<td>0.12 ± 0.07</td>
</tr>
<tr>
<td>Li47Na53-Li-ISG</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% glass altered (From B releases)</td>
<td>1.14 ± 0.11%</td>
<td>1.21 ± 0.11%</td>
<td>1.36 ± 0.11%</td>
<td>1.79 ± 0.08%</td>
</tr>
<tr>
<td>Estimated [Na] in solution (mg/L)</td>
<td>52.9 ± 7.2</td>
<td>56.2 ± 7.1</td>
<td>63.2 ± 7.6</td>
<td>82.9 ± 7.0</td>
</tr>
<tr>
<td>[Na in solution] (mg/L)</td>
<td>46.8 ± 0.6</td>
<td>47.6 ± 0.5</td>
<td>50.6 ± 0.5</td>
<td>60.7 ± 2.6</td>
</tr>
<tr>
<td>Difference (mg/l)</td>
<td>-6.1 ± 7.8</td>
<td>-8.6 ± 7.6</td>
<td>-12.2 ± 8.1</td>
<td>-22.2 ± 9.6</td>
</tr>
<tr>
<td>Estimated precipitated (mg)</td>
<td>0.02 ± 0.03</td>
<td>0.03 ± 0.03</td>
<td>0.05 ± 0.03</td>
<td>0.09 ± 0.04</td>
</tr>
</tbody>
</table>

4.5.3. XRD

Both Li-ISG compositions leached at each temperature for 112 d underwent XRD analysis to investigate whether there was any change in wasteform crystallinity after dissolution. As expected from the precipitates at 90 °C being sparse in the SEM images (Section 4.5.1) and secondary phases being absent from the $^6$Li-$^1$H CP-NMR and $^{23}$Na MAS-NMR spectra (Section...
Relating Magnox and international waste glasses

4.5.2) alongside negligible estimated masses of sodium silicate hydrate precipitates (Table 4.7), no detectable crystalline phases were observed in any of the Li-ISG XRD spectra (Figure 4.15). This is consistent with the leached Li-Mg-EM samples (Figure 3.23), which displayed no crystalline secondary phases despite a significantly larger fraction of the glass being altered (Table 4.5) and a significant amount of secondary phase precipitation taking place (Sections 3.4.1 and 3.4.2). Based upon observations of sodium silicate hydrate and calcium silicate hydrates forming on a Ca-Na borosilicate (ISG without Al and Zr) after 12.8 years of dissolution in deionised water at 90 °C, it is expected crystalline secondary phases would eventually form on all Li-ISG and Li-Mg-EM compositions.

![Figure 4.15: XRD spectra of the Li-ISG compositions leached for 112 d, analysed on a low-background plate.](image)

4.6. Discussion

4.6.1. The structure of pristine Li-ISG
The near-identical $^{11}\text{B}$ MAS-NMR spectra and $^{\text{III}}\text{B}/^{\text{IV}}\text{B}$ ratios of pristine Li29Na71-ISG and Li47Na53-ISG showed that varying the Li:Na ratio had no measurable effect on the number of $^{\text{IV}}\text{B}$ species and subsequently the number of species charge compensating the B network (Table 4.6). The minor discrepancy between the $^{\text{III}}\text{B}/^{\text{IV}}\text{B}$ ratios of ISG and the Li-ISG compositions was attributed to differences in thermal history and small variations in the B to total alkali metal ratios within error of those measured$^{163,186}$. Further, the minor discrepancy between the $^{\text{III}}\text{B}/^{\text{IV}}\text{B}$ ratios of the two batches of Li29Na71-ISG was attributed to differences in their B to total alkali metal ratios within error of those measured (Table 4.6). The consistency of the shape of the $^{\text{III}}\text{B}$ doublet between samples also suggested there was no significant change in the proportion of ring to non-ring $^{\text{III}}\text{B}$ species with the Li:Na ratio. These results were therefore consistent with pristine Mg-EM, Li50Na50-Mg-EM and Li60Na40-Mg-EM. The significant differences between the respective $^{\text{III}}\text{B}/^{\text{IV}}\text{B}$ ratios of the Li-Mg-EM and Li-ISG compositions (Figure 4.10b) was attributed to differences in their glass making conditions, elemental compositions.
Relating Magnox and international waste glasses

(particularly Mg and Ca\(^{46}\)) and their B to total alkali metal ratios. The similarities between the Li-Mg-EM \(^{11}\)B spectra were previously attributed to Na preferentially charge compensating \(^{IV}\)B units whilst Li preferentially modifies the Si-network, based upon observations of single and binary alkali borosilicates in the literature\(^{25,32,38,174}\). In such a system, when Li is substituted for Na the majority of the \(^{IV}\)B units remain charge compensated by Na. This is consistent with the \(^{23}\)Na MAS-NMR spectra of the pristine Li-ISG compositions and ISG showing there was no change in the structural role of Na as the Li:Na increased (Figure 4.13a). Further, the near-identical \(^{23}\)Na spectra of the Li-ISG and Li-Mg-EM compositions showed that Na fulfilled the same structural role in all compositions studied (Figure 4.13b). It should be noted that whilst there was a higher concentration of Na than \(^{IV}\)B species in pristine Mg-EM, ISG and Li\(_{29}\)Na\(_{71}\)-ISG, there was a higher concentration of \(^{IV}\)B species than Na in pristine Li\(_{50}\)Na\(_{50}\)-Mg-EM, Li\(_{60}\)Na\(_{40}\)-Mg-EM and Li\(_{47}\)Na\(_{53}\)-ISG.

It was noted that whilst there was no change in the \(^{7}\)Li MAS-NMR linewidth between the Li-Mg-EM samples (Figure 3.15a), the \(^{7}\)Li MAS-NMR spectra of Li\(_{47}\)Na\(_{53}\)-ISG were wider than those of Li\(_{29}\)Na\(_{71}\)-ISG (Figure 4.7). Assuming \(^{7}\)Li MAS-NMR linewidths are not affected by Li diffusion at ambient temperatures, this increase in linewidth can be attributed to the average Li-Li distance decreasing as the Li contents of the glass increases: the decrease in Li-Li distance results in an increase in homogeneous dipolar coupling and subsequently an increase in \(^{7}\)Li linewidth\(^{184}\). When interpreting this increase in linewidth between the Li-ISG compositions, it should be noted again that the number of Na is higher than the number of \(^{IV}\)B species for Li\(_{29}\)Na\(_{71}\)-ISG but lower than the number of \(^{IV}\)B species for Li\(_{47}\)Na\(_{53}\)-ISG. It was expected that once Li charge compensates the B network in place of Na in Li\(_{47}\)Na\(_{53}\)-ISG, there was a higher degree of mixing amongst Li and Na and the average Li-Li distance decreased compared with Li\(_{29}\)Na\(_{71}\)-ISG; resulting in an increased \(^{7}\)Li linewidth in Li\(_{47}\)Na\(_{53}\)-ISG compared with Li\(_{29}\)Na\(_{71}\)-ISG. The absence of a change in the linewidth of the \(^{23}\)Na spectra of the two Li-ISG compositions may be attributed to homogeneous dipolar coupling not being as strong for Na as in Li\(^{184}\). Contrastingly, the Na concentrations of both Li-Mg-EM compositions were lower than the concentrations of \(^{IV}\)B species. As such, when the Li:Na ratio was increased in Li-Mg-EM, there was already a fraction of Li charge compensating the B network and this resulted in a negligible change in the average Li-Li distance\(^{184}\).
4.6.2. Precipitates controlling aqueous durability

Whilst there were significant structural differences between the pristine Li-ISG and Li-Mg-EM glasses arising from differences in composition and glassmaking conditions, the normalised elemental releases of the leachates alongside SEM images and MAS-NMR spectra of the leached glasses highlighted profound differences in dissolution behaviour between the two analogue types. Although $^{23}$Na MAS-NMR, $^6$Li-$^1$H CP-NMR, SEM and EDS demonstrated there were amorphous alteration products forming at both 40 and 90 °C after just 7 d for both Li-Mg-EM compositions, the alteration products appeared few in the SEM images of the leached Li-ISG compositions and were not detectable through either NMR or XRD.

The $^{23}$Na MAS-NMR spectra of all Li-Mg-EM samples leached at 90 °C (Figure 3.21b and d) demonstrated a sodium silicate hydrate phase was precipitating from solution (see Chapter 3). However, the estimated masses of Na in a precipitated phase for the Li-ISG compositions were either within error of zero or negligibly small (Table 4.7). As such, it was expected that a sodium silicate hydrate phase also precipitates on the Li-ISG glasses, but the rate of precipitation was so slight that these phases could only be observed once a significant fraction of the glass had been altered. This was consistent with the rate of dissolution of the Li-ISG compositions being an order of magnitude lower than the rate of dissolution of the Li-Mg-EM compositions and the absence of this phase from the 40 °C leached Li-Mg-EM samples.

As Mg was absent from ISG and Li-ISG, the macroporous magnesium silicate layer which began forming after just 7 d at 40 °C on the Li-Mg-EM compositions was absent from the leached Li-ISG samples. As discussed in Section 3.5.3, as this magnesium silicate layer precipitates it consumes significant amounts of Si from the leachant, which in turn fuels further hydrolysis of the glass or alteration layers to increase the rate of glass dissolution and lower aqueous durability. Combined with interdiffusion reactions across the passivating alteration layer, this precipitation is expected to control the residual rate of dissolution and results in poor aqueous durability throughout dissolution when the pristine glass or leachant contains Mg$^{47,49,50,102}$. In the literature, it has been shown that in a Mg-EM system where Ca has been substituted for Mg at various Ca:Mg ratios that the initial dissolution rate did not change with the Ca:Mg ratio$^{46}$. This shows that the difference in aqueous durability between the Li-Mg-EM and Li-ISG compositions is not attributable to differences in pristine glass structure. Similarly, whilst a Li-bearing phase was shown to precipitate at 40 and 90 °C after 7 and 112 d respectively onto Li50Na50-Mg-EM (Section 3.5.3), no such phase was detected for the Li-ISG
compositions leached at either temperature for 112 d. This suggests that Mg-phase precipitation causes Li to be incorporated into secondary phases.

4.6.3. Differences in dissolution of the B network and the effects of Li

In addition to the presence of Mg in the Li-Mg-EM compositions resulting in the precipitation of secondary phases which substantially accelerated dissolution, the substitution of Li for Na in ISG at realistic and excess Li:Na ratios had significant effects on dissolution behaviour which differed from those observed for the Li-Mg-EM compositions. This suggests that a clear relationship between the dissolution behaviour of the two analogue types cannot be defined simply through comparing leachate compositions and pristine structures. When considering changes in dissolution kinetics associated with substituting Li for Na at an excess ratio, it should be noted that for the Li-Mg-EM compositions there was a deviation away from an equimolar Li:Na ratio (1.0 to 1.5) but for the Li-ISG compositions there was a deviation towards an equimolar ratio (0.4 to 0.9).

For the Li-Mg-EM glasses leached at long duration at 90 °C, $^{11}$B MAS-NMR spectra showed that $^{III}$B species leached more readily than $^{IV}$B species (see Section 3.5.2). This effect was attributed to Li preferentially modifying the Si network and leaching more readily than charge compensating Na, resulting in faster dissolution of $^{III}$B units through enhanced glass hydration whilst the Na-compensated $^{IV}$B units remained largely unaffected. This effect could not be attributed to $^{III}$B units having an inherently lower chemical durability than $^{IV}$B units as the B network of Mg-EM leached congruently after 112 d at 90 °C. However, the B network appeared to dissolve congruently at 40 °C. It was hypothesised preferential dissolution of $^{III}$B units was also taking place at 40 °C but the magnitude of glass alteration was insufficient for this effect to be measurable. Similarly, dissolution of the B network of both Li-ISG compositions appeared congruent at 40 and 90 °C (Figure 4.11) but the magnitude of dissolution appeared insufficient to ascertain whether dissolution was incongruent.

Owing to the respective preferences of Li to modify the Si network and Na to charge compensate the B network, substituting Li for Na in ISG resulted in a more depolymerised Si network which presented less of a barrier to the inward diffusion of water species and permitted faster hydration of the glass network. Additionally, Li is expected to be more weakly bonded to the glass network in its modifying role than Na in its charge compensating role and the preferential ion-exchange of Li over Na may result in Li leaching out of the glass before Na to
leave a hydrated relict glass structure faster than in a Li-free composition. As low amounts of energy are required to hydrolyse the bonds of the B network, Li promoted the release of B such that the normalised B releases of both Li-ISG and Li-Mg-EM compositions were consistently approximately twice those of ISG and Mg-EM respectively (Figure 4.2 and Figure 3.4 respectively). This demonstrated that the presence of Li had a significant negative impact on aqueous durability across a range of significantly different analogue compositions.

For Li29Na71-ISG, as there were more Na than IVB units the majority of IVB units would have remained compensated by Na; demonstrating that the faster glass hydration brought about by Li modifying the Si network still has a marked impact on the Na-compensated B network. Whilst the Li-Mg-EM compositions displayed a drop in the normalised Si releases compared to Mg-EM at 90 °C (Figure 3.4d), the steady state apparent Si solubility limit of ISG and the Li-ISG compositions appeared similar (Figure 4.2d). The normalised Si releases reached their respective apparent solubility limits at similar values for all Li-ISG and Li-Mg-EM compositions. However, the Li-ISG compositions reached their apparent limit after 7 d at 90 °C and 28 d at 40 °C, in contrast to 14 d at 90 °C and 7 d at 40 °C for the Li-Mg-EM compositions. Whilst the normalised Na releases of Mg-EM and Li50Na50-Mg-EM remained within error of each other throughout dissolution at 90 °C, the residual release rate of Na from ISG was significantly higher than those of both Li-ISG compositions (Figure 4.2c). For Li-ISG it appeared that Li was promoting dissolution of the B network through increasing the rate of glass hydration whilst simultaneously suppressing the residual release of Na, regardless of whether the number of Na exceeded the number of IVB.

The similarity of the 23Na MAS-NMR spectra of ISG and both Li-ISG compositions demonstrated the role of Na did not change with the substitution of Li for Na (Figure 4.13). As such, in Li29Na71-ISG the fraction of Li charge compensating IVB units is expected to be small. Despite promoting the release of B through the previously discussed hydration effects, the drop in the residual Na release rate of the Li-ISG compositions relative to ISG suggests that in addition to these hydration effects having a limited impact on the Na-compensated IVB units, the substitution of Li into ISG also limited the release of charge compensating Na during the residual rate regime. As such, there appeared to be a mixed alkali effect wherein the substitution of Li for Na in Li-ISG resulted in a reduction in the mobility of Na and subsequently the rate of Na diffusion out of the glass, an effect which was most visible during the residual rate
Relating Magnox and international waste glasses

The higher normalised B releases but similar normalised Na releases of Li50Na50-Mg-EM compared with Mg-EM suggested that the enhanced glass hydration brought about by the presence of Li in the Li-Mg-EM compositions was an important mechanism but the reduction of the mobility of Na through a mixed alkali effect in the Li-Mg-EM compositions was not. Notably, increasing the Li:Na ratio from 0.4 to 0.9 in Li-ISG had a significantly different effect on the B and Na releases to increasing the Li:Na ratio from 1.0 to 1.5 in Li-Mg-EM. Initially increased normalised B and Na releases were observed for Li60Na40-Mg-EM relative to Li50Na50-Mg-EM which converged as dissolution progressed, with the releases converging slower at 40 °C than at 90 °C. For Li-ISG, the normalised B and Na releases for Li47Na53-ISG were lower than Li29Na71-ISG and the residual rates of B and Na releases for Li47Na53-ISG appeared subtly lower (Figure 4.2). Li47Na53-ISG displayed similar behaviour in the normalised Li releases to the Li-Mg-EM compositions, with initial releases which were negligibly higher than those of Li29Na71-ISG which later converged to identical values after 14 d (Figure 4.2b).

The initial increases in the B, Li and Na releases of Li60Na40-Mg-EM compared with Li50Na50-Mg-EM were attributed to the further substitution of Li intensifying the previously discussed hydration effects and the excess Li contents was concluded to have no long-term effect on aqueous durability once a passivating alteration layer component had formed and rendered these hydration effects less relevant. Contrastingly, a decrease in the B and Na normalised releases and lack of significant change in the Li and Si normalised releases for Li47Na53-ISG compared with Li29Na71-ISG demonstrated that further substituting Li for Na towards an equimolar ratio in Li-ISG intensified the Li-Na mixed alkali effect to outweigh the previously discussed hydration effects, reduce the normalised B and Na releases for Li47Na53-ISG relative to Li29Na71-ISG throughout dissolution and improve aqueous durability. For Li, the mixed alkali effect appeared to be equally offset by the hydration effects and as such no change in the normalised Li releases was observed. The persistence of these hydration and mixed alkali effects throughout the residual rate regime suggested that the alteration layers formed in the Li-ISG compositions after 112 d at 90 °C were insufficiently dense or passivating to present a significant barrier to dissolution and render the hydration and mixed alkali effects irrelevant.
4.7. Summary

It was shown that changing the Li:Na ratio of the Li-ISG analogues had no effect on the ratio of $^{\text{III}}\text{B}$ to $^{\text{IV}}\text{B}$ units and consequently the number of species charge compensating the B network remained constant. This was consistent with the Li-Mg-EM analogues in suggesting Li charge compensated the B network in place of Na once the Li:Na ratio was increased and the concentration of Na dropped below that of the $^{\text{IV}}\text{B}$ units. Similarly, $^{23}\text{Na}$ MAS-NMR suggested no change in the role of Na with a changing Li:Na ratio. Contrastingly, the B network of both Li-ISG analogues leached congruently at both 40 and 90 °C. However, the extent of glass alteration was considered insufficient to ascertain whether incongruent dissolution was taking place.

Consistent with the Li-Mg-EM analogues, the substitution of Li into ISG reduced aqueous durability (B releases) but decreased the release rate of Na at longer leaching durations at 90 °C. However, substituting in further Li for Na to an excess Li:Na ratio in Li-ISG improved aqueous durability measured through both the B and Na releases at both 40 and 90 °C; opposite to the effect observed for the Li-Mg-EM analogues. Whilst the presence of Li had a negative impact on aqueous durability at 90 °C, likely through enhancing glass hydration, a mixed alkali effect was also present which reduced the Na releases and improved aqueous durability as the Li:Na ratio was increased towards an equimolar value.

The significantly poorer aqueous durability of the Li-Mg-EM analogues compared to the Li-ISG analogues was attributed to the precipitation of a magnesium silicate layer on both Li-Mg-EM analogues at both 40 and 90 °C; where such a layer consumes significant amounts of Si from solution as it forms to fuel further hydrolysis of the glass network. Significant amounts of a sodium silicate hydrate phase were shown to precipitate at 90 °C for the Li-Mg-EM analogues but this phase was absent from the Li-ISG compositions. Such a Na-bearing phase was expected to form for the Li-ISG analogues but the extent of glass alteration was thought to be insufficient for it to be observed. Whilst a Li-bearing phase precipitated on the Li-Mg-EM analogues at 40 and 90 °C, it was expected the incorporation of Li into secondary phases was enhanced by the precipitation of a magnesium silicate.
5. Evaluating the temperature dependence of waste glass dissolution

The work presented in this chapter has been published in the Journal of Non-Crystalline solids and has been modified for use in this dissertation\textsuperscript{187}.

5.1. Introduction

The 24-component complex simulant Magnox waste glass of a simulated 25 wt.% waste loading, MW25 (nominal composition given in Table 5.1), was fabricated on an inactive full-scale replica of the WVP at Sellafield Ltd (see Sections 1.1 and 2.2.2). In producing MW25, inactive isotopes of fission products as well as corrosion products and process additives were used in the simulant HAL. Fission products present in the active HAL at less than 1 wt.% were omitted from the simulant HAL, with the exceptions of Te and the REEs. REEs were represented using a commercial nitrate mixture (La, Nd, Pr, Sm and Y). Transuranic elements were omitted due to their activity, as well as Pd and Rh due to their cost\textsuperscript{11,15}.

Table 5.1: Nominal oxide wt.% composition of MW25\textsuperscript{15}.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Oxide wt.%</th>
<th>Oxide</th>
<th>Oxide wt.%</th>
<th>Oxide</th>
<th>Oxide wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>4.41</td>
<td>Li\textsubscript{2}O</td>
<td>4.12</td>
<td>RuO\textsubscript{2}</td>
<td>0.77</td>
</tr>
<tr>
<td>B\textsubscript{2}O\textsubscript{3}</td>
<td>17.04</td>
<td>MgO</td>
<td>4.68</td>
<td>[SO\textsubscript{4}]\textsuperscript{3-}</td>
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</tr>
<tr>
<td>BaO</td>
<td>0.48</td>
<td>MoO\textsubscript{3}</td>
<td>1.44</td>
<td>SiO\textsubscript{2}</td>
<td>46.83</td>
</tr>
<tr>
<td>CeO\textsubscript{2}</td>
<td>1.13</td>
<td>Na\textsubscript{2}O</td>
<td>8.46</td>
<td>Sm\textsubscript{2}O\textsubscript{3}</td>
<td>0.39</td>
</tr>
<tr>
<td>Cr\textsubscript{2}O\textsubscript{3}</td>
<td>0.6</td>
<td>Nd\textsubscript{2}O\textsubscript{3}</td>
<td>1.86</td>
<td>SrO</td>
<td>0.28</td>
</tr>
<tr>
<td>Cs\textsubscript{2}O</td>
<td>1.07</td>
<td>NiO</td>
<td>0.37</td>
<td>TeO\textsubscript{2}</td>
<td>0.17</td>
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<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
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<td>[PO\textsubscript{4}]\textsuperscript{3-}</td>
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<td>Y\textsubscript{2}O\textsubscript{3}</td>
<td>0.18</td>
</tr>
<tr>
<td>La\textsubscript{2}O\textsubscript{3}</td>
<td>0.58</td>
<td>Pr\textsubscript{2}O\textsubscript{3}</td>
<td>0.56</td>
<td>ZrO\textsubscript{2}</td>
<td>1.41</td>
</tr>
</tbody>
</table>

Many dissolution experiments have taken place at significantly higher temperatures than those expected in a GDF in order to accelerate dissolution under the assumption that the underlying dissolution processes would be the same at both temperatures but merely accelerated at higher temperatures\textsuperscript{3,16,46,74,91,104}. Further, lower temperature studies have focussed on selectively probing initial glass dissolution rates by taking place at lower SA/V ratios or in single-pass flow-through experiments\textsuperscript{108,109,188}. However, changes in dissolution temperature have been shown to have marked impacts on both the initial and long-term dissolution rates of glasses at both near to or far from saturation conditions\textsuperscript{40,48,63,105–107}. 

139
In the previous two chapters, dissolution experiments on simplified analogue compositions took place at both an estimated GDF temperature (40 °C) and an accelerated dissolution temperature (90 °C) to investigate whether the observed effects of Li on aqueous durability occurred consistently at both temperatures. Whilst these Li effects appeared to be consistent across the temperature range studied, these experiments showed there were considerable differences in the concentrations of mobile species within the leachates between 40 and 90 °C. The experiments presented in this chapter aimed to investigate the effects of dissolution temperature on the kinetics of dissolution and the formation of secondary phases as well as the Arrhenius-type dependency of dissolution of MW25.

Dissolution experiments took place at 40 and 90 °C to investigate the dissolution behaviour of MW25 at estimated GDF and accelerated dissolution temperatures respectively. As the same leachates would undergo an isotopic study (presented in Chapter 7), a static batch sampling methodology was used (Section 2.8). To investigate the Arrhenius temperature dependence of MW25 dissolution and the consistency of the dissolution processes across this temperature range, experiments also took place using the standard static batch leaching methodology at the intermediate temperatures of 70 and 80 °C (Section 2.7). An intermediate SA/V of 2000 m⁻¹ was used in both sets of experiments to probe all stages of dissolution (excluding the rate resumption regime).

The MW25 used in these experiments (VTR pour 36, campaign 10) was supplied by Sellafield Ltd as monolithic shards and had previously undergone routine characterisation. Compositional analysis had demonstrated MW25 was within error of its nominal composition and SEM displayed an average bubble surface area coverage of 1.45 %. XRD and EDS analysis showed MW25 contained a crystalline RuO₂ phase and Cr-Fe-Mg-Ni-rich spinel phases which accounted for approximately 1.3 % of the glass in total, whilst no yellow phase was detected. In calculating the geometric surface areas of the powders for the SA/V ratios, a measured density of 2.65 g/cm³ was used.
5.2. Pristine MW25 characterisation

5.2.1. XRD

Pristine MW25 underwent XRD analysis to confirm the phases reported in the literature were observable in the prepared fraction\(^{15}\) as well as to later provide a comparison with the XRD spectra of the leached samples. The characteristic peak locations and ICDD numbers of the matched phases appeared consistent with those reported in the literature\(^{15}\), with the exception of a reported Ni-Cr-Fe spinel phase (Mg-free spinel) which could not be found in the ICDD database.

![X-ray diffractogram of pristine washed and sized MW25](image)

*Figure 5.1: X-ray diffractogram of pristine washed and sized MW25 acquired using 10 ± 1 mg of sample on a low-background plate. Letters correspond to the characteristic peaks of crystalline phases: “R” RuO\(_2\) (ICDD [040-1290]), “D” Donathite ((Fe,Mg)(Cr,Fe)\(_2\)O\(_4\), ICDD [022-0349]) and “M” Mg-Fe-Cr oxide ((Mg,Fe)\(_2\)Cr\(_{1.8}\)O\(_4\), ICDD [071-1257]) or MgCr\(_2\)O\(_4\) (ICDD [077-0007]).*

5.2.2. SEM of prepared glass powders

SE images were acquired not only to provide comparisons with the leached glass samples, but also to assess the effectiveness of the washing methodology. No adhering fines were visible on any washed and sized MW25 particles (Figure 5.2).

![Secondary electron SEM images of pristine washed and sized MW25](image)

*Figure 5.2: Secondary electron SEM images of pristine washed and sized MW25.*
5.3. MW25 dissolution experiments

5.3.1. Leachate concentrations and pH
Washed and sized (75 to 150 µm) MW25 powders were leached in initially pure deionised water at a SA/V of 2000 m⁻¹ for between 6 h and 28 d at 70 and 80 °C (using the same methodology as the Li-Mg-EM experiments, see Section 2.7) and for between 6 h and 464 d at 40 and 90 °C (using a static batch sampling methodology, see Section 2.8). The concentrations of the major constituents of MW25 with Ca and common contaminants within the 70 and 80 °C leachates were measured by ICP-MS (²⁷Al, ¹¹B, ¹³⁷Ba, ⁴³Ca, ¹⁴⁰Ce, ⁵³Cr, ¹³³Cs, ⁵⁶Fe, ¹³⁹La, ⁷Li, ²⁴Mg, ⁹⁵Mo, ²³Na, ¹⁴⁲Nd, ⁶⁰Ni, ³¹P, ¹⁴¹Pr, ¹⁰¹Ru, ²⁹Si, ¹²⁵Te, ⁸⁹Y and ⁹⁰Zr alongside ²⁰⁸Pb and ⁶⁶Zn), whilst the concentrations of major glass species within the 40 and 90 °C leachates were measured by ICP-OES (Al, B, Ca, Li, Mg, Mo, Na, Si and Te). Concentration data were then treated and normalised following the methodology outlined in Section 2.5.5.

Many of the constituent elements of MW25 had low concentrations within the leachates: Te at 40 °C (ICP-OES), Al and Ca at 40 and 90 °C (ICP-OES) and Ce, Fe, La, Nd, Pr and Y at 70 and 80 °C (ICP-MS) were all within one standard deviation of their respective average blank concentrations. Additionally, Mg concentrations at shorter durations (6 h and 1 d) at 70 and 80 °C and longer durations (126 and 464 d) at 90 °C were within one standard deviation of their respective average blank Mg concentrations. All other elements were present in the leachates at significant concentrations (blank concentrations were less than 10 % of the sample concentrations) which were well above their respective detection limits.

For the ICP-OES analyses, average blank concentrations of less than 0.3 µg/ml were measured for all elements except Ca and Te which observed average blank concentrations of less than 1.0 µg/ml. Triplicate sample RSD values for B, Li, Na and Si were less than 10 % for all triplicates except 7 d at 40 °C and 6 h at 90 °C, which were less than 12.5 %. For Mo, triplicate RSD values were less than 20 % but exceeded 10 % in four triplicates at 40 °C and one triplicate at 90 °C. The triplicate RSD values for Al, Ca and Te frequently exceeded 20 %. Triplicate RSD values for Mg at 40 °C were mixed, exceeding 10 % only once in one leaching vessel but thrice in another. At 90 °C, Mg RSD values exceeded 20 % consistently from 28 d onwards. As the experiments took place in acid cleaned PFA (Savillex, US) leaching vessels, leachates were not analysed for common metal contaminants (Pb and Zn).

For the ICP-MS analysis, all elements observed average blank concentrations less than
0.5 µg/ml, with the exceptions of Na, Si and Ca which observed average concentrations less than 1.5 µg/ml, 7.0 µg/ml and 150.0 µg/ml respectively. With the exceptions of two triplicates, triplicate sample RSD values less than 10 % were observed for B, Ba, Cr, Fe, Li, Mg, Mo, Na, Pb, Si, Te, Y and Zn. Triplicate RSD values for Al, Ca, Ce, Cs, La, Nd, Ni, P, Pr and Ru frequently exceeded 10 %. Pb and Zn concentrations were less than 0.015 µg/ml and 0.350 µg/ml respectively in the blanks and samples and did not appear to increase with dissolution time or temperature.

The normalised releases of the most mobile elements within MW25 (B, Li, Mo and Na) measured at each dissolution temperature are given in Figure 5.3. Using B as a tracer of glass dissolution, as it is expected to not be significantly incorporated into any secondary phases\textsuperscript{50}, it was clear that the magnitude of glass alteration increased significantly with dissolution temperature. At 90 °C, the mobile species appeared to leach initially congruently at 6 and 12 h, whereafter the normalised Li and Na releases increased at a slower rate than the normalised B and Mo releases such that Na had the lowest releases of the four species. However, the residual release rate of Na appeared higher than that of Li, such that the normalised Li and Na releases were within error of each other again after 464 d. Whilst the apparent congruent release of B and Mo persisted until 28 d, after this time the normalised Mo releases appeared to diverge from the B releases with time. Interestingly, apparent congruent initial releases were not observed at any other temperature.

After 6 h and 1 d at 80 °C, Na and Li observed the highest and lowest normalised releases of the mobile species respectively whilst B and Mo were leached congruently. As with the 90 °C results, the normalised Li and Na releases at 80 °C increased more slowly than the normalised B and Mo releases such that the normalised releases of B, Na and Mo were within error of one another after 7 d but after this time the normalised B and Mo releases were higher. However, at 80 °C the normalised Li releases remained the lowest of the four species throughout dissolution. Further, the apparent congruent release of Mo and B persisted only until 14 d, at which point the normalised Mo releases exceeded those of B. The same trends were also visible at 70 °C, with the exception that the normalised B and Mo releases remained within error throughout dissolution (except at 1 d where the normalised Mo release was 0.02 g/m\textsuperscript{2} higher but this difference was considered negligible).
Evaluating the temperature dependence of waste glass dissolution

Figure 5.3: Normalised elemental releases for Li (Squares), B (Triangles), Na (Circles) and Mo (Diamonds) measured using ICP-OES in the 40 °C (Blue) and 90 °C (Red) leachates and ICP-MS in the 70 °C (Green) and 80 °C (Orange) leachates. The four parts of the image display the same data with different scaling on the vertical and horizontal axes, with the top panel displaying the longest leaching durations for all experiments undertaken and the bottom panel displaying the shortest. Points are plotted as an average measurement (triplicate leaching vessels at 70 and 80 °C, two sets of triplicate leachates sampled from duplicate leaching vessels at 40 and 90 °C) with errors given to one standard deviation.
Contrastingly, at 40 °C at 6 and 12 h, Li displayed the highest normalised releases whilst Na and B both displayed the lowest; with Mo falling within error of Li and Na but not B. As with all other temperatures probed, the normalised Li and Na releases increased slower than the normalised B releases such that at 7 d all four species had normalised releases within error of one another. After 7 d, the incongruent release of the mobile species became more evident with time. The normalised Li and Na releases remained within error of one another but after 28 d and 126 d respectively they were less than the normalised B releases. Interestingly, the normalised Mo releases remained within error of the normalised Li and Na releases throughout dissolution (with the exception of Na at 28 d) but within error of the normalised B releases only from 7 d onwards. The large errors associated with the 464 d measurements resulted in all four normalised releases being within error of each other, despite appearing to diverge with dissolution time.

The normalised Si releases (Figure 5.4a) demonstrated that more time was required at lower temperatures to reach a lower steady state apparent Si solubility limit in solution than at higher temperatures; requiring 28 d at 40 °C, 14 d at 70 °C and 7 d at both 80 and 90 °C. Whilst the normalised Si releases at 90 °C were initially higher than those at 80 °C, from 7 d onwards the releases were in error of one another for the durations probed. After 28 d at 90 °C, the concentration of Si in solution decreased with time such that the normalised Si releases at 464 d were marginally lower than at 28 d. At 40 °C, the 28 and 464 d normalised Si releases were within error of one another.

Relatively large normalised Te releases were observed at all temperatures except 40 °C, with values approximately one third those of the normalised Li releases at each temperature (Figure 5.4b). However, due to the relatively low Te concentrations in solution, the Te concentrations were not blank corrected. Notably, the decreasing concentration of Te in solution after 28 d at 90 °C eventually to a near-zero concentration at 464 d demonstrated that during the residual rate regime Te was precipitating from solution at a faster rate than it was being leached. The experiments at 70 and 80 °C were evidently too short to observe whether measurable Te precipitation was taking place. The 40 °C Te concentrations were omitted as many of these measurements were indistinguishable from the blank concentrations.

At 90 °C, the pH of the leachant remained constant with dissolution time (Figure 5.4c). Similarly, at 80 °C although there was a spike in the leachant pH at 1 d of dissolution,
measurements at subsequent intervals remained within error of the 6 h value. At 40 °C and 70 °C a more gradual increase in pH was observed, with the leachant pH reaching their long-term values after 7 d and 1 d respectively. From 7 d onwards, the pH of the 40 and 90 °C leachates remained within error of one another and the 70 °C leachates remained more alkaline than the 80 °C leachates; with the 70 and 80 °C observing a lower pH than the 40 and 90 °C leachates.

Figure 5.4: Normalised Si releases (a), normalised Te releases (b) and leachant pH (c) for the 90 °C (Red triangles), 80 °C (Orange squares), 70 °C (Green circles) and 40 °C (Blue diamonds) leachates. Points in (a) and (b) are plotted as the average value (triplicate leaching vessels at 70 and 80 °C, two sets of triplicate leachates sampled from duplicate leaching vessels at 40 and 90 °C) with errors given to one standard deviation. In (c) the 70 and 80 °C points are plotted as the average value from the triplicate pH measurements with errors given to one standard deviation, whilst the 40 and 90 °C points consist of only one measurement at each sampling interval and were assigned an error of ±0.1 pH units.

The low concentrations and large RSD values associated with the Al and Mg concentrations meant no definitive trends could be ascertained from their normalised releases: the normalised Mg releases were at similar values for all temperatures probed (with the exception of 7 d at 40 °C) and appeared to remain approximately constant with dissolution time, whilst the normalised Al releases appeared to not change with dissolution time. Normalised Fe, Ni and Ru releases varied insignificantly with both dissolution time and temperature.
For the normalised releases of Ba at 70 and 80 °C (Figure 5.5a), the effect of dissolution temperature on the normalised releases appeared almost negligible despite the releases increasing with dissolution time. For Cr and Cs, a slight temperature effect was visible, although this appeared minimal. Similarly, although the 70 and 80 °C normalised releases of the lanthanides (Figure 5.5b) and Y (Figure 5.5c) increased with dissolution time, their concentrations within solution were low and temperature effects were almost negligible. These effects are attributed to the low degree of solubility of these elements in solution and their high retention rates within the alteration layers. It should be noted that the releases for these elements (except Ba and Cr) were not blank corrected due to their low concentrations.

Figure 5.5: Normalised Ba, Cr and Cs releases (a), normalised lanthanide (Ce, La, Nd and Pr) releases (b) and normalised Y releases (c) for the 70 °C (vacant markers) and 80 °C (filled markers) leachates. Points are plotted as the average value of the triplicate leaching vessels with errors given to one standard deviation.

5.3.2. Arrhenius plots and activation energies

An Arrhenius plot of the natural logarithm of the 6 h dissolution rates against the reciprocal of
absolute temperature displayed excellent Arrhenius-type behaviour for B and Mo (Figure 5.6a). Activation energies (Table 5.2) for mobile glass species (B, Li, Mo and Na) were produced from the 6 h release rates through a non-linear least squares regression (equation given in Section 2.7.4) of a plot of the 6 h dissolution rate against the reciprocal of absolute temperature (Figure 5.6b). The Arrhenius-type behaviour of B and Mo was reflected in the low errors associated with their activation energies of 44.6 ± 2.9 and 46.3 ± 4.9 kJmol⁻¹ respectively (Table 5.2). Whilst Li displayed Arrhenius-type behaviour as well, the error associated with its activation energy was larger at 53.1 ± 10.0 kJmol⁻¹. However, the Arrhenius plot of Na appeared to display some degree of non-Arrhenius behaviour: the steep slope between 40 and 70 °C corresponded to a high activation energy of 67.4 ± 10.8 kJmol⁻¹ but was followed by a nearly horizontal region between 70 and 90 °C. An activation energy could not be calculated for the latter temperature range, as it had a negative slope.

![Figure 5.6: Arrhenius plots (a) and concentration plots (b) of the 6 h dissolution rates of B, Li, Mo and Na at 40, 70, 80 and 90 °C against the reciprocal of absolute temperature (1/T). Points represent average values (triplicate leaching vessels at 70 and 80 °C, two sets of triplicate leachates sampled from duplicate leaching vessels at 40 and 90 °C) with errors given to one standard deviation. Lines in (a) are linear trendlines and do not represent linear regressions. Lines in (b) represent non-linear least squares regressions used (for all elements except Na, which used linear regression between 40 and 70 °C) to obtain the activation energies.](image-url)
Table 5.2: Table of the activation energies (Ea) obtained from the non-linear least squares regressions (Figure 5.5b) for B, Li and Mo. The Ea for Na was instead obtained through linear regression of the 40 and 70 °C points. Errors represent one standard deviation from the non-linear least squares fit, with the errors on the Na Ea having been propagated from the errors on the concentration of Na in the leachates.

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>Li</th>
<th>Mo</th>
<th>Na (40 to 70 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ea (kJmol⁻¹)</td>
<td>44.6 ± 2.9</td>
<td>53.1 ± 10.0</td>
<td>46.3 ± 4.9</td>
<td>67.4 ± 10.8</td>
</tr>
</tbody>
</table>

5.4. Characterisation of leached and pristine samples

5.4.1. SEM and EDS
Secondary electron images at high magnification were taken of the pristine MW25 surface as well as MW25 leached at 70 and 80 °C for each leaching duration to investigate the effects of dissolution temperature on the nature of the alteration products formed and the kinetics of their formation. EDS analysis took place on the same samples to identify the compositions of the secondary phases and potentially assist in distinguishing between alteration products and the crystalline phases already present in pristine MW25.

After some initial roughening of the glass surface, a macroporous layer gradually formed which wholly covered the surfaces of the glass particles (Figure 5.7). This layer appeared similar to that observed for the Li-Mg-EM samples at 40 and 90 °C (see Section 3.4.1) and matured in terms of thickness (as visually judged from pore depth) and pore size with dissolution time. Notably, the layer appeared to form and mature at 70 °C following the same processes as at 80 °C but merely abated at 70 °C. That is, the mechanisms of secondary phase formation appeared the same at 70 and 80 °C but the kinetics of secondary phase formation at 70 °C were slower such that the 70 °C leached surface at a given time resembled the 80 °C surface from the previous interval (for example, Figure 5.7e resembled Figure 5.7i).
At lower magnifications, clusters of secondary phase precipitates and significant cracking of the glass surfaces were visible after 28 d at both 70 and 80 °C (Figure 5.8). Cracking appeared more extensive in the 80 °C leached glass particles, with a greater number of cracks which also appeared deeper than those of the 70 °C leached particles.

Figure 5.8: Secondary electron SEM images of MW25 leached for 28 d at 70 °C (a) and 80 °C (b).

BSE images of washed and sized pristine MW25 revealed a significant number of crystalline phases (Figure 5.9). As expected from the XRD analysis and literature reports, EDS analysis of these phases (Figure 5.10) confirmed they were needle-like RuO₂ (Figure 5.10a Spot 2) and spinel phases rich in Cr, Fe and Ni (Figure 5.10b Spot 2). However, these spinel phases were noted to contain less Mg than the pristine glass (Figure 5.10a and b spot 1).

Figure 5.9: Backscattered electron SEM images of pristine MW25. Numbers in (a) and (b) correspond to spots numbers in the EDS analysis (Figure 5.10a and b respectively).
Evaluating the temperature dependence of waste glass dissolution

In addition to the crystalline phases present in the pristine glass, BSE images of MW25 leached for 28 d at 70 and 80 °C (Figure 5.11a and b respectively) displayed further evidence for significant cracking after dissolution and clusters of secondary phase precipitates.

Consistent with EDS analysis of the leached Li-Mg-EM glass surfaces, the leached MW25 surfaces were depleted in B and Na whilst being enriched in Mg (Figure 5.12). This confirmed that a similar macroporous magnesium silicate layer to that observed in the Li-Mg-EM experiments was also forming on MW25. Whilst it could be expected this layer on MW25 likely also contained low solubility elements absent from the Li-Mg-EM compositions (such as Ba, Cs, Cr, Fe and Nd), there was no evidence for this in the EDS spectra. Further, analysis of the leached glass surfaces was partly convoluted by the frequent presence of crystalline phases beneath the alteration products. Due to the significant variation in the concentration of Mg measured for multiple spots on the same glass particle, an activation energy for the precipitation of the magnesium silicate phase could not be calculated. Again, such variations within the same samples meant differences between the compositions of the leached glass surfaces at 70 and 80 °C could not be observed.
5.4.2. XRD

XRD analysis of the MW25 powders leached at each temperature for 28 d (Figure 5.7) displayed the same RuO$_2$ and spinel phases as found in the pristine glass (Figure 5.1). As expected from the Li-Mg-EM experiments in Chapter 3, the magnesium silicate alteration products formed on MW25 were not detected through XRD analysis and no crystalline alteration products were detected in the 40, 80 or 90 °C leached samples. However, at 70 °C at approximately 29.5 ° (2θ) an additional phase was detected (marked by “T” in Figure 5.7). A previous study attributed a significantly smaller peak in a similar location to a spinel phase.$^{15}$
However, none of the Mg-Fe-Cr-Ni phases of any stoichiometry in the International Centre for Diffraction Data (ICDD) database matched this peak acceptably. Instead, this peak matched well with the characteristic peaks of either tellurite or a lanthanum (or other rare earth element) tellurium oxide phase, as was consistent with the normalised Te releases decreasing with time during the later dissolution regimes at 90 °C (Figure 5.4b). Leaching the glass for only 28 d appeared insufficient for significant amounts of a Te-bearing phase to precipitate consistently and for this result to be reproducible at other temperatures. Based upon the 90 °C normalised Te releases, it was expected such a crystalline phase would also form in detectable quantities at higher temperatures after longer dissolution times. The low concentrations of Te in solution and the composition of these phases (either TeO₂ or a REE-Te) strongly suggested the precipitation of Te did not have an impact on the rate of glass alteration at any temperature.

Figure 5.13: X-ray diffractograms of MW25 leached for 28 d at 40, 70, 80 and 90 °C. Spectra were acquired using 10 ± 1 mg of sample on a low-background plate. As 40 and 90 °C 28 d leached powders were not available as the experiments were ongoing, powders from another study were used which had been leached under similar conditions to those of the 70 and 80 °C MW25 experiments described herein. Letters correspond to the characteristic peaks of crystalline phases: “R” RuO₂ (ICDD [040-1290]), “D” Donathite ((Fe,Mg)(Cr,Fe)₂O₄, ICDD [022-0349]), “M” Mg-Fe-Cr oxide ((Mg,Fe)₂Cr₁.₈O₄, ICDD [071-1257]) or MgCr₂O₄ (ICDD [077-0007]) and “T” (located on the 70 °C line) TeO₂ (ICDD [008-0484]) or La-Te oxide (ICDD [016-0572]).

5.5. Discussion

5.5.1. Temperature dependence of mobile species release

5.5.1.1. Boron and the alkali metals

In aluminoborosilicate glasses, alkali metals either depolymerise the Si network through forming NBO or charge compensate tetrahedral network forming species such as Al or B. Rather than a random mixing of alkalis in Li-Na borosilicates, Li is expected to preferentially form NBOs in the Si network whereas Na is expected to preferentially charge compensate tetrahedral Al or B network units. These preferences have been suggested to effect nanoscale heterogeneity through forming Li-Si rich domains in a Na-rich borosilicate matrix.
These alkalis are expected to leach via interdiffusion reactions: the reactive inward diffusion of protonated water species (H\(^+\)/H\(_3\)O\(^+\)), ion-exchange between protons and glass species, and the outward diffusion of the glass species\(^{64,65}\). The diffusive nature of this process causes it to be initially rapid, and Li and Na initially observed some of the highest releases of any glass species across all temperatures probed (Figure 5.3).

Network formers, such as B, are not expected to leach via interdiffusion reactions but rather hydrolysis reactions between water species and network bonds\(^{57}\). However, B leached at a similar rate to the alkali metals during the initial stages of dissolution at all temperatures probed (Figure 5.3). This is attributable to the low energy barrier associated with the B-O-Si bond permitting similar rates of B hydrolysis and alkali metal interdiffusion\(^{38,57}\). The activation energies of interdiffusion and B hydrolysis likely differed and resulted in subtle differences in their Arrhenius-type behaviour\(^3\). Such a difference would cause changes in the rate of B hydrolysis relative to the rate of interdiffusion as the dissolution temperature is varied, as was consistent with changes in the normalised releases of B relative to the releases of Li and Na with dissolution temperature observed during the initial stages of dissolution (Figure 5.3).

The effective diffusivities of glass and protonated water species, and subsequently the rate of interdiffusion, were expected to exhibit Arrhenius-type behaviour\(^3\). As the rate of interdiffusion is dependent upon the activity of protons in solution, interdiffusion is a selective process with rates which differ depending upon: the diffusivities of the water and glass species within the glass, leachant temperature, leachant pH and the Arrhenius temperature dependence of the activation energy of interdiffusion. Whilst interdiffusion is initially the dominant dissolution mechanism over hydrolysis, previous studies have suggested that as dissolution temperature or pH is increased the time required for hydrolysis to become the dominant dissolution mechanism over interdiffusion is reduced\(^3,57\). Again, this is consistent with the observed changes in the normalised B releases relative to the normalised Li and Na releases with dissolution temperature (Figure 5.3). Additionally, interdiffusion reactions have been suggested to be the dominant dissolution mechanism during the initial stage of dissolution for significantly shorter periods of time when the leachant is initially dilute deionised water compared with an aqueous solution containing Si at its steady-state apparent solubility limit\(^71\).

After 6 and 12 h of dissolution at 40 °C, the normalised Li releases exceeded both the normalised B and Na releases (Figure 5.3). This suggested that ion-exchange reactions were
still initially rapid at this temperature. The discrepancy between the rates of Li and Na interdiffusion may be attributed to differences in the diffusivities of Li and Na within the glass, potentially arising from the smaller ionic radius and lower mass of Li. Further, this may also be attributed to Na in its charge compensation role being more strongly bonded to the glass network than Li in its network modifying role. After 6 h and 1 d of dissolution at 70 and 80 °C, the normalised releases of Li and Na were lower and higher respectively than the normalised B releases. This may be attributed to Li having a higher diffusivity within the glass than Na at lower temperatures, but the diffusivity of Na increased more with the dissolution temperature than the diffusivity of Li such that the diffusivity of Na was eventually higher. However, after 6 and 12 h of dissolution at 90 °C, the releases of B, Li and Na were apparently congruent.

Although the rate of interdiffusion was initially more rapid that the rate of hydrolysis, it was expected that as the dissolution temperature increased hydrolysis would be favoured to interdiffusion such that, for a given dissolution time, the initial releases of B, Li and Na would be apparently congruent. The higher normalised releases of Li than B and Na at 40 °C and the apparently congruent releases of these species at 90 °C during the initial rate regime were in good agreement with this view, whilst the initially higher normalised releases of Na than B and Li at 70 and 80 °C appeared to contradict it. Further, Na did not exhibit Arrhenius-type behaviour, with a negative slope in the Na Arrhenius plot between 70 and 90 °C compared to a steep positive slope between 40 and 70 °C and the high activation energy associated with it (Figure 5.6 and Table 5.2). It was possible this change in behaviour was caused by the increased rate of B hydrolysis at higher temperatures controlling or promoting the initial release of charge compensating Na, resulting in a change in the Arrhenius-type behaviour of Na at higher temperatures and subsequently negligible changes to the initial normalised Na releases with temperature between 70 and 90 °C. That is, the initial release of Na, which preferentially charge compensated the B network, was promoted by the enhanced release rate of B at higher temperatures such that the releases of Na observed significantly different temperature dependence between 70 and 90 °C compared with between 40 and 70 °C.

As Li instead preferentially modified the Si network, the same change in activation energy at 70 °C as Na was not observed for Li and instead Li exhibited Arrhenius-type behaviour across all temperatures probed. As such, this suggested that changes in temperature affected Na
Evaluating the temperature dependence of waste glass dissolution
differently to other mobile glass species. This was consistent with the view that whilst Na and Li both leach via interdiffusion reactions, their different structural preferences meant they observed different dissolution processes even at lower temperatures\(^\text{38}\). As Li and Na observed significant differences in the temperature dependence of their releases, the activation energies of Li and Na (between 40 and 70 °C) differed significantly.

Based upon observations of a sodium silicate hydrate phase precipitating from solution onto the Li-Mg-EM compositions at 90 °C after 7 d (see Chapter 3), it was expected that a similar Na-bearing precipitate would also form during the MW25 dissolution experiments. This phase appeared to only precipitate onto the Li-Mg-EM compositions in measurable masses at higher temperatures, but in doing so removed significant masses of Na from solution even after just 7 d of dissolution. As such, this suggested that as the dissolution temperature increased in the MW25 dissolution experiments, the rate of sodium silicate hydrate precipitation increased significantly as well. The increased mass of precipitated Na with temperature was likely significantly less than the increase in the Na releases associated with the increasing rate of interdiffusion with temperature and was likely too small to offset the effect of B controlling the initial release of charge compensating Na, but might have measurably impacted the Na releases throughout dissolution at higher temperatures and contributed to the negative slope of the Na Arrhenius plot observed between 70 and 90 °C. Contrastingly, only a small mass of Li was expected to be removed from solution during the precipitation of a Li-bearing phase onto the Li-Mg-EM compositions after 112 d at 40 °C and 7 d at 90 °C (see Figure 3.16). Owing to the high concentrations of Li in solution and the slow rate of Li-bearing phase precipitation, the removal of Li from solution in the MW25 experiments was not expected to measurably impact the Li releases in any of the dissolution regimes at any temperature.

At all temperatures, the normalised Li and Na releases increased at a slower rate than the normalised B releases. This was consistent with the view that the rate of interdiffusion diminished more rapidly with time than the rate of hydrolysis; an effect which was more prominent at higher temperatures, where the rate of hydrolysis was enhanced and dominated more rapidly\(^\text{67}\). At 40 °C the normalised Li and Na releases were lower than the normalised B releases after 28 and 7 d respectively, before apparent congruent dissolution was again observed at 464 d; potentially due to the large errors associated with these measurements. This was consistent with the observation that Li initially leached more than Na at 40 °C due to its higher
diffusivity at this lower temperature and role as a more weakly bonded network modifier in the glass. Contrastingly, at 90 °C incongruent releases were clearly visible after just 7 d, with Na observed to be the least released of the four mobile species followed by Li. However, the residual rate of Na release was higher than that of Li such that after 464 d of dissolution at 90 °C their normalised releases were within error once again. The higher residual rate of Na release than Li release at 90 °C may be attributed to a combination of the previously discussed B effect and the diffusivity of Na at higher temperatures being higher than the diffusivity of Li\(^96\). However, Li remained the least leached of the mobile species throughout dissolution at 70 and 80 °C. Again, this difference was attributed to the increased rate of B hydrolysis at higher temperatures controlling the release of charge compensating Na.

Until after 7 d of dissolution, the leachant pH at 40 °C was lower than that at 90 °C (Figure 5.4c). Such a pH effect might have further contributed to the Li interdiffusion reactions being favoured over hydrolysis at 40 °C. Similarly, the leachant pH at 70 and 80 °C were lower than at 90 °C, with a negligible difference in pH between the 70 and 80 °C leachants. However, even after just 6 h of dissolution, the measured pH at all temperatures were well in excess of 9.0. This suggested that hydrolysis should quickly be favoured to interdiffusion even at lower temperatures\(^3\), but the higher normalised Li releases than normalised B releases at 40 °C contradicted this.

### 5.5.1.2. Molybdenum

The low solubility of Mo in borosilicate glasses causes it to commonly exist as tetrahedral polyanions (commonly [MoO\(_4\)]\(^2-\)) without bonding to the glass matrix or even other polyanions. Such tetrahedra tend to be charged compensated by alkali metals\(^11,22,34,178\). As such, they preferentially exist in alkali metal-rich regions or channels which present depolymerised cationic domains within the modified random network\(^27,191\). This preference effects the low degree of solubility of Mo in borosilicate glasses through promoting phase separation and affords the rapid transport of Mo through the glass. Consequently, this gives rise to a high activity coefficient for Mo and a high degree of solubility in water; thereby reducing the aqueous durability of Mo-containing wasteforms\(^22\). In cationic domains sufficiently rich in alkali metals and Mo beyond the solubility limit of Mo, metastable phases can form which subsequently result in the precipitation of crystalline alkali metal molybdates and chromates during vitrification to form “yellow phase” of a high water solubility\(^22,192\). Yellow phase formation was not observed in the production of MW25, liking owing to its low MoO\(_3\) contents
Evaluating the temperature dependence of waste glass dissolution

(1.4 wt.%) in comparison to other waste glass compositions in which yellow phase has been observed\textsuperscript{15,192}. However, as alkali metal molybdates are found in both amorphous and crystalline phases, the absence of detectable amounts of yellow phase from MW25 does not necessarily mean Mo is well-incorporated into the glass network\textsuperscript{191}. The presence of non-crystalline alkali metal molybdates in the cationic domains of MW25 resulted in the rapid release of Mo at all temperatures (Figure 5.3). As the depolymerised alkali-rich channels likely presented less of a barrier to the inward diffusion of water species than the borosilicate network, they permitted rapid hydration and subsequent ion-exchange reactions between protonated water species and glass modifying species. This hydration and dissociation of the charge compensating alkali metals from the molybdates combined with the absence of networks bonds afforded the rapid diffusion of Mo out of the hydrated cationic domains, likely giving rise to the poorer aqueous durability of Mo-containing glasses\textsuperscript{34}. As such, it was noted the dissolution of Mo was consistently rapid across all temperatures probed.

The release rates of Mo from the modifier-rich domains were similar to the rates of interdiffusion and B network hydrolysis whilst the glass altered at its most rapid initial rate; with Mo initially having the joint highest normalised releases alongside Li at 40 °C, whilst apparently congruent dissolution of Mo and B was observed initially at 70, 80 and 90 °C. At 70 °C, the apparently congruent release of B and Mo persisted throughout dissolution (with the exception of at 1 d). Whereas at 80 and 90 °C, this apparent congruent dissolution continued until 14 and 126 d respectively whereat the normalised Mo releases were greater than and less than the normalised B releases respectively. Further, at 90 °C the normalised B and Mo releases diverged with time after 28 d, with the 464 d Mo releases remaining within error of both the 28 and 126 d Mo releases. At 40 °C, Mo observed apparently congruent dissolution with B and Li after 7 d and with Na at all durations except 126 d. Whilst lower and higher dissolution temperatures favoured interdiffusion and hydrolysis reactions respectively during the initial rate regime, the release of Mo appeared to consistently be a dominant dissolution process alongside both interdiffusion and hydrolysis across all temperatures probed. Differences between the release rates of the alkali metals and Mo became more apparent with dissolution time. This demonstrated a difference in the mechanisms governing their releases: the rate of Mo dissolution appeared to slow at a similar rate to the rate of B hydrolysis, with the rate of interdiffusion slowing more rapidly. This consistent behaviour across all temperatures

158
Evaluating the temperature dependence of waste glass dissolution

probed suggested the energy barrier associated with leaching Mo was similar to that of B network hydrolysis and that it was not necessary for the Mo polyanions to be exchanged with water species in an interdiffusion reaction. Rather, the Mo tetrahedra merely diffused out of the glass in a process similar to the hydrolysed B network; as supported by the similar activation energies of B and Mo (Table 5.2). Consequently, during the later dissolution regimes, the normalised Li and Na releases increased at a slower rate than the normalised B and Mo releases and effected incongruent dissolution which became more apparent with dissolution time and temperature. The almost negligible change in the Mo releases after 28 d and the discrepancy between the normalised B and Mo releases at 126 and 464 d at 90 °C may be attributed to a highly passivating altered layer component forming after approximately 28 d. Such a layer would limit the inward and outward transportation of water and glass species to reactive diffusion through its nanoporous network\textsuperscript{37,58}, through which the reactive diffusion of Mo would be slowed in comparison to B due to the significantly larger ionic radius of Mo. It was expected a similar passivating altered layer would form at lower temperatures and incongruent B and Mo dissolution would be visible if leached for a sufficient period time, as supported by the Arrhenius-type behaviour of Mo (Figure 5.6).

5.5.1.3. **Silicon**

Rather than presenting an intrinsic glass property, the steady state apparent solubility limit of Si in solution is dependent upon wasteform and leachant composition, leachant temperature and pH, and SA/V and as such evolves gradually with dissolution time\textsuperscript{78}. Whilst the leachant pH at 40 and 90 °C were within error after 7 d, significant differences in the apparent Si solubility limit may be attributed to differences in temperature and therefore rates of Si network hydrolysis. Notably, although the leachant pH at 90 °C were higher than those at 80 °C, the normalised Si releases at 80 and 90 °C were within error of each other from 7 d onwards (Figure 5.4a). This suggested that at higher temperatures a change in temperature had a smaller impact on the apparent Si solubility limit in solution than at lower temperatures, to the extent that the apparent Si solubility limits at 80 and 90 °C were within error of one another.

When interpreting the steady state concentration of Si, it should be considered that due to the MgO contents of MW25 (4.5 wt.%) significant amounts of magnesium silicate precipitated rapidly from solution at all temperatures (see Section 5.4.1). This consumption of Si from solution fuels further hydrolysis of either the pristine glass or the alteration layers, contributing to the higher rate of dissolution of Mg-containing glasses compared to Mg-free compositions.
After 464 d at 90 °C, the Si concentrations were lower than at 28 and 126 d and similar to the 7 d value (Figure 5.4a). This showed that the precipitation of Si from solution was taking place at a faster rate than the continued hydrolysis of the alteration layers.

5.5.1.4. Tellurium

Under certain glassmaking conditions and in sufficient concentrations alongside alkali and alkaline earth metals, Te acts as a glass forming element in three or four-fold coordination24,193,194. Whilst Te can alloy with platinum group elements, preferentially Pd, to form insoluble inclusions during vitrification, Ru preferentially oxidises to form RuO₂ and Pd and Rh are both absent from MW2534,36. Further, in the absence of Pd, Te is not expected to form TeO₂35. Whilst a small amount of Ru-Te-O may form35, the large normalised releases of Te (Figure 5.4b) demonstrated that Te exists as a water soluble phase within MW25. As displayed by the decreasing normalised Te releases with time at 90 °C, significant amounts of Te precipitated from solution (Figure 5.4b); likely as TeO₂ or a REE-Te (Figure 5.13), although crystalline tellurium sulphide (Te₄.₀₈S₂₇.₉₂) and tellurium oxide sulphide ((TeO₂)SO₄) phases have been observed after the long-term (nearly 26 years) dissolution of SON6841.

5.5.1.5. Less soluble elements

Mg and Al displayed similar normalised releases which appeared to be unaffected by changes in dissolution temperature. As with the alkali metals, alkaline earth metals are expected to leach via interdiffusion reactions57. However, Mg has been shown to fulfil both network former and charge compensating roles in Mg-EM and, by extension, MW2546. This implies Mg in a network forming role might leach through hydrolysis reactions. The similar normalised releases of Mg across all temperatures probed suggested that as the temperature was increased, the rate of Mg precipitation increased to offset the associated increased rate of Mg release. In aluminoborosilicates, Al fulfils an intermediary network modifying role similar to B and as such leaches through network hydrolysis reactions57. The high energy barrier associated with breaking the Si-O-Al bond and the tendency of dissolved Si and Al to precipitate as zeolite secondary phases resulted in Al having low normalised releases at all temperatures probed166,195. The large errors associated with the Al concentrations meant no significant trends could be discerned.

Ba displayed significantly higher concentrations and normalised releases than Mg at 70 and 80 °C, but also appeared to be unaffected by changes in temperature (Figure 5.5a). The higher releases of Ba than Mg may be attributed to Ba not being incorporated into secondary phases
in as large quantities as Mg. Cr and Cs observed similar normalised releases (Figure 5.5a), which were higher at 80 °C than at 70 °C. These low release rates suggested Cs-molybdates and chromates likely did not exist as a highly water soluble phase. However, at both 70 and 80 °C, the rate of Cs release appeared to remain constant with time, rather than displaying distinct regimes as in the releases of Li and Na. The low Cr releases, as well as the seemingly constant Fe and Ni releases, may be attributed to these elements being present in insoluble Cr-Fe-Mg-Ni spinel phases\(^\text{15}\) (Figure 5.13). As Ru exists in MW25 as crystalline RuO\(_2\)\(^\text{15}\), the high aqueous durability of this crystalline phase likely effected the low normalised Ru releases. The REEs (in this case Ce, La, Nd, Pr and Y) displayed the lowest normalised releases of any species from MW25 at 70 and 80 °C (Figure 5.5b and c). Notably, a difference between the concentrations at each temperature was observable and the release rates of these elements appeared to slow to a residual rate after 7 d of dissolution at both temperatures.

5.5.2. The kinetics of alteration
The hydrolysis of B, interdiffusion of Li and dissolution of Mo were shown to exhibit Arrhenius-type behaviour (Figure 5.6). However, the interdiffusion of Na displayed non-Arrhenius behaviour: a large activation energy was associated with the steep slope of Na Arrhenius plot between 40 and 70 °C, then an almost horizontal region with a negative slope was observed in the Arrhenius plot between 70 and 90 °C (Figure 5.6). Such a region showed that at higher temperatures, the initial releases of Na were significantly less affected by changes in temperature than at lower temperatures. As discussed in Section 5.5.1.1, this behaviour may be attributed to the initial Na releases at higher temperatures being affected by the precipitation of Na-bearing secondary phases and B controlling the release of charge compensating Na.

From these initial concentrations, an activation energy of 44.6 ± 2.9 kJmol\(^{-1}\) was calculated for the hydrolysis of B (Table 5.2). The activation energy for the dissolution of Mo was very close to this value at 46.3 ± 4.9 kJmol\(^{-1}\) and supported the view that B and Mo observed similar dissolution processes, as eluded to by similarities in their normalised releases until later dissolution regimes at 90 °C (Figure 5.3). The activation energy for the interdiffusion of Li fell within error of those of both B and Mo at 53.1 ± 10.0 kJmol\(^{-1}\), although it is unclear whether this is due to the large error associated with this energy.

Surface-controlled reactions, in this case network hydrolysis, and pure diffusive transport in the glass are expected to have associated activations energies of approximately 60 and 10 kJmol\(^{-1}\).
respectively, with activation energies between 15 and 50 kJmol\(^{-1}\) presenting a “mixed reaction”\(^{10}\). Whilst the activation energies calculated for B and Mo were within the range of a mixed reaction, they were lower than those calculated using B releases for Magnox waste glasses leached at a near-neutral pH or a pH of 12.1 at approximately 60 and 64 kJmol\(^{-1}\) respectively\(^3,^{10}\) as well as those calculated for immobilised low activity waste glasses at 52 to 56 kJmol\(^{-1}\)\(^{107}\).

The lower, mixed reaction activation energies calculated for B and Mo implied that the rate of inward diffusion of water species into the glass significantly affected the rate of B network hydrolysis and Mo dissolution. Whilst this view is consistent with elemental profiles of leached glass cross-sections reported in the literature, wherein the B hydrolysis front is present in a hydrated glass layer ahead of the stronger Si hydrolysis front\(^3,^{74}\), the activation energies were closer to that of a surface-controlled reaction and suggested the inward diffusion of water species was not necessarily an initially rate limiting mechanism for B hydrolysis and Mo dissolution.

The activation energy for the interdiffusion of Li fell towards the higher end of values reported for interdiffusion reactions in waste glasses (30 to 50 kJmol\(^{-1}\))\(^3,^{66,96}\). This activation energy also fell within error of both a Magnox waste glass leached at a near-neutral pH\(^3,^{110}\) and a mixed reaction, implying that interdiffusion was not initially rate limited solely by the inward diffusion of water species. Rather, this was consistent with the view that as these waste glasses had a high degree of network polymerisation, ion-exchange preceded glass hydration and as such the rate of ion-exchange strongly influenced the rate of interdiffusion\(^57,^{96}\). Had these experiments taken place under experimental conditions designed to selectively investigate the initial dissolution rates of MW25, the activation energies calculated using Li could be expected to differ more from those of B and Mo.

Contrastingly, an activation energy for the interdiffusion of Na between 40 and 70 °C of 67.4 ± 10.8 kJmol\(^{-1}\) was calculated; falling well within the range of a surface-controlled reaction. This difference in Arrhenius-type behaviour between Li and Na is thought to demonstrate that their dissolution processes differ even at lower temperatures, as is consistent with literature observations of different elemental profiles for Li and Na in cross-sections of leached glass\(^38\). Such a difference likely arose due to the higher diffusivity of Li at lower temperatures and Na being more strongly bonded to the B network in its preferential charge compensation role and
subsequently displaying a higher activation energy than Li in its more weakly bonded Si network modifying role\textsuperscript{32,38,96,190}. This effect was not visible at higher temperatures due to the previously discussed B effect and secondary phase precipitation affecting the initial releases of Na.

The Arrhenius-type behaviour observed for B, Li and Mo suggested consistency amongst the dissolution mechanisms occurring across the range temperatures investigated, with lower dissolution temperatures observing the same mechanisms as at higher temperature but abated. However, such a view neglects differences between the Arrhenius temperature dependence of the activation energies of hydrolysis and interdiffusion which effect differences in the rate of B hydrolysis relative to the rate of Li interdiffusion with dissolution temperature.

5.5.3. Temperature dependence of secondary phase formation

At both 70 and 80 °C, a magnesium silicate macroporous layer began forming during the initial rate regime (Figure 5.8), which appeared similar to that observed for the Li-Mg-EM compositions (Figure 3.7). Whilst this layer for MW25 likely contained many of the lower solubility elements not present in the Li-Mg-EM compositions, this layer was shown to be a magnesium silicate in both the Li-Mg-EM compositions and MW25 (Figure 3.10 and Figure 5.12). This layer appeared to evolve following the same mechanisms at both 70 and 80 °C, with simply slowed kinetics of formation at 70 °C; as was consistent with the Arrhenius-type behaviour of B, Li and Mo, which suggested the same dissolution mechanisms were taking place across the range of temperatures investigated. As with the Li-Mg-EM compositions, the formation of this layer appeared to present an ineffective barrier to dissolution and its formation consumed significant amounts of Si from solution to fuel further hydrolysis of the glass\textsuperscript{47,48,50}, resulting in MW25 having significantly poorer aqueous durability than its Mg-free equivalent SON68\textsuperscript{37,57}. The significant amounts of precipitated sodium silicate hydrate observed for the Li-Mg-EM compositions and Na borosilicates in the literature\textsuperscript{40} suggested a similar phase must also be forming on MW25. The Li-Mg-EM compositions demonstrated the formation of this phase was highly temperature dependent as it was detected at 90 °C but not 40 °C. Similarly, a Li-bearing phase was shown to precipitate only after 112 d at 40 °C but after just 7 d at 90 °C in the Li-Mg-EM experiments. These results suggested such Li and Na-bearing phases only formed at higher temperatures during the MW25 dissolution experiments. Whilst Li appeared to be removed from solution in small masses in the Li-Mg-EM experiments, the mass of Na in secondary phases was significantly larger; possibly affecting both the initial and long-term Na
releases, and subsequently the Na activation energy, at higher temperatures in the MW25 experiments.

5.6. Summary

It was shown that the releases of B and Mo exhibited Arrhenius type behaviour across the temperature range studied, with activation energies of 44.6 ± 2.9 and 46.3 ± 4.9 kJmol⁻¹ respectively. This initially suggested consistency amongst the dissolution processes taking place at all temperatures probed, with the dissolution processes being accelerated as the temperature increased. However, it was observed that the rate of Li interdiffusion varied significantly relative to the rate of B hydrolysis as the temperature was varied; with B hydrolysis taking place more rapidly relative to interdiffusion as the temperature was increased. This was attributable to subtle differences between the activation energies of hydrolysis and interdiffusion effecting measurable differences between their Arrhenius-type behaviour. Whilst Li also exhibited Arrhenius type behaviour, a high activation energy was associated with the Na releases between 40 and 70 °C and non-Arrhenius behaviour was observed for Na between 70 and 90 °C; demonstrating that the initial release processes of Li and Na differed across the temperature range probed. The non-Arrhenius behaviour of Na at higher temperatures was attributed to the initial release of charge compensating Na being controlled by the rate of B network hydrolysis, thereby resulting in the initial Na releases being insusceptible to changes in temperature between 70 and 90 °C. As such, the dissolution processes of Na appeared inconsistent across the temperature range probed.

The rates of Li and Na interdiffusion diminished more rapidly with time than the rate of B hydrolysis at all temperatures probed. Alongside the activation energies, this suggested that the inward diffusion of water species played some role in determining the rates of interdiffusion and B hydrolysis during the initial rate regime but was not strictly rate-limiting. The presence of non-crystalline alkali molybdates within depolymerised regions of glass resulted in Mo being amongst the most mobile elements and leaching with releases comparable to those of B at all temperatures. Further, a macroporous magnesium silicate layer, similar to that observed in the Li-Mg-EM experiments, was shown to form on the leached glass particles at both 70 and 80 °C. The similar appearance of the layer at both temperatures suggested it formed through the same mechanisms at each temperature but merely abated at lower temperatures.
6. **Probing diffusion throughout aqueous glass dissolution.**

The majority of the work presented in the chapter is currently under review in NPJ Materials Degradation.

**6.1. Introduction**

A number of mechanistic kinetic waste glass dissolution models exist but many are contradictory with regards to the predicted structures of the alteration layers at high reaction progress and dominant mechanisms of dissolution\(^{57}\). The predicted residual rates of dissolution differ depending upon whether dissolution is congruent through network hydrolysis reactions with a supersaturated interfacial film of water (interfacial dissolution-precipitation model\(^{83-86}\)) or if dissolution is incongruent through dominant interdiffusion reactions during the initial moments of dissolution and again during the residual rate regime (interdiffusion based model); with some models (such as the GRAAL model) predicting interdiffusion reactions during the residual rate regime across a highly passivating, nanoporous hydrated glass interphase are rate limiting alongside the precipitation of secondary phases\(^{37,38,58,62,64,65}\). As such, it was expected that the isotopic signatures of the leachates would evolve differently depending upon whether kinetic isotopic fractionation due to diffusion (incongruent dissolution) was taking place or if only equilibrium isotopic fractionation due to the precipitation of secondary phases (congruent dissolution) was taking place.

To investigate whether measurable isotopic fractionation was taking place during the dissolution of waste glasses and whether this fractionation could be used to investigate the mechanisms of glass alteration, Li and B isotope fingerprinting techniques were first applied to glass leachates in a simplistic proof of concept dissolution experiment\(^{133,152}\). As Li\(_{50}\)Na\(_{50}\)-Mg-EM had been shown to be an excellent seven-component analogue of MW25 in Chapter 3, in the experiments in this chapter a Li\(_{50}\)Na\(_{50}\)-Mg-EM composition enriched in \(^{6}\)Li to a nominal equimolar \(^{7}\)Li:\(^{6}\)Li ratio (\(\delta^{7}\)Li of -918.90 \(\%\)), named \(^{6}\)Li-Mg-EM (Table 6.1), was fabricated and leached. All other isotopes in \(^{6}\)Li-Mg-EM were at natural abundance. The isotopic enrichment of \(^{6}\)Li in \(^{6}\)Li-Mg-EM allowed for easier \(^{6}\)Li MAS-NMR and \(^{6}\)Li-\(^{1}\)H CP-NMR studies on the pristine and leached samples for an investigation into the Li-bearing phase which precipitated from solution (see Chapter 3). A simplified analogue with deionised water leachant was used rather than a complex waste glass to afford a simpler interpretation of the isotopic signatures of the leachates.
Table 6.1: Nominal cation atomic percent (at.%) composition of $^6$Li-Mg-EM compared with Li50Na50-Mg-EM (Chapter 3) and Mg-EM$^{46}$. Isotopes of all elements except Li were nominally assumed to be at natural abundance.

<table>
<thead>
<tr>
<th>Element/Isotope</th>
<th>Mg-EM</th>
<th>Li50Na50-Mg-EM</th>
<th>$^6$Li-Mg-EM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>4.87</td>
<td>4.87</td>
<td>4.87</td>
</tr>
<tr>
<td>B</td>
<td>27.58</td>
<td>27.58</td>
<td>27.58</td>
</tr>
<tr>
<td>La</td>
<td>1.72</td>
<td>1.72</td>
<td>1.72</td>
</tr>
<tr>
<td>$^7$Li</td>
<td>0.00</td>
<td>7.11</td>
<td>3.85</td>
</tr>
<tr>
<td>$^6$Li</td>
<td>0.00</td>
<td>0.58</td>
<td>3.85</td>
</tr>
<tr>
<td>Mg</td>
<td>6.54</td>
<td>6.54</td>
<td>6.54</td>
</tr>
<tr>
<td>Na</td>
<td>15.38</td>
<td>7.69</td>
<td>7.69</td>
</tr>
<tr>
<td>Si</td>
<td>43.91</td>
<td>43.91</td>
<td>43.91</td>
</tr>
</tbody>
</table>

6.2. $^6$Li-Mg-EM fabrication, XRD and $^{29}$Si MAS-NMR

Whilst the annealed $^6$Li-Mg-EM appeared optically clear, as $^6$Li-Mg-EM was produced following the same methodology as the other Li-Mg-EM samples, XRD analysis of the $^6$Li-Mg-EM fines also showed the main characteristic peak of synthetic α-cristobalite (ICDD card [082-1408]) was present at approximately 22.3° (2θ) (Figure 6.1a). Similar to Li50Na50-Mg-EM-2, analysis of washed and sized $^6$Li-Mg-EM demonstrated this fraction was free from detectable crystalline phases (Figure 6.1a). As with the Li-Mg-EM samples, the crystallinity of the $^6$Li-Mg-EM fines was considered negligible as the washed and sized fraction would be leached. Further, EDS analysis of the Li-Mg-EM fines and washed and sized fractions had demonstrated there was not an enrichment of Si in the fines associated with this crystalline phase (Section 3.2.1.3). No cristobalite peak was present in the $^{29}$Si MAS-NMR spectrum of the $^6$Li-Mg-EM fines (Figure 6.1b), as was consistent with the spectra of the Li-Mg-EM samples displaying a crystalline content less than 1 wt.% (Section 3.2.1.2).

Figure 6.1: XRD spectra of the fines and washed and sized fraction of $^6$Li-Mg-EM (a) and the $^{29}$Si MAS-NMR spectrum of the fines of $^6$Li-Mg-EM (b). “C” in (a) corresponds to the characteristic peak of synthetic α-cristobalite (ICDD card [082-1408]). Analysis of the fines in (a) used a weighed mass of fines on a low-background plate, whilst analysis of the washed and sized fraction did not.
6.3. Pristine $^6$Li-Mg-EM characterisation

6.3.1. Laser diffraction and density analyses

A median particle size of 132.8 µm with a uniform particle size distribution (Figure 6.2) was measured for washed and sized $^6$Li-Mg-EM. Again, this was slightly higher than the geometric mean particle size of 112.5 µm but was consistent with the Li-Mg-EM particle sizes (Table 3.2). A density of $2.47 \pm 0.03$ g/cm$^3$ was measured for $^6$Li-Mg-EM. This was within error of those measured for both Li50Na50-Mg-EM batches and the average Li50Na50-Mg-EM density of $2.51 \pm 0.06$ g/cm$^3$ (Table 3.4).

![Particle size distribution](image)

*Figure 6.2: Particle size distribution for washed and sized $^6$Li-Mg-EM.*

6.3.2. Compositional analyses

Polished resin-mounted pieces of $^6$Li-Mg-EM first underwent EPMA analysis to obtain the concentrations of all elements except B and Li and then LA-ICP-MS analysis to obtain the concentrations of B and Li to ensure the composition of $^6$Li-Mg-EM was close to its nominal composition (Table 6.2). A technique was selected to represent each oxide based upon the recoveries and RSD values. EPMA reported excellent recoveries and RSD values (less than 10 %) for all oxides measured and so was chosen to represent all oxides except B and Li, which were too light to be measured. As the LA-ICP-MS results were normalised to the EPMA SiO$_2$ concentration, excellent recoveries were observed for both B and Li. However, the LA-ICP-MS RSD values were poor and frequently exceeded 10 %, as was consistent with the LA-ICP-MS results of the Li-Mg-EM batches. Despite this, the excellent recoveries demonstrated that $^6$Li-Mg-EM was close to its nominal composition. The low RSD values of the EPMA analysis suggested that the glass was homogeneous.

As $^7$Li was measured for Li in the LA-ICP-MS analysis, the measured concentration of Li in $^6$Li-Mg-EM needed to be corrected. As NIST610 was used to calibrate the instrument, the
measured Li concentrations were first multiplied by 0.9272 (fraction of $^7\text{Li}$ in NIST610 assuming a $^7\text{Li}/^6\text{Li}$ ratio of 12.7307, calculated from a reported $\delta^{7}\text{Li}$ of 32.5 ‰ assuming a $^7\text{Li}/^6\text{Li}$ of 12.3307, see Section 6.3.3.1) to obtain the $^7\text{Li}$ concentrations. The $^7\text{Li}$ concentrations were then divided by 0.5072 (fraction of $^7\text{Li}$ in $^6\text{Li}$ EM calculated from a measured $^7\text{Li}/^6\text{Li}$ ratio of 1.029) to obtain the corrected concentration of Li in $^6\text{Li}$-Mg-EM. All other elements were assumed to be at the same isotopic abundances in NIST610 and $^6\text{Li}$-Mg-EM for simplicity.

Table 6.2: Table of the nominal and measured oxide wt.% compositions of $^6\text{Li}$-Mg-EM presented alongside the technique used to measure the concentration of that oxide, the recoveries for each oxide and the RSD associated with each average measurement. Errors are given to 1σ on the measured oxide wt.% composition as calculated from the 36 points analysed in the EPMA analysis or the 9 points analysed in the LA-ICP-MS analysis.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Oxide</th>
<th>Nominal oxide wt.%</th>
<th>Measured oxide wt.%</th>
<th>Recoveries</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPMA</td>
<td>Al$_2$O$_3$</td>
<td>5.24</td>
<td>5.51 ± 0.23</td>
<td>105.1%</td>
<td>4.1%</td>
</tr>
<tr>
<td>LA-ICP-MS</td>
<td>B$_2$O$_3$</td>
<td>20.25</td>
<td>19.21 ± 2.63</td>
<td>94.9%</td>
<td>13.7%</td>
</tr>
<tr>
<td>EPMA</td>
<td>La$_2$O$_3$</td>
<td>5.91</td>
<td>6.35 ± 0.32</td>
<td>107.4%</td>
<td>5.0%</td>
</tr>
<tr>
<td>LA-ICP-MS</td>
<td>Li$_2$O</td>
<td>2.35</td>
<td>2.40 ± 0.37</td>
<td>102.0%</td>
<td>15.3%</td>
</tr>
<tr>
<td>EPMA</td>
<td>MgO</td>
<td>5.56</td>
<td>6.10 ± 0.21</td>
<td>109.7%</td>
<td>3.5%</td>
</tr>
<tr>
<td>EPMA</td>
<td>Na$_2$O</td>
<td>5.03</td>
<td>4.84 ± 0.37</td>
<td>96.3%</td>
<td>7.7%</td>
</tr>
<tr>
<td>EPMA</td>
<td>SiO$_2$</td>
<td>55.66</td>
<td>54.87 ± 1.36</td>
<td>98.6%</td>
<td>2.5%</td>
</tr>
</tbody>
</table>

6.3.3. Pristine isotopic characterisation

6.3.3.1. Alkali fusion and HF digestion

Four full-procedure replicates took place for the K$_2$CO$_3$ fusion, AG MP-50 Li column chromatography and subsequent Li isotope MC-ICP-MS analysis of washed and sized $^6\text{Li}$-Mg-EM powders to obtain a pristine $^6\text{Li}$-Mg-EM Li isotopic composition. ICP-OES analysis of the four sets of fusion supernatants and residues showed Li recoveries (calculated using the measured pristine glass composition) in the fusion supernatants were between 84 and 96 %, with negligible Li recoveries in the fusion residues (less than 0.2 %). Whilst it was known that the incomplete recovery of B would not yield measurable isotopic fractionation, it was not known whether this would be the case for Li. The high B recoveries measured in the fusion supernatants were attributed to an error in diluting the B calibration standard.

The volumes of each fusion supernatant required for 4 ng Li were prepared, loaded onto the AG MP-50 columns and a Li fraction was eluted (Section 2.12.3.4). Despite a large estimated mass of K relative to Li being loaded onto the columns, the columns were loaded with masses significantly less than their capacity (3 ml of AG MP-50 resin at a capacity of 1.5 mEq/ml). ICP-OES analysis of the pre-Li cuts, post-Li cuts and Li fractions from the column
Probing diffusion throughout aqueous glass dissolution.

chromatography of these samples showed that two of the four \(^6\)Li-Mg-EM fusion supernatant Li fractions contained K (526.9 and 8.0 ng/ml respectively) whilst the other two contained no measurable K.

Each fusion supernatant Li fraction then underwent Li isotope MC-ICP-MS analysis to obtain an average pristine glass \(\delta^7\)Li value of \(-916.52 \pm 0.32\ \%_o\) (\(^7\)Li/\(^6\)Li ratio of 1.029 \pm 0.004 assuming a \(^7\)Li/\(^6\)Li ratio of 12.330 for L-SVEC\(^{132,133}\), Table 6.3) relative to NIST 8545 L-SVEC. Despite two of the fusion supernatant Li fractions containing measurable concentrations of K, a matrix effect was not visible; presumably due to the low K concentration. Further, despite the Li recoveries of the four fusions differing, three of the four replicates were within error of one another and all supernatants had an excellent degree of precision. The difference between fusion 1 and the other three fusions (\(-0.3\ \%_o,\) Table 6.3) was considered negligible and may be attributed to contamination during any of the alkali fusion or subsequent sample purification steps. The low error of the average \(\delta^7\)Li value demonstrated a high level of internal consistency and suggested that Li was not fractionating during the alkali fusion process; unwanted isotopic fractionation would likely be difficult to replicate precisely with different Li recoveries. Owing to the high degrees of precision and internal consistency of these results, the average pristine Li isotopic composition of \(^6\)Li-Mg-EM obtained through alkali fusion was considered reliable and representative of the pristine glass.

To confirm the accuracy of the \(\delta^7\)Li value obtained through alkali fusion and ensure that \(\text{K}_2\text{CO}_3\) fusion flux was not effecting measurable isotopic fractionation, washed and sized \(^6\)Li-Mg-EM powders underwent HF digestion alongside SGR-1b (Section 2.11.2). The prepared single replicate HF digests were each loaded onto the AG MP-50 columns in duplicate, with 4 ng Li loaded based upon their nominal or measured pristine powder compositions without the concentrations of the digests being measured by ICP-OES. The duplicate Li fractions of the SGR-1b and \(^6\)Li-Mg-EM HF digests were then analysed for Li isotopes by MC-ICP-MS (Table 6.3). The \(\delta^7\)Li values obtained for the \(^6\)Li-Mg-EM HF digest were in excellent agreement with those obtained through alkali fusion at \(-916.45 \pm 0.09\ \%_o\) (\(^7\)Li/\(^6\)Li ratio of 1.030 \pm 0.001); demonstrating that no measurable Li isotopic fractionation was taking place during alkali fusion. As such, the pristine glass Li isotopic composition would be represented by the average alkali fusion value. Analysis of the SGR-1b digest gave an average \(\delta^7\)Li value of 3.47 \pm 3.28 \%o. Whilst this is similar to a value of 3.6 \pm 0.4 \%o reported in the literature\(^{200}\), others have reported
values between 4.7 and 5.0 ‰. The poor reproducibility and large errors associated with the SGR-1b HF digest measurements, which were alluded to by the range of literature values, meant that the SGR-1b digest could not be used to assess the accuracy of the $^6\text{Li}$-Mg-EM digest. However, as Li isotope analysis of HF digested samples is a frequently employed technique, the excellent agreement between the $\delta^7\text{Li}$ values obtained with a high degree of precision through alkali fusion and HF digestion of $^6\text{Li}$-Mg-EM was considered sufficient evidence for the accuracy of this pristine glass $\delta^7\text{Li}$ value.

Table 6.3: Table showing the Li isotope MC-ICP-MS results for the four $^6\text{Li}$-Mg-EM alkali fusions, the $^6\text{Li}$-Mg-EM digest run in duplicate and the SGR-1b digest run in duplicate. $\delta^7\text{Li}$ values are relative to NIST SRM 8545 L-SVEC. Each alkali fusion was analysed in triplicate, with an average value being calculated from all twelve measurements. Each HF digest (one HF digest passed through the columns in duplicate) was analysed in duplicate, with an average value calculated from all four measurements. Errors are given to 2σ. $^7\text{Li}/^6\text{Li}$ ratios were calculated assuming a $^7\text{Li}/^6\text{Li}$ ratio of 12.330 for L-SVEC.

<table>
<thead>
<tr>
<th>Fusion or digest number</th>
<th>$^6\text{Li}$-Mg-EM alkali fusions</th>
<th>$^6\text{Li}$-Mg-EM digests</th>
<th>SGR-1b digests</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^7\text{Li}$ (‰)</td>
<td>$^7\text{Li}/^6\text{Li}$</td>
<td>$\delta^7\text{Li}$ (‰)</td>
</tr>
<tr>
<td>1</td>
<td>-916.26 ± 0.15</td>
<td>1.033 ± 0.002</td>
<td>-916.41 ± 0.07</td>
</tr>
<tr>
<td>2</td>
<td>-916.58 ± 0.09</td>
<td>1.029 ± 0.001</td>
<td>-916.48 ± 0.04</td>
</tr>
<tr>
<td>3</td>
<td>-916.60 ± 0.04</td>
<td>1.028 ± 0.001</td>
<td>-916.45 ± 0.09</td>
</tr>
<tr>
<td>4</td>
<td>-916.62 ± 0.07</td>
<td>1.028 ± 0.001</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>-916.52 ± 0.32</td>
<td>1.029 ± 0.004</td>
<td>-916.45 ± 0.09</td>
</tr>
</tbody>
</table>

6.3.3.2. BCR-1, BCR-2 and SGR-1b fusions

To further assess whether the alkali fusion methodology effected isotopic fractionation, BCR-1, BCR-2 and SGR-1b also underwent alkali fusion. ICP-OES analysis of the BCR and SGR-1b fusion supernatants displayed poor recoveries for Li (42 to 60 %) for all fusions and B for the BCR fusions (52 to 62 %); with B appearing to be completely recovered in the SGR-1b fusions (104 to 123 %). These low recoveries may be attributed to the lack of recommended B and Li concentrations for these standards, with the Li and B concentrations for each standard compiled from literature values. Owing to the low Li contents of these standards, large volumes of solution needed to be dried down to yield 4 ng Li and as such large estimated masses of K were loaded onto the columns. However, ICP-OES analysis of the pre-Li cuts, post-Li cuts and Li fractions from the BCR column elutions showed that the Li fractions contained no K but instead some fractions contained Al, Ca, Mn, Na and P.

The Li fractions of the BCR-1 and BCR-2 alkali fusion supernatants were analysed for Li isotopes by MC-ICP-MS and gave average $\delta^7\text{Li}$ values of 7.75 ± 0.56 ‰ and -254.08 ± 458.65 ‰ respectively (Table 6.4). These values deviated significantly from the $\delta^7\text{Li}$ values of
2.4 to 2.7 ‰ and 2.6 to 3.5 ‰ reported in the literature for BCR-1 and BCR-2 respectively. When interpreting these results, it should be considered that BCR-1 and BCR-2 nominally contain approximately 9.4 and 12.9 µg/g Li respectively and that the Li contents (and consequently the inverse of the mass of K loaded onto the columns) of $^6$Li-Mg-EM was three orders of magnitude higher than those of the BCR standards. As the K$_2$CO$_3$ flux was reported to contain no Li and the BCR-2 $\delta^7$Li values deviated from their target by hundreds of ‰, this effect could not be attributed to the K$_2$CO$_3$ flux. Further, the excellent agreement between the $^6$Li-Mg-EM alkali fusion and HF digest $\delta^7$Li values demonstrated that this effect was not caused by isotopic fractionation during alkali fusion. As such, this implied that whilst the columns were not overloaded with K in the $^6$Li-Mg-EM elutions, loading very high masses of K onto the columns in the BCR elutions shifted the elution curves such that all the Li was not collected within a single Li fraction and other elements (particularly Al and Na) were present in the collected Li fraction. In BCR-1 this effect was small (approximately 5 ‰ offset), but due to the higher K load of the BCR-2 fusions this effect was significantly larger (approximately -250 ‰ offset).

For SGR-1b, three of the five fusion supernatants were in agreement with the values obtained via HF digestion (Table 6.4) and were within the range of values reported in the literature (3.6 to 5.0 ‰); suggesting there was no isotopic fractionation during alkali fusion. The two SGR-1b fusions which deviated from the literature values (approximately -10 ‰ offset) may be attributed to the previously discussed effect of the high mass of K loaded onto the columns.

As a test, alkali fusions of SGR-1b and a Li plasma standard (see Section 6.3.3.3) were eluted through the columns twice alongside an SGR-1b digest and a pure Li plasma standard to test whether this was a matrix effect (Table 6.5). Analysis of the Li fractions showed unreliable

<table>
<thead>
<tr>
<th>Fusion number</th>
<th>BCR-1 Fusions</th>
<th>BCR-2 Fusions</th>
<th>SGR-1b Fusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.99 ± 0.24</td>
<td>-60.70 ± 0.59</td>
<td>-9.19 ± 0.60</td>
</tr>
<tr>
<td>2</td>
<td>7.50 ± 0.19</td>
<td>-495.81 ± 0.12</td>
<td>4.01 ± 0.79</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>4.28 ± 0.28</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>3.77 ± 0.46</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>-6.18 ± 0.26</td>
</tr>
<tr>
<td>Average</td>
<td>7.75 ± 0.56</td>
<td>-254.08 ± 458.65</td>
<td>-0.66 ± 12.04</td>
</tr>
</tbody>
</table>

As a test, alkali fusions of SGR-1b and a Li plasma standard (see Section 6.3.3.3) were eluted through the columns twice alongside an SGR-1b digest and a pure Li plasma standard to test whether this was a matrix effect (Table 6.5). Analysis of the Li fractions showed unreliable
results for all samples (previous analysis of the Li standard had given a value of 90.8 ± 5.2 ‰). This suggested that K was shifting the Li elution curve and that eluting even the non-fusion samples through the columns twice would result in the incomplete recovery of Li. Contrastingly, the comparably low mass of K loaded alongside Li for the ⁶Li-Mg-EM alkali fusions did not affect the Li elution curve for these samples and the columns worked for these samples as intended; as is reflected by the high degree of internal consistency between the δ⁷Li values of these fusions and excellent agreement with the HF digest δ⁷Li values.

Table 6.5: Table showing the Li isotope MC-ICP-MS results relative to NIST 8545 L-SVEC for the samples eluted through the columns twice. A single replicate of each Li fraction was analysed. Errors are given to 2σ.

<table>
<thead>
<tr>
<th></th>
<th>δ⁷Li (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGR-1b digest</td>
<td>-3.42 ± 0.26</td>
</tr>
<tr>
<td>SGR-1b fusion</td>
<td>1.77 ± 0.30</td>
</tr>
<tr>
<td>Pure Li standard</td>
<td>78.36 ± 0.32</td>
</tr>
<tr>
<td>Li standard fusion</td>
<td>67.19 ± 0.30</td>
</tr>
</tbody>
</table>

6.3.3.3. **Standard addition fusions**

Standard addition fusions took place to verify the accuracy of the ⁶Li-Mg-EM leachate and pristine glass Li isotope measurements in relation to the L-SVEC standard through fabricating two mixing lines: ⁶Li-Mg-EM mixed with SGR-1b and ⁶Li-Mg-EM mixed with a Li plasma standard. As these mixing lines covered a range of δ⁷Li values, the δ¹⁷Li scale was used instead (see Section 2.13.2). The former mixing line kept the mass of powder constant and focussed on δ¹⁷Li values near pristine ⁶Li-Mg-EM, whilst the latter mixing line covered a wider range of δ¹⁷Li values. As such, the Li concentrations of the supernatants, and subsequently the Li:K ratio loaded onto the columns, varied in the former mixing line but did not in the latter. The ⁶Li-Mg-EM with Li standard mixing line reported good Li recoveries (between 85 and 97 %), whilst the ⁶Li-Mg-EM with SGR-1b mixing line reported poorer recoveries (58 to 85 %); as was expected from the poor Li recoveries in the pure SGR-1b fusions (Section 6.3.3.2).

The ⁶Li-Mg-EM with SGR-1b mixing line appeared close to its nominal targets at high fractions of ⁶Li-Mg-EM, but the pure SGR-1b fusion deviated significantly from values reported in the literature (Figure 6.3a). This deviation appeared to be caused by contamination from another sample, as previous SGR-1b fusions had not yielded such negative δ⁷Li values (Table 6.4). Ignoring this pure SGR-1b value, the gradient of the measured mixing line appeared less than that of the nominal mixing line such that the fusions deviated more from their respective targets (isotopically lighter) as the fraction of ⁶Li-Mg-EM in the sample (x) was decreased. Whilst the
pure Li plasma standard fusion was relatively close to its target, a similar effect was visible in the $^6$Li-Mg-EM with Li plasma standard mixing line (Figure 6.3b): all but one of the mixed fusions were isotopically lighter than their nominal target values, deviating the most at intermediate ($x = 0.35$ and $0.56$) values. The isotopically heavy $x = 0.56$ fusion may be attributed to contamination between samples, as all samples were loaded onto the columns at the same nominal Li:K ratios.

![Figure 6.3: Measured (Orange) and nominal (Blue) standard addition mixing lines for $^6$Li-Mg-EM mixed with SGR-1b (a) and $^6$Li-Mg-EM mixed with a Li plasma standard (b). Results are relative to NIST 8545 L-SVEC. Error bars are given to 2$\sigma$ but are too small to be visible on the scale used.](image)

Both mixing lines appeared non-linear, with mixed-sample fusions appearing isotopically lighter than their nominal targets. However, as it was the evolution of the Li isotopic signature of the $^6$Li-Mg-EM leachates in relation to that of the pristine $^6$Li-Mg-EM glass which was of interest, these non-linear mixing lines were not considered to impact the interpretation of the results from the $^6$Li-Mg-EM experiments. Such non-linear mixing lines would only impact the interpretation of the results if comparisons of the magnitudes of isotopic fractionation were made between isotopically spiked ($^6$Li-Mg-EM) and natural abundance (MW25) samples.
6.3.3.4. $^{11}\text{B}/^{10}\text{B$ LA-MC-ICP-MS

To obtain the B isotopic composition of $^6\text{Li-Mg-EM}$, twelve spots were laser ablated from three resin-mounted pristine $^6\text{Li-Mg-EM}$ pieces and analysed for B isotopes by MC-ICP-MS relative to NIST SRM 610 (Section 2.13.6). An average $\delta^{11}\text{B}$ of $-0.89 \pm 0.18$ ‰ ($^{11}\text{B}/^{10}\text{B$ ratio of 4.045 $\pm 0.001$ assuming a $^{11}\text{B}/^{10}\text{B$ of 4.049$ for NIST 610$^{146,160}$ was measured for $^6\text{Li-Mg-EM}$. The high B concentration of $^6\text{Li-Mg-EM}$ afforded isotope ratio determination with an excellent degree of precision (2σ of 0.10 to 0.20 ‰ on each measurement), which is reflected in the low error associated with the average $\delta^{11}\text{B$ value (2σ of 0.18 ‰); demonstrating the glass was isotopically homogeneous with respect to B. Contrastingly, higher errors were associated with the NIST 610 measurements (2σ of 0.70 to 1.50 ‰), presumably due to its significantly lower B contents. Regardless, the NIST 610 measurements displayed an excellent degree of internal consistency as well ($\delta^{11}\text{B$ of $0.06 \pm 0.96$ ‰). However, the B contents (elemental wt.%) of $^6\text{Li-Mg-EM}$ was nominally a factor of approximately 170 times higher than in NIST 610$^{146}$. Further, there is no certified $^{11}\text{B}/^{10}\text{B$ ratio for NIST 610 and the compiled $\delta^{11}\text{B$ values for NIST 610 relative to NIST 951 in the literature range from -0.78 to 0.00 ‰$^{146}$. This significant concentration mismatch and difference in matrix between $^6\text{Li-Mg-EM}$ and NIST 610 might have effected a matrix effect, which, in light of the range of compiled $\delta^{11}\text{B$ values for NIST 610, has been assigned a conservative error of 5.00 ‰ when compared to the leachates.

6.4. Leachate analyses

$^6\text{Li-Mg-EM}$ powders (75 to 150 µm) were leached in deionised water at 90 °C with a SA/V of 2000 m$^{-1}$ for between 6 h and 98 d in a static batch sampling methodology (see Section 2.9.1).

6.4.1. Concentrations and pH

The concentrations of the $^6\text{Li-Mg-EM$ constituent elements (Al, B, La, Li, Mg, Na and Si) within the leachates were analysed by ICP-MS and treated following the methodology in Section 2.9.4. Whilst B, Li, and Na were present at concentrations above their respective detection limits and significant from their respective blank concentrations (greater than three standard deviations above their respective average blank concentrations), it was noted that the concentrations of Mg and Al were frequently indistinguishable from the blanks. The majority of the La concentrations were indistinguishable from the blank concentrations but as the 0.05 and 0.50 ng/ml La calibration standard intensities were indistinguishable from the 0.00 ng/ml standard (0.1 M HNO$_3$ with 0.3 M HF blank), essentially a single-point calibration took place for La and the sample La concentrations were significantly overestimated. Similarly, despite
the majority of the leachate Si concentrations appearing to be significant from the blank Si concentrations, the 0.05 and 0.50 ng/ml Si calibration standard concentrations were indistinguishable from the 0.00 ng/ml standard. Consequently, many of the Si concentrations in the samples appeared either significantly underestimated or overestimated. As such, it was assumed Si reached its steady state apparent solubility limit after 14 d based upon the Si concentrations from Li50Na50-Mg-EM leached at 90 °C (Section 3.3). As Si was expected to be present at high concentrations within the leachates, this may be attributed to the large dilution factor used and poor detection limit of Si with ICP-MS. Average blank concentrations (not dilution factor corrected) were: below detection for Li, less than 0.01 ng/ml for Al and B, less than 0.25 ng/ml for Mg and Na, less than 0.50 ng/ml for Si and less than 80.00 ng/ml for La. RSD values were less than 12.5 % for B and Li for all but two triplicates, less than 20 % for Na for all but three triplicates, and frequently exceeded 20 % for all other elements.

As ⁶Li-Mg-EM was of the same nominal elemental composition as Li50Na50-Mg-EM and was only leached at 90 °C (whilst Li50Na50-Mg-EM was leached at 40 and 90 °C), the normalised elemental releases of ⁶Li-Mg-EM did not vary significantly from those of Li50Na50-Mg-EM; of which, a more in-depth discussion is presented in Sections 3.3 and 3.5. The normalised B, Li and Na releases of the duplicate leaching vessels were in good agreement with one another throughout dissolution (Figure 6.4). Whilst the normalised B and total Li releases appeared similar for ⁶Li-Mg-EM and Li50Na50-Mg-EM, the normalised Na releases for ⁶Li-Mg-EM were over twice of those of Li50Na50-Mg-EM. This may be attributed to the Na concentrations measured in the longer duration samples significantly exceeding the highest concentration calibration standard and as such being overestimated. The normalised ⁶Li and ⁷Li releases remained within error of each other until 98 d (or 70 d in the refreshed leachant experiment), whereas the normalised ⁷Li releases were higher. This appeared to be caused by the low errors associated with the 70 and 98 d measurements, in contrast to the larger errors at shorter durations. No trends were visible in the normalised Al or Mg releases. Further, the normalised La and Si releases were omitted as many of the leachates had releases either below the average blank concentration or were improbably large.

The non-refreshed leachant experiment showed a residual rate of B, Li and Na release was reached after 28 d (Fig 6.4). Notably, the normalised releases of these mobile species after 70 d in the refreshed leachant experiment were at values similar to those observed after just 7 d of
Initial dissolution of the glass. This demonstrated that after 28 d of dissolution, a passivating alteration layer component had formed which acted as a significant barrier to dissolution. Further, this layer was robust enough to retain its passivating nature after being significantly disturbed by the leachant being refreshed.

As pH measurements were only taken for the initial leachant, after 28 d in vessel 1 (before refreshing the leachant) and after a total of 98 d of dissolution (70 d in the refreshed leachant experiment), pH trends could not be discerned (Figure 6.5). These pH values appeared slightly higher than those observed for Li50Na50-Mg-EM leached at 90 °C, which displayed a negligible drop in pH with time (less than 0.25 pH units between 7 and 112 d, Figure 3.6).
Probing diffusion throughout aqueous glass dissolution.

![Figure 6.5: Measured pH of the leachants from vessel 1 (Blue) and vessel 2 (Orange) in the $^{6}$Li-Mg-EM experiments. Points at 0 d correspond to the initial leachant pH. The vacant markers at 0 and 70 d correspond to the refreshed leachant experiments. Points are plotted as the average of the triplicate aliquots with errors conservatively given to ±0.1 pH units.](image)

Whilst Na was shown to precipitate as a sodium silicate hydrate phase during the dissolution of Li50Na50-Mg-EM at 90 °C (Section 3.4.2.4), $^{6}$Li-$^{1}$H CP-NMR analysis of these leached powders displayed a weak signal but demonstrated a Li-bearing phase was also precipitating from solution (Section 3.4.2.2). However, the decreasing leachate Li/Na ratio in the $^{6}$Li-Mg-EM experiments suggested the rate of Li-bearing phase precipitation was faster than the rate of sodium silicate hydrate precipitation relative to their respective dissolution rates (Figure 6.6a). As B is not expected to be incorporated into secondary phases in significant masses but rather adsorbed onto the surface of alteration products50,123,129, the leachate Li/B ratio decreased at a faster rate than the Li/Na ratio and suggested Li was incorporated into a secondary phase rather than adsorbed (Figure 6.6b). The initially increasing leachate Li/Mg and Li/Al ratios suggested that the rates of magnesium silicate and Al-bearing phase precipitation initially exceeded the rate of Li-bearing phase precipitation (Figure 6.6c and d). However, this view neglects that the rates of Li and Na interdiffusion differ due to differences in their preferential roles within the glass and the higher diffusivity of Na than Li at higher temperatures (as discussed in Section 5.5.1.1). Additionally, the decreasing Li/B ratio could also be attributed to a higher rate of B hydrolysis than Li interdiffusion. The almost negligible changes to the Li/Na and Li/B ratios from 28 d onwards may simply be attributed to the significantly slower rates of glass dissolution and secondary phase precipitation during the residual rate regime, but may also reflect that differences between the dissolution processes of B, Li and Na become less relevant once a highly passivating altered layer interphase forms.
Figure 6.6: The Li/Na (a), Li/B (b), Li/Mg (c) and Li/Al (d) ratios calculated from their respective concentrations (µg/ml) measured in the ⁶Li-Mg-EM leachates. Points are plotted as the averages of the triplicate aliquots taken from each vessel, with each vessel plotted separately (Vessel 1 (Blue) and vessel 2 (Orange)) and errors given to 1σ. Vacant diamond markers correspond to the refreshed leachant experiment, in which after the 28 d leachates were sampled from vessel 1 the leachant was refreshed with fresh deionised water and the glass was leached for a further 70 d.

6.4.2. Li isotopes

Following Li ion-exchange column chromatography, Li fractions of all ⁶Li-Mg-EM leachates were analysed for Li isotopes by MC-ICP-MS and treated following the methodology given in Section 2.13.2. Figure 6.7a gives the temporal evolution of the Li isotopic signature of the leachates relative to the pristine glass Li isotopic composition (given in Section 6.3.3.1). Additionally, the use of an isotope-concentration cross plot illustrated the change, or lack of, in the isotopic composition of the leachates with concentration (Figure 6.7b).

After 6 h of dissolution, significant concentrations of Li had been leached into solution but the Li isotopic composition of the leachates remained within error of the pristine glass (Figure 6.7). The absence of measurable isotopic fractionation suggested that dissolution was initially
congruent. If dissolution in such a system were incongruent through interdiffusion reactions, then kinetic isotopic fractionation due to the enhanced diffusion of $^6\text{Li}$ would be expected and the leachates would be isotopically lighter than the pristine glass (below the pristine glass line). Between 6 h and 7 d, the concentration of Li in solution significantly increased and the leachates became isotopically heavier with time. This may be attributed to an equilibrium isotope effect where the precipitation of Li-bearing phases which preferentially contained $^6\text{Li}$ resulted in the leachant becoming enriched in $^7\text{Li}$ with time\textsuperscript{119,120}.

![Figure 6.7: Temporal evolution of the Li isotopic signature of the $^6\text{Li}$-Mg-EM leachates (a) and evolution of the Li isotopic signature of the leachates as a function of Li concentration (blank and mass loss corrected) change (b). The measured pristine glass composition is given as a dashed line, with the dashed lines above and below this representing the 2$\sigma$ errors on this measurement. Each leaching vessel is plotted as a separate line (vessel 1 (Blue) and vessel 2 (Orange)). Vacant markers represent the refreshed leachant experiment, in which the leachant was refreshed with fresh deionised water in vessel 1 after the 28 d aliquots were taken and the glass was leached for a further 70 d. In (a), each individual triplicate aliquot point is plotted with an error given to 2$\sigma$, with the solid and dashed lines representing the average value for each duration in vessels 1 and 2 respectively. In (b), points are plotted as average values with errors given to 1$\sigma$ on the concentration data (horizontal axis) and 2$\sigma$ on the isotopic data (vertical axis). The arrows in (b) indicate time.]

Whilst $^6\text{Li}$-Mg-EM altered at its residual rate after 28 d, after 7 d the leachates became isotopically lighter with time whilst the leachate Li concentration continued to increase. In particular, in vessel 3 a small increase in Li concentration was observed between 7 and 98 d but
there was a significant decrease in the $\delta^7$Li value of the leachates. This indicated a different dissolution process began operating during the later stage of dissolution. During the additional 70 d leaching after refreshing the leachant, the leachant contained Li at concentrations similar to after the initial 7 d of leaching but the Li isotopic signature of the leachates were only slightly heavier than the pristine glass. These results showed that a highly passivating alteration layer interphase had formed after 28 d which limited the transport of water and glass species to and from the pristine glass interface respectively. This interphase not only inhibited the rate of dissolution, but the decrease in the Li isotopic composition of the leachates coinciding with its formation at 28 d and 98 d in the non-refreshed leachant experiment demonstrated that these glass species were forced to reactively diffuse through its presumably nanoporous structure; effecting kinetic isotopic fractionation due to diffusion for all glass species diffusing from the pristine glass interface into the leachant.

### 6.4.3. B isotopes

All $^6$Li-Mg-EM leachates underwent B sublimation prior to B isotope MC-ICP-MS analysis (Section 2.13.4). The temporal evolution of the isotopic signature of the leachates are presented alongside a concentration-isotope cross plot in Figure 6.8a and b respectively. As the pristine glass $\delta^{11}$B values from LA-MC-ICP-MS were reported with respect to bracketing NIST 610 measurements but the leachate $\delta^{11}$B measurements were bracketed by NIST 951 measurements, a $\delta^{11}$B of 0.00 ‰ for NIST 610 relative to NIST 951 was assumed for simplicity. However, it should be considered that there are a range of compiled $\delta^{11}$B values in the literature for NIST610 (-0.78 to 0.00 ‰ relative to NIST 951), which contribute to the error on the pristine glass $\delta^{11}$B value when comparing it with the $\delta^{11}$B values of the leachates on the NIST 951 scale. As such, owing to this range of $\delta^{11}$B values and the matrix mismatch between $^6$Li-Mg-EM and NIST 610 during the LA-MC-ICP-MS analysis (Section 6.3.3.4), a conservative 5.00 ‰ error was assigned to the pristine $^6$Li-Mg-EM $\delta^{11}$B value. However, this large error resulted in all leachates being within error of the pristine glass $\delta^{11}$B value at all durations. As such, these results cannot be used to discern whether dissolution was initially congruent or incongruent, but rather only the trends of the isotopic signatures can be examined.
Figure 6.8: Temporal evolution of the B isotopic signature of the $^6$Li-Mg-EM leachates (a) and evolution of the B isotopic signature of the leachates as a function of B concentration (blank and mass loss corrected) change (b). The measured pristine glass composition is given as a dashed line, with the errors on this measurement given to 2σ but not visible as they exceeded the scale used (± 5.00 ‰). Each leaching vessel is plotted as a separate line (vessel 1 (Blue) and vessel 2 (Orange)). Vacant markers represent the refreshed leachant experiment, in which the leachant was refreshed with fresh deionised water in vessel 1 after the 28 d aliquots were taken and the glass was leached for a further 70 d. In (a), each individual triplicate aliquot point is plotted with errors given to 2σ, with the solid and dashed lines representing the average for each duration in vessels 1 and 2 respectively. Points with red borders are outliers and have been excluded from the average lines in (a) and (b) based upon the agreement of the other duplicate points. In (b), points are plotted as the average value with errors given to 1σ on the concentration data (horizontal axis) and 2σ on the isotopic data (vertical axis). The arrows in (b) indicate time.

Between 6 h and 28 d, the leachant $\delta^{11}$B values increased gradually with time and significant concentrations of B were leached into solution (Figure 6.8). Without an accurate $\delta^{11}$B value for the pristine glass, it was not known whether dissolution was initially congruent or incongruent. However, the Li isotopic signatures (Figure 6.7) suggested dissolution was initially congruent and the increasing $\delta^{11}$B values were caused an equilibrium isotope effect of $^{10}$B preferentially adsorbing onto the surface of secondary phases$^{117,123,129}$. Whilst the $\delta^7$Li values began decreasing after 7 d, the $\delta^{11}$B values decreased significantly between 28 and 98 d in the non-refreshed leachant experiment despite the 28 and 98 d B concentrations being within error of one another. This decrease for B coincided with $^6$Li-Mg-EM altering at its residual rate after 28 d and Si reaching its steady state apparent solubility limit after 14 d (as shown by Li50Na50-Mg-EM). Additionally, the 70 d refreshed leachant experiment leachates had B concentrations
Probing diffusion throughout aqueous glass dissolution.

similar to those after 6 h of initial dissolution but had lower δ^{11}B values. This was consistent with the Li results in demonstrating kinetic isotopic fractionation caused by reactive diffusion through a nanoporous, passivating alteration layer interphase was taking place for all glass species leaching from the pristine glass. As the maximum δ^7Li and δ^{11}B values were observed at different times, this provided evidence that these isotope ratio trends were not attributable to changes in leachant pH. The contrasting shapes of the isotope-concentration cross plots for Li and B provided further evidence that they leached through different dissolution processes.

6.4.4. Mg isotopes
Following Mg column chromatography, all 6Li-Mg-EM leachates were analysed for Mg isotopes by MC-ICP-MS (Figure 6.9). However, many of the eluted Mg fractions contained too little Mg to be analysed. Further, some of the samples had precipitated from solution and blocked the nebuliser, producing a low degree of reproducibility amongst the measurements. Whilst the Mg isotopic signatures appeared to evolve following a similar trend to the B isotopic signature, as only one 28 d aliquot of the six aliquots taken was successfully analysed trends could not be discerned using these results. Many of the samples could not be reanalysed as all of the samples were aspirated in the first instance. As such, Mg isotope analysis of the pristine glass did not take place.

![Figure 6.9: Temporal evolution of the Mg isotopic signatures (δ^{26}Mg (a) and δ^{25}Mg values (b)) of the 6Li-Mg-EM leachates. Each leaching vessel is plotted as a separate line (vessel 1 (Blue) and vessel 2 (Orange)). Vacant markers represent the refreshed leachant experiment, in which the leachant was refreshed with fresh deionised water in vessel 1 after the 28 d aliquots were taken and the glass was leached for a further 70 d. Each individual point is plotted (where measured) with errors given to 2σ. The solid and dashed lines represent the means for each duration in vessels 1 and 2 respectively.](image-url)
6.5. Characterisation of leached and pristine samples

As these were static-batch sampling dissolution experiments, only 98 d total leaching time (refreshed and non-refreshed leachant experiment) samples were available for analysis.

6.5.1. SEM

Secondary electron SEM images of the 98 d leached $^6$Li-Mg-EM surfaces (Figure 6.10) showed the same macroporous magnesium silicate layer had formed as on the Li-Mg-EM compositions (Section 3.4.1). No differences between the surfaces of the refreshed and non-refreshed leachant samples were visible.

![SEM images](image)

Figure 6.10: Secondary electron SEM of $^6$Li-Mg-EM leached for 98 d in the refreshed leachant experiment (a) and the experiment without refreshing the leachant (b).

6.5.2. NMR

6.5.2.1. $^{11}$B-NMR

The leached $^6$Li-Mg-EM $^{11}$B MAS-NMR spectra were consistent with those of the leached Li-MG-EM samples in displaying a decrease in the $^{III}$B/$^{IV}$B ratio after dissolution (Figure 6.11). No differences in the $^{III}$B/$^{IV}$B ratio between the refreshed and non-refreshed leachant samples were apparent.

![NMR spectra](image)

Figure 6.11: $^{11}$B MAS-NMR spectra of pristine $^6$Li-Mg-EM (Black) and $^6$Li-Mg-EM leached for a total of 98 d after refreshing the leachant after 28 d (Blue) and without refreshing the leachant (Red). Spectra were normalised to the intensities of their $^{IV}$B peaks.
6.5.2.2. $^{6}\text{Li MAS-NMR, }^{6}\text{Li-}^{1}\text{H CP-NMR and }^{6}\text{Li-}^{1}\text{H CP MAS-NMR}$

$^{6}\text{Li-}^{1}\text{H CP-NMR of leached }^{6}\text{Li-Mg-EM (without refreshing the leachant, Figure 6.12a) showed a significantly stronger signal than observed for }^{6}\text{Li}_{50}\text{Na}_{50}\text{-Mg-EM. Whilst some measurable polarisation was visible for the fines, this was considered negligible. In comparison to single-pulse }^{6}\text{Li MAS-NMR experiments, the }^{6}\text{Li-}^{1}\text{H CP MAS-NMR signal from the leached sample was small but non-negligible (Figure 6.12b). However, normalised to the same scale, the }^{6}\text{Li-}^{1}\text{H CP MAS-NMR spectra of both the leached sample and fines were wider than the }^{6}\text{Li MAS-NMR of both the fines and leached sample (Figure 6.12c).}$

![Figure 6.12: $^{6}\text{Li-}^{1}\text{H CP-NMR (a) and }^{6}\text{Li MAS-NMR with }^{6}\text{Li-}^{1}\text{H CP MAS-NMR (b and c) of }^{6}\text{Li-Mg-EM fines (Red for MAS-NMR and Magenta for CP-NMR and CP MAS-NMR) and 98 d leached }^{6}\text{Li-Mg-EM without refreshing the leachant (Blue for MAS-NMR and Black for CP-NMR and CP MAS-NMR). The intensity of the spectra in (a) and (b) have been adjusted to the mass of sample analysed and number of acquisitions, whilst spectra in (c) have been normalised to the same intensity.}"

6.6. Discussion

6.6.1. Initially congruent dissolution

Despite significant concentrations of Li having been leached into solution after 6 h of dissolution, this was not accompanied by any measurable isotopic fractionation and the Li
isotopic composition of the leachates remained within error of that of the pristine glass (Figure 6.7). As such, this suggested that dissolution was initially congruent or apparently congruent. This was consistent with the interfacial dissolution-precipitation model of dissolution, which predicted congruent dissolution through an interfacial film of water controls the initial rate of dissolution. In interdiffusion based models of dissolution, dissolution is instead initially incongruent through interdiffusion reactions (inward diffusion of protonated water species, ion exchange reactions between water and glass species and the subsequent outward diffusion of glass species) across a layer hydrated glass preceding a Si hydrolysis front. If interdiffusion reactions were taking place, it could be expected that the enhanced diffusion of $^6$Li over $^7$Li (owing to its lower mass), would result in kinetic isotopic fractionation such that the leachates would initially be isotopically lighter (lower $\delta^7$Li values) than the pristine glass.

Whilst the B isotopic compositions of the leachates at 6 and 12 h were within error of that of the pristine glass (assuming an error of 0.00 ‰ on the pristine glass isotopic composition), the large error of 5.00 ‰ assigned to the B isotopic composition of the pristine glass resulted in all leachates at all durations probed being within error of the pristine glass. As such, only the trends of the B results could be investigated and these initial B releases could not be used to distinguish between congruent and incongruent dissolution. However, as elemental profiles of cross-sections of leached glasses have shown that glass Li leaches in a wide interdiffusion curve in the hydrated glass ahead of a sharp B hydrolysis front (see Figure 6.13a), it seemed probable that if the Li isotopes leached congruently from the glass then so would the B isotopes. Further, as there is a larger relative difference in mass between $^6$Li and $^7$Li than $^{10}$B and $^{11}$B, the magnitude of kinetic isotopic fractionation due to diffusion could be expected to be larger for Li than B.

Although these results appeared consistent with models of congruent glass dissolution, it should be considered that in interdiffusion based models of dissolution the initial period interdiffusion controls the rate of dissolution over hydrolysis is expected to be shorter at higher dissolution temperatures. As such, at 90 °C interdiffusion reactions might have controlled the rate of dissolution for a time insufficient to effect measurable isotopic fractionation.

### 6.6.2. Secondary phase precipitation and adsorption

The leachates becoming isotopically heavier with respect to Li with time (increase of the $\delta^7$Li values) between 6 h and 7 d were consistent with dissolution continuing to be congruent
alongside the dominant removal of Li from solution. As a sodium silicate hydrate was shown to precipitate from solution throughout dissolution for Li50Na50-Mg-EM at 90 °C (Section 3.4.2.4) and B was not expected to be removed from solution in significant masses\(^5\), the decreasing Li/Na and Li/B ratios (Figure 6.6) were consistent with a Li-bearing phase precipitating from solution onto the surface of the glass during this time. This was consistent with the \(^6\)Li-\(^1\)H spectra of Li50Na50-Mg-EM leached at 90 °C under similar conditions which displayed evidence for a Li-bearing phase precipitating after just 7 d (Section 3.4.2.2). The preferential incorporation of \(^6\)Li into the secondary phases resulted in the leachates becoming enriched in \(^7\)Li with time and the \(\delta^{7}\)Li value increasing between 6 h and 7 d\(^119,120\). As this increasing \(\delta^{7}\)Li value was not preceded by any measurable isotopic fractionation, it was expected dissolution continued to be congruent and no measurable diffusive isotopic fractionation was present to offset this increase.

The B isotopic signature of the leachant increased gradually between 6 h and 28 d. Although significant masses of B were not expected to be incorporated into any secondary phases under the experimental conditions used\(^5\), B is known to adsorb onto the surface of clays with a strong pH dependency\(^129\). As with the precipitation of the Li-bearing phase, as \(^10\)B preferentially adsorbed onto the surface of secondary phases the leachant became enriched in \(^11\)B and the \(\delta^{11}\)B value in solution increased with time. Again, this was consistent with dissolution continuing to be congruent coupled with the absorption of B.

**6.6.3. Interdiffusion as a rate limiting dissolution mechanism**

If dissolution continued to be congruent, Li-bearing secondary phases continued to precipitate and B continued to be adsorbed onto secondary phases, the leachant would continue to be enriched in \(^7\)Li and \(^{11}\)B with time (as depicted in Figure 6.13b). As such, in congruent models of glass dissolution which exclude diffusive transport as a rate-limiting mechanism, only a drop in leachant pH, dissolution of secondary phases or continued congruent glass dissolution unaccompanied by further secondary phase precipitation could make the leachant isotopically lighter with time. However, after 7 and 28 d the leachant \(\delta^{7}\)Li and \(\delta^{11}\)B values respectively reached their maxima and the leachant started to become isotopically lighter with time. The leachant pH values for \(^6\)Li-Mg-EM (Figure 6.5) and Li50Na50-Mg-EM (Section 3.3) suggested that this effect was not due to a decreasing leachant pH. Additionally, this was supported by the \(\delta^{7}\)Li and \(\delta^{11}\)B values reaching their respective maximum values at different times, which would not be possible if their subsequent decrease were solely caused by a pH effect. As the secondary
phases precipitated from the leachant and there was no notable change in the leaching vessel environment between 7 and 98 d (7 and 28 d for the refreshed leachant experiment), it seemed implausible these secondary phases would spontaneously dissolve and release $^6$Li and $^{10}$B without an external driving force. The decreasing Li/Na and Li/B ratios during this time suggested that the precipitation of Li-bearing phases persisted throughout the later dissolution regimes, which was supported by the $^6$Li-$^1$H CP-NMR spectrum of 112 d 90 °C leached Li50Na50-Mg-EM having a higher intensity than the 7 d spectrum (Section 3.4.2.2). Therefore, the leachates becoming isotopically lighter with time could only be attributed to kinetic isotopic fractionation caused by diffusive transport.

The magnitude of kinetic isotopic fractionation due to diffusion for both B and Li was large enough to entirely offset the continued equilibrium isotopic fractionation caused by adsorption onto or incorporated into secondary phases respectively and make the leachant isotopically lighter with time. These significant light isotopic fractionations coupled with small changes in the B and Li concentrations were well illustrated in the isotope-concentration cross plots for Li and B (Figure 6.7b and Figure 6.8b respectively).

After the extended leaching for an additional 70 d, the leachates from the refreshed leachant experiment had lower B and Li concentrations than observed after 12 h and 7 d respectively of
initial dissolution of the pristine glass. This demonstrated that a highly passivating alteration layer interphase had formed after 28 d which limited to transport of water and glass species to and from the pristine glass interface respectively and was robust enough to retain its passivating nature after being significantly disturbed through refreshing the leachant. This observation was consistent with other dissolution experiments which involved leachant renewal\textsuperscript{77}. This passivating interphase was expected to form between 7 and 28 d of dissolution, as was consistent with the Si concentration in solution reaching a steady state apparent solubility limit after 14 d in the Li-Mg-EM experiments (Section 3.3).

The passivating alteration layer interphase not only inhibited the rate of glass alteration, but the magnitude of B and Li diffusive isotopic fractionation coinciding its formation demonstrated that all glass species, and by extension the interdiffusion water species, were forced to reactively diffuse through its tight nanoporous structure from the pristine glass interface into the leachant\textsuperscript{37,58}. Owing to their lower masses, $^{10}$B and $^6$Li diffused through this layer faster than $^{11}$B and $^7$Li respectively to enrich the leachant in $^6$Li and $^{10}$B after 7 and 28 d respectively. As such, this result was consistent with models of glass dissolution which predict the residual rate of alteration is controlled by interdiffusion reactions across a highly passivating altered layer interphase coupled with the destruction of this layer through network hydrolysis reactions fuelled by the precipitation of Si-bearing secondary phases\textsuperscript{37,48,57}. In this view, the inward reactive diffusion of water species to the pristine glass presents a rate limiting mechanism. As diffusive isotopic fractionation was observed for both B and Li, this implies diffusion plays a key role for all glass species passing through this interphase regardless of their prior role within the glass and the isotopes of all outwardly diffusing glass species leach from the glass incongruently (as in Figure 6.13a).

The $\delta^7$Li and $\delta^{11}$B values in solution after 70 d in the ‘refreshed leachant experiment’ were similar to the initial 12 h $\delta^7$Li values and isotopically lighter than the initial 6 h $\delta^{11}$B values respectively. Whilst the decreasing $\delta^7$Li and $\delta^{11}$B values in solution after 28 d in the non-refreshed leachant experiment strongly suggested diffusive isotopic fractionation affected the isotopic signatures measured in the refreshed leachant experiment leachates, it was not possible to investigate what proportion of these isotopic signatures was caused by the dissolution of $^6$Li and $^{10}$B-rich secondary phases brought about by refreshing the leachant with pure deionised water. As the refreshed leachate $\delta^7$Li values were isotopically heavier than the pristine glass,
this showed that significant amounts Li-bearing secondary phase precipitation took place during this additional 70 d of leaching. Consequently, as the leachant was not sampled immediately after refreshing the leachant, these refreshed leachate isotopic signatures could not be attributed to kinetic isotopic fractionation due to diffusion. The initial formulation of the interfacial dissolution-precipitation model excluded interdiffusion reactions and diffusive transport through a passivating relict hydrated glass interphase as rate limiting mechanisms. A later version of this model then predicted that once Si reached its steady state apparent solubility limit in solution, a component of the precipitated gel layer behind the interfacial film of water and congruent dissolution front (see Figure 6.13b) may densify into a passivating component which limits transport to reactive diffusion similar to the densified hydrated glass layer in some interdiffusion-based models (see Figure 6.13a). However, if the measured diffusive isotopic fractionation for both B and Li was caused by diffusion through a densified precipitated alteration layer component behind a congruent dissolution front, Li and B would experience the same diffusive barrier at the same time and the δ7Li and δ11B values in solution should have begun to decrease simultaneously. As such, despite the isotopic signatures of the leachates suggesting dissolution was initially congruent, the decreasing δ7Li and δ11B values provided evidence for diffusive transport being rate-limiting during the residual rate regime which could not have come from congruent dissolution and alteration layer structures as described by the interfacial dissolution-precipitation model. Instead, the δ7Li and δ11B values in solution decreasing at 7 and 28 d respectively may be consistent with incongruent dissolution and a passivating hydrated glass interphase as described by an interdiffusion-based model of glass dissolution. In some interdiffusion-based models of glass dissolution such as the GRAAL model, the passivating alteration layer interphase forms in the hydrated glass layer ahead of the Si network hydrolysis front wherein the Li interdiffusion curve and B hydrolysis front occur (see Figure 6.13a). As the leachant δ7Li values began decreasing after 7 d, this implied that the innermost part of the hydrated glass layer (contacting the pristine glass interface) began densifying into a passivating interphase first after the Si concentration in solution had reached its steady state apparent solubility limit; as was consistent with the GRAAL model. As the Li interdiffusion curve preceded the B hydrolysis front in the hydrated glass layer, the passivating hydrated glass interphase densified and grew until it encompassed the Li interdiffusion curve
Probing diffusion throughout aqueous glass dissolution.

prior to encompassing the B hydrolysis front; resulting in Li being forced to reactively diffuse outwards through this interphase and the $\delta^7$Li value in solution decreasing after 7 d whilst the release of B remained unaffected and the $\delta^{11}$B value in solution continued to increase until 28 d. After 28 d, the passivating hydrated glass interphase densified and grew to eventually also encompass the B hydrolysis front, B was forced to reactively outward diffuse through this layer and the $\delta^{11}$B value in solution decreased. As such, the $\delta^{11}$B value in solution decreased at a later time than the $\delta^7$Li value. It could be expected that the temporal evolution of the isotopic signatures of other alkali metals which preferentially charge compensate the B network and leach alongside the B hydrolysis front, such as K$^{38}$, would be similar to B. Once the residual rate regime is reached (after 28 d in this case), this passivating hydrated glass interphase is expected to be fully densified and form through interdiffusion reactions at the same rate it is dissolved through hydrolysis of the glass network such that the magnitude of kinetic isotopic fractionation across this interphase should remain constant.$^{48,57}$

6.7. Summary

It was shown through simplistic experiments that Li and B isotope fingerprinting techniques could be applied to the glass leachates of a simplified analogue to investigate whether diffusive processes were taking place during dissolution. The Li isotopic signatures of the leachates initially remained within error of that of the pristine glass and suggested Li isotopes initially leached congruently from the glass. Both Li and B isotopic signatures initially increased with time, as was consistent with congruent dissolution alongside secondary phase precipitation. After 7 and 28 d, the Li and B leachate isotopic signatures respectively decreased with time. Combined with the 70 d refreshed-leachate concentrations being comparable to those of the 7 d leachates, this was attributed to the formation of a highly passivating alteration layer component beginning to form after 7 d. Such an interphase was expected to force glass species to reactively diffuse into solution, thereby effecting significant kinetic isotopic fractionation. As the Li and B isotopic signatures peaked at different times, this observation could not be attributed to a pH effect. Further, combined with the $^6$Li-$^1$H CP-NMR results of Li50Na50-Mg-EM demonstrating that the precipitation of a Li-bearing phase continued throughout all dissolution regimes, it was shown that these isotopic signatures could not be the result of a passivating alteration layer component behind a congruent dissolution front. Rather, these results appeared consistent with interdiffusion-based models of dissolution.
An isotopic investigation into the temperature dependence of dissolution

7. An isotopic investigation into the temperature dependence of dissolution

7.1. Introduction

The simplistic proof of concept isotope experiment presented in Chapter 6 provided strong evidence for interdiffusion presenting a key process during the residual dissolution of $^{6}$Li-Mg-EM at 90 °C. As such, it was demonstrated that isotope fingerprinting techniques could be applied to simplistic glass leachates to investigate whether kinetic isotopic fractionation due to diffusion was taking place and distinguish between congruent dissolution through an interfacial dissolution-precipitation model and incongruent dissolution through an interdiffusion based model. This suggested that these techniques could be applied to investigate the dissolution processes of complex waste glass compositions.

In this chapter, the Li isotope fingerprinting techniques employed in Chapter 6 were applied to investigate the dissolution mechanisms of MW25. Whilst the post-process analyses of leached glass samples and normalised elemental releases presented in Chapters 3 and 5 suggested Li50Na50-Mg-EM was an excellent simplified analogue of MW25, it was also necessary to investigate whether the dissolution processes of $^{6}$Li-Mg-EM were similar to MW25 to further understand the relationship between simplified analogues and the complex glasses they aimed to represent. Further, the interpretation of the isotopic signatures of the MW25 leachates may be convoluted by the complex composition and structure of MW25 and a comparison to the isotopic signatures of simplified analogue leachates might afford a more sophisticated interpretation of these results.

Experiments took place at both an estimated GDF temperature and accelerated leaching temperature (40 and 90 °C respectively) to investigate the effects of leachant temperature on the dissolution mechanisms of MW25; by extension investigating the validity of applying data from experiments conducted under accelerated leaching conditions to predict waste package lifespans in a GDF over geological timescales. The powders and leachates which underwent isotopic analyses herein were the same as those in the 40 and 90 °C experiments described in Chapter 5. An in-depth discussion of the leachate concentration data, the Arrhenius-type behaviour of MW25 dissolution and post-process analyses of the leached MW25 powders are presented in Chapter 5 alongside the 70 and 80 °C MW25 experiments. As such, this chapter
aimed to use isotope fingerprinting techniques to provide an additional dimension with which
to understand the temperature dependence of dissolution of MW25 and build upon Chapter 5.

7.2. Isotopic analyses

7.2.1. Li and Mg isotopes of NGM
As many of the elements present in the MW25 alkali fusion supernatants and leachates had not
been eluted through the columns before (Cr, Cs, Fe, Mo, Ni and REEs represented by Ce), their
effects on the Li and Mg elution curves were tested alongside the largest mass of Li and smallest
mass of Mg which could be loaded onto the columns without adverse effects through the mock
complex waste glass matrix NGM (“Nuclear Glass Matrix”).

Initially, the volumes of NGM required to yield masses of 56, 149, 298 and 707 ng Mg (39,
104, 208 and 494 ng Li, masses of other elements given in Table 2.2) were prepared, loaded
onto the AG MP-50 columns, eluted for Li and Mg fractions and analysed by MC-ICP-MS (see
Sections 2.12.3.3 and 2.13.3). Analysis of the 1 ml pre-Li and post-Li fractions for
concentrations by MC-ICP-MS gave Li and Na concentrations indistinguishable from 2 %
HNO₃, deionised water and 0.7 M HCl blanks; demonstrating that even for the 494 ng Li
sample, all the Li remained within the collected Li fractionation without Na contamination. Li
isotope MC-ICP-MS analysis of the four NGM samples showed no change in the δ⁷Li values
with the mass of Li loaded (Table 7.1), confirming the calibrated elution procedure for the
columns functioned as intended even at high Li masses. Further, the concentration of Na in the
Li fractions appeared almost constant across all four samples (Table 7.1). Alongside a
decreasing [Li]/[Na] ratio with the mass of Li loaded, this demonstrated that higher Li loads did
not cause the Na elution curve to overlap with the collected Li fraction. However, the duplicate
IAPSO seawater standards (loaded 5 ng Li) eluted through the columns alongside the NGM
standards significantly deviated from their target value (18.5 ± 3.2 ‰ and 21.2 ± 1.1 ‰ with a
target of 31.0 ± 0.5 ‰); suggesting significant amounts of Na were present in the seawater
Li fractions. The large errors associated with the first two NGM measurements in Table 7.1
may be attributed to these measurements being destabilised by high Na concentrations in the
prior seawater measurements. Whilst this test demonstrated higher Li loads did not significantly
affect the Li elution curve, the AG MP-50 resin in the columns needed to be changed and a
second Li test would be needed to investigate whether the Li elutions at lower masses of Li
loaded would be affected by the elements in NGM.
An isotopic investigation into the temperature dependence of dissolution

After changing and cleaning the resin, the volumes of 500 times diluted NGM required for 5 ng Li were loaded in triplicate onto the AG MP-50 columns alongside IAPSO seawater (3 ng Li) in triplicate. Li fractions were eluted, prepared and analysed for Li isotopes by MC-ICP-MS (see Sections 2.12.3.3 and 2.13.3) alongside an Aristar Li plasma standard (the same Li standard which was used in fabricating NGM and was not eluted through the columns). Two of the three NGM $\delta^7$Li values were within error of the Aristar Li standard, with one NGM $\delta^7$Li value being approximately 1‰ lighter than in the Aristar standard (Table 7.1). Similarly, the triplicate IAPSO seawater $\delta^7$Li values were approximately 2‰ lighter than their target value (measured seawater $\delta^7$Li values of 27.8 ± 0.2, 28.8 ± 0.3 and 28.4 ± 0.3‰). As both the NGM and seawater standards were offset by similar values, this suggested either the molarity of the HCl used deviated from 0.7 M or a very small fraction of the Li was not being collected in the Li fraction. However, this was thought to aptly demonstrate that the other elements in NGM did not significantly affect the Li elution curve either at large or small masses of Li loaded. To mitigate this offset in the Li column chromatography of the MW25 leachates, all alkali fusions and all HF digests, the 0.7 M HCl was titrated again, the Li fraction collected from the columns in future runs was increased by 2 ml from 13 to 15 ml and before and after each Li fraction a 1 ml pre- and post-Li cut was collected in each column run. Further, IAPSO seawater standards (3.5 ng Li) would be eluted through the columns in duplicate alongside each set of four samples per set of six columns to check whether the samples were isotopically fractionating in the columns, whether this 1 or 2‰ offset was still present, how this offset evolved as more samples were run through the columns and confirm the external reproducibility of each column run.

Table 7.1: Table of the mass of Li in the prepared NGM standards loaded onto the AG MP-50 columns and eluted for Li. $\delta^7$Li values represent average values from the duplicate measurements for the variable Li load samples and the triplicate measurements for the 5 ng Li load samples and Aristar Li. Errors are given to 2σ. The concentrations of Li and Na measured in the undiluted Li fractions by MC-ICP-MS (V) in the first set of NGM Li fractions are also given alongside the Na/Li ratio of that Li fraction.

<table>
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<th>Loaded mass of Li (ng)</th>
<th>$\delta^7$Li (‰)</th>
<th>Conc. of Na in Li fraction (V)</th>
<th>Conc. of Li in Li fraction (V)</th>
<th>[Na]/[Li] in Li fraction</th>
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</thead>
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<td>39</td>
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<td>1.5</td>
<td>70</td>
<td>0.021</td>
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<tr>
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<td>7.0</td>
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<tr>
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<td>1.1</td>
<td>978</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>-2.76 ± 0.57</td>
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<td></td>
</tr>
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<td>5</td>
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<tr>
<td>Aristar Li (Measured, not loaded)</td>
<td>-1.40 ± 0.66</td>
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</tbody>
</table>
The Mg fractions from the initial NGM elutions (56, 149, 298 and 707 ng Mg NGM loaded onto AG MP-50 resin) were analysed for Mg isotopes by MC-ICP-MS alongside the Cambridge 1 standard (the same Mg standard used in fabricating Mg). Whilst the Na, Al and Cr concentrations within the eluted Mg fractions remained constant with the mass of Mg loaded, the Ni/Mg ratio increased with the mass of loaded Mg (Table 7.2). However, the concentrations of Ni in these fractions were low and considered negligible under the wet plasma conditions used. Despite the higher Ni/Mg ratio, the $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values of the 707 ng Mg loaded NGM standard were within error of those of Cambridge 1 and demonstrated there was no significant Ni matrix effect (Table 7.2). However, as the mass of Mg loaded decreased, the $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values of NGM became significantly isotopically heavier. This might be attributed to a small fraction of Mg being retained by the columns, which would not be noticeable at higher Mg loadings. This could not be attributed to Na, as a Na matrix effect would make the $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values isotopically lighter.

As it appeared more than 700 ng Mg would need to be loaded onto the columns to produce

<table>
<thead>
<tr>
<th>Mass of Mg loaded (ng)</th>
<th>$\delta^{25}\text{Mg}$</th>
<th>$\delta^{26}\text{Mg}$</th>
<th>Concentration in Mg fraction (V)</th>
<th>Ratio in Mg fraction</th>
<th>Concentration in Mg fraction (V)</th>
<th>Ratio in Mg fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na</td>
<td>Al</td>
<td>Cr</td>
<td>Ni</td>
<td>[Na]/[Mg]</td>
<td>[Al]/[Mg]</td>
</tr>
<tr>
<td>56</td>
<td>0.11</td>
<td>0.07</td>
<td>0.002</td>
<td>0.015</td>
<td>0.136</td>
<td>0.087</td>
</tr>
<tr>
<td>149</td>
<td>0.13</td>
<td>0.06</td>
<td>0.002</td>
<td>0.035</td>
<td>0.093</td>
<td>0.043</td>
</tr>
<tr>
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<td>0.13</td>
<td>0.07</td>
<td>0.002</td>
<td>0.070</td>
<td>0.052</td>
<td>0.028</td>
</tr>
<tr>
<td>707</td>
<td>0.12</td>
<td>0.11</td>
<td>0.002</td>
<td>0.165</td>
<td>0.028</td>
<td>0.025</td>
</tr>
<tr>
<td>Cambridge 1 (Measured)</td>
<td>-1.32 ± 0.04</td>
<td>-2.53 ± 0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3620</td>
<td>-1.34 ± 0.05</td>
<td>-2.61 ± 0.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1671</td>
<td>-1.27 ± 0.03</td>
<td>-2.47 ± 0.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>776</td>
<td>-1.48 ± 0.05</td>
<td>-2.90 ± 0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cambridge 1 (Measured)</td>
<td>-1.31 ± 0.03</td>
<td>-2.53 ± 0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cambridge 1 (Literature)</td>
<td>-1.33 ± 0.07</td>
<td>-2.58 ± 0.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
reproducible results, subsequent tests took place on AG 50W-X12 resin columns using 3620, 1671 and 776 ng of Mg in NGM. Additionally, approximately 4500 ng Mg of the standard CCS2 was loaded onto the columns in triplicate. Mg fractions were the analysed for Mg isotopes by MC-ICP-MS. All CCS2 measurements fell within error of literature values ($\delta^{26}\text{Mg}$ of $-2.67 \pm 0.19$, $-2.66 \pm 0.13$ and $-2.73 \pm 0.13$ %o with a target of $-2.71$ %o). Whilst the $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values of the 3620 and 1671 ng Mg loaded NGM standards fell within error of Cambridge 1, the values of the 776 ng Mg NGM standard did not (Table 7.2). This suggested that for both AG MP-50 and AG 50W-X12 columns significantly more than 700 ng Mg would need to be loaded to produce reproducible results. Owing to the low Mg concentrations within the MW25 leachates, many of the triplicates had insufficient Mg contents for column chromatography even if the triplicate aliquots were to be combined. As such, Mg isotope analysis of pristine MW25 and the MW25 leachates did not take place.

7.2.2. Pristine MW25 isotopic analyses

7.2.2.1. Alkali fusion and HF digestion

Following the acceptable B and Li recoveries of the K$_2$CO$_3$ fusion test run on MW25 (see Section 2.11.1), alkali fusion was used to obtain the Li isotopic signature of pristine MW25. Four full-procedure replicates of washed and sized MW25 were alkali fused before being eluted through the AG MP-50 columns and analysed for Li isotopes by MC-ICP-MS. ICP-OES analysis of the four fusion supernatants reported recoveries between 88 and 105 % for B and 79 and 93 % for Li with negligible masses of B and Li within the fusion residues. Li recoveries were noted to be similar to those found for the four $^6\text{Li}$-Mg-EM fusion supernatants (Section 6.3.3.1). The volume of each MW25 fusion supernatant required for 4 ng Li was prepared and eluted through the columns (Section 2.12.3.3). As with the $^6\text{Li}$-Mg-EM alkali fusions, the K:Li ratio of the loaded samples was low and the columns were loaded with elemental masses significantly less than their 1.5 mEq/ml capacity. ICP-OES analysis showed negligible masses of all elements within the pre-Li cuts, post-Li cuts and Li fractions from the column chromatography of the four MW25 fusions. MC-ICP-MS of the four fusion Li fractions yielded an average pristine glass $\delta^7\text{Li}$ value of $8.24 \pm 0.47$ %o relative to L-SVEC ($^7\text{Li}/^6\text{Li}$ ratio of 12.432 $\pm 0.006$ assuming a $^7\text{Li}/^6\text{Li}$ ratio of 12.330 for L-SVEC, Table 7.3). As with the $^6\text{Li}$-Mg-EM alkali fusions, the low error on this $\delta^7\text{Li}$ value reflected the excellent degree of internal consistency and agreement amongst the four full-procedure fusion replicates; with three of the four fusions being within error of one another. Again, the difference between fusion 3 and
An isotopic investigation into the temperature dependence of dissolution

fusions 1 and 2 (~0.3 to 0.5 ‰) was small enough to be considered negligible in light of the excellent agreement between the other fusions. The slightly isotopically heavy average δ^7Li value for MW25 was thought to be caused by the Li precursor used in fabricating MW25 slightly deviating from natural abundance.

Table 7.3: Table showing the Li isotope MC-ICP-MS results for the four MW25 alkali fusions, the MW25 digest and the SGR-1b digest. δ^7Li values are relative to NIST SRM 8545 L-SVEC. Each alkali fusion was analysed in triplicate, with an average value being calculated from all twelve measurements. Each HF digest (one HF digest passed through the columns in duplicate) was analysed in duplicate, with an average value calculated from all four measurements. Errors are given to 2σ. ^7Li/^6Li ratios were calculated assuming a ^7Li/^6Li ratio of 12.330 for L-SVEC^132,133.

<table>
<thead>
<tr>
<th>Fusion or digest number</th>
<th>MW25 alkali fusions</th>
<th>MW25 digests</th>
<th>SGR-1b digests</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ^7Li (‰)</td>
<td>δ^7Li (‰)</td>
<td>δ^7Li (‰)</td>
</tr>
<tr>
<td>1</td>
<td>8.20 ± 0.07</td>
<td>8.12 ± 0.15</td>
<td>1.79 ± 0.79</td>
</tr>
<tr>
<td>2</td>
<td>7.95 ± 0.27</td>
<td>7.64 ± 0.35</td>
<td>3.38 ± 0.27</td>
</tr>
<tr>
<td>3</td>
<td>8.52 ± 0.21</td>
<td>8.24 ± 0.47</td>
<td>7.88 ± 0.60</td>
</tr>
<tr>
<td>4</td>
<td>8.29 ± 0.38</td>
<td>7.88 ± 0.60</td>
<td>2.59 ± 1.91</td>
</tr>
<tr>
<td>Average</td>
<td>8.24 ± 0.47</td>
<td>7.88 ± 0.60</td>
<td>2.59 ± 1.91</td>
</tr>
</tbody>
</table>

HF digestion of MW25 alongside SGR-1b took place to confirm the accuracy of the MW25 δ^7Li value obtained through alkali fusion (Section 2.11.2). It was noted that after the final digestion step, a small number of colourless grains remained in the digestion vial for MW25. These were assumed to be the spinel phases present in pristine MW25 which would contain negligible masses of Li. Further, it could be expected that if such phases did not dissolve under repeated high temperature acid digestions, they would not dissolve in deionised water at 90 °C. As such, the Li in the digested portion of MW25 was expected to contain all of the leachable Li of pristine MW25. After loading the volumes of each diluted digest required for 4 ng Li onto the AG MP-50 columns and eluting the Li fractions, Li fractions were analysed for Li isotopes by MC-ICP-MS. The MW25 δ^7Li values obtained through HF digestion appeared to be in excellent agreement with those obtained through alkali fusion (average δ^7Li value of 7.88 ± 0.60 ‰ and ^7Li/^6Li ratio of 12.427 ± 0.007, Table 7.3); demonstrating all of the Li in MW25 was likely recovered in the digested fraction, no measurable isotopic fractionation took place during alkali fusion and the average alkali fusion δ^7Li value was accurate. As with the SGR-1b digest which accompanied the ^6Li-Mg-EM digest (Table 6.3), the average δ^7Li value for the SGR-1b digest was within error of literature values (3.6 to 5.0 ‰^152,200,201) but the measurements had poor reproducibility (2.59 ± 1.91 ‰) and could not be used to assess the accuracy of the MW25 digest δ^7Li value. However, as the MW25 and ^6Li-Mg-EM δ^7Li values
obtained through alkali fusion and HF digestion were both in excellent agreement with a high degree of internal consistency, the HF digests of the samples alone were considered sufficient evidence for the accuracy of the pristine glass δ^7Li values obtained through alkali fusion.

**7.2.2. ^{11}B/^{10}B LA-MC-ICP-MS**

LA-MC-ICP-MS took place to obtain the B isotopic signature of resin-mounted pristine MW25 pieces (Section 2.13.6). An average δ^{11}B value of -0.57 ± 0.24 ‰ relative to NIST 610 (^{11}B/^{10}B ratio of 4.047 ± 0.001, assuming a ratio of 4.049 for NIST 610^{146,160}) was found from 20 spots ablated from the two pieces of MW25. Each measurement was determined with a high degree of precision (2σ = 0.10 to 0.13 ‰) and had excellent internal consistency (2σ = 0.24 ‰ on the average measurement); demonstrating MW25 was isotopically homogeneous with respect to B. However, as with the ^{6}Li-Mg-EM LA-MC-ICP-MS measurements, MW25 nominally contained approximately 150 times more B than NIST610. Combined with the compiled literature δ^{11}B values for NIST 610 covering a range of values (-0.78 to 0.00 ‰ relative to NIST 951^{146}), an error of 5.00 ‰ was assigned to the pristine MW25 δ^{11}B value. As an error of 5.00 ‰ on the ^{6}Li-Mg-EM δ^{11}B value covered the range of the leachate δ^{11}B values entirely (Sections 6.3.3.4 and 6.4.3), it was decided that B isotope MC-ICP-MS would not take place on the MW25 leachates.

**7.2.3. MW25 leachate ratios and Li isotopes**

MW25 powders were leached in deionised water at 40 and 90 °C for between 6 h and 464 d using a static batch sampling methodology (Section 2.8). An in-depth discussion of the leachate concentration data is presented as part of the MW25 temperature effects study in Chapter 5. Here, the temporal evolution of the ratios of the concentrations and Li isotopic signatures of the leachates are presented. Unlike the ^{6}Li-Mg-EM Li isotope analysis, only one aliquot from each triplicate was analysed for Li isotopes in these MW25 experiments. As discussed in Chapter 5, at 90 °C the leachate pH remained constant with time whilst at 40 °C there was an increase in leachant pH to a constant long-term value from 7 d onwards (Figure 7.1a). Whilst the leachant Li/Na ratio at 90 °C increased to a maximum after 7 d then decreased with time, the exact opposite trend was visible in the 40 °C leachates (Figure 7.1b). However, the trends of the Li/B ratios at 40 and 90 °C appeared similar but offset to lower values in the 90 °C leachates (Figure 7.1c). It should also be considered that Si reached its steady state apparent solubility limit after 28 d at 40 °C and 7 d at 90 °C (Figure 5.4a) and mobile glass species (B, Li, Mo and Na) appeared to be released at their residual rates after 28 d at both 40
An isotopic investigation into the temperature dependence of dissolution

and 90 °C (Figure 5.3).

Assuming small masses of B were adsorbed onto secondary phases, the similar Li/B ratio trends observed at both temperatures suggests that the fraction of leached Li being incorporated into secondary phases was similar at both 40 and 90 °C from 7 d onwards. Between 6 h and 7 d, the 40 °C Li/B ratio appeared to decline more rapidly than at 90 °C, suggesting a higher fraction of leached Li was being incorporated into secondary phases at 40 °C than at 90 °C during this time. The lower 6 h Li/B ratio at 90 °C may not solely be attributed to an initially higher fraction of Li being incorporated into secondary phases, owing to differences in the Arrhenius-type behaviours of Li interdiffusion and B hydrolysis effecting different initial release rates for Li relative to B as the temperature was varied (see Chapter 5). Based upon the similarity of the trends of the Li/B ratios at both temperatures, the differences in the Li/Na ratio trends between 40 and 90 °C may be attributed to the rate of precipitation of sodium silicate hydrate (see Figure 3.20) changing relative to the rate of Li-bearing phase precipitation with temperature. It should also be considered that the diffusivity of Li within the glass was expected to be higher than that of Na at lower temperatures but lower than that of Na at higher temperatures.96

Figure 7.1: Leachate pH (a), Li/Na ratios (b) and Li/B ratios (c). Ratios were calculated from their respective blank corrected concentrations (µg/ml). Lines are plotted for each of the duplicate leaching vessels at 40 °C (Blue triangles and Orange Circles) and 90 °C (Blue diamonds and Orange squares). As leachate pH measurements consisted of single measurements, they were assigned errors of ±0.1 pH units. Points in the ratio plots are given as average values from the triplicate aliquot measurements with errors given to 1σ.
An isotopic investigation into the temperature dependence of dissolution

As alluded to by the similar Li/B ratios at both temperatures, the trends of the Li isotopic signatures of the leachates appeared similar at both temperatures (Figure 7.2). After 6 h of dissolution at both temperatures, significant Li concentrations were present in solution and the leachates were isotopically lighter than the 90 °C leachates. Further, the 40 °C leachates were isotopically lighter than the 90 °C leachates. This showed that the leaching of Li was initially incongruent. Between 6 h and 28 d, the leachate δ²⁷Li values increased until the 90 °C values were within error of the pristine glass and the 40 °C were slightly isotopically lighter than the pristine glass. This is attributable to ⁶Li being preferentially incorporated into secondary phases due to an equilibrium isotopic effect. However, unlike the ⁶Li-Mg-EM leachates, no light isotopic fractionation from incongruent dissolution was visible at either temperature during the later dissolution regimes: the δ²⁷Li values of the leachates increased slightly between 7 and 28 d at 40 °C, the 126 d δ²⁷Li values were within error of the 28 d δ²⁷Li values at both temperatures and the 464 d δ²⁷Li values were significantly isotopically heavier than the 126 d δ²⁷Li values at both temperatures.

![Figure 7.2: Temporal evolution of the Li isotopic signature of the MW25 leachates. The measured pristine MW25 Li isotopic signature is given as a dotted line, with the dashed lines above and below it representing the 2σ error associated with this measurement. Lines are plotted for each of the duplicate leaching vessels at 40 °C (Blue triangles and Orange Circles) and 90 °C (Blue diamonds and Orange squares). Points are plotted for each leachate analysed for Li isotopes from each triplicate, with errors given to 2σ calculated from the triplicate MC-ICP-MS measurements of each leachate.](image)

7.3. Discussion

7.3.1. Initially incongruent dissolution

The isotopically light leachates at 6 h of dissolution demonstrated that dissolution was initially incongruent through interdiffusion reactions at both temperatures, with kinetic isotopic
fractionation arising from the enhanced outward diffusion of $^6$Li across a hydrated glass layer ahead of the Si hydrolysis front$^{37,57}$. Further, the isotopically lighter 40 °C leachates suggested interdiffusion controlled the initial rate of dissolution for a longer time at this lower temperature. This was consistent with the view that at lower temperatures interdiffusion controls the initial rate of dissolution for a longer period of time$^{3,71}$ and thereby effects more kinetic isotopic fractionation due to diffusion.

If the isotopic signature of the leachates was within error of that of the pristine glass, this would suggest dissolution was initially congruent and no interdiffusion reactions were taking place. This was the case for the Li isotopic signatures of the 90 °C $^6$Li-Mg-EM leachates, which suggested that dissolution was initially congruent through an interfacial dissolution-precipitation model (Chapter 6); seemingly contradicting the isotopically light MW25 leachates which suggested dissolution was initially incongruent through an interdiffusion-based model. It should be considered that after 6 h of dissolution, the concentrations of major mobile glass species, particularly B, in the $^6$Li-Mg-EM leachates (Li, B and Na at 18.2, 106.2 and 62.0 µg/ml respectively) were significantly higher than in the 90 °C MW25 leachates (Li, B and Na at 6.5, 19.7 and 21.5 µg/ml respectively). Although a leachate pH measurement was not taken at 6 h in the $^6$Li-Mg-EM experiment, these initial releases suggested that the leachant pH rose more rapidly from its starting value (pH of approximately 5.00 to 7.00) to its constant long-term value (as suggested by the pH of the 6 h and 464 d 90 °C MW25 leachates remaining constant and the 7 and 112 d 90 °C Li50Na50-Mg-EM leachates decreasing negligibly with time) in the $^6$Li-Mg-EM experiment than in the 90 °C MW25 experiment. Consequently, the more rapid rise in pH for the $^6$Li-Mg-EM leachant coupled with the MW25 results suggested that interdiffusion reactions were also taking place during the dissolution of $^6$Li-Mg-EM but the leachant pH rose so rapidly that interdiffusion controlled the initial rate of dissolution for a significantly shorter time than in the 90 °C MW25 experiment; a time period which was insufficient to produce measurable diffusive isotopic fractionation.

7.3.2. Congruent dissolution with secondary phases precipitation

At both temperatures, the Li isotopic signatures of the leachates increased significantly between 6 h and 7 d (Figure 7.2). This was consistent with the $^6$Li-Mg-EM leachates and was attributable to congruent dissolution through network hydrolysis controlling dissolution alongside the precipitation of Li-bearing secondary phases preferentially removing $^6$Li from solution. As the leachates were isotopically lighter than the pristine glass at 6 h, congruent dissolution without
the precipitation of Li-bearing phases would also make the leachates isotopically heavier with time. However, as $^6\text{Li}-^1\text{H}$ CP-NMR demonstrated Li was being incorporated into secondary phases during the dissolution of Li50Na50-Mg-EM at both 40 and 90 °C (Figure 3.16) and a similar trend was visible in the isotopically heavy $^6\text{Li}$-Mg-EM leachates (Figure 6.7), it was expected that at both 40 and 90 °C some Li was being incorporated into secondary phases during the dissolution of MW25. This was supported by the decreasing leachate Li/B ratios observed at both temperatures (Figure 7.1c). However, diffusive isotopic fractionation from interdiffusion might have been occurring but was entirely offset by equilibrium isotopic fractionation from secondary phase precipitation.

Notably, between 6 h and 28 d the average increase in the $\delta^7\text{Li}$ value of the 40 °C leachates was twice that of the 90 °C leachates (Figure 7.2). This may be attributed to a larger fraction of the leached Li being incorporated into secondary phases at 40 than at 90 °C; as was supported by the leachate Li/B ratios between 6 h and 28 d decreasing approximately twice as fast at 40 than at 90 °C. In the $^6\text{Li}$-Mg-EM experiment, at 7 d the Li isotopic signatures of the leachates reached a maximum value and subsequently decreased with dissolution time. This was attributed to the formation a highly passivating hydrated glass interphase which presented a barrier to dissolution and limited the transport of glass and water species to reactive diffusion through its nanoporous structure. However, the $\delta^7\text{Li}$ values of the MW25 leachates at both temperatures continued increasing between 6 h and 28 d. This appeared to suggest that the alteration layers formed in the MW25 experiments were insufficiently passivating and dense to present a diffusive barrier to dissolution and as such the leachates continued to become isotopically heavier with time due to dominant congruent dissolution alongside continued secondary phase precipitation.

Whilst the $\delta^7\text{Li}$ values of the leachates at 28 and 126 d were within error of one another at both temperatures, there was a significant increase in the leachate $\delta^7\text{Li}$ values between 126 and 464 d such that the 90 °C leachates were isotopically heavier than the pristine glass and the 40 °C leachates were within error of the isotopic signature of the pristine glass. Again, this may be attributed to the continued precipitation of Li-bearing secondary phases taking place alongside dominantly congruent dissolution during the later dissolution regimes. Notably, the trends of the leachate isotopic signatures and Li/B ratios at both temperatures appeared the same from 28 and 7 d onwards respectively. This suggested from 7 d onwards similar fractions of leached Li
were incorporated into secondary phases and the subsequent heavy isotopic fractionation caused by secondary phase precipitation was similar at both temperatures. That is, the leachates became isotopically heavier at the same rates and times at both temperatures despite different kinetics of dissolution and Si reaching its steady state apparent solubility limit at different times at each temperature.

Calculating theoretical 126 d δ^7Li values through interpolating the 28 and 464 d results yielded heavier 126 d δ^7Li values than those observed (on average 0.6 and 0.8 ‰ heavier at 40 and 90 °C respectively). It may be speculated from these results that heavy equilibrium isotopic fractionation from secondary phase precipitation between 28 and 126 d was equally offset by diffusive isotopic fractionation arising from reactive diffusion through a passivating alteration layer interphase. However, this speculation is most likely negligible such that these results are most suggestive of dissolution in the residual rate regime continuing to be congruent alongside the precipitation of Li-bearing secondary phases; with the alteration layers being insufficiently passivating to present a nanoporous diffusive barrier. The similarities of the isotopic trends at 40 and 90 °C suggested that the same dissolution mechanisms took place at both temperatures.

7.4. Summary

It was shown through the initially isotopically light leachates that interdiffusion processes took place during the initial rate regime such that dissolution was initially incongruent. Further, the isotopically lighter leachates at 40 °C than at 90 °C suggested interdiffusion controlled the initial dissolution rate for a longer period of time at 40 °C; as was consistent with a higher rate of Li interdiffusion relative to the rate of B hydrolysis at 40 °C than at 90 °C. Consistent with the ⁶Li-Mg-EM leachates, the leachates became isotopically heavier with time during the initial rate regime. This was attributed to dissolution subsequently being congruent alongside secondary phase precipitation. However, the leachates at both temperatures continued to become isotopically heavier with time during the later dissolution regimes as was also consistent with dissolution continuing to be congruent alongside secondary phase precipitation. These results therefore suggested that the alteration layer formed did not present a diffusive barrier to dissolution such that interdiffusion was not a rate limiting process at long leaching durations at either temperature. The similar isotopic trends and Li/B ratios at both temperatures suggested similar fractions of Li-bearing phases were precipitated at both temperatures and that the same dissolution processes were taking place at both temperatures.
8. Conclusions and future work

8.1. Simplified analogues and the effects of Li

For the Li-Mg-EM simplified analogues, it was shown that the proportion of \(^{III}\)B to \(^{IV}\)B units, and consequently the number of species charge compensating the B network, remained constant in all pristine glass compositions investigated regardless of their Li:Na ratio. This result was consistent with literature observations of Na preferentially charge compensating the B network in alkali borosilicates and Li preferentially modifying the Si network. However, the observed lower concentration of Na than \(^{IV}\)B units in both Li-Mg-EM compositions implied that at higher Li:Na ratios, Li merely charge compensated the \(^{IV}\)B network in place of Na. At longer leaching durations at 90 °C, it was shown that \(^{III}\)B units leached more readily than \(^{IV}\)B units in the Li-Mg-EM compositions. As such an effect was not observed during the dissolution of Mg-EM\(^{46}\), it was concluded that Li enhanced glass hydration and the rate of glass dissolution. Consequently, the rate of dissolution of \(^{III}\)B units increased whilst the leaching of Na-compensated \(^{IV}\)B units remained unaffected. It was expected that similar incongruent dissolution of the B network may be occurring for the Li-Mg-EM analogues at 40 °C, but the extent of glass alteration at this lower temperature appeared insufficient to observe it.

Faster rates of glass alteration, as measured through the B releases, during the initial stages of dissolution were observed for the Li-Mg-EM analogues relative to Mg-EM but the rates of Na release from Li50Na50-Mg-EM and Mg-EM appeared similar. This was consistent with Li preferentially depolymerising the Si network in the pristine glass and leaching more readily than Na in its’ charge compensation role, thereby permitting faster glass hydration and dissolution than in a Li-free analogue whilst the Na-compensated B units and release rate of Na remained largely unaffected. Li60Na40-Mg-EM was shown to have higher initial B, Li and Na releases compared with Li50Na50-Mg-EM. This was attributed to the previously discussed depolymerisation and hydration effects intensifying with higher Li contents such that the release of Na was also somewhat affected. However, despite the residual rates of dissolution at both 40 and 90 °C being higher in the Li-Mg-EM compositions than in Mg-EM, the residual rates of dissolution of both Li-Mg-EM compositions were similar. It was concluded this was caused by a similar passivating alteration layer forming for both compositions, regardless of differences in initial glass dissolution rates, which made these hydration effects significantly less relevant. As such, it was concluded that increasing the Li:Na ratio had no long-term impact on the
Conclusions and future work

aqueous durability of the glasses. Further, a simplified analogue of MW25 should contain Li to more accurately reflect the dissolution processes of MW25.

Consistent with the Li-Mg-EM results, it was shown that changing the Li:Na ratio in Li-ISG had no effect on the ratio of $^{11}$B to $^{13}$B units. This was confirmed through $^{23}$Na MAS-NMR, which demonstrated there was no change in the role of Na with a changing Li:Na ratio in both the Li-Mg-EM and Li-ISG compositions; showing Na fulfilled the same preferential charge compensation role to the B network in all Li-Mg-EM and Li-ISG compositions investigated. However, the B network of both Li-ISG compositions was shown to leach congruently at both 40 and 90 °C. As was consistent with Mg-EM and the Li-Mg-EM compositions, substituting Li into ISG was shown to reduce aqueous durability, as measured through the normalised B releases, but the residual release rate of Na from ISG was significantly higher than from both Li-ISG compositions. Further, the substitution of Li for Na to an excessively high Li:Na ratio in Li-ISG was shown to result in an increase in aqueous durability as measured through the B and Na releases; an opposite effect to that observed for Li-Mg-EM. This was attributable to a Li-Na mixed alkali effect, which was not present for the Li-Mg-EM compositions.

A magnesium silicate layer was shown to precipitate on the Li-Mg-EM compositions at both 40 and 90 °C, effecting the significantly poorer aqueous durability of the Li-Mg-EM compositions relative to Li-ISG through consuming Si from solution and fuelling hydrolysis of the glass network during the later dissolution regimes. Significant amounts of Na were shown to precipitate from solution as an amorphous sodium silicate hydrate for the Li-Mg-EM compositions leached at 90 °C but not at 40 °C or for the Li-ISG compositions. Such a phase was expected to form on all compositions at both temperatures probed but the magnitude of alteration was considered insufficient to observe it. Similarly, Li was shown to precipitate from solution for Li50Na50-Mg-EM at long duration at both 40 and 90 °C but not for the Li29Na71-ISG at either temperature. However, the precipitation of these Li and Na-bearing phases was not expected to significantly impact dissolution kinetics.

8.2. Probing the dissolution mechanisms of simplified and complex glasses

The simplistic proof of concept dissolution experiment and isotopic analyses presented in Chapter 6 demonstrated that isotope fingerprinting techniques could be used to directly probe diffusion throughout dissolution of the simplified analogue $^6$Li-Mg-EM. The absence of isotopic fractionation in the initial leachates suggested that the dissolution of $^6$Li-Mg-EM was
initially congruent alongside the precipitation of secondary phases. However, the leachates becoming isotopically lighter with time with respect to Li and B after 7 and 28 d respectively combined with the concentrations from the refreshed leachant experiment being comparable to the 7 d leachates after 70 d of further dissolution demonstrated a highly passivating alteration layer interphase had formed. This robust interphase limited the outward transport of all glass species to reactive diffusion; effecting kinetic isotopic fractionation through the enhanced diffusion of lighter isotopes. Combined with the pH measurements of the Li50Na50-Mg-EM leachates, the different peaks in the Li and B isotopic signatures of the leachates demonstrated that this decrease was not due to a pH effect and dissolution during the later dissolution regimes was incongruent following an interdiffusion-based model of glass dissolution. The $^6$Li-$^1$H CP-NMR results of Li50Na50-Mg-EM leached for 7 and 112 d at 90 °C (Chapter 3) demonstrated secondary phase precipitation continued during the later dissolution regimes and as such these isotopic results could not have been caused by a passivating interphase behind a congruent dissolution as described by an interfacial dissolution-precipitation model of dissolution.

Contrastingly, the 40 and 90 °C MW25 leachates were initially isotopically light with respect to Li and showed that dissolution was incongruent through an interdiffusion-based model. Based upon incongruent dissolution in the MW25 leachates and differences between the 90 °C leachate concentrations of MW25 and $^6$Li-Mg-EM, it was concluded that the leachant pH increased more rapidly in the $^6$Li-Mg-EM experiments such that interdiffusion controlled the initial rate of dissolution for a time insufficient to effect measurable diffusive isotopic fractionation and dissolution was apparently congruent. Whilst the MW25 leachates were consistent in showing dissolution was subsequently congruent alongside secondary phase precipitation, the MW25 leachates continued to become isotopically heavier with time rather than decreasing during the later dissolution regimes; as was consistent with continued congruent dissolution. This suggested that the alteration layers formed for MW25 at longer leaching durations were insufficiently passivating to limit dissolution to reactive diffusion.

**8.3. The effects of dissolution temperature on MW25**

In addition to investigating the effects of excess Li contents on the aqueous durability MW25, the effects of dissolution temperature on the kinetics and mechanisms of MW25 dissolution also needed to be understood. In the initial temperature study presented in Chapter 5, the releases of B and Mo from MW25 were shown to exhibit Arrhenius-type behaviour between

205
40°C and 90°C with activation energies of 44.6 \( \pm \) 2.9 and 46.3 \( \pm \) 4.9 kJ mol\(^{-1}\) respectively. These initial results first suggested that the same dissolution mechanisms were taking place across all temperatures probed, but were merely accelerated at higher temperatures. However, it was noted there were significant changes in the rate of B hydrolysis relative to the rate of Li interdiffusion as the dissolution temperature was varied. This subtle difference in Arrhenius behaviour was attributed to the difference between the temperature dependence of the activation energies of hydrolysis and interdiffusion. Notably, whilst a high activation energy was associated with the Na releases between 40 and 70 °C, Na displayed non-Arrhenius behaviour at higher temperatures and demonstrated its release processes differed from Li even at lower temperatures. This was attributed to the rate of hydrolysis of the B network at higher dissolution temperatures controlling the initial release of charge compensating Na compared with lower temperatures; rendering the dissolution of Na less susceptible to temperature changes above 70 °C. Therefore, the same dissolution processes were not consistent for Na across the range of temperatures studied. At all temperatures, the rates of Li and Na interdiffusion decreased faster than the rate of B hydrolysis and suggested B hydrolysis was not rate-limiting during the initial rate regime. Additionally, the same magnesium silicate macroporous layer as in the Li-Mg-EM experiments was shown to form through the same mechanisms at 70 and 80 °C, but merely abated at 70 °C.

The subsequent isotopic study of the MW25 40 and 90 °C leachates presented in Chapter 7 appeared in good agreement with many of the views initially suggested by the concentration data. Most notably, the Li isotopic signatures of the leachates at 40 and 90 °C displayed the same trends and as such were consistent in demonstrating that the same underlying dissolution mechanisms were taking place at both temperatures. The isotopically lighter 40 °C leachates demonstrated interdiffusion controlled the initial rate of dissolution for a longer period of time at this lower temperature, as was initially suggested by the rate of Li interdiffusion being faster than the rate of B hydrolysis at 40 °C. Additionally, the similar trends of the Li isotopic signatures at both temperatures during the later dissolution regimes was consistent with the leachate Li/B ratios in suggesting a similar fraction of leached Li was incorporated into secondary phases at each temperature. Combined with the observation of the same macroporous layer forming at 70 and 80 °C, this suggests consistency amongst the fraction of secondary phases formed at each temperature. However, essentially opposite trends for the Li/Na ratios at
each temperature appeared to contradict this. As such, it was concluded that the mechanisms of dissolution were consistent across the range of temperatures studied, higher dissolution temperatures merely accelerated dissolution as intended and accelerated dissolution data could be applied to model the dissolution of glasses in GDF conditions.

8.4. Concluding remarks on analogues and probing dissolution mechanisms

The results from the Li mechanistic studies demonstrated that when Li was included in the glass composition it had a significant negative impact on aqueous durability, regardless of analogue type (Mg-EM or ISG). However, significant differences in the effects of further increasing the Li:Na ratio of these analogue types suggested that comparisons of pristine glass structures and leachates compositions alone cannot explain the differences in dissolution behaviour and effects of excess Li on Li-Mg-EM and Li-ISG. This also requires a consideration of the relationship between significantly different glass compositions giving rise to dissolution kinetics that are significantly affected by secondary phase precipitation. Further, the suggested presence of a highly passivated alteration layer component without a mixed alkali effect during the dissolution of the Li-Mg-EM compositions was the opposite case to that observed for the Li-ISG compositions. As such, these results suggested that a relationship between the dissolution behaviours, in particular the effects of excess Li concentrations, of Li-Mg-EM and Li-ISG could not be simply defined. Similarly, significant differences between the trends of the Li isotopic signatures of the $^6$Li-Mg-EM and MW25 leachates at 90 °C suggested differences in the structures of the alteration layers formed and the mechanisms underlying both initial and residual glass dissolution. Whilst these results demonstrated that isotope fingerprinting techniques can elucidate the mechanisms of dissolution of both simplified and complex waste glasses, these results suggested more information, such as structural information on the alteration layers, was still required to define a clear relationship between analogues and complex glasses with confidence.

8.5. Future work

The isotope fingerprinting techniques employed herein showed excellent potential for understanding the mechanisms by which nuclear waste glasses dissolve. However, significant differences in the trends of the Li isotopic signatures of the leachates from the $^6$Li-Mg-EM and MW25 experiments presented in Chapter 6 and 7 respectively highlighted a clear need to further understand the differences in dissolution mechanisms between these two compositions.
Conclusions and future work

Additionally, these techniques could be applied to investigate the dissolution mechanisms of the post operational clean out (POCO) complex waste glasses produced as part of the end of reprocessing activities at Sellafield Ltd. Owing to their high Mo contents and low aqueous durability, designing an optimal GDF disposal strategy for the POCO glasses may present a challenge. Further, only a small amount of work has taken place on characterising the aqueous durability of these glasses. As such, the kinetics and mechanisms of dissolution of the POCO glasses may significantly differ from those of MW25 and need to be investigated.

It is expected that isotope analysis of other isotopes within the MW25 leachates may afford an improved interpretation of the Li isotope results. As such, future work would first focus on B isotope analysis of the MW25 leachates. Whilst the pristine glass B isotopic signatures of $^6$Li-Mg-EM and MW25 obtained through LA-MC-ICP-MS appeared precise, the large errors (5 ‰) associated with these isotopic signatures meant interpretation of the B isotopic signatures of the $^6$Li-Mg-EM leachates was limited and B isotope analysis of the MW25 leachates did not take place. As such, the alkali fusions supernatants of MW25 would also need to undergo B isotope analysis to confirm the accuracy of the pristine glass B isotopic signatures. To this end, B column chromatography would need to take place, with current work focussing on calibrating AG 50W-X8 and Amberlite IRA743 resin columns to handle the difficult alkali fusion sample matrix.

To better understand the mechanisms governing the residual rate of dissolution of MW25, static batch sampling dissolution experiments could take place on MW25 using leachants initially enriched to Si to a concentration similar to the apparent steady state Si solubility limit for MW25 at each temperature as required. This would inhibit dissolution to its residual rate, affording an improved understanding of the mechanisms governing the residual rate regime. Further, post-process analyses of the leached glasses through Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and atom probe tomography would provide detailed elemental or isotopic profiles of leached glass cross-sections. Not only would such profiles provide complementary information on how elements are leached from these glasses, but this would also provide key insights into the structures of the alteration layers and how this differed between analogues and complex glasses; thereby producing a complete picture of glass alteration alongside the isotopic signatures of the leachates which could be used to modify an existing contemporary model of glass dissolution to include an isotopic term.
References


References


References


Supplementary tables

A. EDS quantification tables and additional spectra

*Supplementary table 1:* Examples of the EDS analyses of the glass fines and washed and sized fractions of the full-Li MW base glass and Li50Li50-Mg-EM-1 to demonstrate no enrichment of Si in the fines.

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226
B. Pristine glass compositions

Supplementary table 2: Measured Li-Mg-EM pristine glass compositions with recoveries reported for ICP-OES, LA-ICP-MS and EPMA analyses.

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Supplementary tables

Supplementary table 3: Measured Li-ISG pristine glass compositions with recoveries reported for ICP-OES and EPMA analyses.

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Oxide wt% with 1σ error measured using ICP-OES

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% recoveries ICP-OES

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<td>103.02%</td>
<td>100.98%</td>
<td>101.01%</td>
</tr>
<tr>
<td>ZrO2</td>
<td>94.55</td>
<td>93.74</td>
<td>95.79</td>
<td>90.23</td>
<td>ZrO2</td>
<td>115.22%</td>
<td>118.74%</td>
<td>112.43%</td>
<td>111.89%</td>
</tr>
</tbody>
</table>

% recoveries EPMA

Supplementary table 4: Measured oxide wt.% RSD values and recoveries measured using EPMA and LA-ICP-MS for 6Li-Mg-EM.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>EPMA</th>
<th>LA-ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxide wt.%</td>
<td>RSD</td>
</tr>
<tr>
<td>Al2O3</td>
<td>5.51</td>
<td>4.1%</td>
</tr>
<tr>
<td>B2O3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>La2O3</td>
<td>6.35</td>
<td>5.0%</td>
</tr>
<tr>
<td>Li2O</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>6.10</td>
<td>3.5%</td>
</tr>
<tr>
<td>Na2O</td>
<td>4.84</td>
<td>7.7%</td>
</tr>
<tr>
<td>SiO2</td>
<td>54.87</td>
<td>2.5%</td>
</tr>
</tbody>
</table>
C. ICP-OES calibration standards

**Supplementary table 5:** Concentrations of the single-element plasma standards, stock calibration standard and series of calibration standards used for the ICP-OES analysis of the MW25 leachates.

<table>
<thead>
<tr>
<th>Concentrations (µg/ml)</th>
<th>Li</th>
<th>B</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Mo</th>
<th>Cs</th>
<th>Te</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP-standard</td>
<td>1001</td>
<td>100</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>6000</td>
<td>2000</td>
<td>8000</td>
<td>172.4</td>
<td>999</td>
<td>100</td>
</tr>
<tr>
<td>Stock</td>
<td>10000</td>
<td>40000</td>
<td>30000</td>
<td>4000</td>
<td>4000</td>
<td>60000</td>
<td>10000</td>
<td>8000</td>
<td>172.4</td>
<td>999</td>
<td>100</td>
</tr>
<tr>
<td>Standard 1</td>
<td>5000</td>
<td>20000</td>
<td>15000</td>
<td>2000</td>
<td>2000</td>
<td>30000</td>
<td>10000</td>
<td>4000</td>
<td>2000</td>
<td>100</td>
<td>0.100</td>
</tr>
<tr>
<td>Standard 1.5</td>
<td>2500</td>
<td>10000</td>
<td>7500</td>
<td>1000</td>
<td>1000</td>
<td>15000</td>
<td>5000</td>
<td>2000</td>
<td>1000</td>
<td>0.050</td>
<td>3x10^-4</td>
</tr>
<tr>
<td>Standard 1.75</td>
<td>1250</td>
<td>5000</td>
<td>3750</td>
<td>0.050</td>
<td>0.005</td>
<td>0.750</td>
<td>0.250</td>
<td>1.000</td>
<td>0.050</td>
<td>0.025</td>
<td>1.5x10^-4</td>
</tr>
<tr>
<td>Standard 2</td>
<td>0.500</td>
<td>2000</td>
<td>1500</td>
<td>0.020</td>
<td>0.002</td>
<td>0.300</td>
<td>0.100</td>
<td>0.400</td>
<td>0.020</td>
<td>0.010</td>
<td>6x10^-7</td>
</tr>
<tr>
<td>Standard 2.5</td>
<td>0.250</td>
<td>1000</td>
<td>0.750</td>
<td>0.010</td>
<td>0.001</td>
<td>0.150</td>
<td>0.050</td>
<td>0.200</td>
<td>0.010</td>
<td>0.005</td>
<td>3x10^-9</td>
</tr>
<tr>
<td>Standard 3</td>
<td>0.050</td>
<td>200</td>
<td>0.150</td>
<td>0.002</td>
<td>2x10^-4</td>
<td>0.030</td>
<td>0.010</td>
<td>0.040</td>
<td>0.002</td>
<td>0.001</td>
<td>6x10^-6</td>
</tr>
<tr>
<td>Standard 4</td>
<td>0.005</td>
<td>0.020</td>
<td>0.015</td>
<td>2x10^-4</td>
<td>2x10^-4</td>
<td>0.003</td>
<td>0.001</td>
<td>0.004</td>
<td>2x10^-4</td>
<td>1x10^-4</td>
<td>6x10^-7</td>
</tr>
<tr>
<td>Standard 5</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Concentrations (µg/ml)</th>
<th>Li</th>
<th>B</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stock</td>
<td>20</td>
<td>28</td>
<td>40</td>
<td>0.08</td>
<td>0.08</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>Standard 1</td>
<td>5</td>
<td>7</td>
<td>10</td>
<td>0.02</td>
<td>0.02</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Standard 1.5</td>
<td>2.5</td>
<td>3.5</td>
<td>5</td>
<td>0.01</td>
<td>0.01</td>
<td>7.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Standard 2</td>
<td>1</td>
<td>1.4</td>
<td>2</td>
<td>0.004</td>
<td>0.004</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Standard 2.5</td>
<td>0.5</td>
<td>0.7</td>
<td>1</td>
<td>0.002</td>
<td>0.002</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Standard 3</td>
<td>0.1</td>
<td>0.14</td>
<td>0.2</td>
<td>0.0004</td>
<td>0.0004</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Standard 4</td>
<td>0.01</td>
<td>0.014</td>
<td>0.02</td>
<td>0.00004</td>
<td>0.00004</td>
<td>0.03</td>
<td>0.0001</td>
</tr>
<tr>
<td>Standard 5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Supplementary table 6: $^6$Li-Mg-EM calibration standard for ICP-OES analysis of the $^6$Li-Mg-EM fusions fabricated using single-element plasma standards and a blank K$_2$CO$_3$ fusion supernatant.

<table>
<thead>
<tr>
<th>Concentration (µg/ml)</th>
<th>Li</th>
<th>B</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stock</td>
<td>10</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td>5</td>
<td>125</td>
<td>0</td>
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<tr>
<td>Standard 1</td>
<td>2</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>1</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>Standard 2</td>
<td>1</td>
<td>5</td>
<td>2.5</td>
<td>2.5</td>
<td>0.5</td>
<td>12.5</td>
<td>0</td>
</tr>
<tr>
<td>Standard 3</td>
<td>0.5</td>
<td>2.5</td>
<td>1.25</td>
<td>1.25</td>
<td>0.25</td>
<td>6.25</td>
<td>0</td>
</tr>
<tr>
<td>Standard 4</td>
<td>0.25</td>
<td>1.25</td>
<td>0.625</td>
<td>0.625</td>
<td>0.125</td>
<td>3.125</td>
<td>0</td>
</tr>
<tr>
<td>Standard 5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Supplementary tables

**Supplementary table 7:** First set of calibration standards for ICP-OES analysis of the BCR-1 and BCR-2 fusion supernatants and residues, fabricated by diluting single-element plasma standards with blank fusion supernatant.

<table>
<thead>
<tr>
<th>Concentration (µg/ml)</th>
<th>Li</th>
<th>B</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>K</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stock</td>
<td>0.06</td>
<td>0.03</td>
<td>90</td>
<td>80</td>
<td>50</td>
<td>500</td>
<td>5</td>
<td>60</td>
<td>130</td>
</tr>
<tr>
<td>Standard 1</td>
<td>0.06</td>
<td>0.03</td>
<td>90</td>
<td>80</td>
<td>50</td>
<td>500</td>
<td>5</td>
<td>60</td>
<td>130</td>
</tr>
<tr>
<td>Standard 2</td>
<td>0.03</td>
<td>0.015</td>
<td>45</td>
<td>40</td>
<td>25</td>
<td>250</td>
<td>2.5</td>
<td>30</td>
<td>65</td>
</tr>
<tr>
<td>Standard 3</td>
<td>0.015</td>
<td>0.0075</td>
<td>22.5</td>
<td>20</td>
<td>12.5</td>
<td>125</td>
<td>1.25</td>
<td>15</td>
<td>32.5</td>
</tr>
<tr>
<td>Standard 4</td>
<td>0.0075</td>
<td>0.00375</td>
<td>11.25</td>
<td>10</td>
<td>6.25</td>
<td>62.5</td>
<td>0.625</td>
<td>7.5</td>
<td>16.25</td>
</tr>
<tr>
<td>Standard 5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Supplementary table 8:** Second set of calibration standards for ICP-OES analysis of the BCR-1 and BCR-2 fusion supernatants and residues, fabricated by diluting single-element plasma standards with blank fusion supernatant.

<table>
<thead>
<tr>
<th>Concentration (µg/ml)</th>
<th>Al</th>
<th>B</th>
<th>Ca</th>
<th>Li</th>
<th>Mn</th>
<th>Na</th>
<th>P</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stock (new)</td>
<td>22.5</td>
<td>1.5</td>
<td>15</td>
<td>3.75</td>
<td>1</td>
<td>550</td>
<td>35</td>
<td>1600</td>
</tr>
<tr>
<td>Standard 1</td>
<td>4.5</td>
<td>0.3</td>
<td>3</td>
<td>0.75</td>
<td>0.2</td>
<td>110</td>
<td>7</td>
<td>320</td>
</tr>
<tr>
<td>Standard 2</td>
<td>2.25</td>
<td>0.15</td>
<td>1.5</td>
<td>0.375</td>
<td>0.1</td>
<td>55</td>
<td>3.5</td>
<td>160</td>
</tr>
<tr>
<td>Standard 3</td>
<td>1.125</td>
<td>0.075</td>
<td>0.75</td>
<td>0.1875</td>
<td>0.05</td>
<td>27.5</td>
<td>1.75</td>
<td>80</td>
</tr>
<tr>
<td>Standard 4</td>
<td>0.5625</td>
<td>0.0375</td>
<td>0.375</td>
<td>0.09375</td>
<td>0.025</td>
<td>13.75</td>
<td>0.875</td>
<td>40</td>
</tr>
<tr>
<td>Standard 5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Supplementary table 9:** ICP-OES calibration standards used in the analysis of the SGR-1b fusion supernatants and residues.

<table>
<thead>
<tr>
<th>Concentration (µg/ml)</th>
<th>Al</th>
<th>B</th>
<th>Ca</th>
<th>Li</th>
<th>Mn</th>
<th>Na</th>
<th>P</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stock</td>
<td>22.5</td>
<td>1.5</td>
<td>15</td>
<td>3.75</td>
<td>1</td>
<td>550</td>
<td>35</td>
<td>1600</td>
</tr>
<tr>
<td>Standard 1</td>
<td>4.5</td>
<td>0.3</td>
<td>3</td>
<td>0.75</td>
<td>0.2</td>
<td>110</td>
<td>7</td>
<td>320</td>
</tr>
<tr>
<td>Standard 2</td>
<td>2.25</td>
<td>0.15</td>
<td>1.5</td>
<td>0.375</td>
<td>0.1</td>
<td>55</td>
<td>3.5</td>
<td>160</td>
</tr>
<tr>
<td>Standard 3</td>
<td>1.125</td>
<td>0.075</td>
<td>0.75</td>
<td>0.1875</td>
<td>0.05</td>
<td>27.5</td>
<td>1.75</td>
<td>80</td>
</tr>
<tr>
<td>Standard 4</td>
<td>0.5625</td>
<td>0.0375</td>
<td>0.375</td>
<td>0.09375</td>
<td>0.025</td>
<td>13.75</td>
<td>0.875</td>
<td>40</td>
</tr>
<tr>
<td>Standard 5</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Supplementary table 10: Calibration standards for analysis of the pre-Li, post-Li and Li fractions of the \(^{6}\)Li-Mg-EM, MW25, BCR-1 and BCR-2 column procedures. Standards were fabricated from fusion supernatants.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Al (ng/ml)</th>
<th>B (ng/ml)</th>
<th>K (Max)</th>
<th>Li (ng/ml)</th>
<th>Na (ng/ml)</th>
<th>Si (ng/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard 4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Standard 3</td>
<td>0.08</td>
<td>10.49</td>
<td>294.49</td>
<td>1.09</td>
<td>3.68</td>
<td>15.23</td>
</tr>
<tr>
<td>Standard 2</td>
<td>0.16</td>
<td>20.98</td>
<td>588.99</td>
<td>2.17</td>
<td>7.35</td>
<td>30.47</td>
</tr>
<tr>
<td>Standard 1</td>
<td>0.33</td>
<td>41.95</td>
<td>1177.97</td>
<td>4.35</td>
<td>14.71</td>
<td>60.93</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard</th>
<th>Al (ng/ml)</th>
<th>B (ng/ml)</th>
<th>Ba (ng/ml)</th>
<th>K (Max)</th>
<th>Li (ng/ml)</th>
<th>Mg (ng/ml)</th>
<th>Mo (ng/ml)</th>
<th>Na (ng/ml)</th>
<th>Si (ng/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard 4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>Standard 3</td>
<td>0.025</td>
<td>5.8</td>
<td>0.025</td>
<td>297.4</td>
<td>1.9</td>
<td>0.025</td>
<td>1.1</td>
<td>6.7</td>
<td>10.8</td>
</tr>
<tr>
<td>Standard 2</td>
<td>0.05</td>
<td>11.6</td>
<td>0.05</td>
<td>594.9</td>
<td>3.7</td>
<td>0.05</td>
<td>2.3</td>
<td>13.5</td>
<td>21.6</td>
</tr>
<tr>
<td>Standard 1</td>
<td>0.1</td>
<td>23.2</td>
<td>0.1</td>
<td>1189.7</td>
<td>7.5</td>
<td>0.10</td>
<td>4.6</td>
<td>26.9</td>
<td>43.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard</th>
<th>Al (ng/ml)</th>
<th>B (ng/ml)</th>
<th>Ca (ng/ml)</th>
<th>K (Max)</th>
<th>Li (ng/ml)</th>
<th>Mn (ng/ml)</th>
<th>Na (ng/ml)</th>
<th>P (ng/ml)</th>
<th>Si (ng/ml)</th>
<th>V (ng/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard 4</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
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<td>Standard 3</td>
<td>1528.7</td>
<td>1.3</td>
<td>194.2</td>
<td>1180326</td>
<td>3.5</td>
<td>144.6</td>
<td>11777</td>
<td>543.5</td>
<td>48878.6</td>
<td>280.4</td>
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<td>3057.4</td>
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<td>388.3</td>
<td>2360652</td>
<td>6.9</td>
<td>289.2</td>
<td>23554</td>
<td>1087</td>
<td>97757.2</td>
<td>560.7</td>
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<tr>
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<td>6114.8</td>
<td>5.1</td>
<td>776.7</td>
<td>4721304</td>
<td>13.8</td>
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<td>47107.9</td>
<td>2173.9</td>
<td>195514.5</td>
<td>1121.4</td>
</tr>
</tbody>
</table>
D. ICP-OES recoveries

**Supplementary table 11:** Percent recoveries in the MW25 test run alkali fusion supernatant and residue measured using ICP-OES. Recoveries are relative to the nominal composition of MW25$^{15}$.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>B</th>
<th>Ba</th>
<th>Li</th>
<th>Mg</th>
<th>Mo</th>
<th>Na</th>
<th>Si</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>% recovery in supernatant</td>
<td>0.6%</td>
<td>77.6%</td>
<td>6.9%</td>
<td>84.1%</td>
<td>0.4%</td>
<td>103.6%</td>
<td>95.8%</td>
<td>45.1%</td>
<td>0.7%</td>
</tr>
<tr>
<td>% recovery in residue</td>
<td>13.2%</td>
<td>0.8%</td>
<td>22.4%</td>
<td>2.3%</td>
<td>41.3%</td>
<td>0.6%</td>
<td>3.0%</td>
<td>6.7%</td>
<td>7.2%</td>
</tr>
<tr>
<td>% missing</td>
<td>86.1%</td>
<td>21.6%</td>
<td>70.7%</td>
<td>13.6%</td>
<td>58.3%</td>
<td>-4.3%</td>
<td>1.2%</td>
<td>48.2%</td>
<td>92.1%</td>
</tr>
</tbody>
</table>

**Supplementary table 12:** Percent recoveries in the MW25 test run alkali fusion supernatant and residue measured using ICP-OES with a set of calibration standards in a K$_2$CO$_3$ matrix. Recoveries are relative to the nominal composition of MW25$^{15}$.

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>Li</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>% recovery in supernatant</td>
<td>75.2%</td>
<td>81.6%</td>
<td>87.9%</td>
</tr>
<tr>
<td>% recovery in residue</td>
<td>0.6%</td>
<td>2.4%</td>
<td>1.1%</td>
</tr>
<tr>
<td>% recovery missing</td>
<td>24.2%</td>
<td>16.0%</td>
<td>11.0%</td>
</tr>
</tbody>
</table>

**Supplementary table 13:** Supernatant and residues recoveries from the four potassium carbonate fusions of $^6\text{Li}$-Mg-EM, measured using ICP-OES.

<table>
<thead>
<tr>
<th>Fusion no.</th>
<th>Recovered in supernatant (%)</th>
<th>AL</th>
<th>B</th>
<th>Li</th>
<th>Mg</th>
<th>Na</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fusion 1</td>
<td>2.2%</td>
<td>162.3%</td>
<td>90.9%</td>
<td>0.0%</td>
<td>91.7%</td>
<td>55.7%</td>
<td></td>
</tr>
<tr>
<td>Fusion 2</td>
<td>2.7%</td>
<td>168.2%</td>
<td>95.4%</td>
<td>0.1%</td>
<td>98.1%</td>
<td>56.9%</td>
<td></td>
</tr>
<tr>
<td>Fusion 3</td>
<td>2.9%</td>
<td>156.3%</td>
<td>88.2%</td>
<td>0.0%</td>
<td>88.9%</td>
<td>52.4%</td>
<td></td>
</tr>
<tr>
<td>Fusion 4</td>
<td>2.0%</td>
<td>148.6%</td>
<td>84.0%</td>
<td>0.0%</td>
<td>83.2%</td>
<td>46.4%</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fusion no.</th>
<th>Recovered in residue (%)</th>
<th>AL</th>
<th>B</th>
<th>Li</th>
<th>Mg</th>
<th>Na</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fusion 1</td>
<td>4.5%</td>
<td>0.2%</td>
<td>0.2%</td>
<td>7.1%</td>
<td>0.0%</td>
<td>0.0%</td>
<td></td>
</tr>
<tr>
<td>Fusion 2</td>
<td>1.7%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>2.5%</td>
<td>0.0%</td>
<td>0.0%</td>
<td></td>
</tr>
<tr>
<td>Fusion 3</td>
<td>3.8%</td>
<td>0.0%</td>
<td>0.1%</td>
<td>6.1%</td>
<td>0.0%</td>
<td>0.0%</td>
<td></td>
</tr>
<tr>
<td>Fusion 4</td>
<td>7.3%</td>
<td>0.0%</td>
<td>0.2%</td>
<td>11.6%</td>
<td>0.0%</td>
<td>0.0%</td>
<td></td>
</tr>
</tbody>
</table>
**Supplementary table 14: ICP-OES recoveries of the BCR-1 and BCR-2 supernatants from their first analysis.**

<table>
<thead>
<tr>
<th>% recovered in supernatant</th>
<th>Al</th>
<th>B</th>
<th>Ba</th>
<th>Ca</th>
<th>Fe</th>
<th>Li</th>
<th>Mg</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR-1 F-1</td>
<td>2.3%</td>
<td>34.7%</td>
<td>0.0%</td>
<td>0.9%</td>
<td>0.0%</td>
<td>58.5%</td>
<td>0.0%</td>
<td>6.2%</td>
</tr>
<tr>
<td>BCR-1 F-2</td>
<td>2.0%</td>
<td>37.8%</td>
<td>0.0%</td>
<td>1.2%</td>
<td>0.0%</td>
<td>55.9%</td>
<td>0.0%</td>
<td>15.8%</td>
</tr>
<tr>
<td>BCR-2 F-1</td>
<td>1.7%</td>
<td>34.1%</td>
<td>0.0%</td>
<td>0.6%</td>
<td>0.0%</td>
<td>44.8%</td>
<td>0.0%</td>
<td>16.9%</td>
</tr>
<tr>
<td>BCR-2 F-2</td>
<td>1.2%</td>
<td>37.6%</td>
<td>0.0%</td>
<td>1.2%</td>
<td>0.0%</td>
<td>46.1%</td>
<td>0.0%</td>
<td>15.3%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>% recovered in residue</th>
<th>Mo</th>
<th>Na</th>
<th>P</th>
<th>Si</th>
<th>Sr</th>
<th>Ti</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR-1 F-1</td>
<td>0.0%</td>
<td>82.3%</td>
<td>94.5%</td>
<td>83.3%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>106.5%</td>
<td>0.1%</td>
</tr>
<tr>
<td>BCR-1 F-2</td>
<td>0.0%</td>
<td>79.4%</td>
<td>93.3%</td>
<td>85.6%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>112.5%</td>
<td>0.2%</td>
</tr>
<tr>
<td>BCR-2 F-1</td>
<td>81.7%</td>
<td>65.7%</td>
<td>90.8%</td>
<td>96.3%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>99.7%</td>
<td>0.1%</td>
</tr>
<tr>
<td>BCR-2 F-2</td>
<td>84.5%</td>
<td>67.9%</td>
<td>92.9%</td>
<td>102.3%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>105.0%</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

**Supplementary table 15: ICP-OES recoveries of the BCR-1 and BCR-2 supernatants from their second analysis.**

<table>
<thead>
<tr>
<th>% recovered in supernatant</th>
<th>Al</th>
<th>B</th>
<th>Ca</th>
<th>Li</th>
<th>Mn</th>
<th>Mo</th>
<th>Na</th>
<th>P</th>
<th>Si</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR-1 F-1</td>
<td>6.5%</td>
<td>59.6%</td>
<td>1.2%</td>
<td>60.7%</td>
<td>7.0%</td>
<td>69.6%</td>
<td>122.6%</td>
<td>87.1%</td>
<td>44.1%</td>
<td>162.2%</td>
</tr>
<tr>
<td>BCR-1 F-2</td>
<td>5.3%</td>
<td>54.2%</td>
<td>1.5%</td>
<td>64.3%</td>
<td>23.9%</td>
<td>17.8%</td>
<td>117.2%</td>
<td>83.7%</td>
<td>42.0%</td>
<td>166.5%</td>
</tr>
<tr>
<td>BCR-2 F-1</td>
<td>4.5%</td>
<td>52.3%</td>
<td>0.6%</td>
<td>45.4%</td>
<td>24.9%</td>
<td>98.2%</td>
<td>110.0%</td>
<td>85.3%</td>
<td>50.2%</td>
<td>143.3%</td>
</tr>
<tr>
<td>BCR-2 F-2</td>
<td>3.2%</td>
<td>61.1%</td>
<td>1.8%</td>
<td>42.4%</td>
<td>17.6%</td>
<td>99.9%</td>
<td>109.0%</td>
<td>84.4%</td>
<td>53.3%</td>
<td>156.0%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>% recovered in residue</th>
<th>Mo</th>
<th>Na</th>
<th>P</th>
<th>Si</th>
<th>Sr</th>
<th>Ti</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR-1 F-1</td>
<td>0.1%</td>
<td>0.0%</td>
<td>0.2%</td>
<td>0.0%</td>
<td>0.2%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.1%</td>
</tr>
<tr>
<td>BCR-1 F-2</td>
<td>0.1%</td>
<td>0.0%</td>
<td>0.2%</td>
<td>0.0%</td>
<td>0.2%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.1%</td>
</tr>
<tr>
<td>BCR-2 F-1</td>
<td>0.1%</td>
<td>0.0%</td>
<td>0.1%</td>
<td>0.0%</td>
<td>0.2%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.3%</td>
</tr>
<tr>
<td>BCR-2 F-2</td>
<td>0.1%</td>
<td>0.0%</td>
<td>0.1%</td>
<td>0.0%</td>
<td>0.1%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.2%</td>
</tr>
</tbody>
</table>
Supplementary table 16: Percent recoveries of the SGR-1b fusion supernatants and residues calculated from the nominal composition of SGR-1b assuming a 31.25 % LOI.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>B</th>
<th>Ca</th>
<th>Li</th>
<th>Mn</th>
<th>Na</th>
<th>P</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGR-1b-S-1</td>
<td>28.81%</td>
<td>116.10%</td>
<td>14.83%</td>
<td>58.86%</td>
<td>126.84%</td>
<td>99.54%</td>
<td>35.64%</td>
<td>82.66%</td>
</tr>
<tr>
<td>SGR-1b-S-2</td>
<td>24.75%</td>
<td>104.03%</td>
<td>1.91%</td>
<td>46.93%</td>
<td>142.67%</td>
<td>84.05%</td>
<td>28.96%</td>
<td>73.34%</td>
</tr>
<tr>
<td>SGR-1b-S-3</td>
<td>31.00%</td>
<td>107.76%</td>
<td>15.78%</td>
<td>47.56%</td>
<td>134.00%</td>
<td>82.55%</td>
<td>29.79%</td>
<td>75.73%</td>
</tr>
<tr>
<td>SGR-1b-S-4 rerun</td>
<td>27.28%</td>
<td>114.16%</td>
<td>13.31%</td>
<td>47.63%</td>
<td>131.57%</td>
<td>95.05%</td>
<td>36.16%</td>
<td>77.11%</td>
</tr>
<tr>
<td>SGR-1b-S-5 rerun</td>
<td>12.51%</td>
<td>122.47%</td>
<td>12.50%</td>
<td>42.09%</td>
<td>131.57%</td>
<td>95.05%</td>
<td>36.16%</td>
<td>77.11%</td>
</tr>
<tr>
<td>SGR-1b-R-1 rerun</td>
<td>1.96%</td>
<td>0.00%</td>
<td>1.90%</td>
<td>6.92%</td>
<td>23.24%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>SGR-1b-R-2 rerun</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.31%</td>
<td>0.00%</td>
<td>16.17%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>SGR-1b-R-3 rerun</td>
<td>3.84%</td>
<td>0.00%</td>
<td>2.06%</td>
<td>0.00%</td>
<td>18.24%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>SGR-1b-R-4 rerun</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.41%</td>
<td>0.00%</td>
<td>15.73%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>SGR-1b-R-5 rerun</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.26%</td>
<td>0.00%</td>
<td>18.89%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
</tbody>
</table>

Supplementary table 17: Supernatant and residues recoveries from the four potassium carbonate fusions of MW25, measured using ICP-OES.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>B</th>
<th>Ba</th>
<th>Li</th>
<th>Mg</th>
<th>Mo</th>
<th>Na</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>% recovered in supernatant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW25 Fusion 1</td>
<td>0.55%</td>
<td>88.55%</td>
<td>4.66%</td>
<td>87.72%</td>
<td>0.33%</td>
<td>109.76%</td>
<td>94.41%</td>
<td>45.96%</td>
</tr>
<tr>
<td>MW25 Fusion 2</td>
<td>0.73%</td>
<td>104.79%</td>
<td>3.22%</td>
<td>92.86%</td>
<td>0.57%</td>
<td>113.67%</td>
<td>102.43%</td>
<td>47.06%</td>
</tr>
<tr>
<td>MW25 Fusion 3</td>
<td>0.87%</td>
<td>96.69%</td>
<td>4.34%</td>
<td>86.16%</td>
<td>0.83%</td>
<td>104.90%</td>
<td>94.51%</td>
<td>44.76%</td>
</tr>
<tr>
<td>MW25 Fusion 4</td>
<td>1.18%</td>
<td>91.18%</td>
<td>7.20%</td>
<td>79.56%</td>
<td>1.75%</td>
<td>98.47%</td>
<td>90.24%</td>
<td>41.72%</td>
</tr>
<tr>
<td>% recovered in residue</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW25 Fusion 1</td>
<td>14.40%</td>
<td>0.23%</td>
<td>23.95%</td>
<td>1.39%</td>
<td>64.20%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>9.87%</td>
</tr>
<tr>
<td>MW25 Fusion 2</td>
<td>7.06%</td>
<td>0.01%</td>
<td>12.78%</td>
<td>0.78%</td>
<td>31.96%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>7.28%</td>
</tr>
<tr>
<td>MW25 Fusion 3</td>
<td>2.52%</td>
<td>0.00%</td>
<td>9.22%</td>
<td>0.23%</td>
<td>10.53%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>3.31%</td>
</tr>
<tr>
<td>MW25 Fusion 4</td>
<td>0.92%</td>
<td>0.00%</td>
<td>5.14%</td>
<td>0.00%</td>
<td>4.43%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>1.39%</td>
</tr>
</tbody>
</table>
E. Alkali fusion masses loaded onto the columns and ICP-OES of Li cuts

Supplementary table 18: Masses of elements loaded onto the columns from the $^6$Li-Mg-EM alkali fusions alongside the volume of 100 times diluted sample prepared to yield that mass of elements.

<table>
<thead>
<tr>
<th>Volume prepared (µl)</th>
<th>Mass loaded onto column</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Fusion 1</td>
<td>12.0</td>
</tr>
<tr>
<td>Fusion 2</td>
<td>11.5</td>
</tr>
<tr>
<td>Fusion 3</td>
<td>12.4</td>
</tr>
<tr>
<td>Fusion 4</td>
<td>13.0</td>
</tr>
</tbody>
</table>

Supplementary table 19: Masses of elements loaded onto the columns from the BCR alkali fusions alongside the volume of supernatant prepared (undiluted).

<table>
<thead>
<tr>
<th>V prepared (µl)</th>
<th>Mass loaded with 4 ng Li (ng)</th>
<th>K (Estimated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>B</td>
</tr>
<tr>
<td>BCR-1 F-1</td>
<td>152.4</td>
<td>2312</td>
</tr>
<tr>
<td>BCR-1 F-2</td>
<td>144.8</td>
<td>.5</td>
</tr>
<tr>
<td>BCR-2 F-1</td>
<td>3015</td>
<td>1770</td>
</tr>
<tr>
<td>BCR-2 F-2</td>
<td>278.6</td>
<td>.5</td>
</tr>
<tr>
<td>BCR-3 F-1</td>
<td>2284</td>
<td>3015</td>
</tr>
<tr>
<td>BCR-3 F-2</td>
<td>298.7</td>
<td>.6</td>
</tr>
</tbody>
</table>

Supplementary table 20: Masses of elements loaded onto the columns from the SGR-1b alkali fusions alongside the volume of supernatant prepared (undiluted).

<table>
<thead>
<tr>
<th>V prepared (µl)</th>
<th>Mass loaded with 4 ng Li (ng)</th>
<th>K (Estimated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>B</td>
</tr>
<tr>
<td>Fusion 1</td>
<td>9.4</td>
<td>457.6</td>
</tr>
<tr>
<td>Fusion 2</td>
<td>11.7</td>
<td>488.3</td>
</tr>
<tr>
<td>Fusion 3</td>
<td>11.6</td>
<td>605.3</td>
</tr>
<tr>
<td>Fusion 4</td>
<td>11.5</td>
<td>530.1</td>
</tr>
<tr>
<td>Fusion 5</td>
<td>14.7</td>
<td>275.7</td>
</tr>
</tbody>
</table>
Supplementary table 21: ICP-OES analysis of the pre-Li cuts, post-Li cuts and Li fractions from the $^6$Li-Mg-EM fusion AG MP-50 column chromatography alongside the two accompanying IAPSO seawater standards.

Concentrations (ng/ml) corrected for blanks and dilution factors

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>B</th>
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Supplementary table 22: ICP-OES analysis of the pre-Li cuts, post-Li cuts and Li fractions from the BCR-1 and BCR-2 fusion AG MP-50 column chromatography alongside the two accompanying IAPSO seawater standards.

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Supplementary table 23: Masses of elements loaded onto the columns from the MW25 alkali fusions alongside the volume of 100 times diluted sample prepared to yield that mass of elements.

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<th>Mg</th>
<th>Mo</th>
<th>Na</th>
<th>Si</th>
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**Supplementary table 24: ICP-OES analysis of the pre-Li cuts, post-Li cuts and Li fractions from the MW25 fusion AG MP-50 column chromatography alongside the two accompanying IAPSO seawater standards.**

**Concentrations (ng/ml) corrected for blanks and dilution factors**

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