

# Volatilities of Trace Elements in Silicate Melts



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The loss rates of volatile elements from silicate melts are of considerable interest to a number of branches of volcanology, petrology, and geochemistry. In the volcanic context emanation coefficients are used as empirical measures of the extent of loss of individual elements in the gas phase. In geochemistry and cosmochemistry relative loss rates control the pattern of element depletions during melting and core segregation on asteroids and proto planets. Incorporation of such differentiated, pre-melted bodies probably influenced the well-known pattern of volatile element depletion in the Silicate Earth.

This study makes two independent measurements of the volatilities of the elements Ag, Bi, Cd, Cr, Cu, Ga, Ge, In, Mo, Pb, Sn, Tl, V, W and Zn, in molten silicate. The first includes a series of high pressure (1.5GPa) metal–silicate partitioning experiments used to determine the activities of trace elements in silicate melts. The second involves direct measurement of volatile loss from a representative basaltic melt at oxygen fugacities applicable to planetary formation.

Results from this study show that some elements (e.g. indium) are less volatile than previously thought, while others (e.g. copper) are more so. Applying these results to volatile depletion in the Silicate Earth reconciles the supposed overabundance of indium, as suggested by condensation temperatures. Comparing depletion of the Silicate Earth relative to CI meteorites shows a remarkably consistent trend with the measured volatility factors, suggesting that evaporative volatile loss occurred during planetary formation, most likely from planetesimals.

The volatile loss data from this study also support the observation of volatile depletion in lunar basalts. Such agreement provides additional evidence that the Moon experienced some degree of volatile loss during its accretion after the giant impact by *Theia*.





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The loss rates of volatile elements from silicate melts are of considerable interest to a number of branches of volcanology, petrology, and geochemistry. Despite this importance, volatility data are sparse and the use of theoretical condensation temperatures as proxies for volatility is problematic due to their limited applicability to evaporation. To address these shortcomings, this study has experimentally measured trace element volatile loss from silicate melts. In pursuit of this aim, two approaches have been undertaken: high pressure metal–silicate partitioning experiments permitting the measurement of trace element activities in silicate melt (from which their volatilities may be computed) and direct measurement of volatile loss from molten silicate at one atmosphere pressure. To directly measure volatile loss a gas mixing stirring furnace has been designed and assembled. The volatilities obtained have been used to interpret the volatile depletion pattern of the Silicate Earth relative to CI chondrites, and also the pattern imparted on the Earth’s Moon during its formation.

During planetary formation, as a precursor to accretion, both major and trace elements condensed in the solar nebula according to their volatilities and solubilities in the earliest-forming stable major-element phases. By considering a slowly cooling cloud of solar composition, the temperature at which 50% of the mass of each element has condensed can be computed using thermochemical data, assuming equilibrium with and, in most cases, ideal behaviour in the condensed phases [Anders and Grevesse 1989; Yoneda and Grossman 1995; Lodders 2003]. A radial temperature profile in the proto-Solar System resulted in large-scale heterogeneity, with the most volatile elements condensing in the outer solar system [Palme and O’Neill 2014].

During terrestrial planet formation, a typical semi–molten planetary embryo would have possessed a magma ocean [Li and Agee 1996; Li and Agee 2001; Wade and Wood 2005; Rubie *et al.* 2015] and undergone depletion of volatile trace elements due to atmospheric loss, by either

Jean's escape, hydrodynamic loss [Hunten 1993], or from shock waves caused by giant impacts [Genda and Abe 2003]. Discounting differentiation and sequestration of siderophile elements into a metallic core, then episodes of volatile loss and enrichment from unprocessed material should be sufficient to describe the observed trace element depletion, relative to CI chondrite, in the bulk Silicate Earth (BSE). The volatilities from silicate melts of the trace elements of interest to this study have so far remained unmeasured.

Formation of the Earth's Moon by a giant impact [Stephenson 1987; Halliday 2000; Canup and Asphaug 2001; Canup 2004; Wade and Wood 2016] 4.5 Gyr ago would have resulted in widespread melting of the mantle and an ejected cloud of molten silicate material heated by up to 1000 to 3000 K [Melosh 1990; Canup 2001; Canup and Asphaug 2001; Pahlevan and Stevenson 2007]. All volatile elements would have remained in the vapour phase while the moon accreted and while the precise conditions of formation are unconstrained, volatile depletion of the Moon relative to the BSE should be observed in Lunar samples. It has long been known that the moon is depleted in volatile elements, but this study will compare the degree of depletion of each element to the measured volatility.

To measure the activity coefficients of the sixteen trace elements in various silicate melts, an experimental campaign was undertaken to measure the trace element partition coefficients between carbon-saturated iron metal and silicate melt at high temperature and pressure. Starting mixtures comprising a range of CMAS compositions were prepared and doped with trace elements at abundances between 50 and 5000  $\mu\text{g.g}^{-1}$ . These high pressure experiments were conducted in a  $\frac{1}{2}$ " Boyd-England type piston cylinder apparatus operated at a temperature of 1650°C and a pressure of 1.5 GPa.

The epsilon model of Zhongting 2001 was used to compute activity coefficients for the trace elements in carbon-saturated iron metal. These values were combined with the partition coefficients and available thermochemical data and FeO activities to compute activity coefficients of the trace elements in silicate melt. Some values for epsilon-carbon have been revised using the results from four experiments conducted in carbon-free capsules. Solubility experiments were performed to ensure that trace elements of interest were obeying Henry's law. Absolute values of the activity coefficients have been determined, and those exhibiting a trend with melt composition have been modelled using linear regression. Some elements show a

strong dependence on melt composition (e.g. Mo, W, Cr, V) while others show very little (e.g. Cu and Sb).

To directly measure trace element volatility, a one atmosphere gas-mixing furnace was designed and built. A key requirement of the furnace was the capability to stir a crucible of silicate melt at temperatures up to 1700°C at a range of oxygen fugacities applicable to planetary formation. By measuring the loss of volatile elements to the vapour phase this apparatus provided direct measurement of trace element volatility, or effusion rate, from silicate melts. Previous workers [Dingwell *et al.* 1994] have built *in situ* stirring mechanisms integrated with gas-mixing furnaces, but the design presented here offers a number of advantages and improvements, such as: an entirely gas-tight assembly to maintain  $fO_2$  as well as facilitate working with toxic or reactive gases (e.g.  $H_2$ ,  $SO_4$ ); a rapid-quenching mechanism; low-cost of consumables; and strongly-supported end caps that can be adapted to a wide range of experiments.

Volatile loss experiments were undertaken using a natural basalt sample doped with the trace elements of interest. Experiments were performed in a Ni crucible at 1300°C and a range of  $\log(fO_2)$  values from  $-7$  to  $-13$  atm. At this temperature the Fe–FeO buffer is at  $-10.5$  and Ni–NiO at  $-6.5$  atm. To interpret and compare the volatile loss experiments the volatility factor is defined as the concentration of a trace element in the experimental charge after 60 minutes, divided by the starting concentration. All of the trace elements show a pronounced decrease in the volatility factor, and an increase in volatility, at lower values of oxygen fugacity. Most striking is how the volatile loss results show that some elements previously thought to be highly volatile, such as indium, are actually measured to be less volatile than other elements such as copper.

Evaluation of the volatility factors shows that they are effective predictors of volatile depletion during planetary formation. A plot of volatility factor against bulk Silicate Earth depletion shows a surprisingly near linear trend in log-log space. Outlier refractory elements such as Mo and W are most likely sequestered into the core. A further noteworthy observation is the bulk Silicate Earth's enrichment in the most volatile elements, which could have accompanied the addition of  $2 \pm 1\%$  of Earth's C, H and some noble gases [Marty 2012] and/or the “late veneer” which delivered  $\sim 0.5\%$  of Earth's highly siderophile elements after core formation ceased [Wang *et al.* 2013].

Applying the volatility factors to volatile depletion of the low-Ti lunar basalts also shows a linear trend, suggesting that these materials experienced substantial outgassing. Looking for the same correlation with bulk silicate Moon compositions shows less agreement, but such comparisons are complicated by the many estimates required to compute a BSM composition.

Both of the experimental campaigns in this study required analysis of both major and trace elements in all solid phases. Major and minor elements were analysed by electron probe microanalysis (EPMA) [Castaing 1952], while trace elements were analysed using laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) [Gray 1985; Jackson et al 1992].

The particular characteristics of the experimental products of this study resulted in a need for specialized EPMA analysis. In particular, dendritic textures dispersed throughout some of the quenched glasses, and the undesired influence of secondary fluorescence, precluded the direct analysis by EPMA. The software PENEPMAS was used to model results from spot analyses distributed across hypothetical quench textures, and the statistical uncertainty of multiple spots to be determined. This treatment limited the relative uncertainty introduced by sample heterogeneity to 5%.

Trace element analysis was performed by LA–ICP–MS, and while analysis of homogenous glasses is routine and well characterised, the analysis of iron metal for volatile elements has required the fabrication of matrix matched iron standards. Characterisation of these standards for the trace element of interest has allowed optimisation of the laser ablation sampling conditions, as well as provided guidance regarding analytical accuracy. To improve the accuracy of the analysis, a set of correction curves were determined by regression and applied to these data to effectively improve deviations in relative accuracy from over 500% to less than 100% for some volatile elements.

The contents of this thesis are my own work, except where otherwise stated.

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## Table of Contents

|       |                                                           |    |
|-------|-----------------------------------------------------------|----|
| 1     | Volatilities of Trace Elements in Silicate Melts.....     | 1  |
| 1.1   | Introduction.....                                         | 1  |
| 1.2   | Planetary Formation Overview .....                        | 1  |
| 1.3   | Condensation vs Vaporisation .....                        | 5  |
| 1.3.1 | Condensation in the Solar Nebula .....                    | 6  |
| 1.3.2 | Vaporisation from Accreted Bodies.....                    | 10 |
| 1.4   | Specific Problems of Interest .....                       | 12 |
| 1.4.1 | Trace Element Composition of the Silicate Earth.....      | 12 |
| 1.4.2 | The Formation of the Earth's Moon.....                    | 13 |
| 1.5   | Proposed Route of Enquiry.....                            | 13 |
| 1.5.1 | Knudsen Effusion Cell Mass Spectrometry .....             | 14 |
| 1.5.2 | Direct Volatile Loss .....                                | 15 |
| 1.5.3 | Metal–Silicate–Vapour Partitioning.....                   | 15 |
| 1.6   | Silicate Melt Activity.....                               | 17 |
| 1.6.1 | Previous Measurements of Activity in Silicate Melts ..... | 17 |
| 1.7   | The Epsilon Model.....                                    | 18 |
| 1.7.1 | Activity and Activity Coefficients .....                  | 19 |
| 1.7.2 | The Epsilon Model Calculation.....                        | 20 |
| 1.8   | Summary .....                                             | 23 |



|       |                                                    |    |
|-------|----------------------------------------------------|----|
| 2     | EPMA Analysis of Glass and Metal Samples.....      | 25 |
| 2.1   | Introduction.....                                  | 25 |
| 2.2   | EPMA Analysis of Homogenous CMAS+Fe Glass .....    | 26 |
| 2.3   | EPMA Analysis of Dendritic Quench Textures.....    | 26 |
| 2.3.1 | PENEPMA Simulations.....                           | 29 |
| 2.4   | EPMA Analysis of Trace Elements in Iron Metal..... | 36 |
| 2.4.1 | Analytical Conditions.....                         | 37 |
| 2.4.2 | WDS Spectrometer Configuration.....                | 37 |
| 2.4.3 | Line Selection and Interferences .....             | 39 |
| 2.4.4 | Background Positions.....                          | 43 |
| 2.4.5 | Detection Limits .....                             | 45 |
| 2.5   | Summary .....                                      | 46 |
| 3     | LA-ICP-MS Analysis of Glass and Metal Samples..... | 47 |
| 3.1   | Introduction.....                                  | 47 |
| 3.2   | Instrumentation .....                              | 47 |
| 3.2.1 | Laser Ablation Instrument .....                    | 48 |
| 3.2.2 | ICP-MS .....                                       | 48 |
| 3.3   | Analytical Methodology.....                        | 49 |
| 3.4   | Analysis of Glass Samples .....                    | 50 |
| 3.4.1 | Standards .....                                    | 50 |

|       |                                                 |    |
|-------|-------------------------------------------------|----|
| 3.4.2 | Sampling .....                                  | 51 |
| 3.4.3 | Detection Limits .....                          | 52 |
| 3.4.4 | Discussion .....                                | 53 |
| 3.5   | Analysis of Iron Metal .....                    | 53 |
| 3.5.1 | Fabrication of In-House Iron Standards .....    | 54 |
| 3.5.2 | Characterising Iron Standards .....             | 58 |
| 3.5.3 | Accepted Standard Compositions .....            | 59 |
| 3.5.4 | Characterisation of Iron Metal Ablation .....   | 62 |
| 3.5.5 | Accuracy of Iron Analysis by LA-ICP-MS .....    | 68 |
| 3.5.6 | Concentration Correction Curves .....           | 78 |
| 3.5.7 | Discussion and Future Directions of Study ..... | 79 |
| 3.6   | Conclusion .....                                | 81 |
| 4     | Metal-Silicate Partitioning Experiments .....   | 83 |
| 4.1   | Introduction .....                              | 83 |
| 4.2   | Starting Compositions .....                     | 84 |
| 4.2.1 | Trace Elements .....                            | 86 |
| 4.2.2 | Experiment Starting Mixtures .....              | 87 |
| 4.3   | High Pressure Experiments .....                 | 88 |
| 4.3.1 | Quench Rate .....                               | 89 |
| 4.3.2 | Typical Experimental Charge .....               | 91 |

|       |                                                                         |     |
|-------|-------------------------------------------------------------------------|-----|
| 4.4   | Analysis .....                                                          | 92  |
| 4.4.1 | Quench Textures in Glass .....                                          | 92  |
| 4.4.2 | Major Element Compositions .....                                        | 93  |
| 4.5   | Calculating Activity Coefficients .....                                 | 98  |
| 4.5.1 | Determining Common Thermochemical Terms.....                            | 101 |
| 4.6   | Calculating Revised Epsilons and Gamma-Zeros.....                       | 106 |
| 4.6.1 | Calculation of Gamma-Zero Values from Binary Phase Diagrams .....       | 107 |
| 4.6.2 | Computing Gamma-Zero with the Miedema Thermodynamic Model.....          | 108 |
| 4.6.3 | Calculated Gamma Zero Values.....                                       | 110 |
| 4.6.4 | Revising Epsilon-Carbon Values.....                                     | 116 |
| 4.6.5 | Revise Epsilon-Carbon Values by Modelling Free Energy .....             | 118 |
| 4.7   | Computing Thermochemical Data.....                                      | 124 |
| 4.7.1 | Computing $\log K_f(\text{liquid})$ from $\log K_f(\text{solid})$ ..... | 124 |
| 4.7.2 | Computing $\log K_f(\text{liquid})$ From Vapour Data.....               | 125 |
| 4.8   | Thermochemical Data Summary.....                                        | 127 |
| 4.8.1 | Silver (Ag).....                                                        | 127 |
| 4.8.2 | Bismuth (Bi) .....                                                      | 128 |
| 4.8.3 | Cadmium (Cd).....                                                       | 128 |
| 4.8.4 | Chromium (Cr) .....                                                     | 129 |
| 4.8.5 | Copper (Cu) .....                                                       | 130 |

|        |                                                                  |     |
|--------|------------------------------------------------------------------|-----|
| 4.8.6  | Gallium (Ga) .....                                               | 131 |
| 4.8.7  | Germanium (Ge) .....                                             | 131 |
| 4.8.8  | Indium (In) .....                                                | 132 |
| 4.8.9  | Molybdenum (Mo).....                                             | 132 |
| 4.8.10 | Lead (Pb) .....                                                  | 133 |
| 4.8.11 | Antimony (Sb) .....                                              | 134 |
| 4.8.12 | Tin (Sn).....                                                    | 135 |
| 4.8.13 | Thallium (Tl).....                                               | 135 |
| 4.8.14 | Vanadium (V).....                                                | 136 |
| 4.8.15 | Tungsten (W).....                                                | 137 |
| 4.8.16 | Zinc (Zn) .....                                                  | 137 |
| 4.9    | Silicate Melt Activity Coefficients and Composition Models ..... | 139 |
| 4.9.1  | Silver ( $\gamma\text{AgO}_{0.5}$ ) .....                        | 141 |
| 4.9.2  | Bismuth ( $\gamma\text{BiO}_{1.5}$ ).....                        | 141 |
| 4.9.3  | Cadmium ( $\gamma\text{CdO}$ ) .....                             | 142 |
| 4.9.4  | Chromium ( $\gamma\text{CrO}$ ).....                             | 143 |
| 4.9.5  | Copper ( $\gamma\text{CuO}_{0.5}$ ).....                         | 143 |
| 4.9.6  | Gallium ( $\gamma\text{GaO}_{1.5}$ ).....                        | 143 |
| 4.9.7  | Germanium ( $\gamma\text{GeO}_2$ ).....                          | 144 |
| 4.9.8  | Indium ( $\gamma\text{InO}_{1.5}$ ) .....                        | 144 |

|        |                                                                                   |     |
|--------|-----------------------------------------------------------------------------------|-----|
| 4.9.9  | Molybdenum ( $\gamma\text{MoO}_2$ ) .....                                         | 144 |
| 4.9.10 | Lead ( $\gamma\text{PbO}$ ) .....                                                 | 145 |
| 4.9.11 | Antimony ( $\gamma\text{SbO}_{1.5}$ ) .....                                       | 145 |
| 4.9.12 | Tin ( $\gamma\text{SnO}_2$ ) .....                                                | 145 |
| 4.9.13 | Thallium ( $\gamma\text{TlO}_{0.5}$ ) .....                                       | 146 |
| 4.9.14 | Vanadium ( $\gamma\text{VO}_{1.5}$ ) .....                                        | 147 |
| 4.9.15 | Tungsten ( $\gamma\text{WO}_3$ ) .....                                            | 147 |
| 4.9.16 | Zinc ( $\gamma\text{ZnO}$ ) .....                                                 | 147 |
| 4.10   | Trace Element Activity Figures .....                                              | 149 |
| 4.11   | Discussion .....                                                                  | 157 |
| 4.11.1 | Computed Values of Gamma–Zero .....                                               | 157 |
| 4.11.2 | Activity Uncertainties .....                                                      | 159 |
| 4.11.3 | Comparison to Previous Work .....                                                 | 160 |
| 4.11.4 | Trends and Patterns .....                                                         | 161 |
| 4.11.5 | Physical Melt Models .....                                                        | 162 |
| 4.12   | Summary .....                                                                     | 163 |
| 5      | Design, Construction and Application of a One Atmosphere Gas Mixing Furnace ..... | 165 |
| 5.1    | Introduction .....                                                                | 165 |
| 5.2    | Furnace Design .....                                                              | 166 |
| 5.2.1  | Tube Furnace .....                                                                | 170 |

|       |                                          |     |
|-------|------------------------------------------|-----|
| 5.2.2 | Furnace Controller .....                 | 170 |
| 5.2.3 | Furnace Tube End Caps .....              | 171 |
| 5.2.4 | Stirring Mechanism.....                  | 173 |
| 5.2.5 | Crucible .....                           | 174 |
| 5.2.6 | Quenching Mechanism .....                | 175 |
| 5.2.7 | Temperature Monitoring System.....       | 175 |
| 5.3   | Furnace Characterisation.....            | 182 |
| 5.3.1 | Furnace Temperature .....                | 182 |
| 5.3.2 | Vertical Temperature Profile .....       | 182 |
| 5.3.3 | External Thermocouple Calibration.....   | 183 |
| 5.3.4 | Stirrer Length Extension .....           | 184 |
| 5.4   | Volatile Loss Experiments .....          | 187 |
| 5.4.1 | Source Material.....                     | 187 |
| 5.4.2 | Experiment Preparation .....             | 190 |
| 5.4.3 | Quenching.....                           | 192 |
| 5.4.4 | Oxygen Fugacity .....                    | 192 |
| 5.5   | Results.....                             | 194 |
| 5.5.1 | Analysis and Homogeneity Assessment..... | 194 |
| 5.5.2 | Trace Element Homogeneity .....          | 196 |
| 5.5.3 | Surface Scans.....                       | 197 |

|       |                                                                        |     |
|-------|------------------------------------------------------------------------|-----|
| 5.5.4 | Capsule Scans.....                                                     | 198 |
| 5.5.5 | Time Series Results.....                                               | 199 |
| 5.5.6 | Introducing the Volatility Factor .....                                | 201 |
| 5.5.7 | Variation in Volatility Factor with Oxygen Fugacity .....              | 202 |
| 5.6   | Calculating Volatile Element Vapour Pressure.....                      | 204 |
| 5.6.1 | Correction for Non-Ideality Using Activity Coefficients.....           | 207 |
| 5.7   | Discussion .....                                                       | 214 |
| 5.7.1 | Copper and Indium.....                                                 | 214 |
| 5.7.2 | Non-Ideal Behaviour of Volatile Trace Elements .....                   | 216 |
| 5.8   | Summary .....                                                          | 218 |
| 6     | Earth's volatile Contents Established by Melting and Vaporisation..... | 219 |
| 6.1   | Introduction.....                                                      | 219 |
| 6.2   | Experimental Conditions and Summary of Results .....                   | 220 |
| 6.3   | Relative Volatilities of Copper and Indium.....                        | 222 |
| 6.4   | Volatile Loss from Planets and Planetesimals.....                      | 224 |
| 6.5   | Volatile Depletion in the Silicate Earth.....                          | 226 |
| 6.6   | Summary .....                                                          | 228 |
| 7     | Peripheral Insights and Direction for Future Study.....                | 229 |
| 7.1   | Peripheral Applications.....                                           | 229 |
| 7.1.1 | Volatile Loss during the Moon-Forming Giant Impact.....                | 229 |

|       |                                                   |     |
|-------|---------------------------------------------------|-----|
| 7.1.2 | Volatile Degassing from Molten Planetesimals..... | 233 |
| 7.1.3 | Glass Reference Materials.....                    | 235 |
| 7.1.4 | Gas Speciation during Volatile Loss .....         | 235 |
| 7.1.5 | Thermochemical Data .....                         | 237 |
| 7.1.6 | Volcanic Systems.....                             | 237 |
| 7.2   | Direction of Future Work.....                     | 238 |
| 7.2.1 | Isotopic Analysis.....                            | 238 |
| 7.2.2 | Improved Stirring Furnace Experiments .....       | 239 |
| 7.3   | Conclusion .....                                  | 240 |
|       | References.....                                   | 243 |



## Table of Figures

|                                                                                             |    |
|---------------------------------------------------------------------------------------------|----|
| Figure 1.1—BSE/CI Chondrite vs 50% Condensation Temperature .....                           | 10 |
| Figure 1.2—Molten Silicate–Vapour Equilibrium .....                                         | 16 |
| Figure 1.3—Metal–Silicate Equilibrium .....                                                 | 16 |
| Figure 2.1—Quench Texture Formation Schematic.....                                          | 27 |
| Figure 2.2—Typical Sample Showing Quench Texture .....                                      | 28 |
| Figure 2.3a—High Resolution BSE Images of Quench Textures .....                             | 28 |
| Figure 2.3b—High Resolution BSE Images of Quench Textures.....                              | 29 |
| Figure 2.4—PENEPMA Simulated Quench–Texture.....                                            | 30 |
| Figure 2.5—Assessment of Matrix Correction Routine by Pearson Correlation.....              | 31 |
| Figure 2.6a—Al <sub>2</sub> O <sub>3</sub> Concentration from 100 PENEPMA Simulations ..... | 33 |
| Figure 2.6b—CaO Concentration from 100 PENEPMA Simulations .....                            | 33 |
| Figure 2.6c—FeO Concentration from 100 PENEPMA Simulations.....                             | 34 |
| Figure 2.6d—MgO Concentration from 100 PENEPMA Simulations .....                            | 34 |
| Figure 2.6e—SiO <sub>2</sub> Concentration from 100 PENEPMA Simulations .....               | 35 |
| Figure 2.7—Minimum Number of Points Required to Reach Minimum Uncertainty .....             | 36 |
| Figure 2.8—Assessment of Detector Linearity .....                                           | 38 |
| Figure 2.11a—Transition Row Elements on PET .....                                           | 41 |
| Figure 2.11b—Transition Row Elements on LIF.....                                            | 41 |
| Figure 2.12—Tungsten and Silicon on TAP .....                                               | 42 |

|                                                                                     |    |
|-------------------------------------------------------------------------------------|----|
| Figure 3.1—Quench Texture in Standard BW162A .....                                  | 56 |
| Figure 3.2—Quench Texture in Standard G3A1 .....                                    | 56 |
| Figure 3.3—Quench Texture in Standard G3Pb1 .....                                   | 57 |
| Figure 3.4—Ablation Rate of 99.999% Iron Wire .....                                 | 63 |
| Figure 3.5—Ablation Crater in Iron (50µm, 200 shots, 1.4 J.cm <sup>-2</sup> ).....  | 64 |
| Figure 3.6—Ablation Crater in Iron (50µm, 200 shots, 5.8 J.cm <sup>-2</sup> ).....  | 65 |
| Figure 3.7—Ablation Crater in Iron (50µm, 200 shots, 8.3 J.cm <sup>-2</sup> ).....  | 65 |
| Figure 3.8—Ablation Crater in Iron (50µm, 200 shots, 24.9 J.cm <sup>-2</sup> )..... | 66 |
| Figure 3.9—Analytical Accuracy by On-Sample Fluence .....                           | 67 |
| Figure 3.10—Ablation Scan of Iron Standard G3A1 .....                               | 68 |
| Figure 3.12a—Analytical Accuracy Assessment—Ag .....                                | 70 |
| Figure 3.12b—Analytical Accuracy Assessment—Bi.....                                 | 70 |
| Figure 3.12c—Analytical Accuracy Assessment—Cd .....                                | 71 |
| Figure 3.12d—Analytical Accuracy Assessment—Cr.....                                 | 71 |
| Figure 3.12e—Analytical Accuracy Assessment—Cu .....                                | 72 |
| Figure 3.12f—Analytical Accuracy Assessment—Ga .....                                | 72 |
| Figure 3.12g—Analytical Accuracy Assessment—Ge .....                                | 73 |
| Figure 3.12h—Analytical Accuracy Assessment—In .....                                | 73 |
| Figure 3.12i—Analytical Accuracy Assessment—Mo .....                                | 74 |
| Figure 3.12j—Analytical Accuracy Assessment—Pb.....                                 | 74 |

|                                                                                                             |     |
|-------------------------------------------------------------------------------------------------------------|-----|
| Figure 3.12k—Analytical Accuracy Assessment—Sb .....                                                        | 75  |
| Figure 3.12l—Analytical Accuracy Assessment—Sn .....                                                        | 75  |
| Figure 3.12m—Analytical Accuracy Assessment—Tl .....                                                        | 76  |
| Figure 3.12n—Analytical Accuracy Assessment—V .....                                                         | 76  |
| Figure 3.12o—Analytical Accuracy Assessment—W .....                                                         | 77  |
| Figure 3.12p—Analytical Accuracy Assessment—Zn .....                                                        | 77  |
| Figure 4.1—Starting Compositions ADF Projection.....                                                        | 85  |
| Figure 4.2—Piston Cylinder Assembly.....                                                                    | 89  |
| Figure 4.3—Piston–Cylinder Quench Rate.....                                                                 | 90  |
| Figure 4.4—Typical Experimental Charge .....                                                                | 91  |
| Figure 4.5—Sample FM1108 Showing Quench Crystal Texture .....                                               | 92  |
| Figure 4.6—Silicate Melt Composition ADF Ternary Diagram .....                                              | 93  |
| Figure 4.7—Wood and Wade 2013: $\gamma$ FeO Contours on the ADF Ternary .....                               | 102 |
| Figure 4.8—Computing Gamma Zero from a Miscibility Gap .....                                                | 108 |
| Figure 4.9—Iron–Silver Phase Diagram.....                                                                   | 110 |
| Figure 4.10—Iron–Indium Phase Diagram .....                                                                 | 112 |
| Figure 4.11—Iron–Lead Phase Diagram .....                                                                   | 113 |
| Figure 4.12—Major Oxide Composition Ranges .....                                                            | 119 |
| Figure 4.13—Gibbs Free Energy of Metal–Silicate Partitioning at 1923 K—Measured vs<br>Modelled Values ..... | 121 |

|                                                                                                        |     |
|--------------------------------------------------------------------------------------------------------|-----|
| Figure 4.14—Model of $\text{AgO}_{0.5}$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary | 149 |
| Figure 4.15—Model of $\text{BiO}_{1.5}$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary | 149 |
| Figure 4.16—Model of $\text{CdO}$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary       | 150 |
| Figure 4.17—Model of $\text{CuO}_{0.5}$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary | 150 |
| Figure 4.18—Model of $\text{CrO}$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary       | 151 |
| Figure 4.19—Model of $\text{GaO}_{1.5}$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary | 151 |
| Figure 4.20—Model of $\text{GeO}_2$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary     | 152 |
| Figure 4.21—Model of $\text{InO}_{1.5}$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary | 152 |
| Figure 4.22—Model of $\text{MoO}_2$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary     | 153 |
| Figure 4.23—Model of $\text{PbO}$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary       | 153 |
| Figure 4.24—Model of $\text{SnO}_2$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary     | 154 |
| Figure 4.25—Model of $\text{TlO}_{0.5}$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary | 154 |
| Figure 4.26—Model of $\text{VO}_{1.5}$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary  | 155 |
| Figure 4.27—Model of $\text{WO}_3$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary      | 155 |
| Figure 4.28—Model of $\text{ZnO}$ Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary       | 156 |
| Figure 4.29—Iron–Bismuth Phase Diagram                                                                 | 158 |
| Figure 5.1—Stirring Furnace Overview                                                                   | 167 |
| Figure 5.2—Furnace Top End Cap and Stirring Mechanism                                                  | 168 |
| Figure 5.3—Furnace Bottom End Cap and Quench Mechanism                                                 | 169 |
| Figure 5.4—Furnace Photographs                                                                         | 170 |

|                                                                                   |     |
|-----------------------------------------------------------------------------------|-----|
| Figure 5.5—Furnace Controller Circuit Diagram.....                                | 171 |
| Figure 5.6—Temperature Monitor Block Diagram .....                                | 177 |
| Figure 5.7—Monitor Box Circuit Diagram.....                                       | 178 |
| Figure 5.8—Temperature Probe Circuit Diagram .....                                | 179 |
| Figure 5.10—Stirring Furnace Vertical Temperature Profiles .....                  | 183 |
| Figure 5.11—Stirring Furnace Internal Thermocouple vs External Thermocouple ..... | 184 |
| Figure 5.12—Starting Material “EB” .....                                          | 187 |
| Figure 5.13—Typical Volatile Loss Experiment Sample .....                         | 195 |
| Figure 5.14—Typical Laser Ablation Scan at Glass Surface.....                     | 198 |
| Figure 5.15—Typical Laser Ablation Scan at Glass–Crucible Interface.....          | 199 |
| Figure 5.16—Time Series of Volatile Loss: Ag, Cu, and In.....                     | 201 |
| Figure 5.17—Volatility Factor vs Oxygen Fugacity .....                            | 203 |
| Figure 5.18—Total Partial Pressure of Trace Element Gases .....                   | 206 |
| Figure 5.19—Total Partial Pressure for Trace Element Gases.....                   | 208 |
| Figure 5.20—Vapour Pressure vs Volatile Loss: $\log(fO_2)=-7$ .....               | 210 |
| Figure 5.21—Vapour Pressure vs Volatile Loss: $\log(fO_2)=-9$ .....               | 211 |
| Figure 5.22—Vapour Pressure vs Volatile Loss: $\log(fO_2)=-11$ .....              | 212 |
| Figure 5.23—Vapour Pressure vs Volatile Loss: $\log(fO_2)=-13$ .....              | 213 |
| Figure 5.24—Copper and Indium Ideal Behaviour .....                               | 215 |
| Figure 5.26—Copper and Indium with Modelled Activity Coefficients.....            | 216 |

|                                                                         |     |
|-------------------------------------------------------------------------|-----|
| Figure 6.1—Evaporation and Condensation during Planetary Accretion..... | 220 |
| Figure 6.2—Volatile Loss Time Series .....                              | 221 |
| Figure 6.2—Modification to Figure from Palme and O’Neill 2014 .....     | 223 |
| Figure 6.4—BSE/CI Chondrite vs Measured Volatility Factors.....         | 227 |
| Figure 7.1—Lunar Basalt Depletion vs Volatility Factor.....             | 232 |
| Figure 7.2—BSM Depletion vs Volatility Factor .....                     | 233 |

## Table of Tables

|                                                                        |    |
|------------------------------------------------------------------------|----|
| Table 2.1—Glass Analytical Conditions .....                            | 26 |
| Table 2.2—PENEPMA Simulation Sample Compositions .....                 | 30 |
| Table 2.3—Magnitude of Matrix Correction Uncertainty .....             | 31 |
| Table 2.5—Trace Element Lines and Standards .....                      | 37 |
| Table 2.6—Spectrometer Configuration .....                             | 37 |
| Table 2.7—PHA Settings .....                                           | 39 |
| Table 2.8—Ti, V, and Cr Overlap Ratios.....                            | 40 |
| Table 2.9—Background Position Summary.....                             | 43 |
| Table 2.10—Cameca Spectrometer Positions .....                         | 44 |
| Table 2.11—Detection Limit Terms .....                                 | 45 |
| Table 2.12—EPMA Detection Limits for Trace Elements in Iron .....      | 46 |
| Table 3.1—General LA-ICP-MS Conditions .....                           | 50 |
| Table 3.2—Glass Analysis Masses and Dwell Times .....                  | 52 |
| Table 3.3—Glass Detection Limits.....                                  | 53 |
| Table 3.4—Third Party Iron Reference Materials Used in This Study..... | 54 |
| Table 3.5—Summary of Fabricated In-House Iron Standards.....           | 58 |
| Table 3.6a—Standard Compositions .....                                 | 60 |
| Table 3.6b—Standard Compositions (cont....) .....                      | 61 |
| Table 4.1—Intermediary End Member Compositions.....                    | 84 |

|                                                                                                           |     |
|-----------------------------------------------------------------------------------------------------------|-----|
| Table 4.2—Starting Compositions .....                                                                     | 85  |
| Table 4.3a—Trace Element Mixture “A” .....                                                                | 86  |
| Table 4.3b—Trace Element Mixture “F” .....                                                                | 86  |
| Table 4.3c—Trace Element Mixture “B” .....                                                                | 86  |
| Table 4.4—Experiment Starting Mixture Compositions .....                                                  | 87  |
| Table 4.5—Major Element Silicate Melt Compositions .....                                                  | 94  |
| Table 4.6—Silicate Melt Trace Element Compositions .....                                                  | 95  |
| Table 4.7—Carbon-Saturated Iron Trace Element Compositions .....                                          | 96  |
| Table 4.8—Trace Element Partition Coefficients.....                                                       | 97  |
| Table 4.9—Oxidation States of Trace Elements in Silicate Melts .....                                      | 98  |
| Table 4.10—Activity Coefficients of FeO in Silicate Melt Compositions at 1923 K.....                      | 103 |
| Table 4.11—Values and References for Gamma-Zero and Epsilon-Carbon.....                                   | 106 |
| Table 4.12—Summary of Models of Free Energy by Melt Composition .....                                     | 120 |
| Table 4.13—Revised Epsilon-Carbon Values .....                                                            | 123 |
| Table 4.14—Summary of Thermodynamic Values.....                                                           | 127 |
| Table 4.15—Activity Coefficients of Liquid Oxides in Silicate Melts at 1923 K .....                       | 140 |
| Table 4.16—Summary of Computed Activity Coefficients of Liquid Oxides in Silicate Melts at<br>1923 K..... | 140 |
| Table 4.17—Models of Trace Element Activity Coefficients in Silicate Melts .....                          | 141 |
| Table 5.1—EB Major Element Composition .....                                                              | 188 |



|                                                                                                               |     |
|---------------------------------------------------------------------------------------------------------------|-----|
| Table 5.2—Starting Material EBT1 Composition .....                                                            | 190 |
| Table 5.3—Nickel Crucible Trace Element Composition.....                                                      | 191 |
| Table 5.4—Stirring Furnace Experiment List .....                                                              | 194 |
| Table 5.5—Major Element Composition of all Volatile Loss Experimental Glasses.....                            | 196 |
| Table 5.6—Volatile Loss Experiments Trace Element Compositions.....                                           | 197 |
| Table 5.7—Computed Volatility Factors (60 Minute Experiments) .....                                           | 202 |
| Table 5.8—Gas Species Present in Computed Total Pressures .....                                               | 205 |
| Table 5.9—Activity Coefficients from Models at EB Composition.....                                            | 207 |
| Table 7.1—Low-Ti Lunar Basalt Composition.....                                                                | 231 |
| Table 6.2—Correlation between Angrite NWA7533/CI Depletion and Volatility Factors by<br>Oxygen Fugacity ..... | 234 |



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## 1 Volatilities of Trace Elements in Silicate Melts

### 1.1 Introduction

The vaporisation of volatile elements from silicate melts is of considerable interest to volcanology, petrology, and geochemistry. In this study the volatilities of 16 elements (Ag, Bi, Cd, Cr, Cu, Ga, Ge, In, Mo, Pb, Sn, Tl, V, W and Zn, which are mostly post-transition metals<sup>1</sup>, with some transition metals and refractory elements included for comparative purposes) have been measured using two approaches: metal–silicate partitioning, and direct volatile loss. These measurements offer insight to the formation of the Earth and Moon as well as the other terrestrial planets.

The highly volatile elements were classified in the 1920s and 30s by Goldschmidt and Russel [Lodders *et al.* 2009] to include H, He, C, O, N, as well as the rare gasses. While those elements and their volatile compounds (e.g. H<sub>2</sub>O) are widely referred to in the Earth Sciences as *volatiles*, they are not the focus of this study.

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### 1.2 Planetary Formation Overview

The field of planetary chemistry is focussed on understanding interactions between the chemical elements throughout every stage of planetary formation: the pre–solar nebula; solar accretion and ignition; the protoplanetary disc; and planetary accretion, formation, and differentiation. While our current level of understanding [Turekian and Holland 2013] has naturally focussed on our own solar system, there is also much interest in extra–solar planets, the discovery of which is ongoing at an extraordinary rate [Kane *et al.* 2016].

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<sup>1</sup> There is no IUPAC approved name for these elements, but the approximate grouping fits between the transition metals and the non-metals, and is characterised by high electronegativity and low melting point. From this study the group includes: Cu, Zn, Ga, Ge, Ag, Cd, In, Sn, Sb, Tl, Pb, and Bi.

The Earth accreted from asteroidal and protoplanetary bodies over a timescale of 70-100 Myr [Chambers 2001; Chambers 2004; Kleine *et al.* 2004]. Meteorites represent remnants from this process, and based on observations of igneous, metallic and achondritic meteorites, many of these asteroidal components formed within a few Myr of the origin of the solar system. During their formation they underwent an early phase of melting and vaporisation, with heating produced by both kinetic and radiogenic sources, such as the decay of  $^{26}\text{Al}$  [Ghosh and McSween 1998; Kleine *et al.* 2009]. For example the asteroid Vesta appears to have formed within 4 Myr of the origin of the solar system and to have undergone melting and volcanism for a further 35 M.yr [Roszjar *et al.* 2016].

As a precursor to accretion, both major and trace elements condensed to solid phases in the early protoplanetary disk. The condensation order of the elements depends on their volatility as well as their solubility in stable major element phases. By considering a slowly cooling cloud of solar composition, the temperature at which 50% of the mass of each element has condensed can be computed using thermochemical data [Lodders 2003]. Models of mid-plane temperature profiles [Fromang *et al.* 2002] show differences of several hundred degrees between models, as well as several hundred degrees between the orbital radii of Venus and Mars. The broad-scale trend of 50% condensation temperature (50%CT) predicts that outer rocky bodies should be volatile-rich, while the inner rocky bodies should be volatile-poor. However, 50%CT values are insufficient to explain the volatile content of the terrestrial planets alone [Lodders 1998; Marty 2011], especially with regards to the isotopic abundance of different elements, as discussed later.

During the early stages of planetary accretion, gas, dust, and condensed solids at various length scales, accreted to form the planets we observe today. The exact mechanism of accretion, such as pairwise sticking or collective effects, as well as evolution of characteristic particle sizes, are

topics of ongoing scientific debate. At the moment of writing the ROSETTA [Glassmeier *et al.* 2007] spacecraft has ended a 12.5 year mission by “landing” on the comet 67P/Churyumov-Gerasimenko [Altwegg *et al.* 2015], while returning tantalising surface imagery<sup>2</sup> showing boulders of intermediate size (3 meters) that suggests the comet body formed via a continuous accretion process.

Timing of accretion is especially important as this controlled the accumulation of condensed phases prior to the removal of interplanetary dust and gas within 100 Myr. This clearing of the inner solar system resulted in wholesale changes to conditions within the protoplanetary disc, with temperature, pressure, dust, and oxygen fugacity all being strong controls on the kinetics of vaporisation and evaporation, and thus degrees of isotopic fractionation in condensed phases. While there are some fractionation signatures showing that accreted bodies retain chondritic isotopic signatures, such as silver-palladium, [Schönbächler 2010], it is necessary to invoke complex models of heterogeneous accretion to explain other isotopic systems such as chromium and strontium. Attempts at constraining those models (see Schönbächler 2010 and references therein) result in uncorrelated isotopic systems, or overly-complex explanatory models, which the author of this study suggests reflects the ultimately chaotic nature of condensation, accretion, volatilisation, and late addition that inevitably occurred to various extents during formation of our solar system.

In contrast, later stages of planetary formation were defined by extensive oligarchic growth [Kokubo and Ida 1998] ending with a decrease in the rate of collisions and an increase in the occurrence of *giant impacts*. Throughout the Earth’s protracted accretion un-melted and

---

<sup>2</sup> “Rosetta spacecraft prepares to land on comet, solve lingering mysteries | Science | AAAS”, <http://www.sciencemag.org/news/2016/09/rosetta-spacecraft-prepares-land-comet-solve-lingering-mysteries>, retrieved 2016-10-02

previously melted, differentiated bodies were added by impacts which became progressively more violent, terminating with the giant impact (or impacts) which led to formation of the Moon [Canup and Asphaug 2001; Cuk *et al.* 2016]. Modelling of the accretion process and application of constraints based on the partitioning of siderophile elements between core and silicate mantle leads to the conclusion that the Earth was periodically covered by a “magma ocean” of molten silicate [Li and Agee 1996; Li and Agee 2001; Wade and Wood 2005; Rubie *et al.* 2015]. Models of the giant impact also suggest that this will have led to wholesale melting of the silicate Earth and extremely high surface temperatures with partial vaporisation of the silicate melt [Canup 2004]. The conclusion that volatile elements were partially vaporised from the Earth and its precursors at one or more periods during its growth is therefore inescapable.

While isotopic fractionation does not always occur during vaporisation, there is some confirmation of volatile loss provided by existing isotopic data for Noble gasses [Tucker and Mukhopadhyay 2014] as well as zinc [Paniello *et al.* 2012]. Furthermore, potassium isotopes show clear evidence [Wang and Jacobsen 2016] of vaporisation during the Moon-forming giant impact.

In conclusion, the elemental and isotopic composition of the Earth, relative to primitive material, can be explained as a combination of the following processes: accretion of material condensed under a range of conditions in the early solar system, volatile loss from accreted material, differentiation and core formation, collisional erosion, later addition of volatile-rich material from the outer solar system, and acute volatilisation caused by giant impacts. To add another degree of complication, some of these processes would have occurred slowly under equilibrium conditions, while others were rapid and dominated by kinetic effects, obscuring further any measurable remnants of isotopic and elemental fractionation.

Despite considerable efforts [above refs plus Palme and O'Neill 2003; O'Neill and Palme 2008; Halliday 2004; Halliday 2013] reconciling these processes to explain all aspects of the chemical and isotopic compositions of the terrestrial planets has so far proved elusive.

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### 1.3 Condensation vs Vaporisation

Separating the effects of condensation and vaporisation requires the identification of characteristic isotopic or elemental signatures for each process in material remnants. An isolated chemical system at equilibrium, consisting of both vapour and condensed phases will undergo continual exchange between phases, with the rate of vaporisation matching that of condensation. It is unlikely that such idealised conditions were ubiquitous during planetary formation, with pressure, temperature, presence of dust, hydrogen fugacity, and kinetic effects, all influencing degrees of isotopic and elemental fractionation. There is most certainly additional complexity to these processes, since experimental studies [Hashimoto 1989; Davis *et al.* 1990; Wang *et al.* 1999] have shown that both evaporation and condensation can leave some, none, or reversed (relative to Rayleigh fractionation) elemental or isotopic signatures in the final condensed phase.

The evaporative flux of a single element (or isotope) from a condensed phase is given by the Hertz-Knudsen equation [Hirth and Pound 1963]:

$$J_i^e = \frac{\sum_j n_j \gamma_{ij}^e P_{ij,\text{sat}}}{\sqrt{2\pi m_{ij} RT}}$$

This expression computes the evaporative flux of element  $i$  per unit area  $J_i^e$  and introduces the evaporation coefficient  $\gamma_{ij}^e$  which represents kinetic alteration of the evaporation rate, and takes

values  $\leq 1$ . The other values are:  $n_j$  number of atoms of  $i$  in the  $j^{\text{th}}$  gas molecule;  $P_{ij,\text{sat}}$  saturation vapour pressure of  $j$ ;  $m_{ij}$  molecular weight of  $j$ ;  $R$  gas constant;  $T$  temperature.

Likewise, there is a similar expression for condensation, which includes the condensation coefficient  $\gamma_{ij}^c$  and there is no evidence that this value differs from  $\gamma_{ij}^e$  away from equilibrium [Tachibana *et al.* 2011]. However, determining evaporation coefficients from first principles remains elusive, and as such they must be measured experimentally. Evaporation coefficients have been measured in many chemical systems, but in the Earth Sciences previous workers have conducted measurements of the evaporation coefficients at high temperatures of major elements in the iron–iron wustite [Hashimoto 1989] and olivine [Davis *et al.* 1990; Wang *et al.* 1999] systems.

### 1.3.1 Condensation in the Solar Nebula

The solar composition [Asplund *et al.* 2006] serves as our best estimate of the primitive material that formed the solar system, while the carbonaceous chondrites represent the most primitive of condensed materials, showing depletion of only the most volatile elements: hydrogen, carbon, nitrogen, oxygen, and the rare gases. However, even the most primitive carbonaceous chondrites show some evidence of processing [McSween 1979].

Due to a radial temperature distribution, 50%CT should correlate radially with elemental depletion in terrestrial solar system bodies [Palme and O'Neill 2014]. Once the young sun entered its T-Tauri phase gasses were swept from the inner solar system and condensation was effectively stopped. Certainly this model fits with general observation, as rocky bodies from the outer solar system all appear to be enriched in frozen volatile phases, emphasising that consideration of 50%CT alone can broadly explain large-scale structure in the solar system.



Focussing more on the inner solar system, and elements with 50%CT values between 500 and 1500K, it is observed that while the highly siderophile elements are heavily depleted in silicate phases and are assumed to mostly reside in the Earth's metallic core, some elements, such as indium, are far removed from the general trend. As such, it is not known if their condensation temperatures are incorrect or the Earth underwent some hitherto unidentified mechanism of indium enrichment late in its formation. It should be noted that in general, 50%CT is not well known for all elements, with weak (or unknown) values for the alkalis (Rb, Cs), halogens (F, Cl, Br, I) [Fegley and Lewis 1980] and the trace elements Bi, In, Hg, Pb, Sn and Tl [Lodders 2003].

The 50%CT value is computed [Anders and Grevesse 1989; Yoneda and Grossman 1995] via thermodynamic modelling by cooling a gas of solar composition at  $10^{-4}$  bar in small step-wise decrements, and determining the stable condensed phases at each temperature, equilibrating the gas and condensed phases, and computing the new gas composition. All components are gaseous above 1770K, with the major elements condensing to a small number of refractory phases down to 1500K, namely corundum, hibnonite, perovskite, and gehlenite, respectively. Below 1500K the range of major phases expands to include Fe-Ni metal, enstatite, forsterite, Ca-pyroxene, albite and anorthite. At each step trace elements are equilibrated with the major phases, but due to limited thermochemical knowledge, in many cases it is necessary to assume ideal behaviour in the condensed phases. A further complication to such modelling is the presence (observed in meteorite specimens) of high-abundance, but sparsely distributed phases (e.g.  $\text{WO}_3$  or iridium, osmium and ruthenium nuggets [Sylvester *et al.* 1990]) accounting effectively for total trace element budgets, yet greatly complicating thermochemical modelling.

Figure 1.1 shows concentrations in the bulk silicate Earth (BSE) of moderately volatile elements relative to their concentrations in CI chondrite meteorites, and is based on the original plot by

Palme and O'Neill, recently published in an updated form in Palme and O'Neill 2014. Here, each element's concentration is normalised to a concentration ratio of Mg of 1.0, and plotted against their 50%CT values.

As shown by Figure 1.1, the silicate Earth is strongly depleted in moderately volatile elements such as Pb, Tl, Zn, Sb, Bi and Ag relative to primitive solar system solids as represented by CI chondrite meteorites. In this figure it can be seen that although there is a general trend of declining relative abundance in the silicate Earth with increasing volatility and decreasing condensation temperature, there are many elements which fall below the trend. Such cases are frequently ascribed to extraction into the core, either in segregating Fe-rich metal [Wood *et al.* 2014] during accretion or in the so-called “Hadean matte” that formed during final stages of core formation [O'Neill 1991]. As an example, those elements that are known to partition strongly into both molten Fe metal and liquid FeS at elevated temperature, such as Au, Cu, Ag, and S, are most likely to reside in the core, as compared to Na, K, B, F which show negligible tendency to follow them. Core formation has clearly reduced the concentrations of relatively non-volatile elements such as Fe, Ni, Mo, and W in silicate Earth [McDonough and Sun 1995] so it is reasonable to apply the same principle to the volatile elements.

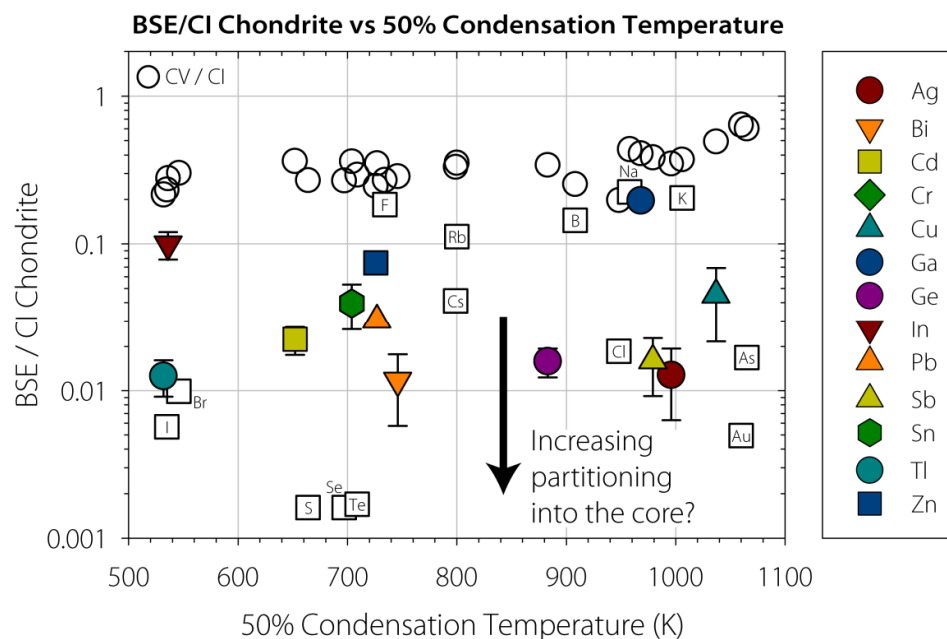
Implicitly, however, this approach relies on the assumption that the moderately volatile elements were added to Earth during accretion by a body of 10-20% of Earth's mass which had CI chondrite ratios of these elements. This body has also been suggested to have been the moon-forming impactor [O'Neill 1991]. Further depletions as shown for Au, Ag and other elements are then ascribed to the core-forming processes mentioned above.

Despite the flexibility of the approach in terms of conditions (pressure, temperature, metal composition) of core formation (which can be varied to match the depletion pattern) the abundances of numerous elements remain difficult to explain. Indium, for example, has a much lower condensation temperature than Zn and is more siderophile and more chalcophile than Zn yet is relatively more abundant in the silicate Earth. In is also much more abundant than Tl despite having similar 50%CT and being both more siderophile and more chalcophile than Tl [Wood *et al.* 2014]. Cs is strongly depleted despite not partitioning significantly into either metal or sulphide [Mills *et al.* 2007], and the same applies to the halogens. Cu and Ag have virtually identical partitioning into sulphide and metal and very similar condensation temperatures, yet Cu is substantially more abundant than Ag.

For comparison, Figure 1.1 also shows the depletion pattern of CV carbonaceous chondrites [Wasson & Kallemeyn 1988], meteorites which are also volatile-depleted relative to CI chondrites and which have never undergone planetary processes of melting and core formation.

Overall, the pattern of abundance in Figure 1.1 cannot be explained solely by addition of volatiles to a CI-like body followed by partial core formation. Of the other processes known to have been involved in differentiation of the Earth, and mentioned in the introduction above, melting is therefore inevitable and must lead to partial vaporisation of the most volatile elements.

Figure 1.1—BSE/CI Chondrite vs 50% Condensation Temperature



Concentration in Bulk Silicate Earth (BSE) relative to CI chondrite meteorites [Palme and O'Neill 2014] and normalised to a concentration ratio of Mg of 1.0 plotted versus their 50% condensation temperatures from a gas of solar system composition. The temperature range has been chosen to include moderately volatile elements, with elements from this study shown by filled symbols. Other elements are shown in square labelled symbols, and for comparison, the abundance in CV meteorites (normalised to CI in the same way) are shown as open circles. Error bars are 1SD.

### 1.3.2 Vaporisation from Accreted Bodies

As outlined in the previous section, condensation alone is insufficient to explain the trace element depletion pattern of the silicate Earth. Undoubtedly, some vaporisation took place in the early solar system, as bodies were heated by dynamic collisions and the release of energy by radiogenic decay. Consideration of planetary differentiation models shows that some feature a shallow magma ocean [Righter 2003], others a deep magma ocean [Li and Agee 2001], while “heterogeneous accretion” proposes no magma ocean at all [Newsom and Sims 1991]. There is strong geochemical evidence [Wood *et al.* 2006] that a scenario involving a deep magma ocean was most likely, and it is expected that this would have accentuated any depletion of trace elements through volatile loss due to high temperatures and some degree of surface turnover.

A simplistic approach to volatilisation from a magma ocean inevitably results in isotopic fractionation of volatiles via Rayleigh fractionation [Hannah *et al.* 2007] which should be most pronounced in the lightest most-volatile elements, which from this study include Cu and Zn.

Despite chemical evidence of a magma ocean, a clear signature of vaporisation in the silicate Earth has so far proven elusive, with Albarede 2009 commenting that trace element depletion in the silicate Earth from volatilisation is unlikely due to a high Mg/Zn ratio and low  $\delta^{66}\text{Zn}$  ratio, when compared to other rocky bodies from the inner solar system.

However, without experimental validation of both  $\gamma_{ij}^e$  and  $\gamma_{ij}^c$  along with the thermodynamic properties of all phases, vaporisation processes can occur without any fractionation, or indeed impart a signature reversed relative to Rayleigh fractionation. As an added complication, such effects are also observed to be element or isotope specific, and unravelling the chemical history requires complete understanding of a complex multi-component system with exact knowledge of the physical and chemical environment in which the vaporisation is occurring.

A simple example highlighting this complexity is measurement of major chemistry vaporisation from CAI-like silicate melts, as investigated by Knight *et al.* 2009. Those workers measured the isotopic fractionation factors of Mg and Si from melts at a range of temperatures (1600-1900°C) and found Si isotope fractionation to be unaffected by temperature, while Mg isotope fractionation showed a significant linear trend with reciprocal temperature. As such, it seems prudent to note that evaporation and condensation coefficients are element and phase-dependent, and resulting in actual volatile fluxes that can only be determined through experimental observation.

A direct analytical solution is not possible since we do not know the evaporation coefficients for all of the trace elements of interest, nor do we know activity models for the condensed phases.

Instead, direct experimental measurement of volatile loss from representative silicate melt at relevant temperature, pressure, and oxygen fugacity, should provide element volatility data that can be applied to planetary processes.

---

## **1.4 Specific Problems of Interest**

To better understand the volatility of trace elements so as to unravel their chemical histories during planetary formation, this study will measure the volatility of the metallic trace elements Ag, Bi, Cd, Cu, In, Pb, Sb, Sn, Tl, and Zn and their activities in silicate melts. These elements are typified by low 50% condensation temperature (50%CT) as well as comprising a mixture of lithophile, chalcophile, and siderophile habits. In addition, the semi-metals Ga and Ge are of interest, as well as the refractory elements Cr, Mo, V, and W, which have been included for comparative purposes.

### **1.4.1 Trace Element Composition of the Silicate Earth**

The bulk composition of the silicate Earth retains a signature of planetary processing, which includes trace element depletion due to sequestration to the core, depletion caused by vaporisation, and the possibility of enrichment by the addition of chondritic, or volatile-rich material after core formation had ceased. For the lithophile elements in this study, partitioning to the core can be mostly neglected, while for those siderophile elements with well-characterised metal-silicate partition coefficients, the degree of core partitioning can be estimated. By measuring the degree of depletion caused by evaporation, and comparing those effects to depletion in the silicate Earth, it is expected that the depletion of these elements can be explained.

### 1.4.2 The Formation of the Earth's Moon

The Moon forming impact [Stephenson 1987; Halliday 2000; Canup and Asphaug 2001; Canup 2004; Wade and Wood 2016] resulted in the formation of our planet's satellite from a combination of the Earth's mantle and remnants of the impactor itself.

Modelling suggests that collision by a fast impactor of  $\frac{1}{4}$  Earth mass, would have melted half the mantle and raised the temperature of the ejected material by 1000K to 3000K [Melosh 1990].

During this dramatic event volatile elements would have formed a high temperature gas cloud while the Moon formed through accretion of debris ejected from the Earth's mantle. If volatile elements remained gaseous after most of the Moon had formed, they would have subsequently condensed and de-orbited back to the Earth's surface. As such, a record of trace element fractionation between the Earth and the Moon should be present in the chemistry of both bodies, overprinted by a complex isotopic fractionation record due to the extreme kinetics of the vaporisation event.

To a first degree, as a means of validating both the experimental results from this study, and (to a first order) validating the giant impact hypothesis, it should be possible to estimate the bulk Moon trace element composition by depleting the bulk silicate Earth composition by an amount commensurate to the volatility measurements from this study.

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## 1.5 Proposed Route of Enquiry

The volatility of a trace element is directly proportional to its partial vapour pressure and evaporation coefficient. Derivation of evaporation coefficients from first principles is generally not possible, while direct measurement of vapour pressure is problematic without highly

specialised apparatus such as a Knudsen effusion cell mass spectrometer [Knudsen 1909; Caloz *et al.* 1997].

### 1.5.1 Knudsen Effusion Cell Mass Spectrometry

The Knudsen cell works by containing a condensed phase (solid or liquid) inside a chamber held at a fixed temperature. A vapour forms in equilibrium with the condensed phase, and this can be sampled after it escapes via a small orifice located in the lid of the cell. Provided the orifice is small relative to the volume of the chamber, equilibrium inside the cell can be maintained, while still allowing the vapour to be sampled. The vapour emerging into a high vacuum chamber forms a molecular beam which can be ionised and directed into a mass spectrometer for analyses. The intensity of the molecular beam is directly proportional to the vapour pressure inside the cell, once the geometry of the orifice relative to the cell has been accounted for.

Knudsen cell effusion mass spectrometry has been applied successfully to measure the thermochemical properties of metals [Fraser and Rammensee 1982] as well as silicate systems [Rammensee and Fraser 1982; Fraser *et al.* 1985; Jacobsen and Costa 2015; Costa *et al.* 2017]. Unfortunately for this study, to measure volatility some knowledge of the thermochemical properties of the condensed phase is also required. In addition, there are two technical obstacles that limit the applicability of this apparatus to this study: one is the identification of a high temperature non-reactive material for the cell and the other is a lack of control over the oxygen fugacity. While the mass spectrometer can (in principle) be used to directly measure the oxygen fugacity, there is little scope for imposing a fixed fugacity on the atmosphere inside the cell itself. Since all of the elements of interest to this study will be present as oxidised species in the



liquid silicate, yet are most abundant in the vapour phase as reduced species, oxygen fugacity will be a significant factor controlling element volatility.

As a result it was determined that the inability to control oxygen fugacity excluded Knudsen cell effusion mass spectrometry from this study.

### 1.5.2 Direct Volatile Loss

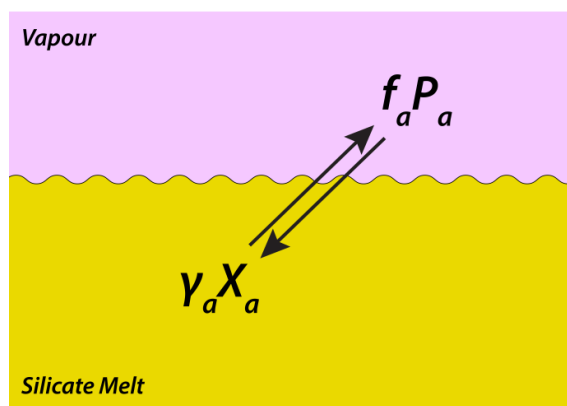
A simpler approach to measuring volatile loss from a condensed phase is to allow vaporisation to proceed under controlled conditions ( $T$ ,  $P$ ,  $f_{O_2}$ ) for some duration of time. To eliminate dependence on diffusion in the melt, a stirring mechanism can be used to ensure a continual turnover of material. At the end of the experiment the composition of the condensed phase can be measured and compared to the starting composition.

This approach has been pursued in this study and is documented in Chapter 5.

### 1.5.3 Metal–Silicate–Vapour Partitioning

Another alternative approach to Knudsen cell mass spectrometry is to consider equilibrium in a silicate–vapour system, as illustrated in Figure 1.2. At equilibrium the partial vapour pressure will depend on the activity of the element in the silicate melt which can be calculated using established thermodynamic relationships [Gibbs 1873a; Gibbs 1873b; Gibbs 1878]. As such, the first objective is to measure the trace element activity coefficients in silicate melt.

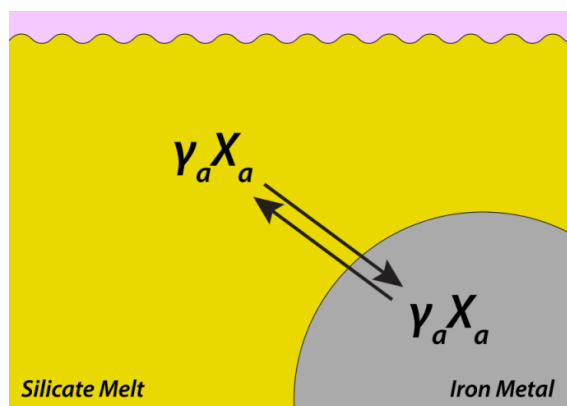
Figure 1.2—Molten Silicate–Vapour Equilibrium



At equilibrium, the fugacity coefficient ( $f_a$ ) and partial pressure ( $P_a$ ) of trace element in the vapour will be determined by the concentration ( $X_a$ ) in the silicate melt as well as the activity coefficient ( $\gamma_a$ ).

Measurement of trace element activity coefficients can be achieved by considering a second equilibrium between silicate melt and a phase with known thermochemical properties. A suitable choice is molten iron metal, since it is immiscible with molten silicate and has been well characterised due to its considerable commercial importance. As such it is well documented in the steelmaking literature. By establishing equilibrium, as depicted in Figure 1.3, between silicate melt and molten iron metal, the activity coefficient in the silicate melt can be determined by measuring the concentration present in each phase.

Figure 1.3—Metal–Silicate Equilibrium



At equilibrium, the chemical potential (not shown) is equal in each phase. This allows the activity coefficient in one phase to be determined provided the concentration ( $X_a$ ) is known in each phase along with the activity coefficient in the other phase. In this study the activity coefficients in iron metal are determined from literature values and used to determine the activity coefficients in the silicate melt.

The exact formalism of this approach is outlined in §1.7 and Chapter 4, but will be based on a series of high pressure experiments to create equilibrium conditions, and accurate analysis of trace element concentrations in both the iron and silicate phases (see Chapters 2 and 3).

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## 1.6 Silicate Melt Activity

Previous studies of crystal-melt partitioning suggest that the generally effective elastic strain model [Blundy and Wood 1994; Wood and Blundy 1997; Blundy and Wood 2003] can deviate from ideal behaviour in some cases [van Westrenen et al 2000].

Such deviation from ideal behaviour may depend on melt composition effects, which previous efforts [Mills 1993] have attempted to explain. Models of trace element activity in silicate melts will provide some insight towards understanding this behaviour and determine whether there exists a strong dependence on melt composition.

### 1.6.1 Previous Measurements of Activity in Silicate Melts

Much work [Campbell *et al.* 1979; Holzheid *et al.* 1994; Holzheid and Palme 1996; Holzheid *et al.* 1997; O'Neill and Eggins 2002; Borisov 2006; Borisov *et al.* 2006; Wood and Wade 2013] has been done to measure trace element activity coefficients in silicate melts. One type of measurement is based on metal saturation. In these experiments a piece of solid iron metal is held in contact with molten silicate at 1 atmosphere, high temperature, and known fixed oxygen fugacity until equilibrium is reached. The combination of melt and metal is quenched and the partitioning of trace elements measured by electron probe microanalysis (EPMA) or laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS). Due to experimental limitations such experiments are typically conducted below the melting point of iron. This approach has only been successfully applied to a small range of elements such as Ni, W, and

Mo, since the more volatile elements are rapidly lost from the experiment in the one-atmosphere furnace.

Performing these metal–silicate equilibrium experiments at high pressure will significantly suppress trace element volatility and should offer considerable improvement on previous measurements.

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## 1.7 The Epsilon Model

Understanding the thermochemical behaviour of liquid iron alloys has been of considerable interest to the steelmaking community [Steelmaking Data Sourcebook 1988] as well as the earth sciences [Wood 1993; Rubie *et al.* 2011]. To compute activity coefficients for trace elements in molten iron alloys an early epsilon model of Wagner [Wagner *et al.* 1952] has been unified by Zhongting [Zhongting 2001] and applied by other workers [Wade and Wood 2005] to understand core formation in the Earth.

Part of this study was the creation of a website (*MetalAct*, <http://earth.ox.ac.uk/~expet/metalact/>) that implements the epsilon model to compute activity coefficients for trace elements in molten iron.

The calculation of Zhongting 2001 is relatively direct, but does depend on known values for activity coefficients and interaction parameters for the major constituents of the alloy.

In this manuscript the activity coefficients are represented for species  $i$  by  $\gamma_i$  and in the text these values are in general (i.e. for any species) referred to as “gamma” and at infinite dilution, “gamma-zero”. The interaction parameters are represented by  $\mathcal{E}_i^j$  which quantifies how much the presence of species  $j$  alters the activity coefficient of species  $i$ ; specifically:  $\mathcal{E}_i^j : X_j \xrightarrow{\text{alters}} \gamma_i$ .

While the interaction parameters are general concepts that apply to any thermodynamic system, the *MetalAct* website only computes activities in molten iron alloys, and for this work the use of carbon-saturated iron in the high pressure experiments results in a focus on the values of  $\mathcal{E}_i^C$  for all of the trace elements in this study.

Values for gamma-zero and interaction-parameters can be found in the literature. Indeed, Boom *et al.* wrote “*More has been published about enthalpies of liquid alloys of iron than of its solid solutions or compounds, which is rather unusual*”.

### 1.7.1 Activity and Activity Coefficients

The activity of a species  $i$  is defined to be:

$$a_i = e^{\frac{\mu_i - \mu_i^\circ}{RT}}$$

Where  $\mu_i$  is the chemical potential of the species  $i$  at the conditions of interest,  $\mu_i^\circ$  is the chemical potential of that species at some defined set of standard conditions,  $R$  is the gas constant,  $T$  is the thermodynamic temperature and  $e$  is the exponential constant. This can also be formulated as:

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

In practice, the activity has the effect of altering the effective composition of the component in the system under consideration. The proportionality constant between activity and actual concentration is called the *activity coefficient*, so with  $X_i$  representing mole fraction we can write:

$$a_i = \gamma_i X_i$$

The activity coefficient depends on the chemical nature of both the solvent and the solute and its magnitude represents a deviation from *ideal mixing* behaviour.

## 1.7.2 The Epsilon Model Calculation

### 1.7.2.1 Preliminary Requirements

The requirement of the epsilon model is to first identify the gamma-zero value, which represents the activity coefficient at infinite dilution in liquid iron.

These values can be found in the literature, with most coming from the *Steelmaking Data Sourcebook* (1988), table 1 on page 278. The *MetalAct* website uses a collection of data files that list the gamma-zero and interaction-parameter values at the reference temperature of 1873K. To convert these to our working temperature  $T \rightarrow T'$  we can use the following expressions ( $T = 1873K$ ):

$$\ln \gamma_i^0(T') = \frac{T}{T'} \ln \gamma_i^0(T) \quad [\text{Eq. 16, p275, Steelmaking Data Sourcebook, 1988}]$$

$$\varepsilon_i^j(T') = \frac{T}{T'} \varepsilon_i^j(T) \quad [\text{Eq. 17, p275, Steelmaking Data Sourcebook, 1988}]$$

### 1.7.2.2 Modelled Gamma-Zero Values

While most gamma-zero values have been experimentally determined, some of the elements of interest to this study are unstable at high temperature, rather toxic, volatile, and mostly insoluble in iron. The Miedema [Miedema *et al* 1980] model is based on the work of [Niessen *et al.* 1983] and applied [Boom 1983] to determine the molar enthalpy of mixing of trace elements in iron. Those authors report good agreement with experimental values, where available, and the Miedema model has withstood considerable scrutiny and review [Colinet *et al.* 1985; Cranshaw 1987; Inaba and Yukawa 1997; Arzpeyma 2011; Arzpeyma *et al.* 2013].

From Arzpeyma's 2013 review paper: “*It is proposed that for systems with no or few experimental thermodynamic property data, a Miedema/Witusiewicz model or Miedema/Hard-Sphere model can be used as thermodynamic property first approximations.*”

A complete treatment of the derivation and calculation of gamma-zero values for the trace elements of interest to this study is presented in Chapter 4.

### 1.7.2.3 Computing the Activity Coefficients

For each sample composition:

1. The composition is converted to mole fraction (if required).
2. The composition is normalised to a total of 1.
3. The  $\ln \gamma_i$  term is computed using Equation [23] from Zhongting 2001:

$$\begin{aligned}
 \ln \gamma_i &= \frac{\Delta G^{\text{ex}}}{RT} - \frac{1}{RT} \sum_{i=2}^N X_i \frac{\partial \Delta G^{\text{ex}}}{\partial X_i} \\
 &= \sum_{i=2}^N \epsilon_i^i (X_i + \ln(1 - X_i)) \\
 &\quad - \sum_{j=2}^{N-1} \sum_{k=j+1}^N \epsilon_j^k X_j X_k \left( 1 + \frac{\ln(1 - X_j)}{X_j} + \frac{\ln(1 - X_k)}{X_k} \right) \\
 &\quad + \sum_{i=2}^N \sum_{\substack{k=2 \\ (k \neq i)}}^N \epsilon_i^k X_i X_k \left( 1 + \frac{\ln(1 - X_k)}{X_k} + \frac{1}{1 - X_i} \right) \\
 &\quad + \frac{1}{2} \sum_{j=2}^{N-1} \sum_{k=j+1}^N \epsilon_j^k X_j^2 X_k^2 \left( \frac{1}{1 - X_j} + \frac{1}{1 - X_k} - 1 \right) \\
 &\quad - \sum_{i=2}^N \sum_{\substack{k=2 \\ (k \neq i)}}^N \epsilon_i^k X_i^2 X_k^2 \left( \frac{1}{1 - X_i} + \frac{1}{1 - X_k} + \frac{X_i}{2(1 - X_i)^2} - 1 \right)
 \end{aligned}$$

4. For each element the  $\ln \gamma_i$  term is computed using Equation [24] from Zhongting 2001:

$$\begin{aligned}
\ln \gamma_i &= \ln \gamma_1 + \frac{1}{RT} \frac{\partial \Delta G^{\text{ex}}}{\partial X_i} \\
&= \ln \gamma_1 + \ln \gamma_i^0 - \varepsilon_i^i \ln(1 - X_i) \\
&\quad - \sum_{\substack{k=2 \\ (k \neq i)}}^N \varepsilon_i^k X_k \left( 1 + \frac{\ln(1 - X_k)}{X_k} - \frac{1}{1 - X_i} \right) \\
&\quad + \sum_{\substack{k=2 \\ (k \neq i)}}^N \varepsilon_i^k X_k^2 X_i \left( \frac{1}{1 - X_i} + \frac{1}{1 - X_k} + \frac{X_i}{2(1 - X_i)^2} - 1 \right)
\end{aligned}$$

5. If desired, the theoretical saturation of carbon is computed using the method described on p604 of Wood 1993 and the computation is then repeated from step (2) using the adjusted composition. Convergence is typically achieved in 4 to 5 iterations.



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## 1.8 Summary

Measuring the trace element activity coefficients in silicate melts can lead to estimation of vapour pressure, and in turn volatility for the trace elements of interest to this study, but knowledge of vaporisation coefficients is required to correctly predict volatile loss. In addition, thermochemical models of the silicate melt, in particular the activities of the trace elements of interest is required.

Volatility of trace elements can offer insight into planetary formation processes and important signature events such as the Moon-forming giant impact.

An epsilon model has been implemented to allow calculation of trace element activities in carbon saturated iron.

To pursue the proposed route of enquiry a series of high pressure metal-silicate partitioning experiments have been performed. To successfully determine the trace element composition of both phases EPMA and LA-ICP-MS have been used for *in situ* sampling of the experimental run products.

The following two chapters (2 and 3) will now be dedicated to introducing the analytical techniques and outlining the methodology employed in this study.

Chapter 4 will contain a thorough treatment of the high pressure experiments and the calculations leading to determination of the trace element activities and dependence, if any, on melt composition.

Chapter 5 outlines the design and construction of a one atmosphere gas mixing stirring furnace and the volatile loss experiments performed to directly measure volatile loss from representative silicate melt at appropriate conditions.

Two key objectives of this project are measurement of trace element activities in silicate melt (see Chapter 4) and evaporation coefficients for the same elements from a representative silicate melt (see Chapter 5).

Finally, Chapters 6 and 7 apply the experimental data to a range of interesting applications including a possible explanation for the depletion of volatile elements in the bulk Silicate Earth, as well as corroborating the depletion of volatile trace elements in the Moon relative to the BSE.

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## 2 EPMA Analysis of Glass and Metal Samples

### 2.1 Introduction

Electron Probe Micro Analysis (EPMA) [Castaing 1952] of experimental product solid samples was performed using the Jeol JXA-8600 electron probe situated at Oxford University department of Archaeology (RLAHA)<sup>3</sup>. The use of EPMA is well established in the Earth sciences [Potts *et al.* 2012] and with care this technique can routinely achieve results with both precision and accuracy to within 2%. In practice, provided the instrument is operating correctly and the background subtraction is adequate, then the dominating limiting factors are uncertainty in the composition of the standard, and uncertainty in the matrix correction routine. Furthermore, in some materials there can be complications arising from secondary fluorescence, where characteristic X-Rays from the excitation volume under the beam, travel up to tens of microns through the material to excite a nearby phase of contrasting composition. Because of these general issues it is determined for the purpose of this study that EPMA data are accurate to within 2-5%.

The microprobe analysis undertaken in this project has fallen into three broad categories: analysis of major elements in homogenous CMAS+Fe glass, analysis of major elements in dendritic crystal quench textures in a glass matrix, and analysis of trace elements in iron, complicated by the presence of blebs enriched in the trace elements of interest.

The rest of this chapter introduces the analytical conditions employed, as well as a discussion of complications and issues surrounding the specific analysis of each material type.

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<sup>3</sup> “Research Laboratory for Archaeology & the History of Art”, <http://www.arch.ox.ac.uk/rlaha.html>, retrieved 2016-08-22

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## 2.2 EPMA Analysis of Homogenous CMAS+Fe Glass

Analysis of homogenous CMAS+Fe glasses for major elements by EPMA is relatively trivial to achieve provided best practices are followed and appropriate standards are available for calibration. To avoid any selective bias, points were allocated uniformly along linear transects, placed at random by this study's author on the featureless surface of the glass. Any visible "flecks" or "blebs" of material, either present in the glass, or embedded during sample preparation, were avoided when programming transects. Analytical conditions were: accelerating voltage of 15kV, beam current of 10nA, and beam size of 5 $\mu$ m. The per-element conditions are summarised below in Table 2.1.

**Table 2.1—Glass Analytical Conditions**

| Element | Line       | Crystal | Standard                                      | Peak Time (s) | BG <sup>a</sup> Time (s) x 2 | BG Fit | BG1 (mm) | BG2 (mm) |
|---------|------------|---------|-----------------------------------------------|---------------|------------------------------|--------|----------|----------|
| Al      | K $\alpha$ | TAP     | Jadeite (NaAlSi <sub>3</sub> O <sub>6</sub> ) | 30            | 15                           | Linear | -0.40    | 0.40     |
| Ca      | K $\alpha$ | PET     | Wollastonite (CaSiO <sub>3</sub> )            | 60            | 30                           | Linear | -0.90    | 0.50     |
| Fe      | K $\alpha$ | LIF     | Hematite (Fe <sub>2</sub> O <sub>3</sub> )    | 60            | 30                           | Linear | -4.00    | 2.00     |
| Mg      | K $\alpha$ | TAP     | Periclase (MgO)                               | 30            | 15                           | Linear | -1.20    | 0.60     |
| Si      | K $\alpha$ | TAP     | Wollastonite (CaSiO <sub>3</sub> )            | 60            | 30                           | Linear | 0.50     | 2.50     |

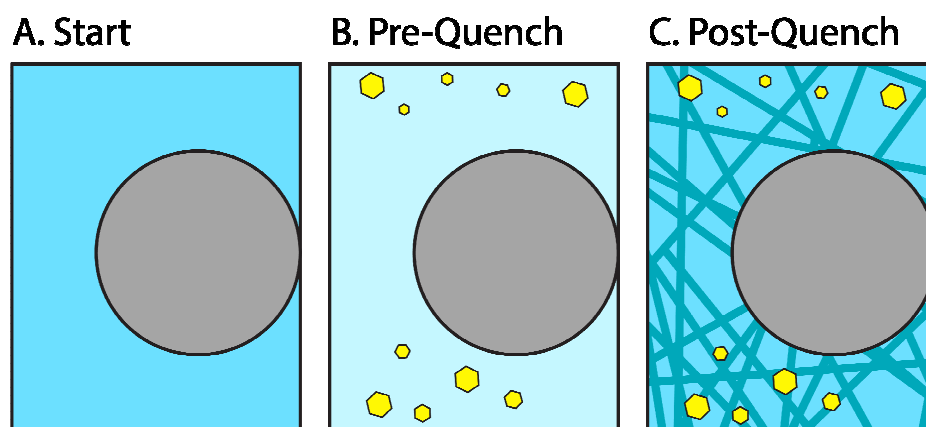
<sup>a</sup>BG=Background

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## 2.3 EPMA Analysis of Dendritic Quench Textures

Experimental samples close to crystal solidus compositions can quench to a fine dendritic texture of crystals in a glass matrix. This is shown schematically in Figure 2.1. To robustly interpret such quench textures, the analytical objective is to recover the major element composition of the original melt at the temperature and pressure of the experiment prior to formation of the quench texture (i.e. the "pre-quench" matrix in Fig 2.1).

Figure 2.1—Quench Texture Formation Schematic



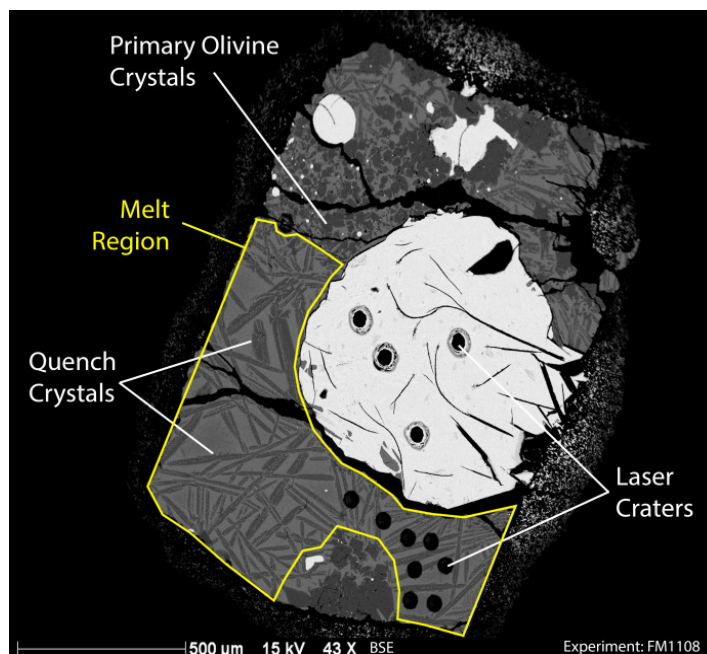
Cartoon showing the three stages of quench crystal formation during a high pressure experiment. At the start of the experiment (A) the material is separated into two immiscible phases. During the experiment some crystal phases may be stabilised at the conditions and primary crystals will slowly grow (B). On quenching the metastable melt forms dendritic quench textures of 2 phases throughout the melt region. The analytical objective of this study is to recreate the composition of the melt in (B) using the texture in (C) while ignoring the loss of material to the primary crystals.

In general, if the two phases present large and well-separate surface areas for analysis, they could be analysed separately, their modal proportions assessed by image analysis, and the bulk composition determined via weighted means. Such a direct approach is not possible for the samples encountered in this study as the quench textures are very finely grained, presenting in some cases a delicate and intimate intergrowth on the scale of tens of nm (see Figures 2.2 and 2.3).

Accepted practice would be to defocus the beam (by up to 20 or even 50  $\mu\text{m}$ ) and allow the larger interaction volume to “average out” the sample composition. This approach violates one of the fundamental assumptions of the EPMA matrix correction, that the sample is assumed to be homogenous, and as such will affect the accuracy of the results. Defocussing also raises the question of what beam size to defocus to, which must depend on the heterogeneity in the sample, and most analysts would simply attempt to estimate it by inspection.

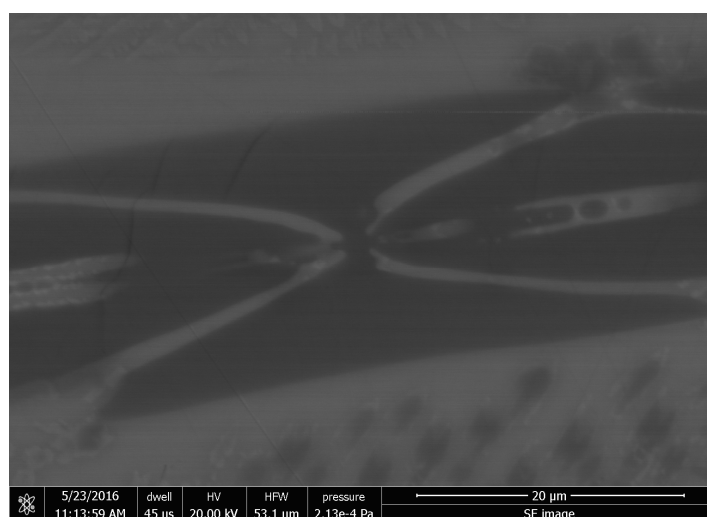
The approach presented here attempts to provide a more rigorous set of constraints on both the accuracy that can be achieved, and the number of points (time) required to achieve that accuracy.

Figure 2.2—Typical Sample Showing Quench Texture



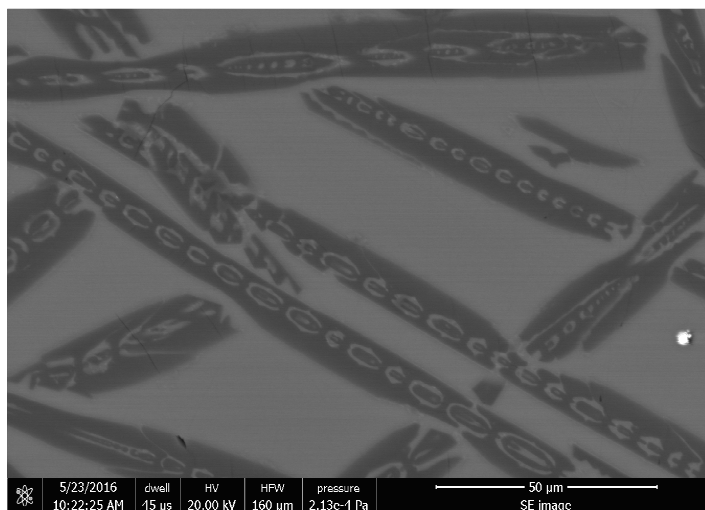
An SEM BSE image of high pressure experiment FM1108 showing a large melt region characterised by extensive dendritic quench texture.

Figure 2.3a—High Resolution BSE Images of Quench Textures



An SEM BSE image of high pressure experiment FM1108 showing a highly magnified region of the dendritic quench texture. The dark phase is an iron-depleted crystal assemblage, while the lighter regions are glass.

Figure 2.3b—High Resolution BSE Images of Quench Textures



An SEM BSE image of high pressure experiment FM1108 showing the dendritic quench texture at medium magnification.

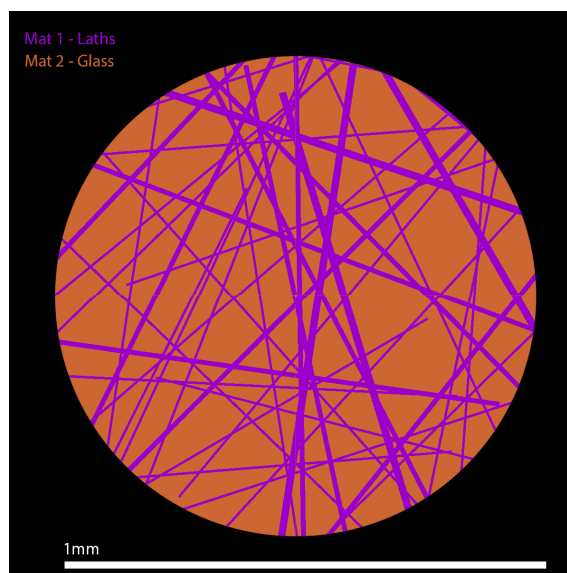
### 2.3.1 PENEPMA Simulations

The PENEPMA 2014 code [Llovet 2006; Llovet and Salvat 2016] is a modified version of PENELOPE [Acosta *et al.* 2001] optimised to simulate electron-atom interactions. The PENEPMA code generates X-Ray spectra equivalent to those measured using EMPA. It has been successfully applied to the interpretation of EPMA analysis [Firouzdor 2010; Llovet 2014].

To undertake a statistical analysis of this dendritic quench texture a synthetic sample was prepared (see Figure 2.3) using PENGEO and a grid of 100 PENEPMA simulations placed uniformly on a 250 x 250 μm grid in the centre of the sample. The thinnest laths are 5 μm, and the thickest 20 μm, across. Modal analysis of the surface was performed using ImageJ [Abràmoff *et al.* 2004] which identified that 71.1% of the surface is glass and 28.9% of the surface is lath. Because all laths are rectangular prisms that extend from the surface to the bottom of the sample block, the modal surface proportions also represent the bulk volume proportions of the two phases. A summary of the sample compositions, including the bulk

composition derived from the modal analysis, is shown in Table 2.2. Of particular importance is the analysed bulk composition, which was determined by simulating a homogenous sample of the bulk composition. The differences in the analysed composition are due to the limitations of the matrix correction. However, it should be noted that all elements are within 1% of their true values, except for MgO which is low by 2% relative.

Figure 2.4—PENEPMMA Simulated Quench-Texture



A rendering of the material geometry file used in PENEPMMA to simulate the dendritic quench textures of interest to this study. The main body is a cylinder 1mm in diameter, intersected by a random arrangement of crystal laths 5, 10, and 20  $\mu\text{m}$  wide. The laths are rectangular prisms so the volume fractions of the solid are equal to that shown at the surface.

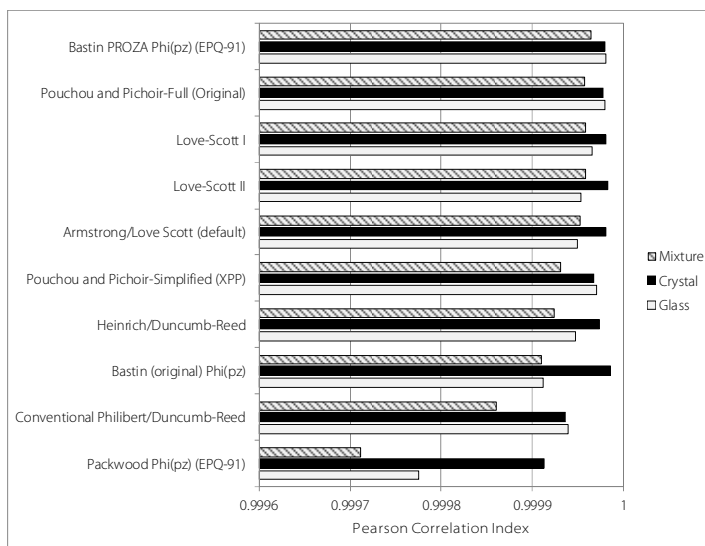
**Table 2.2—PENEPMMA Simulation Sample Compositions**

| Element                 | Glass | Crystal | Mixture |
|-------------------------|-------|---------|---------|
| $\text{Al}_2\text{O}_3$ | 17.0  | 0.0     | 12.1    |
| CaO                     | 22.4  | 0.0     | 15.9    |
| FeO                     | 15.4  | 10.0    | 13.9    |
| MgO                     | 13.3  | 50.0    | 23.9    |
| $\text{SiO}_2$          | 32.1  | 40.0    | 34.4    |
| Total                   | 100.2 | 100.0   | 100.1   |

All concentrations in  $\mu\text{g.g}^{-1}$



Figure 2.5—Assessment of Matrix Correction Routine by Pearson Correlation



PENEPMA simulations were performed on three homogenous materials comprising the three compositions shown in Table 2.2. A series of PENEPMA calibration simulations were also performed and used to compute the material composition using CalcZAF. Compositions were computed using all of the available matrix routines and the Pearson correlation index computed to determine the routine that produced the closest match to the known sample compositions. In this case it was the Bastin PROZA routine.

Table 2.3—Magnitude of Matrix Correction Uncertainty

| Element                        | Simulated Glass |          |                | Simulated Crystal |          |                | Simulated Homogenous Mixture |          |                |
|--------------------------------|-----------------|----------|----------------|-------------------|----------|----------------|------------------------------|----------|----------------|
|                                | Composition     | Analysed | Difference (%) | Composition       | Analysed | Difference (%) | Composition                  | Analysed | Difference (%) |
| Al <sub>2</sub> O <sub>3</sub> | 17.0            | 17.3     | +1.9           | 0.0               | 0.0      |                | 12.1                         | 12.4     | +2.4           |
| CaO                            | 22.4            | 22.5     | +0.7           | 0.0               | 0.0      |                | 15.9                         | 16.1     | +1.1           |
| FeO                            | 15.4            | 15.5     | +0.5           | 10.0              | 10.2     | +2.0           | 13.9                         | 14.0     | +1.0           |
| MgO                            | 13.3            | 13.2     | -0.3           | 50.0              | 49.6     | -0.8           | 23.9                         | 23.7     | -0.6           |
| SiO <sub>2</sub>               | 32.1            | 32.2     | +0.2           | 40.0              | 40.1     | +0.1           | 34.4                         | 34.5     | +0.4           |
| Total                          | 100.2           | 100.8    | +0.6           | 100.0             | 99.9     | -0.1           | 100.1                        | 100.7    | +0.6           |

All concentrations in  $\mu\text{g g}^{-1}$ ; Matrix correction Bastin PROZA; FFAST MACs

### 2.3.1.1 Simulation Results

The PENEPMA simulation outputs a detector file that lists the intensity of each X-Ray line detected with an associated uncertainty. All simulations were run for sufficient time to produce relative intensity uncertainties below 2% RSD. In practice most simulations achieved 0.5% RSD. In addition to the 100 simulated grid points, commensurate simulations were performed on standard materials and the measured intensities used to compute K-ratio values for each element to be analysed. The standard materials and the elements calibrated on each were: Albite–Al, Si; MgO–Mg; Fayalite–Fe; Wollastonite–Ca. The composition of each simulation was computed using CalcZAF [Armstrong *et al.* 2013] configured to use FFAST MAC tables

and the Bastin PROZA matrix correction routine. A table of simulated compositions is included in the Appendix.

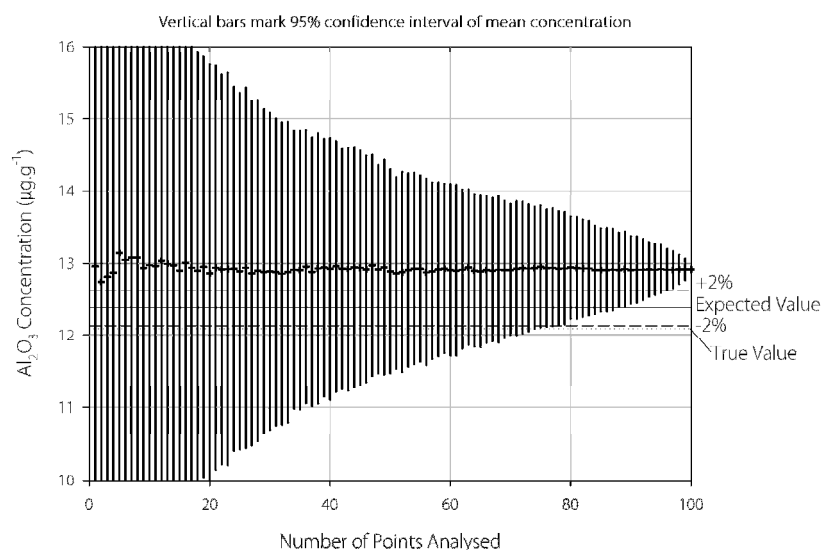
### *2.3.1.2 Statistical Analysis*

The mean of the concentrations can be used to recover the true composition of the bulk sample, provided the number of points is large enough. Assigning an uncertainty to the mean is problematic, since the standard deviation of a binary distribution is dominated by the separation of the two populations and does not decrease as the number of points is increased. Alternatively the standard error in the mean can be used, since this value will decrease as the number of analysis points increases. However, the standard error in the mean will continue to decrease indefinitely, eventually providing an unfeasibly small uncertainty. The analyst must determine at what point the standard error in the mean has started to under estimate the analytical uncertainty.

To remedy these issues a statistical analysis has been conducted to provide answers to these two fundamental concerns: what is the minimum number of points required for the average to represent the true bulk composition? And, what is the maximum number of points, beyond which the standard error in the mean is artificially too small to be meaningful?

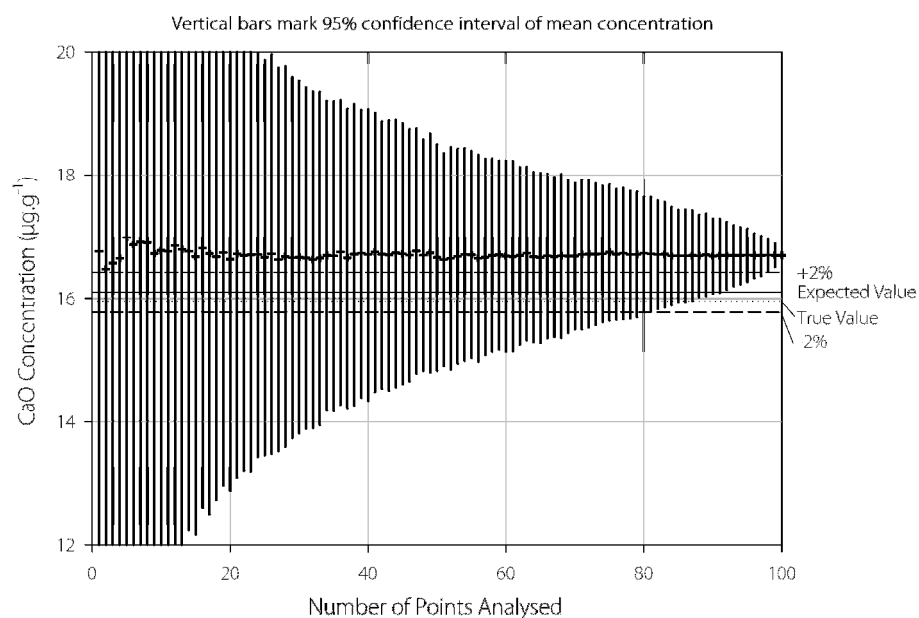
A statistical bootstrapping routine was written in PHP to produce random subsets from the 100 simulated points. The size of the subsets was incremented from 1 to 100 and the script repeated the sampling 1000 times to produce a statistical pool at each subset size. The mean and standard deviation was computed for each pool of subsets, as well as the average uncertainty measured in each pool.

Figure 2.6a— $\text{Al}_2\text{O}_3$  Concentration from 100 PENEPMAs Simulations



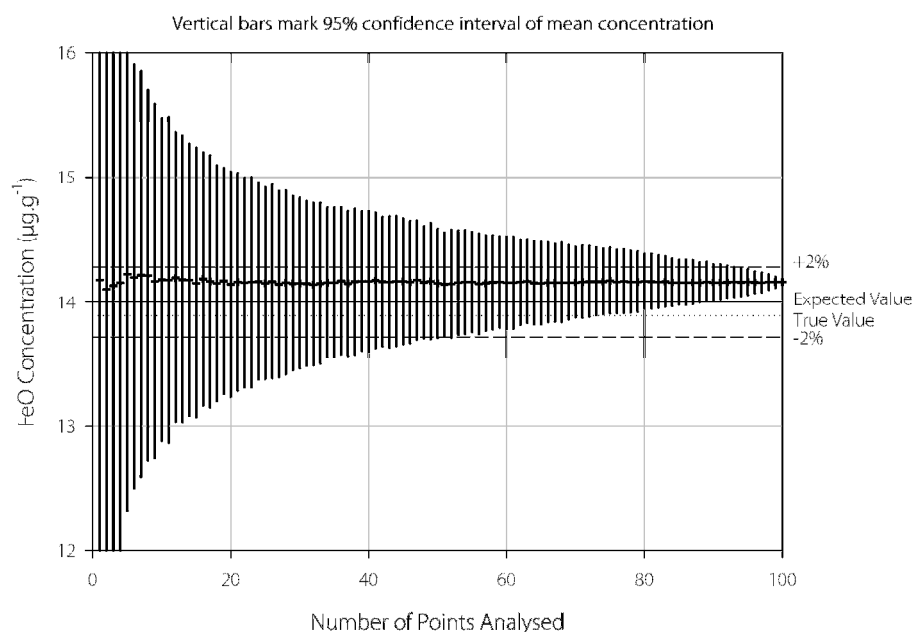
Bootstrapped sample pools of  $\text{Al}_2\text{O}_3$  concentration measured by PENEPMAs simulation of heterogeneous quench textures. The vertical bars show the expected 95% confidence interval by the number of points analysed. The expected value is from a CalcZAF analysis of a homogenous material at the true value concentration.

Figure 2.6b— $\text{CaO}$  Concentration from 100 PENEPMAs Simulations



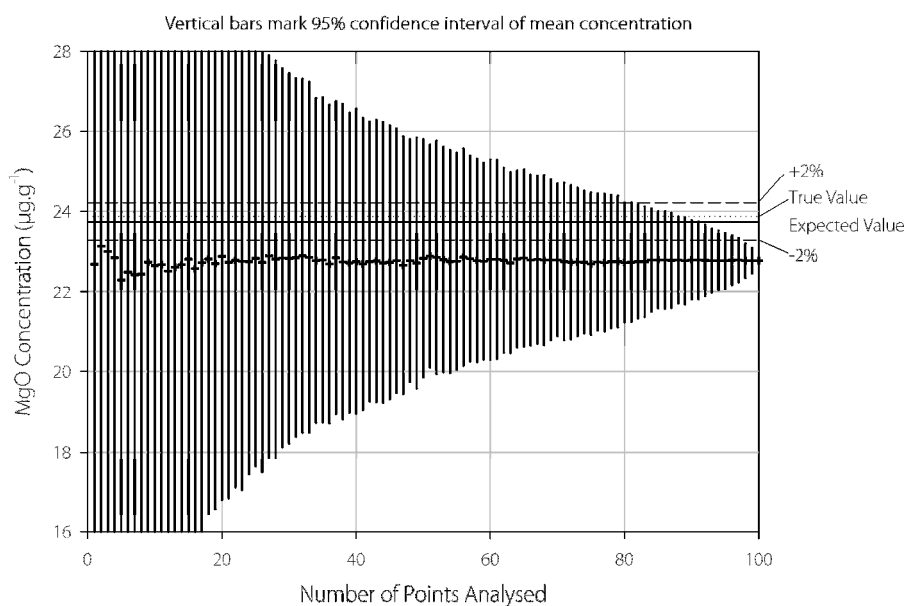
Bootstrapped sample pools of  $\text{CaO}$  concentration measured by PENEPMAs simulation of heterogeneous quench textures. The vertical bars show the expected 95% confidence interval by the number of points analysed. The expected value is from a CalcZAF analysis of a homogenous material at the true value concentration.

Figure 2.6c—FeO Concentration from 100 PENEPMAs Simulations



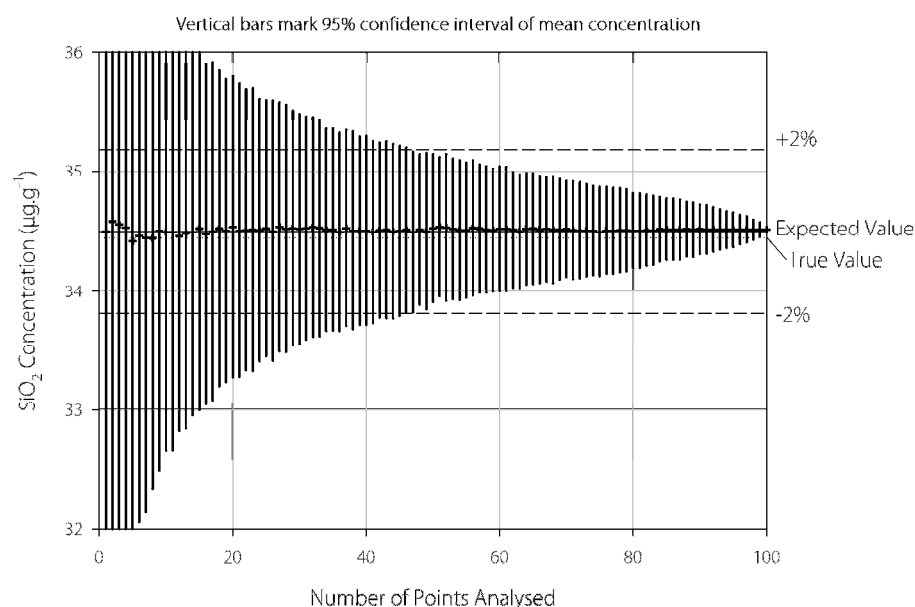
Bootstrapped sample pools of FeO concentration measured by PENEPMAs simulation of heterogeneous quench textures. The vertical bars show the expected 95% confidence interval by the number of points analysed. The expected value is from a CalcZAF analysis of a homogenous material at the true value concentration.

Figure 2.6d—MgO Concentration from 100 PENEPMAs Simulations



Bootstrapped sample pools of MgO concentration measured by PENEPMAs simulation of heterogeneous quench textures. The vertical bars show the expected 95% confidence interval by the number of points analysed. The expected value is from a CalcZAF analysis of a homogenous material at the true value concentration.

Figure 2.6e—SiO<sub>2</sub> Concentration from 100 PENEPMAs Simulations

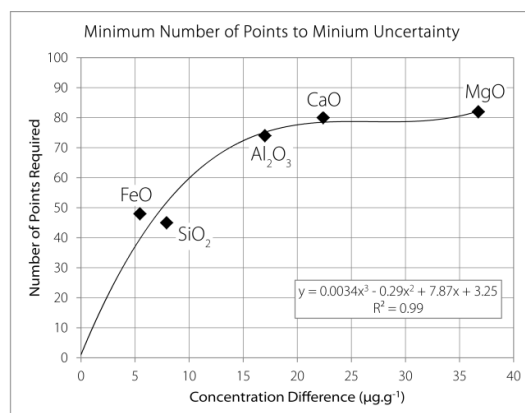


Bootstrapped sample pools of SiO<sub>2</sub> concentration measured by PENEPMAs simulation of heterogeneous quench textures. The vertical bars show the expected 95% confidence interval by the number of points analysed. The expected value is from a CalcZAF analysis of a homogenous material at the true value concentration.

To provide a more accessible interpretation of the bootstrap analysis, Figure 2.7 shows the minimum number of points required to reach the minimum uncertainty for each element in the material. The difference in concentration is determined by the composition of two phases, and as expected, the number of points required trends to zero along with the difference in concentration. The 3<sup>rd</sup> order polynomial has been fitted to guide the eye and provide interpolated values; there is no statistical or physical basis for the 3<sup>rd</sup> order fit.

If the reader encounters a similar quench texture and wishes to ascertain the appropriate number of points to determine the composition, then the fit in Figure 2.7 provides the appropriate guidance. The clear flattening of the curve at N=80 is most likely caused by the limited sample size ( $N_{\max}=100$ ) but may also be caused by the interplay between the sampling statistics and the fundamental reproducibility of the technique.

Figure 2.7—Minimum Number of Points Required to Reach Minimum Uncertainty



Using the bootstrapped statistics for each element the minimum number of points was determined to reach for minimum error for each major element component. This is plotted here against the concentration different between the two phases. There is no justification for the 3<sup>rd</sup> order polynomial fit, except the relationship should collapse to 1 point at 0% concentration difference. The flattening of the trend at N=80 may be due to the number of points (100) in the simulations, or some physical relationship between the spot size and the lath size.

### 2.3.1.3 Implications for Analysis

To effectively analyse these materials the element with the largest difference in concentration between the crystals and the glass determines the number of points required. For these quench textures the value of  $\Delta\text{MgO}=36 \mu\text{g.g}^{-1}$  results in the requirement of at least 80 points. The final minimum uncertainty of the concentration must incorporate both the uncertainty of the sample set as well as the deviation between the analysed composition and the true composition. Since the true composition is unknown for the samples, using the simulations as a guide this study uses an estimated relative uncertainty of  $\pm 5\%$  for each element in the final composition.

## 2.4 EPMA Analysis of Trace Elements in Iron Metal

In this study a number of experimental samples were produced that contained 50 to 5000  $\mu\text{g.g}^{-1}$  of trace elements (see Chapter 3). Quantification of these elements by EPMA requires careful consideration of the host matrix and analytical conditions.

## 2.4.1 Analytical Conditions

To minimise the detection limit for the trace elements of interest the following conditions were used: accelerating voltage 25keV; beam current 300nA; spot size 5 $\mu$ m. The standards and lines for each element are summarised in Table 2.3 below.

**Table 2.5—Trace Element Lines and Standards**

| Element | Crystal | Standard                                                   | Line | Comments                                                                           |
|---------|---------|------------------------------------------------------------|------|------------------------------------------------------------------------------------|
| Ag      | PET     | Ag metal                                                   | La   |                                                                                    |
| Bi      | LIF     | Bi metal                                                   | La   | Bi Ma on PET vs Bi La on LIF at 25keV yields 97 cps/nA vs 270 cps/nA respectively. |
| Cd      | PET     | CdS (77.81% Cd)                                            | La   |                                                                                    |
| Cr      | PET     | Cr metal                                                   | Ka   | Overlap correction for V K $\beta$ .                                               |
| Cu      | LIF     | Cu metal                                                   | Ka   |                                                                                    |
| Ga      | LIF     | Ga metal                                                   | Ka   |                                                                                    |
| Ge      | LIF     | Er <sub>2</sub> Ge <sub>2</sub> O <sub>7</sub> (24.55% Ge) | Ka   |                                                                                    |
| In      | PET     | InSb (48.5% In)                                            | La   |                                                                                    |
| Mo      | PET     | Mo metal                                                   | La   |                                                                                    |
| Pb      | LIF     | PbS (86.6% Pb)                                             | La   | At 25keV, Pb La on LIF shows greater intensity than Pb Ma on PET.                  |
| Sb      | PET     | InSb (51.5% Sb)                                            | La   |                                                                                    |
| Sn      | PET     | Sn metal                                                   | La   |                                                                                    |
| Ti      | LIF     | Ti(Br <sub>2</sub> ) (65.98% Ti)                           | La   | At 25keV, Ti La on LIF shows greater intensity than Ti Ma on PET.                  |
| V       | PET     | V metal                                                    | Ka   |                                                                                    |
| W       | LIF     | W metal                                                    | La   |                                                                                    |
| Zn      | LIF     | Zn metal                                                   | Ka   |                                                                                    |

## 2.4.2 WDS Spectrometer Configuration

Each spectrometer was fitted with a gas-filled proportional counter. The detectors on this microprobe are optimised for counting either high-energy or low-energy X-ray lines. The low-energy counters use P10 gas (10% methane in argon), continuously flowing, at 1atm, with a thin Mylar window. The high-energy counters are sealed with 3atm of xenon and a beryllium window. The spectrometer configuration is outlined in Table 2.6 below.

**Table 2.6—Spectrometer Configuration**

| Spectrometer | Crystal | <sup>a</sup> Secondary Crystal | Counter Gas    | Gas Pressure (atm) | Counter Window |
|--------------|---------|--------------------------------|----------------|--------------------|----------------|
| SP1          | TAP     | LDE                            | P10 / Flow     | 1                  | Mylar          |
| SP2          | TAP     | STE                            | P10 / Flow     | 1                  | Mylar          |
| SP3          | PET     | LIF                            | Xenon / Sealed | 3                  | Beryllium      |
| SP4          | LIF     | PET                            | Xenon / Sealed | 3                  | Beryllium      |

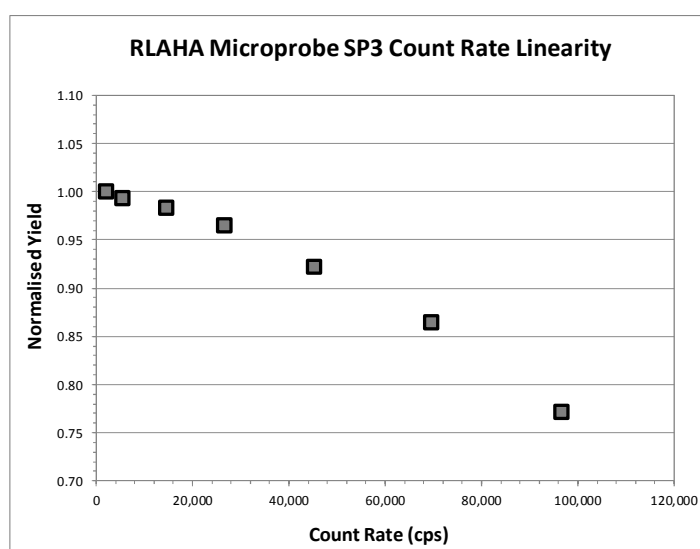
<sup>a</sup>Not used in this study

### 2.4.2.1 Counter Dead Time—Detector Linearity

The sealed xenon proportional counters on SP3 and SP4 are old and their dead-time correction factors are unknown. To ensure that the counter does not become saturated during calibration,

a linearity test was performed to establish the maximum usable count rate. The Cd L $\alpha$  line was measured using the sealed xenon counter on SP3, on a CdS standard at a range of beam currents from 4nA to 220nA. The yield, normalised to the value measured using the lowest beam current, is plotted in Figure 2.8 which shows how the effective yield drops at high count rates due to saturation of the detector. For all work performed using this instrument, count rates on SP3 and SP4 were kept below 20,000 cps.

Figure 2.8—Assessment of Detector Linearity



Sealed xenon proportional counter linearity, on SP3 PET, Cd L $\alpha$ , CdS standard, measured at beam currents from 4nA to 220nA. The yield is lower at higher count rates, possibly due to low xenon pressure in the counter. For analysis using sealed xenon counters on this instrument, the count rate was always kept below 20,000 cps.

#### 2.4.2.2 PHA Table

The pulse height analyser (PHA) settings on the electron probe were carefully adjusted for the energy of each line analysed. The approach of Paul Carpenter (Workshop 2010, [http://epmalab.uoregon.edu/Workshop2010/Presentations/Carpenter\\_Oregon\\_Workshop\\_2010.pdf](http://epmalab.uoregon.edu/Workshop2010/Presentations/Carpenter_Oregon_Workshop_2010.pdf)) was followed: the gain was set to 16, 32, 64, or 128 (depending on X-ray energy) and then the bias adjusted to give a well-shaped peak in the middle of the voltage range, located around 4V, with the escape peak (if present) below the blind value. The PHA was set to integral mode



for all heavy lines, and differential mode (with appropriate voltage window) for lighter lines that may be subject to high-order interferences. A summary of the PHA settings used for all elements investigated over the course of this project are shown in Table 2.6 below.

**Table 2.7—PHA Settings**

| Element | Line       | Spectrometer | Crystal | Bias | Gain | Mode | Blind | Window |
|---------|------------|--------------|---------|------|------|------|-------|--------|
| Ag      | L $\alpha$ | SP3          | PET     | 1790 | 64   | Int  | 1000  | 10000  |
| Al      | K $\alpha$ | SP2          | TAP     | 1720 | 32   | Diff | 2000  | 4000   |
| Bi      | L $\alpha$ | SP4          | LIF     | 1735 | 32   | Int  | 1000  | 10000  |
| Ca      | K $\alpha$ | SP3          | PET     | 1840 | 32   | Int  | 2000  | 10000  |
| Cd      | L $\alpha$ | SP3          | PET     | 1790 | 64   | Int  | 1000  | 10000  |
| Co      | K $\alpha$ | SP4          | LIF     | 1840 | 32   | Int  | 1000  | 10000  |
| Cr      | K $\alpha$ | SP3          | PET     | 1830 | 32   | Int  | 2000  | 10000  |
| Cu      | K $\alpha$ | SP4          | LIF     | 1750 | 32   | int  | 2000  | 10000  |
| Fe      | K $\alpha$ | SP4          | LIF     | 1840 | 32   | Int  | 1000  | 10000  |
| Ga      | K $\alpha$ | SP4          | LIF     | 1770 | 32   | Int  | 1000  | 10000  |
| Ge      | K $\alpha$ | SP4          | LIF     | 1770 | 32   | Int  | 1000  | 10000  |
| In      | L $\alpha$ | SP3          | PET     | 1790 | 64   | Int  | 1000  | 10000  |
| K       | K $\alpha$ | SP3          | PET     | 1840 | 32   | Int  | 2000  | 10000  |
| Mg      | K $\alpha$ | SP1          | TAP     | 1735 | 32   | Diff | 2000  | 4000   |
| Mn      | K $\alpha$ | SP4          | LIF     | 1810 | 32   | Int  | 2000  | 10000  |
| Mo      | L $\alpha$ | SP3          | PET     | 1800 | 64   | Int  | 2000  | 10000  |
| Na      | K $\alpha$ | SP1          | TAP     | 1685 | 64   | Diff | 2000  | 4000   |
| Ni      | K $\alpha$ | SP4          | LIF     | 1760 | 32   | Int  | 2000  | 1000   |
| Pb      | L $\alpha$ | SP4          | LIF     | 1730 | 32   | Int  | 1000  | 10000  |
| Pb      | Ma         | SP3          | PET     | 1800 | 64   | Diff | 2000  | 4000   |
| S       | K $\alpha$ | SP3          | PET     | 1800 | 64   | Diff | 2000  | 4000   |
| Sb      | L $\alpha$ | SP3          | PET     | 1770 | 64   | int  | 1000  | 10000  |
| Si      | K $\alpha$ | SP2          | TAP     | 1710 | 32   | Diff | 2000  | 4000   |
| Sn      | L $\alpha$ | SP3          | PET     | 1775 | 64   | Int  | 1000  | 10000  |
| Ti      | K $\alpha$ | SP3          | PET     | 1830 | 32   | Int  | 2000  | 10000  |
| Ti      | K $\alpha$ | SP3          | PET     | 1830 | 32   | Int  | 2000  | 10000  |
| Ti      | K $\beta$  | SP3          | PET     | 1830 | 32   | Int  | 2000  | 10000  |
| Tl      | L $\alpha$ | SP4          | LIF     | 1750 | 32   | int  | 2000  | 10000  |
| V       | K $\alpha$ | SP3          | PET     | 1830 | 32   | Int  | 2000  | 10000  |
| V       | K $\beta$  | SP3          | PET     | 1830 | 32   | Int  | 2000  | 10000  |
| W       | L $\alpha$ | SP4          | LIF     | 1745 | 32   | Int  | 2000  | 10000  |
| W       | Ma         | SP1          | TAP     | 1680 | 32   | Diff | 1800  | 2000   |
| Zn      | K $\alpha$ | SP4          | LIF     | 1750 | 32   | Int  | 2000  | 10000  |

### 2.4.3 Line Selection and Interferences

Virtual WDS [Reed and Buckley 1996] has been used to choose lines, assess interferences and to select background positions. The program was configured for a JEOL microprobe<sup>4</sup> and the nominal matrix entered as 100 atoms of iron to 1 atom for each of the trace elements. Other

<sup>4</sup> Roland circle = 140mm; xenon counters.

elements present in the calibration standards and possibly present in the samples as contaminants were also included, which included: S, Si, I and Br.

The net intensity (both measured and using Virtual WDS) of the heavy element (Pb, Tl, and Bi)  $M\alpha$  lines on TAP were compared against the  $La$  lines on LIF. Perhaps surprisingly, at 25keV a greater peak-background count rate was measured with the  $La$  lines and for this reason they have been used for analysis in this study. This may be a peculiarity of the old TAP crystals on this instrument, as in general the Pb, Tl, and Bi  $M$  lines would provide superior peak to background ratios.

#### 2.4.3.1 *Ti–V–Cr*

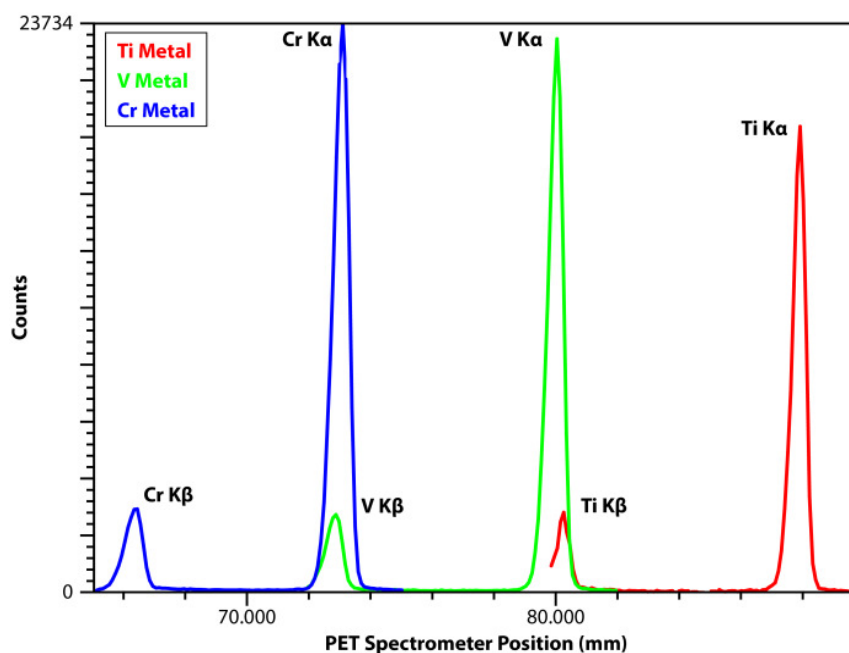
The transition-row metals present a well-known set of interferences where the  $K\beta$  line from the lighter element overlaps the  $K\alpha$  line of the heavier element. The higher-resolution of the LIF crystal allows these overlaps to be resolved, however the range of most spectrometers only extends the LIF crystal down to Mn  $K\alpha$ , while analysis of the lighter transition metals requires that the PET must be used and an overlap correction made. Figure 2.8a shows the overlaps on the elements of interest on the PET crystal, while the Fe and Co lines are already well resolved on the LIF crystal, as shown in Figure 2.8b. Quantification of the magnitude of the overlaps on the SP3 PET crystal is shown in Table 2.4 below, and amounts to 7.7% of Ti  $K\beta$  on V  $K\alpha$  and 8.1% of V  $K\beta$  on Cr  $K\alpha$ .

**Table 2.8—Ti, V, and Cr Overlap Ratios**

| Interference               | Peak Counts                     | Interference Counts           | Interference Percentage |
|----------------------------|---------------------------------|-------------------------------|-------------------------|
| Ti $K\beta$ on V $K\alpha$ | V $K\alpha$ on V metal: 23023   | V $K\alpha$ on Ti metal: 1774 | 7.7%                    |
| V $K\beta$ on Cr $K\alpha$ | Cr $K\alpha$ on Cr metal: 23735 | Cr $K\alpha$ on V metal: 1932 | 8.1%                    |

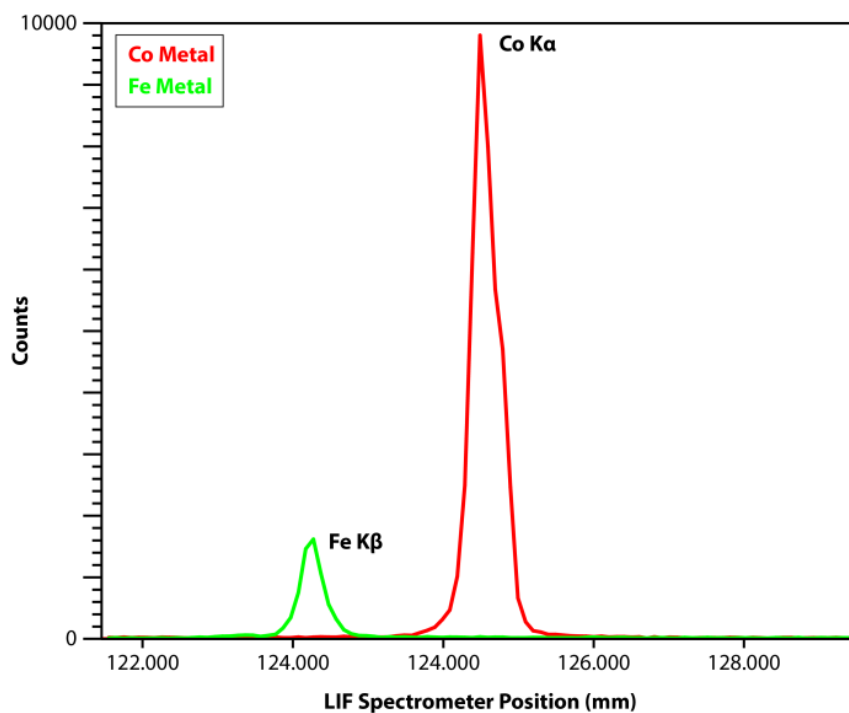
*15kV; 20s counting time; 10nA beam*

Figure 2.11a—Transition Row Elements on PET



A combined plot of X-ray intensities collected on Cr, V, and Ti metal using the same beam conditions with the PET analysing crystal. The chart clearly shows the overlap of Ti on V, and V on Cr. Overlap corrects are required when analysing for these elements.

Figure 2.11b—Transition Row Elements on LIF

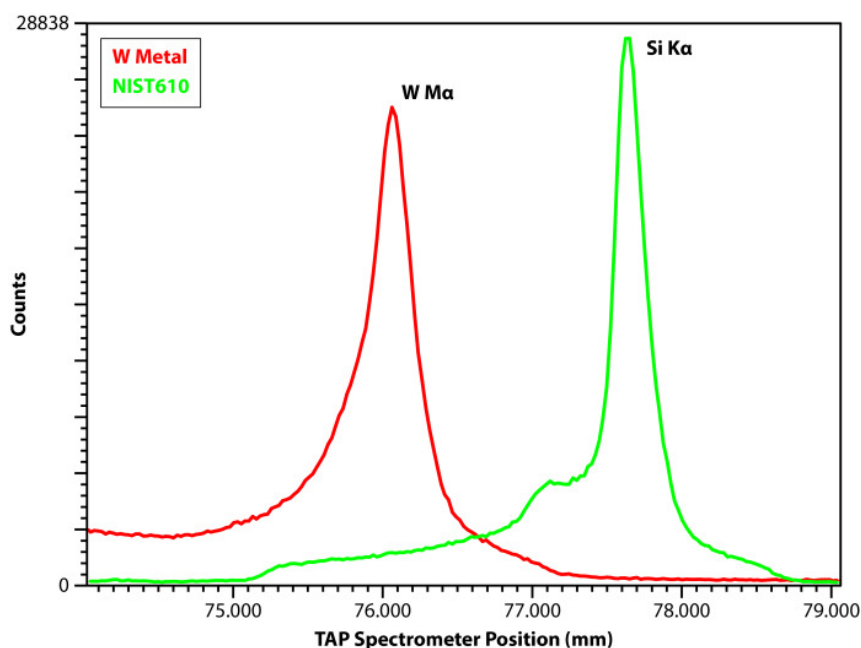


A combined plot of X-ray intensities collected on Co and Fe metal using the same beam conditions with the LIF analysing crystal. The chart clearly shows the separation between the Fe and Co peaks, principally due to the higher resolution of LIF compared to PET. When analysing for Co it is not necessary to perform an overlap correction, however the backgrounds must be carefully placed.

### 2.4.3.2 W–Si

Silicon shows moderately siderophile behaviour and the metal phase in these experimental materials could contain up to a few weight percent, though the exact concentration is not significant. Certified values for the reference material show up to 0.4% silicon: SRM1262b at 0.40%, SRM152A at 0.202%, and SRM65d at 0.370%. As such the location of the Si K $\alpha$  close to the W M $\alpha$  must be investigated. Figure 2.9 shows wave scans on the TAP crystal on W metal and the NIST610. While the peak positions are close, they are sufficiently separate that no overlap correction is required.

Figure 2.12—Tungsten and Silicon on TAP



A combined plot of X-ray intensities collected on W metal and SiO<sub>2</sub> using the same beam conditions with the TAP analysing crystal. The chart clearly shows the separation between the W and Si peaks, however when analysing for each element in the presence of the other, the backgrounds must be carefully placed.

### 2.4.3.3 Mo–S

The iron samples are notionally free of sulphur, but the reference materials may contain a few hundred  $\mu\text{g.g}^{-1}$ . To avoid any interference issues, the well-known S K $\alpha$  line close to Mo L $\alpha$  was assessed and the Mo backgrounds carefully chosen to avoid the peak.

## 2.4.4 Background Positions

The background positions used for calibration and trace element analysis are shown in Table 2.9. In addition, a complete set of wave scans for each element has been included in the Appendix.

**Table 2.9—Background Position Summary**

| Element | Line       | Crystal | BG1 (mm) | BG2 (mm) | Comments                                                                                                                                                                                            |
|---------|------------|---------|----------|----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Ag      | La         | PET     | -2.05    | 1.65     | Minor lines for Cd, Sn and Ti on both sides.                                                                                                                                                        |
| Bi      | La         | LIF     | -2.2     | 1.2      | Ge K $\beta$ 1 very close on low side. Pb La1 very close on high side.                                                                                                                              |
| Cd      | La         | PET     | -1.4     | 1        | Ag L $\beta$ 1 very close on low side, almost an overlap, but not quite. Fe K $\beta$ 2 <sup>nd</sup> on low side, background pulled in slightly to avoid.                                          |
| Cr      | K $\alpha$ | PET     | -1       | 1        | Overlap correction for V K $\beta$ required, if present in sample.                                                                                                                                  |
| Cu      | K $\alpha$ | LIF     | -0.9     | 0.9      |                                                                                                                                                                                                     |
| Ga      | K $\alpha$ | LIF     | -1.03    | 1.7      | Pb Li very close on high side.                                                                                                                                                                      |
| Ge      | K $\alpha$ | LIF     | -1.7     | 1.05     | W L $\beta$ 2 and L $\beta$ 3 lines overlap. Only attempt quant analysis if W present at trace levels.                                                                                              |
| In      | La         | PET     | -0.55    | 0.65     | Cd L $\beta$ 1 very close on low side. Ag L $\beta$ 2 on low side, and Ag L $\beta$ 3 on high side. Calibrate with -1.200 and +0.840.                                                               |
| Mo      | La         | PET     | -1.8     | 3        | S K $\alpha$ very close on low side. Ti Ma very close on right side.                                                                                                                                |
| Pb      | La         | LIF     | -1       | 1.3      | Bi La on low side. Ti La on high side.                                                                                                                                                              |
| Sb      | La         | PET     | -1       | 0.7      | Fe K $\beta$ 2 <sup>nd</sup> order close on high side. Sn L $\beta$ 1 close on low side. In L $\beta$ 3 and L $\beta$ 4 on high side. Cd L $\beta$ 2 on high side. Calibrate with 1.000 and +1.600. |
| Sn      | La         | PET     | -0.7     | 0.7      | In L $\beta$ 1 very close on low side. Cd L $\beta$ 3 on high side. Calibrate with -1.100 and +1.100.                                                                                               |
| Ti      | K $\alpha$ | PET     | -0.95    | 0.65     | Minor lines of Ge, Sb, Cu, and Sn, on either side of peak. Backgrounds should avoid these. Calibrate with -1.000 and +1.000.                                                                        |
| Tl      | La         | LIF     | -1       | 1.5      | Pb La on low side.                                                                                                                                                                                  |
| V       | K $\alpha$ | PET     | -1       | 1        | Overlap correction for Ti K $\beta$ required, if present in sample.                                                                                                                                 |
| W       | La         | LIF     | -1.5     | 1.5      |                                                                                                                                                                                                     |
| Zn      | K $\alpha$ | LIF     | -1.8     | 1.15     |                                                                                                                                                                                                     |

### 2.4.4.1 Cameca Background Positions

Some of these analytical results were verified using the Cameca SX5 electron probe installed in the University of Oxford, Department of Earth Sciences. To do so the background positions have been converted to the Cameca ( $\sin(\theta) \times 10^5$ ) positioning units via Bragg's law [Bragg and Bragg 1913] and the Jeol spectrometer position formula provided in the Jeol microprobe documentation:  $L$  is the spectrometer position in mm,  $R$  is the diameter of the Rowland

Circle in mm,  $d$  is the analysing crystal lattice spacing in the same units as the wavelength  $\lambda$ , and  $n$  is the order of the diffraction.

$$2d \sin \theta = n\lambda \quad (\text{Bragg's Law})$$

$$L = \frac{2R}{2d} \cdot n\lambda \quad (\text{Jeol Position Formula})$$

If converting positions with the same crystal spacing then the conversion is simplified to the following expression:

$$\sin \theta = \frac{n\lambda}{2d} = \frac{L}{2R}$$

To compute the Cameca spectrometer positions the Jeol instrument Rowland circle radius is 140mm, and the crystal lattice spacing values are: LIF  $d=2.0133\text{\AA}$ , and PET  $d=4.3710\text{\AA}$ .

For clarity the Cameca positions have been rounded to the nearest multiple of ten in Table 2.10.

**Table 2.10—Cameca Spectrometer Positions**

| Element   | Crystal    | Line      | Jeol Position (mm) | BG1 (mm)      | BG2 (mm)     | Cameca Position | BG1         | BG2        |
|-----------|------------|-----------|--------------------|---------------|--------------|-----------------|-------------|------------|
| Ag        | PET        | La        | 133.066            | -2.050        | 1.650        | 47523           | -730        | 420        |
| Bi        | LIF        | La        | 79.541             | -2.200        | 1.200        | 28408           | -790        | 430        |
| Cd        | PET        | La        | 126.721            | -1.400        | 1.000        | 45258           | -500        | 360        |
| Cr        | PET        | Ka        | 73.339             | -1.000        | 1.000        | 26193           | -360        | 360        |
| Cu        | LIF        | Ka        | 107.126            | -0.900        | 0.900        | 38259           | -320        | 320        |
| Ga        | LIF        | Ka        | 93.185             | -1.030        | 1.700        | 33280           | -370        | 610        |
| Ge        | LIF        | Ka        | 87.203             | -1.700        | 1.050        | 31144           | -610        | 380        |
| In        | PET        | La        | 120.814            | -0.550        | 0.650        | 43148           | -200        | 230        |
| <i>In</i> | <i>PET</i> | <i>La</i> | <i>120.814</i>     | <i>-1.200</i> | <i>0.840</i> | <i>43148</i>    | <i>-430</i> | <i>300</i> |
| Mo        | PET        | La        | 173.171            | -1.800        | 3.000        | 61847           | -640        | 1070       |
| Pb        | LIF        | La        | 81.707             | -1.000        | 1.300        | 29181           | -360        | 460        |
| Sb        | PET        | La        | 110.164            | -1.000        | 1.600        | 39344           | -360        | 250        |
| <i>Sb</i> | <i>PET</i> | <i>La</i> | <i>110.164</i>     | <i>-1.000</i> | <i>1.000</i> | <i>39344</i>    | <i>-360</i> | <i>570</i> |
| Sn        | PET        | La        | 115.305            | -0.700        | 0.700        | 41180           | -250        | 250        |
| <i>Sn</i> | <i>PET</i> | <i>La</i> | <i>115.305</i>     | <i>-1.100</i> | <i>1.100</i> | <i>41180</i>    | <i>-390</i> | <i>390</i> |
| Ti        | PET        | Ka        | 88.034             | -0.950        | 0.650        | 31441           | -340        | 230        |
| <i>Ti</i> | <i>PET</i> | <i>Ka</i> | <i>88.034</i>      | <i>-1.000</i> | <i>1.000</i> | <i>31441</i>    | <i>-360</i> | <i>360</i> |
| Tl        | LIF        | La        | 83.958             | -1.000        | 1.500        | 29985           | -360        | 540        |
| V         | PET        | Ka        | 80.188             | -1.000        | 1.000        | 28639           | -360        | 360        |
| W         | LIF        | La        | 102.664            | -1.500        | 1.500        | 36666           | -540        | 540        |
| Zn        | LIF        | Ka        | 99.796             | -1.800        | 1.150        | 35641           | -640        | 410        |

*Duplicate rows in oblique indicate the recommended positions for calibration on pure element standards.*

## 2.4.5 Detection Limits

The detection limit computed and reported in the SAMX software is a modified form of the expression from Potts *et al.* 2012, *Microprobe techniques in the Earth Sciences*, and is reproduced here:

$$C_{\text{lim}} = \frac{C_t}{I_t - B_t} \times F \times 3\sqrt{2} \times \sqrt{\frac{B_e}{t_e}} \quad (\text{Equation 2.1})$$

The terms in this expression are outlined in Table 2.11.

**Table 2.11—Detection Limit Terms**

| Term          | Description                                                             | Units           |
|---------------|-------------------------------------------------------------------------|-----------------|
| $\text{bc}_e$ | Beam current on the sample                                              | nanoamps        |
| $\text{bc}_t$ | Beam current on the standard                                            | nanoamps        |
| $C_e$         | Concentration of element in the sample                                  | weight percent  |
| $C_t$         | Concentration of element in the standard                                | weight percent  |
| $F$           | Correction factor $F = C_e / K$                                         | weight percent  |
| $t_e$         | Counting time on the sample peak                                        | seconds         |
| $B_e$         | Intensity of background in the sample                                   | counts / second |
| $B_t$         | Intensity of background in the standard                                 | counts / second |
| $I_e$         | Intensity of peak in the sample                                         | counts / second |
| $I_t$         | Intensity of peak in the standard                                       | counts / second |
| $K$           | K-ratio $K = ((I_e - B_e) / \text{bc}_e) / ((I_t - B_t) / \text{bc}_t)$ | unit less ratio |

### 2.4.5.1 Optimisation of Detection Limits

From Equation 2.1 it can be seen that maximising the counting time on the sample will result in minimising the detection limit. However, due to the square root denominator term, there is a limited return from counting for an extended period. Ultimately the noise-floor of the system itself will eventually dominate and the standard deviation on the background will grow and raise the detection limit.

Typical detection limits achieved on this microprobe are summarised in Table 2.6. These counting times are prohibitive (30 minutes total per point) and it is clear that an alternative technique such as LA-ICP-MS is able to measure more elements at lower detection limits ( $\text{ng.g}^{-1}$ ) in a fraction of the time (60s per point). However, in Chapter 3 this author outlines the many analytical challenges of LA-ICP-MS for analysis of volatile metals, and the trace element method described here is used extensively for characterisation of reference materials.

**Table 2.12—EPMA Detection Limits for Trace Elements in Iron**

| Element | Standard                                       | Crystal | Peak | Peak Time (s) | BG Time (s) x 2 | <sup>a</sup> Det. Lim. ( $\mu\text{g.g}^{-1}$ ) |
|---------|------------------------------------------------|---------|------|---------------|-----------------|-------------------------------------------------|
| Ag      | Ag metal                                       | PET     | La   | 200           | 100             | 55                                              |
| Bi      | Bi metal                                       | LIF     | La   | 200           | 100             | 220                                             |
| Cd      | CdS (77.81% Cd)                                | PET     | La   | 200           | 100             | 55                                              |
| Cr      | Cr metal                                       | PET     | Ka   | 200           | 100             | 25                                              |
| Cu      | Cu metal                                       | LIF     | Ka   | 200           | 100             | 40                                              |
| Ga      | Ga metal                                       | LIF     | Ka   | 200           | 100             | 45                                              |
| Ge      | $\text{Er}_2\text{Ge}_2\text{O}_7$ (24.55% Ge) | LIF     | Ka   | 200           | 100             | 60                                              |
| In      | InSb (48.5% In)                                | PET     | La   | 200           | 100             | 50                                              |
| Mo      | Mo metal                                       | PET     | La   | 200           | 100             | 85                                              |
| Pb      | PbS (86.6% Pb)                                 | LIF     | La   | 600           | 300             | 100                                             |
| Sb      | InSb (51.5% Sb)                                | PET     | La   | 200           | 100             | 75                                              |
| Sn      | Sn metal                                       | PET     | La   | 200           | 100             | 75                                              |
| Tl      | Tl(Br <sub>2</sub> I) (65.98% Tl)              | LIF     | La   | 600           | 300             | 80                                              |
| V       | V metal                                        | PET     | Ka   | 200           | 100             | 15                                              |
| W       | W metal                                        | LIF     | La   | 200           | 100             | 95                                              |
| Zn      | Zn metal                                       | LIF     | Ka   | 200           | 100             | 40                                              |

<sup>a</sup>The average of all detection limits over all sessions, as computed by the XMAS software.

## 2.5 Summary

In this chapter EPMA methods have been introduced for the analysis of homogenous glass, dendritic quench textures in glass, and trace elements in iron metal.

To assess the uncertainties associated with analysing quench textures a series of PENEPMA simulations were performed and the results used to assess the accuracy of averaging results as well as to determine the minimum number of points to analyse on each quench texture.

The successful analysis of trace elements in iron can be achieved with particular care and attention to detail. The detection limits that can be achieved are of use to this study, but the time required (30 minutes per point) becomes prohibitive for large numbers of samples.



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### **3 LA-ICP-MS Analysis of Glass and Metal Samples**

#### **3.1 Introduction**

Of vital importance to this project was the need to accurately determine the trace element composition *in situ* for both glass and metal samples at concentrations as low as  $1 \mu\text{g.g}^{-1}$ . Laser Ablation–Inductively Coupled Plasma–Mass Spectrometry (LA–ICP–MS) [Gray 1985; Jackson et al 1992] was selected due to equipment availability, minimal sample preparation, low detection limits, and widespread use in the Earth Sciences.

This chapter introduces the instrumentation and is then divided into two main sections: the first describes the analytical method used to analyse glass samples for the trace elements of interest to this project; the second outlines the complications encountered using LA–ICP–MS for analysing volatile trace elements in iron metal, fabrication and characterisation of matrix–matched standards to improve the accuracy of quantification, and an overview of the analytical method used for iron metal analysis in this project.

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#### **3.2 Instrumentation**

Analysis was conducted on a New Wave Research (NWR) UP213 laser instrument attached to a Perkin Elmer NexION 400Q ICP–MS, both located at the University of Oxford Earth Sciences department. To improve stability of the instrument a number of optimisations and modifications were made to the laser ablation system, and all those mentioned here are the author’s own work unless otherwise noted.

### 3.2.1 Laser Ablation Instrument

The laser ablation system was based on a solid-state Nd:YAG<sup>5</sup> laser operating at a fundamental wavelength of 1066 nm, with frequency quintupling optics to produce an on-sample wavelength of 213 nm. The laser can fire at up to 10 Hz with individual pulses of 4 ns duration.

The laser ablation sample cell is the “large format” cell from NWR fitted with a custom Perspex sample holder (fabricated by the Earth sciences workshop to Dr Jon Wade’s design) that can accommodate up to nine 25 mm diameter samples. Some of the iron-bearing samples were lifted out by the magnetic “cup” mechanism that is peculiar to this style of cell. To remedy this issue small grub screws were set into the side of the holder to immobilize magnetic samples. Internally the cell uses a short ( $\approx 15$  cm) length of Tygon<sup>6</sup> tubing from the cup to the cell body, while the rest of the transport tubing was converted to 4mm ID uncoloured nylon, which is significantly less permeable to atmospheric gases, notably nitrogen and oxygen, both of which affect ICP stability and sensitivity. The total tubing length from the cell to the ICP was 4m, 2m of which was wound into a 20cm diameter coil to provide moderate signal smoothing. To minimise memory effects, a custom smooth-bore coupling was fabricated from Perspex and fitted to the laser system analyte output to mix argon from the ICP nebuliser gas supply with the analyte as soon as possible following ablation.

### 3.2.2 ICP-MS

The ICP on the NexION featured the standard Perkin Elmer glass torch with 1 mm ID quartz injector. The ICP was run in “hot plasma” conditions, with 1600 W of forward power. The typical nebuliser gas flow was 0.45 L.min<sup>-1</sup> with a helium flow of 0.8 L.min<sup>-1</sup>. The interface was fitted with the same set of nickel cones throughout the duration of this project, which were

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<sup>5</sup> Neodymium-doped yttrium aluminium garnet; Nd:Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>

<sup>6</sup> Trade name, unknown formulation of trade-secret composition.

cleaned on three occasions. The quadrupole mass spectrometer was operated without a collision or reaction cell and the mass spectrum was tuned to a mass resolution of 0.7. Over the course of this project the regular tuning tasks involved swapping over to solution mode to perform the dual-detector calibration as it was not possible to generate sufficient signal for the analogue counting mode. On this particular instrument the pulse counting is not recommended over  $1 \times 10^6$  counts per second (CPS) and stops entirely at  $2 \times 10^6$  CPS. At all times considerable care was taken to keep all signals in the pulse counting mode. The general ICP conditions are summarised in Table 3.1.

---

### **3.3 Analytical Methodology**

To mitigate instrumental drift in the mass spectrometer, standards were analysed every 45–60 minutes and data were saved in time-resolved mode to the XL file format. Data were reduced to sample concentrations using the software package Glitter [GEMOC, Macquarie University, Australia; Griffin *et al.* 2008] and processed in single blocks of standards–samples–standards using linear interpolation of calibration factors.

All standard compositions were retrieved from GeoREM [Jochum *et al.* 2005a] in 2014 and the “GeoREM Preferred” values used throughout this project.

**Table 3.1—General LA-ICP-MS Conditions**

|                          |                                            |
|--------------------------|--------------------------------------------|
| ICP RF Power             | 1600 W                                     |
| Auxilliary Gas Flow (Ar) | 1.2 L.min <sup>-1</sup>                    |
| Plasma Gas Flow (Ar)     | 17 L.min <sup>-1</sup>                     |
| <sup>a</sup> Autolens    | Yes                                        |
| Nebulizer Gas Flow (Ar)  | <sup>b</sup> 0.40-0.85 L.min <sup>-1</sup> |
| Carrier Gas Flow (He)    | 0.8 L.min <sup>-1</sup>                    |
| Laser Wavelength         | 213 nm                                     |
| Laser Repetition Rate    | 5Hz                                        |
| Laser Spot Size          | 25–80µm                                    |
| Laser On-Sample Fluence  | ≈4 J.cm <sup>-2</sup>                      |
| Tuning: Standard         | NIST 610                                   |
| Tuning: ThO/Th           | ≤0.2%                                      |
| Tuning: U/Th             | ≤1.2                                       |

<sup>a</sup>Proprietary ion optics feature; <sup>b</sup>Varies with daily tuning

### 3.4 Analysis of Glass Samples

#### 3.4.1 Standards

The NIST 610 reference glass [Eggins and Shelley 2002; Jochum *et al* 2011] was used for calibration of element yields. This glass is widely used in the Earth Sciences for quantification of LA-ICP-MS analysis and consists of an alkali-rich glass matrix doped with approximately 400 µg.g<sup>-1</sup> of the entire periodic table. The glass is not homogenous for some elements<sup>7</sup> of interest to this study, and as such calibration samples were always taken close to the centre of the mounted glass disc, as per the assessment and advice given in Eggins and Shelley 2002.

In addition to the NIST 610 reference glass, the USGS basaltic glass standards [Guillong *et al.* 2005; Jochum *et al.* 2005b] GSE and GSD were assessed for calibration purposes. The GSE glass provides a closer matrix match to the glass material from the volatile-loss experiments (see Chapter 5) but features low thallium concentration at only 2 µg.g<sup>-1</sup>. The high-pressure partitioning experiments were calibrated using NIST610 and the one-atmosphere volatile-loss

<sup>7</sup> Most notably: Ag, Bi, Cd, Cr, Mo, Pb, Sb, Tl, W, Cu, Cd, and Fe.

experiments were calibrated using GSE-1G. Despite this detail, for all glass analysis in this project only marginal difference in precision or accuracy was observed between NIST 610 and USGS GSE-1G.

The basaltic glass standard BCR-2G [Jochum *et al.* 2005b] was analysed routinely as a secondary standard, as well as the USGS basaltic glass standard GSD-1G.

### 3.4.2 Sampling

The high-pressure experiment run products (see Chapter 4) presented glass surfaces on the order of 1mm x 1mm in area, though marked by characteristic decompression cracks. To analyse this material the laser was aligned on the sample and fired at 5 Hz with a spot size of 50µm. The laser was fired for 40s which excavated a crater approximately 20–30µm deep, with only minimal debris. Prior to ablation a 20s gas blank was collected, and following ablation, the cell was flushed for 120s to ensure signal levels had returned to background.

The quadrupole mass spectrometer measured intensities for the masses of interest in peak hopping mode at the mass values and dwell times listed in Table 3.2. Those masses have been chosen to avoid interferences, maximise yield, and avoid use of the analogue detector for major elements.

Mass  $^{43}\text{Ca}$  was used as the internal standard, and the calcium concentration in each sample was measured using EPMA prior to laser ablation.

**Table 3.2—Glass Analysis Masses and Dwell Times**

| Element | Mass (amu) | Dwell Time (ms) |
|---------|------------|-----------------|
| Si      | 29         | 30              |
| Ca      | 43         | 30              |
| V       | 51         | 30              |
| Cr      | 53         | 30              |
| Fe      | 57         | 30              |
| Cu      | 65         | 30              |
| Zn      | 66         | 30              |
| Ga      | 69         | 30              |
| Ga      | 71         | 30              |
| Ge      | 72         | 30              |
| Ge      | 73         | 30              |
| Mo      | 95         | 30              |
| Mo      | 98         | 30              |
| Ag      | 107        | 30              |
| Cd      | 111        | 30              |
| In      | 115        | 30              |
| Sn      | 118        | 30              |
| W       | 182        | 30              |
| Tl      | 203        | 100             |
| Tl      | 205        | 100             |
| Pb      | 208        | 30              |
| Bi      | 209        | 30              |

### 3.4.3 Detection Limits

When evaluating LA-ICP-MS data the signal intensity varies by spot size, while the gas background depends on multiple factors, such as: ICP-MS tuning; cell leaks; permeation of gases through transfer tubing; outgassing from samples; and memory effects. The detection limits reported by the data reduction software Glitter are shown in Table 3.3 below. Most notable is that all of the detection limit values fall between 1 and  $0.01 \mu\text{g.g}^{-1}$  which was more than suitable for the glass analysis performed in this study.

**Table 3.3—Glass Detection Limits**

| Element | Mass (amu) | Det. Lim. ( $\mu\text{g.g}^{-1}$ ) |
|---------|------------|------------------------------------|
| Ag      | 107        | 0.03                               |
| Bi      | 209        | 0.01                               |
| Cd      | 111        | 0.2                                |
| Cr      | 53         | 1.4                                |
| Cu      | 65         | 0.4                                |
| Ga      | 71         | 0.08                               |
| Ge      | 74         | 0.2                                |
| In      | 115        | 0.01                               |
| Mo      | 95         | 0.06                               |
| Pb      | 208        | 0.02                               |
| Sb      | 121        | 0.05                               |
| Sn      | 118        | 0.08                               |
| Tl      | 203        | 0.05                               |
| V       | 51         | 0.1                                |
| W       | 182        | 0.02                               |
| Zn      | 66         | 0.4                                |

### 3.4.4 Discussion

In general the analysis of glass by LA-ICP-MS is routine and offers good accuracy and precision. For this study the laser was operated in spot mode when analysing metal-silicate partitioning experiments (see Chapter 4) and in scanning mode for the volatile loss experiments (see Chapter 5). In practice there was little difference between the two modes of operation, with the secondary standards BCR-2G and USGS GSD-1G showing good recovery, generally within 20% of the expected concentrations.

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## 3.5 Analysis of Iron Metal

Data reduction with this technique is empirical and depends upon the appropriate choice of a well characterised matrix-matched standard [Longerich *et al* 1996; Devos *et al.* 2004; Sarah *et al.* 2007].

As already introduced, the NIST 600-series glasses provide a convenient SRM for silicate analysis, but are unsuitable for iron analysis due to their low iron content ( $460 \mu\text{g.g}^{-1}$ ), high calcium content ( $^{40}\text{Ca}^{16}\text{O}^1\text{H}$  interference on  $^{57}\text{Fe}$ ) and systemic heterogeneity of the trace

elements of interest, particularly thallium and antimony. The GS-series of basaltic glasses from the US Geological Survey (USGS) improve on the NIST glasses by featuring iron as a major component ( $\approx 10\% \text{ g.g}^{-1}$ ) but they are significantly deficient in thallium ( $\approx 2 \mu\text{g.g}^{-1}$ ) and their matrix is still substantially different from that of iron metal.

Initial naïve attempts to use either NIST610 or GSE-1G for quantified analysis of iron metal resulted in considerable deviations from expected concentrations. For some elements the measured values were over 500% larger than the expected value.

To assess the analytical deficiencies of using glass standards to analyse iron metal samples, and building on other efforts [Wohlgemuth-Ueberwasser *et al.* 2007] this author fabricated and characterised a series of iron metal materials containing 10 to 10,000  $\mu\text{g.g}^{-1}$  of the trace elements of interest to this study.

In addition to the fabricated materials a number of reference materials were procured, and these are listed below in Table 3.4.

**Table 3.4—Third Party Iron Reference Materials Used in This Study**

| Standard | Source      | Trace Elements                       | $\Sigma \text{ Traces (g.g}^{-1}\text{)}$ |
|----------|-------------|--------------------------------------|-------------------------------------------|
| SRM65d   | NIST        | Cr, Cu, Mo, Sn, Zn                   | 0.8                                       |
| SRM152a  | NIST        | Cr, Cu, Mo, Sn, V, Zn                | 0.8                                       |
| SRM1262b | NIST        | Ag, Bi, Cr, Cu, Mo, Sb, Sn, V, W, Zn | 4.3                                       |
| SRM665   | NIST        | Cr, Cu, Mo, Pb, V                    | 0.02                                      |
| Fe Wire  | Goodfellows | Cr, Cu, Ga, Mo, Sn, W                | 0.0007                                    |
| USNM1334 | Meteorite   | Cr, Cu, Ga, Ge, Mo, Sn, W            | 0.04                                      |

### 3.5.1 Fabrication of In-House Iron Standards

The certified reference materials shown in Table 3.4 are useful, but limited in the range of trace elements they contain. The volatile trace elements of most interest to this study (such as Tl, Pb, Ag, and Cd) are rarely, if ever, characterised in iron standards, and at the time of writing this author was unable to locate any additional reference materials. As such, a range of in-house



iron standards were fabricated in the piston cylinder apparatus. All of the fabricated standards are shown in Table 3.5 below.

Metal standards were prepared by mixing oxides of the elements of interest with a mixture of Fe metal (90% by weight) and synthetic Fe-free silicate (10%). The mixtures were placed in capsules of polycrystalline MgO (6 mm OD, 2.5 mm ID) and raised to a pressure of 1.5 GPa at a temperature of 1650°C in a piston-cylinder solid-media high pressure apparatus. Under these conditions the metal melted and dissolved the minor elements, expelling excess oxygen as FeO which dissolved in the molten silicate. Metal and silicate are immiscible and segregated into large physically distinct parts of the capsule. The synthesis was quenched after 30 minutes by cutting power to the graphite furnace. This quenched the sample to below its solidus in ~3 seconds<sup>8</sup>, trapping the trace elements of interest in the metal. The samples were then mounted in 1" diameter acrylic rounds, ground and polished for LA-ICP-MS and microprobe analysis.

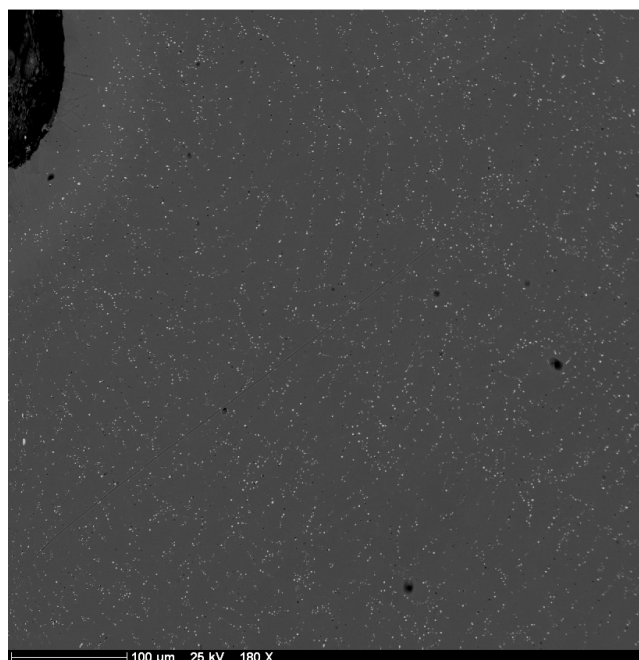
#### *3.5.1.1 In-House Standard Compositions*

The trace elements of interest exhibit varied solubility in iron metal. For this study it is desirable if the trace element concentration exceeds 500  $\mu\text{g.g}^{-1}$  per element so as to be readily analysed by EPMA. While the solubility of a given element can be estimated by assessing the iron binary phase diagram, it is noteworthy to mention that the observed solubility also depends on the kinematics of the quench and the presence of other elements in the material. As such, while a particular molten element may be soluble at the conditions in the piston cylinder, on quenching the trace elements exsolved and formed small blebs 1–10  $\mu\text{m}$  in diameter. The presence and morphology of these blebs varied considerably, and their size and prevalence are documented in Figures 3.1 to 3.3 below.

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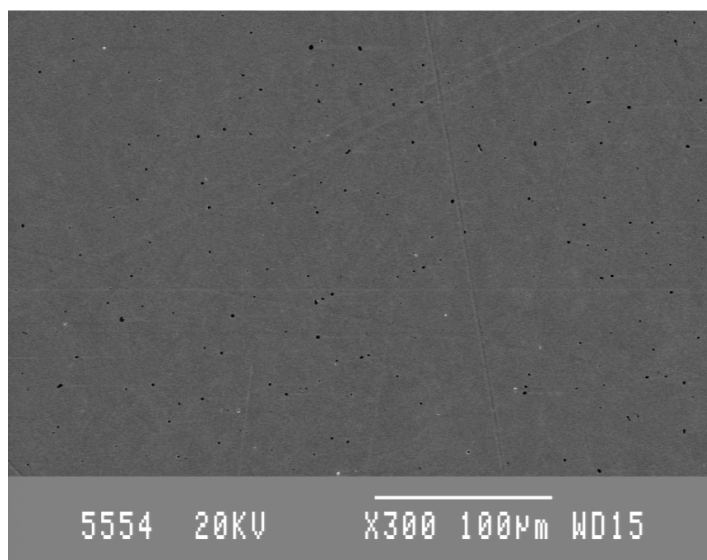
<sup>8</sup> See §4.3.1 in Chapter 4 for measurement of quench rate.

Figure 3.1—Quench Texture in Standard BW162A



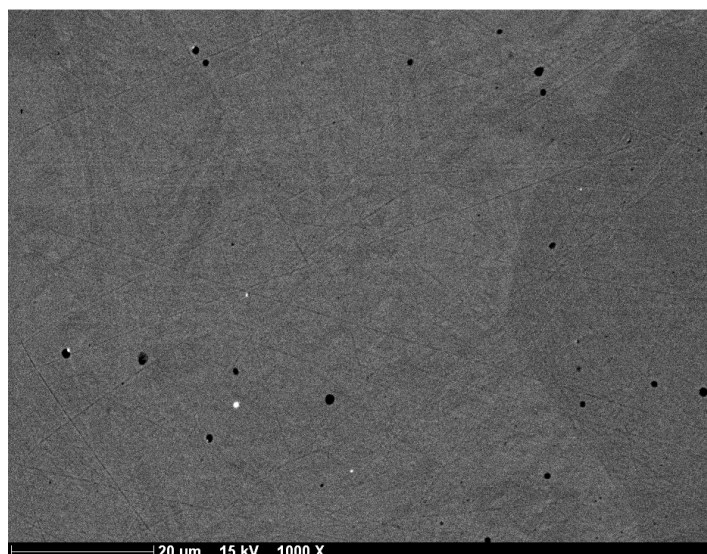
SEM BSE image of quench texture in standard BQ162A. This material contains a relatively high concentration of trace elements totalling to  $2.4 \text{ g.g}^{-1}$  with the balance comprising pure iron metal. The quench texture consists of discrete blebs 1 to  $10 \mu\text{m}$  in diameter that appear to form along the domain boundaries in the iron.

Figure 3.2—Quench Texture in Standard G3A1



SEM BSE image of quench texture in standard G3A1. This material contains  $1.8 \text{ g.g}^{-1}$  of trace elements in a matrix of pure iron. The trace elements in this standard were chosen for their compatibility with iron and were doped at a level below saturation, as estimated from binary phase diagrams and literature data.

Figure 3.3—Quench Texture in Standard G3Pb1



SEM BSE image of quench texture in standard G3Pb1. This material contains  $30 \mu\text{g.g}^{-1}$  of lead in a matrix of pure iron. By lowering the concentration of lead the material presents with fewer blebs and is more homogenous, however the usefulness as a standard decreases.

The successful fabrication strategy of this study was to make one material (G3A1) containing the readily soluble trace elements and then separate materials (G3Ag1, G3Bi1, G3Cd1, G3Tl1, G3Pb1) containing just one each of the more insoluble elements. In the process of making these materials a number of others were fabricated, all of which have been analysed and included in this study, though they failed to contain a high abundance of trace elements homogeneously distributed in the iron matrix. Weighing records for the trace element mixtures of each standard have been included in the Appendix, with a summary included here in Table 3.5.

**Table 3.5—Summary of Fabricated In-House Iron Standards**

| Standard | Source     | Trace Elements                         | $\Sigma$ Traces (g.g <sup>-1</sup> ) |
|----------|------------|----------------------------------------|--------------------------------------|
| G3A1     | This Study | Cr, Cu, Ga, Ge, In, Mo, Sb, Sn, W, Zn  | 1.8                                  |
| A575     | This Study | Ag, Bi, Cd, Cr, Cu, In, Pb, Sb, Tl, Zn | 0.1                                  |
| BW162A   | This Study | Cd, Cr, Cu, In, Pb, Sn, Tl, V, Zn      | 2.4                                  |
| BW163F   | This Study | Ag, Bi, Cu, Ga, Ge, Mo, Sb, W          | 3.3                                  |
| BW1362N  | This Study | Ag, Bi, Cd, Ge, In, Pb, Tl, V, Zn      | 0.4                                  |
| G3Ag1    | This Study | Ag                                     | 0.05                                 |
| G3Bi1    | This Study | Bi                                     | 0.02                                 |
| G3Cd1    | This Study | Cd                                     | 0.0007                               |
| G3Pb1    | This Study | Pb                                     | 0.03                                 |
| G3Tl     | This Study | Tl                                     | 0.06                                 |
| A566     | This Study | Ag, Bi, Cd, Cu, In, Pb, Sb, Tl, Zn     | 0.6                                  |
| A573     | This Study | Ag, Bi, Cd, Cu, In, Pb, Sb, Tl, Zn     | 0.5                                  |
| A572     | This Study | Ag, Bi, Cd, Cu, In, Pb, Sb, Tl, Zn     | 0.4                                  |
| A463     | This Study | Ag, Bi, Cd, Cu, In, Pb, Sb, Tl, Zn     | 0.2                                  |
| A565     | This Study | Ag, Bi, Cd, Cu, In, Pb, Sb, Tl, Zn     | 0.05                                 |

### 3.5.2 Characterising Iron Standards

The iron metal standards were all analysed for trace elements by EPMA, as outlined in Chapter

2. Some trace element concentrations in some standards were below the EPMA detection limits.

To thoroughly characterise the trace element concentrations in these materials, a small fragment of each sample was digested and analysed by solution ICP–MS.

#### 3.5.2.1 Solution ICP–MS Analysis of Iron Metal Standards

For solution ICP–MS analysis a thin 0.5mm slither was cut from each standard material using a diamond cutting wheel. The slithers of material were weighed (average of 4 to 5 mg each) before being washed in 50% hydrofluoric acid (HF) for 30 seconds to remove any remnants of silicate from their surface. They were then rinsed several times in Mili-Q water to remove all HF before being digested in 5ml of 8M nitric acid in a sealed FEP beaker and heated overnight at 90°C. They were then evaporated down to almost dryness before 0.5ml of 16M nitric was added and they were again evaporated down to dryness at 90°C. Finally, 10ml of 2M nitric acid was added and the solution was left at 90°C overnight to complete the process. All acids were quartz distilled grade and purified in-house.

Analysis was performed at the University of Oxford, Earth Sciences Department, quadrupole ICP–MS laboratory on a Perkin Elmer Elan 6100 DRC ICP–MS equipped with an ESI PC3 Peltier for improved oxide ratios. Calibrations were obtained using standard addition analysis where a standard<sup>9</sup> of known trace element concentration was spiked onto replicates at increasing volumes. As a quality check an external standard was prepared using dilutions of the same calibration standards. All blanks, standards and samples were spiked with an internal standard of 1 ng.g<sup>-1</sup> Rh, so that any general instrument drift could be normalised. Dilutions were made using a 2% HNO<sub>3</sub> solution and 18.2 MΩ DI water. Concentrations in solution were divided by the dilution ratios to recover the total mass of trace element present in the original digestion. The weight percent of the trace element in the original iron sample was then trivially computed.

### 3.5.3 Accepted Standard Compositions

The accepted composition of each iron standard is a combination of certificate values and literature values (where available), EPMA concentration (where above detection limit) and solution ICP–MS analysis.

Taking all analytical factors into account, the accepted concentration of each element is computed as the mean of known and trusted values, with the relative uncertainty values combined as relative standard deviations<sup>10</sup>. The accepted compositions of each standard are shown in Table 3.6 below.

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<sup>9</sup> 10 µg.g<sup>-1</sup> ICP–MS-68A and 10 µg.g<sup>-1</sup> ICP–MS-68B.

<sup>10</sup>  $\sigma = \sqrt{\sigma_a^2 + \sigma_b^2}$  with  $\sigma$  expressed as a relative amount.

**Table 3.6a—Standard Compositions**

| Standard | Composition Source              | Fe                   | Fe (a)                | Ag                    | (a)                   | Bi                    | (a)                   | Cd                    | (a)                   | Cr                    | (a)                   | Cu                    | (a)                   | Ga                    | (a)                   | Ge                    | (a)                   | In                    | (a)                   |
|----------|---------------------------------|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| G3A1     | EPMA, Solution ICP              | 98.22                | 0.06                  |                       |                       |                       |                       |                       |                       | 957                   | 144                   | 4688                  | 1642                  | 959                   | 29                    | 464                   | 21                    | 825                   | 116                   |
| G3Ag1    | EPMA, Solution ICP              | 99.95                | 0.01                  | 537                   | 128                   |                       |                       |                       |                       | 22.1                  | 0.6                   | 16.4                  | 5.7                   | 2.02                  | 0.05                  |                       |                       |                       |                       |
| G3B1     | EPMA, Solution ICP              | 99.99                | 0.03                  |                       |                       | 158                   | 402                   |                       |                       | 15                    | 0                     | 28                    | 10                    | 2.15                  | 0.06                  |                       |                       |                       |                       |
| G3Cd1    | Solution ICP                    | 99.99                |                       |                       |                       | 0.66                  | 0.15                  | 7.12                  | 0.31                  | 14                    | 0                     | 15                    | 5                     |                       |                       |                       |                       |                       |                       |
| G3Pb1    | EPMA, Solution ICP              | 99.97                | 0.01                  |                       |                       |                       |                       |                       |                       | 16                    | 0                     | 204                   | 71                    | 2                     |                       |                       |                       |                       |                       |
| G3Ti1    | EPMA, Solution ICP              | 99.94                | 0.01                  |                       |                       |                       |                       |                       |                       | 23                    | 1                     | 11                    | 4                     | 2.48                  | 0.07                  |                       |                       |                       |                       |
| A575     | EPMA, Solution ICP              | 99.92                | 0.02                  | 48                    | 14                    | 78                    | 65                    | 8.4                   | 1.3                   | 18                    | 6                     | 173                   | 21                    |                       |                       |                       |                       | 31                    | 18                    |
| BW162A   | EPMA, Solution ICP              | 97.61                | 0.11                  | 243                   | 0.30                  |                       |                       | 1471                  | 240                   | 792                   | 49                    | 7501                  | 148                   | 1.55                  | 0.19                  | 211                   | 107                   | 2764                  | 184                   |
| BW163F   | EPMA, Solution ICP              | 96.72                | 0.09                  | 2117                  | 268                   | 3134                  | 560                   | 16                    | 1                     | 3                     | 11                    | 8418                  | 103                   | 3277                  | 20                    | 3170                  | 149                   | 0.54                  | 0.19                  |
| BW1362N  | EPMA, Solution ICP              | 99.63                | 0.07                  | 476                   | 91                    | 711                   | 199                   | 335                   | 117                   | 20.8                  | 4.7                   | 15.7                  | 0.8                   | 1.20                  | 0.12                  | 212                   | 106                   | 684                   | 82                    |
| SRM65d   | Certificate, EPMA, Solution ICP | 99.19                | 0.23                  |                       |                       | 0.28                  | 0.065                 |                       |                       | 490                   | 14                    | 504                   | 177                   | 942                   | 0.26                  | 17.5                  | 0.6                   |                       |                       |
| SRM152a  | Certificate, EPMA, Solution ICP | 99.16                | 0.24                  |                       |                       | 0.35                  | 0.080                 |                       |                       | 463                   | 16                    | 239                   | 84                    | 646                   | 0.18                  | 8.7                   | 0.3                   |                       |                       |
| SRM1262b | Certificate, EPMA, Solution ICP | 95.72                | 0.01                  | 14.9                  | 5.6                   | 298                   | 6.9                   | 745                   | 0.32                  | 2950                  | 129                   | 5204                  | 1822                  | 16.9                  | 0.5                   |                       |                       |                       |                       |
| SRM665   | Certificate                     | 99.98                |                       |                       |                       |                       |                       |                       |                       | 72                    |                       | 58                    |                       |                       |                       |                       |                       |                       |                       |
| Fe Wire  | Certificate                     | 99.999               |                       |                       |                       |                       |                       |                       |                       | 3.9                   |                       | 2                     |                       | 0.67                  |                       | 2                     |                       |                       |                       |
| USNM1334 | Solution, Literature            | 99.96                |                       |                       |                       |                       |                       |                       |                       | 49                    | 1                     | 137                   | 48                    | 610                   | 1.7                   | 173                   | 6                     |                       |                       |
| A463     | EPMA, Solution ICP              | 99.79                | 0.10                  | 89                    | 19                    | 289                   | 240                   | 2.50                  | 0.16                  | 18                    | 4                     | 273                   | 96                    | 3.06                  | 0.08                  |                       |                       | 58                    | 21                    |
| A565     | EPMA, Solution ICP              | 99.96                | 0.02                  | 14                    | 27                    | 36                    | 90                    |                       |                       | 23                    | 4                     | 153                   | 56                    |                       |                       |                       |                       | 13                    | 2                     |
| A566     | EPMA, Solution ICP              | 99.43                | 0.15                  | 321                   | 87                    | 679                   | 369                   | 308                   | 1.3                   | 21                    | 4                     | 717                   | 251                   |                       |                       |                       |                       | 258                   | 51                    |
| A572     | EPMA, Solution ICP              | 99.57                | 0.22                  | 296                   | 190                   | 647                   | 617                   | 13.2                  | 0.6                   | 23                    | 3                     | 719                   | 252                   | 16.51                 | 0.45                  |                       |                       | 196                   | 76                    |
| A573     | EPMA, Solution ICP              | 99.45                | 0.08                  | 383                   | 58                    | 807                   | 278                   | 31.7                  | 1.4                   | 23                    | 3                     | 1120                  | 393                   | 2.59                  | 0.07                  |                       |                       | 290                   | 47                    |
| Units    |                                 | (g g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) | (μg g <sup>-1</sup> ) |

**Table 3.6b—Standard Compositions (cont....)**

| Standard | Composition Source              |  |  | Mo   | (a)                      | Pb                       | (a)                      | Sb                       | (a)                      | Sn                       | (a)                      | Ti                       | (a)                      | V                        | (a)                      | W                        | (a)                      | Zn                       | (a)                      |
|----------|---------------------------------|--|--|------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| G3A1     | EPMA, Solution ICP              |  |  | 443  | 31                       | 3.6                      | 0.6                      | 4172                     | 290                      | 2186                     | 141                      |                          |                          | 62                       | 30                       | 480                      | 23                       | 2249                     | 78                       |
| G3Ag1    | EPMA, Solution ICP              |  |  | 240  | 0.08                     |                          |                          | 398                      | 0.73                     |                          |                          |                          |                          |                          |                          |                          |                          | 460                      | 1.24                     |
| G3B1     | EPMA, Solution ICP              |  |  | 3.01 | 0.10                     | 0.66                     | 0.12                     | 3.34                     | 0.22                     |                          |                          |                          |                          |                          |                          | 2.54                     | 0.33                     | 882                      | 0.60                     |
| G3Cd1    | Solution ICP                    |  |  | 2.86 | 0.11                     | 2.25                     | 0.40                     | 3.57                     | 0.46                     |                          |                          | 0.81                     | 0.27                     |                          |                          | 1.17                     | 0.08                     | 11.3                     | 2.7                      |
| G3Pb1    | EPMA, Solution ICP              |  |  | 2    |                          | 290                      | 91                       | 3.00                     | 0.00                     | 3.00                     |                          | 58                       | 10                       |                          |                          |                          |                          | 1220                     | 4.0                      |
| G3Ti1    | EPMA, Solution ICP              |  |  | 3.09 | 0.10                     |                          |                          | 3.26                     | 0.45                     |                          |                          | 600                      | 209                      |                          |                          |                          |                          | 14.7                     | 6.5                      |
| A575     | EPMA, Solution ICP              |  |  | 2.74 | 0.48                     | 108                      | 34                       | 18                       | 0.75                     |                          |                          | 214                      | 26                       |                          |                          | 1.23                     | 0.58                     | 100                      | 24                       |
| BW162A   | EPMA, Solution ICP              |  |  | 2.36 | 0.62                     | 3996                     | 529                      |                          |                          | 2828                     | 106                      | 3208                     | 429                      | 97                       | 21                       |                          |                          | 2306                     | 39                       |
| BW163F   | EPMA, Solution ICP              |  |  | 3048 | 34                       | 15.7                     | 1.3                      | 3705                     | 121                      | 2.14                     | 1.23                     | 14                       | 535                      | 0.55                     | 0.31                     | 4403                     | 78                       | 1.7                      | 2.9                      |
| BW1362N  | EPMA, Solution ICP              |  |  | 3.6  | 0.5                      | 1134                     | 268                      |                          |                          |                          |                          | 491                      | 265                      | 273                      | 31                       | 84                       | 4.1                      | 591                      | 17                       |
| SRM65d   | Certificate, EPMA, Solution ICP |  |  | 234  | 22                       | 2.63                     | 0.47                     | 8.50                     | 0.53                     | 36                       | 0.6                      |                          |                          | 13                       | 0.2                      | 7.1                      | 0.4                      | 43                       | 19                       |
| SRM152a  | Certificate, EPMA, Solution ICP |  |  | 332  | 25                       | 4.16                     | 0.74                     | 5.76                     | 0.46                     | 329                      | 398                      |                          |                          | 10                       | 0.2                      | 2.9                      | 0.4                      | 27                       | 13                       |
| SRM1262b | Certificate, EPMA, Solution ICP |  |  | 614  | 52                       | 3.61                     | 1.11                     | 93.6                     | 1.59                     | 172                      | 11.1                     |                          |                          | 378                      | 12                       | 1020                     | 81                       | 22                       | 6                        |
| SRM665   | Certificate                     |  |  | 50   |                          | 0.15                     |                          |                          |                          |                          |                          |                          |                          | 6                        |                          |                          |                          |                          |                          |
| Fe Wire  | Certificate                     |  |  | 0.17 |                          |                          |                          |                          |                          | 0.21                     |                          |                          |                          |                          |                          | 0.87                     |                          |                          |                          |
| USNM1334 | Solution, Literature            |  |  | 7.09 | 0.17                     |                          |                          |                          |                          | 2.47                     | 0.06                     |                          |                          |                          |                          | 5.03                     | 0.53                     | 6.92                     | 1.16                     |
| A463     | EPMA, Solution ICP              |  |  | 2.28 | 0.08                     | 200                      | 191                      | 32                       | 1                        |                          |                          | 808                      | 531                      |                          |                          |                          |                          | 202                      | 12                       |
| A565     | EPMA, Solution ICP              |  |  | 2.35 | 0.08                     | 50                       | 48                       | 8                        | 1                        |                          |                          | 88                       | 96                       |                          |                          | 1.01                     | 0.07                     | 41                       | 11                       |
| A566     | EPMA, Solution ICP              |  |  | 2.48 | 0.08                     | 739                      | 260                      | 82                       | 25                       |                          |                          | 2378                     | 1177                     |                          |                          |                          |                          | 618                      | 22                       |
| A572     | EPMA, Solution ICP              |  |  | 2.50 | 0.08                     | 549                      | 369                      | 87                       | 2                        |                          |                          | 991                      | 712                      |                          |                          | 0.68                     | 0.03                     | 381                      | 21                       |
| A573     | EPMA, Solution ICP              |  |  | 2.44 | 0.09                     | 702                      | 226                      | 104                      | 30                       |                          |                          | 1406                     | 521                      |                          |                          | 0.74                     | 0.04                     | 618                      | 21                       |
| Units    |                                 |  |  |      | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) | ( $\mu\text{g g}^{-1}$ ) |

### 3.5.4 Characterisation of Iron Metal Ablation

Ablation of iron metal by UV nanosecond laser pulses has been documented in the literature [Jordon and Lunney 1998;] and successfully employed for quantified analysis of both archaeological [Devos *et al.* 2000; Sarah *et al.* 2007] and meteoritic [Campbell and Humayun 1999; Mullane *et al.* 2004; Chernonozhkin *et al.* 2014] materials.

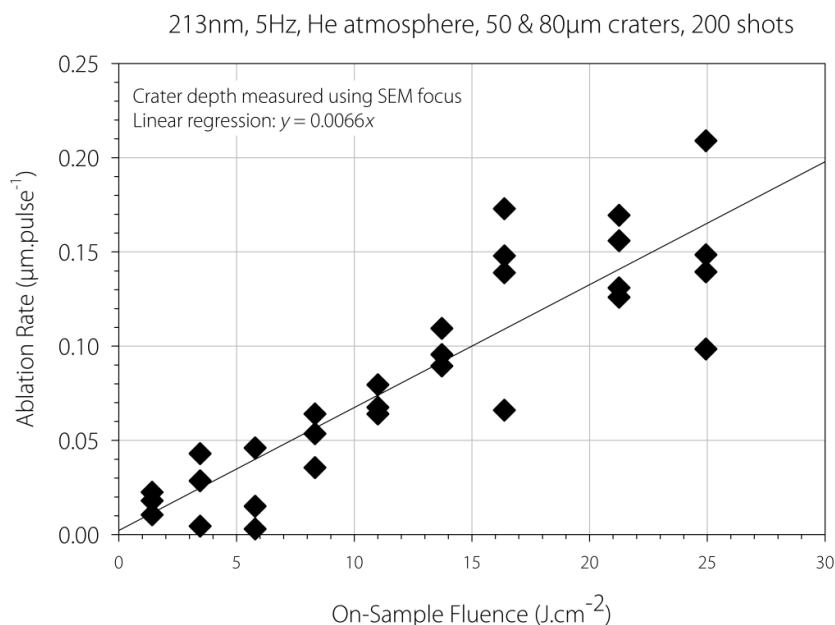
Building on previous work, the ablation characteristics of iron metal were investigated in this study to understand ablation rate and to optimise sample removal. The iron metal samples in some experiments were small (10s to 100s of  $\mu\text{m}$  across) and it was important that sufficient material was removed for analysis without entirely destroying the sample.

#### 3.5.4.1 Iron Ablation Rate

The ablation rate was measured using a piece of 99.999% iron wire. The sample was ablated for 200 pulses at a range of fluence values. The crater depths were measured using SEM focal length while imaging the top and bottom of the crater with secondary electrons. While measuring crater depths in this manner is imprecise compared to scanning white light interferometry [Deck and De Groot 1994] the ablation rate can be reasonably estimated using the regressed linear relationship shown in Figure 3.4.



Figure 3.4—Ablation Rate of 99.999% Iron Wire



The ablation rate of pure iron was measured over a range of fluence values. The crater depth has been measured by SEM focus and repeated three times for each crater. The ablation was performed using a 213nm Nd:YAG laser in a helium atmosphere at spot sizes of 50 and 80µm.

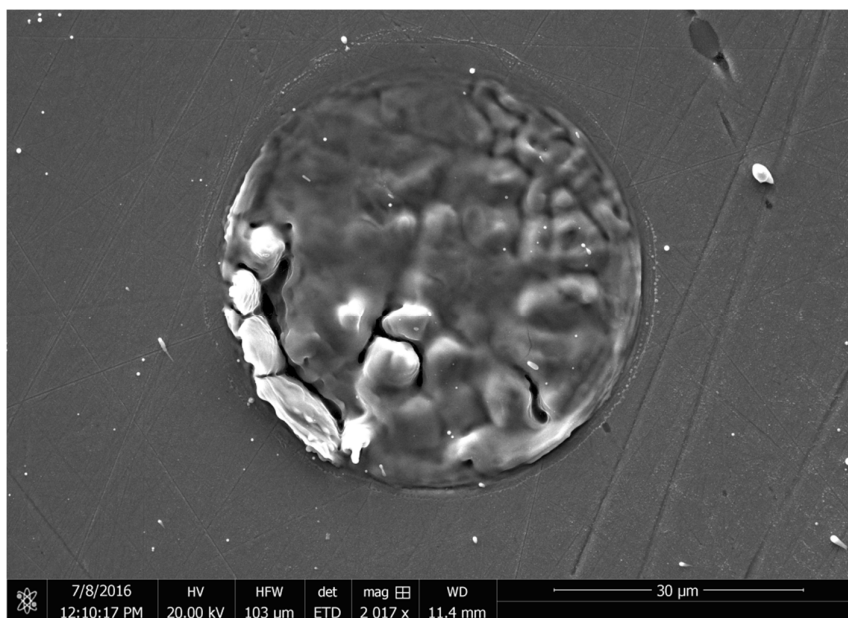
### 3.5.4.2 Iron Ablation Fluence Optimisation

The SEM images in Figures 3.5 to 3.8 show changes in crater morphology for a range of on-sample fluence values. At low fluence ( $1.4 \text{ J.cm}^{-2}$ , Figure 3.5) the laser energy density is only just above the ablation threshold and the crater is very shallow with only a small volume of material removed. At high fluence ( $24.9 \text{ J.cm}^{-2}$ , Figure 3.8) the crater is deep and the molten iron ejected from the crater has formed a *chimney* around the ablation site, increasing the effective crater depth as well as down-hole fractionation. Droplets of iron have been deposited all around the crater in a radial pattern, smothering the area for almost a millimetre in all directions.

At intermediate fluence values (Figures 3.6 and 3.7) the crater floor is very uneven, showing towering features that are possibly correlated with intensity variation of the laser spot profile as their general shape and location appear to be common to most ablation craters made with this instrument.

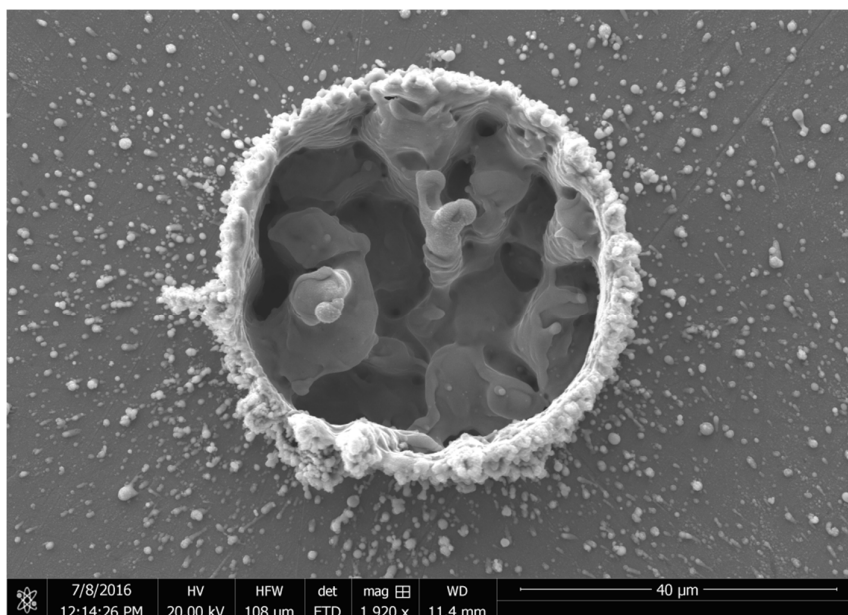
The conclusion drawn from visual inspection of the craters is that lower to intermediate fluence values will be better, resulting in a more controlled ablation, less sample heating and melting, as well as minimal contamination of the surrounding sample with ablation debris.

Figure 3.5—Ablation Crater in Iron (50 $\mu$ m, 200 shots, 1.4 J.cm<sup>-2</sup>)



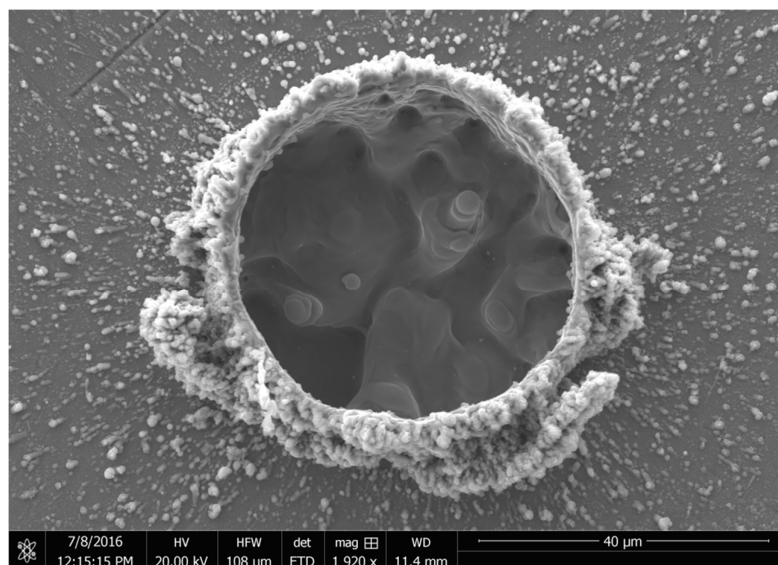
An SEM SE image of a 200-pulse 50 $\mu$ m crater ablated in iron at 1.4 J.cm<sup>-2</sup>. At these conditions the laser energy density is barely above the ablation threshold and only a small volume of material has been removed. There is little evidence of melting and there are very few melt droplets surrounding the crater.

Figure 3.6—Ablation Crater in Iron (50 $\mu$ m, 200 shots, 5.8 J.cm<sup>-2</sup>)



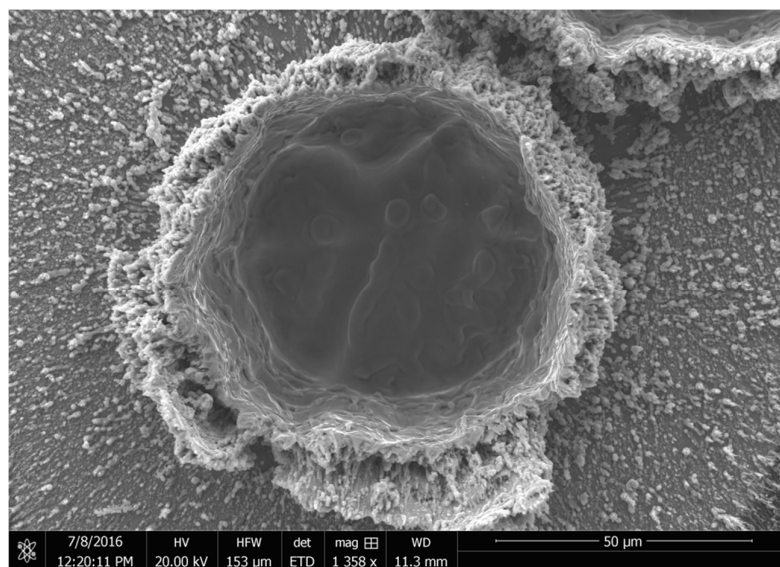
An SEM SE image of a 200-pulse 50 $\mu$ m crater ablated in iron at 5.8 J.cm<sup>-2</sup>. At these conditions the laser energy profile has created a dramatic series of hills and troughs in the bottom of the crater while melted material is deposited around the crater as small (<2 $\mu$ m diameter) droplets.

Figure 3.7—Ablation Crater in Iron (50 $\mu$ m, 200 shots, 8.3 J.cm<sup>-2</sup>)



An SEM SE image of a 200-pulse 50 $\mu$ m crater ablated in iron at 8.3 J.cm<sup>-2</sup>. At these conditions the iron has melted and is deposited as small droplets in a radial pattern surrounding the crater. The material has also formed a *chimney* around the crater, increasing the effective depth of the crater and increasing down-hole fractionation. In addition, the laser energy profile creates a series of hills and troughs in the bottom of the crater.

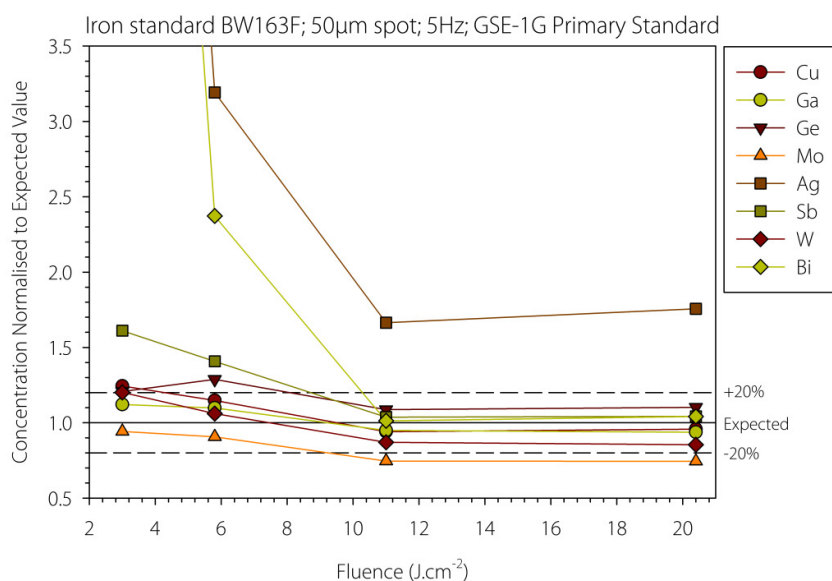
Figure 3.8—Ablation Crater in Iron (50µm, 200 shots, 24.9 J.cm<sup>-2</sup>)



An SEM SE image of a 200-pulse 50µm crater ablated in iron at 24.9 J.cm<sup>-2</sup>. The iron has been melted by the laser and deposited as small droplets in a radial pattern around the crater. The material has also formed a *chimney* around the crater, increasing the effective depth of the crater and increasing down-hole fractionation. The extra energy deposited at this fluence value has melted away most features from the crater floor, which are typically present at lower fluence.

To assess analytical accuracy with on-sample fluence, standard BW163F was analysed in spot mode using a 50µm spot, 5Hz, and GSE-1G as a primary calibration standard. The concentration of each element was normalised by the accepted composition of the standard. The results are plotted in Figure 3.9 and show several interesting features: the volatile elements silver, bismuth, and antimony are all over-estimated at lower fluence values; even at high-fluence values silver is 80% higher than expected; other elements assessed exhibit best analytical accuracy at a fluence of 8J.cm<sup>-2</sup>.

Figure 3.9—Analytical Accuracy by On-Sample Fluence



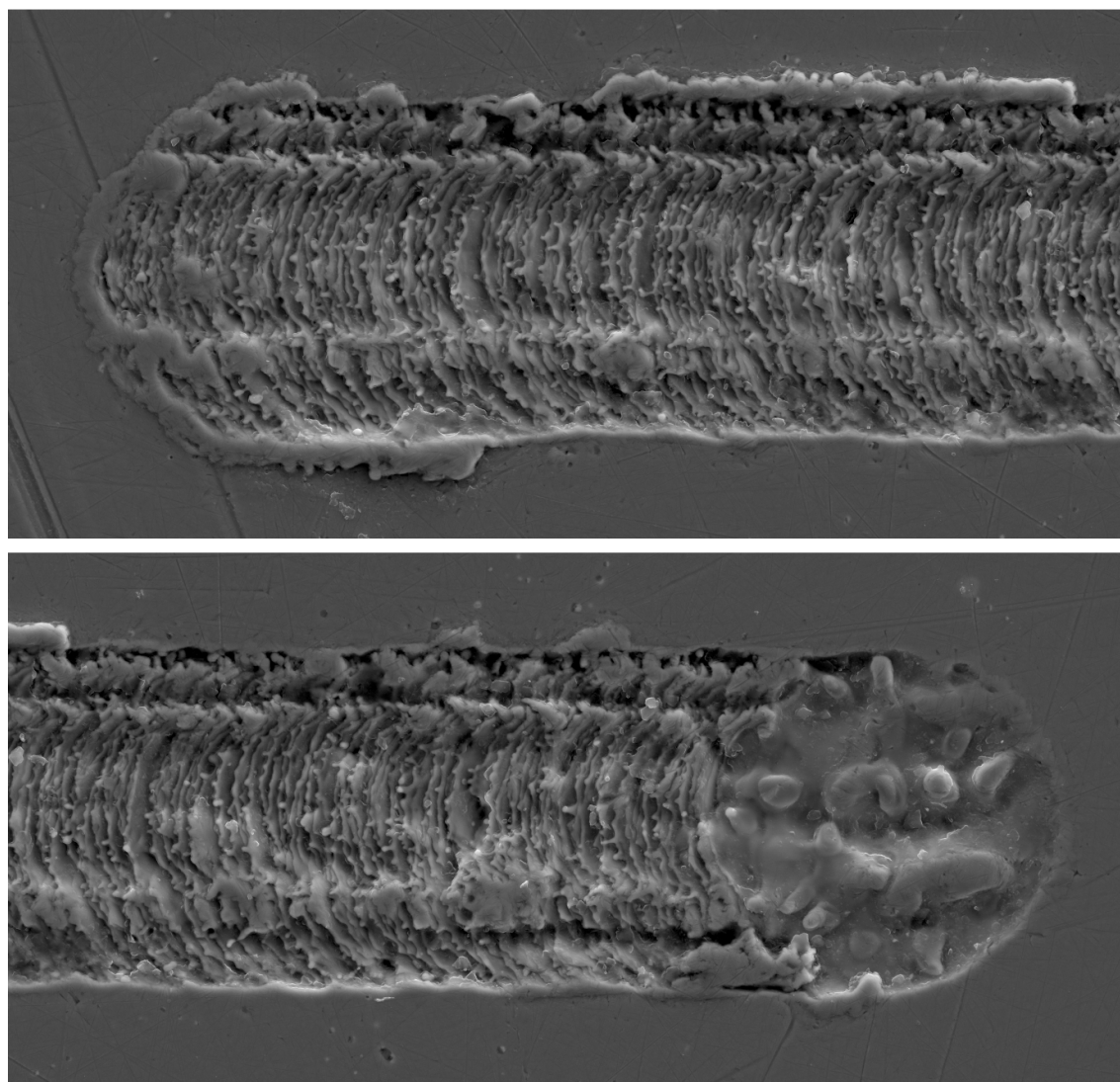
Sample BW162A was analysed using four different fluence values with a 50 $\mu$ m spot, 5Hz, and GSE-1G as primary standard. The analytical accuracy is assessed by normalising the measured concentration to the accepted concentration for each element.

### 3.5.4.3 Scanning Mode

To reconcile the conflicting optimisation requirements, scanning mode has been identified as providing optimal conditions for iron metal analysis. In scanning mode a lower fluence value can be used, with less of the exaggerated over-estimation observed in spot mode. The lower fluence value ensured that ablation was more controlled with less melting and a shallower crater. Less melting during ablation resulted in less incidental sample damage and debris contaminating the sample surface.

The optimised scanning conditions used throughout this study were: 50 $\mu$ m round spot; 5Hz repetition rate; 4J.cm<sup>-2</sup> fluence; and 3 $\mu$ m.s<sup>-1</sup> scan speed.

Figure 3.10—Ablation Scan of Iron Standard G3A1



Laser ablation scan on iron metal standard G3A1. Ablation conditions: 50 $\mu$ m crater, 5Hz, 3 $\mu$ m.s<sup>-1</sup>, 4J.cm<sup>-2</sup>, helium atmosphere. Imaging conditions: FEI SEM, 20kV, SE detector, WD: 11.5mm. Scan shows controlled ablation with minimal melting. Surface has not been cleaned prior to imaging.

### 3.5.5 Accuracy of Iron Analysis by LA-ICP-MS

The iron reference materials and in-house standards were all analysed by LA-ICP-MS using scanning mode as outlined in the previous section. The measured compositions have been compared to the accepted compositions, over the concentration range of interest to this study: 1 to 10,000  $\mu$ g.g<sup>-1</sup>. The comparison figures plot measured concentration against expected

concentration, for two different laser spot sizes. The figures are shown below, one for each trace element, as Figures 3.12a to 3.12p.

Most trace elements, especially the refractory elements, show good agreement between LA-ICP-MS and the accepted composition. For others, and in particular the more volatile elements, there was a marked deviation in the LA-ICP-MS results, with the measured values deviating by up to a few hundred percent (see Ag, Bi, Cd, In, Pb, Sb, and Tl.). This over-estimation of the measured concentration is more involved than the fluence optimisation measurements suggest, as there is also a strong dependence on concentration for most of these elements. Only antimony shows a fixed offset, regardless of concentration, which suggests that the antimony concentration in the primary calibration is wrong by some fixed amount.

The mechanism for over estimating the concentration by LA-ICP-MS is unknown, but is most likely due to the presence of small high-density blebs in the iron matrix. These blebs contain elevated levels of volatile metals (measured qualitatively by SEM) which are ablating more readily than the surrounding iron. This results in preferential removal of the high density material and subsequent over-estimation of the concentration.

Another significant observation afforded by the plots in Figures 3.12a-p is the ability to inspect the overall detection limit of this technique. While the data reduction software reports detection limits less than  $1 \mu\text{g.g}^{-1}$  (see Table 3.3) for a single analysis, elements such as chromium, copper and zinc are observed to have a much higher effective detection limit of 100, 100, and  $50 \mu\text{g.g}^{-1}$  respectively. It is this author's opinion that the high detection limits for these elements are caused by an interference<sup>11</sup> or limitation in the data processing.

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<sup>11</sup> Most probably polyatomic as all isobaric interferences have been accounted for in this study.

Figure 3.12a—Analytical Accuracy Assessment—Ag

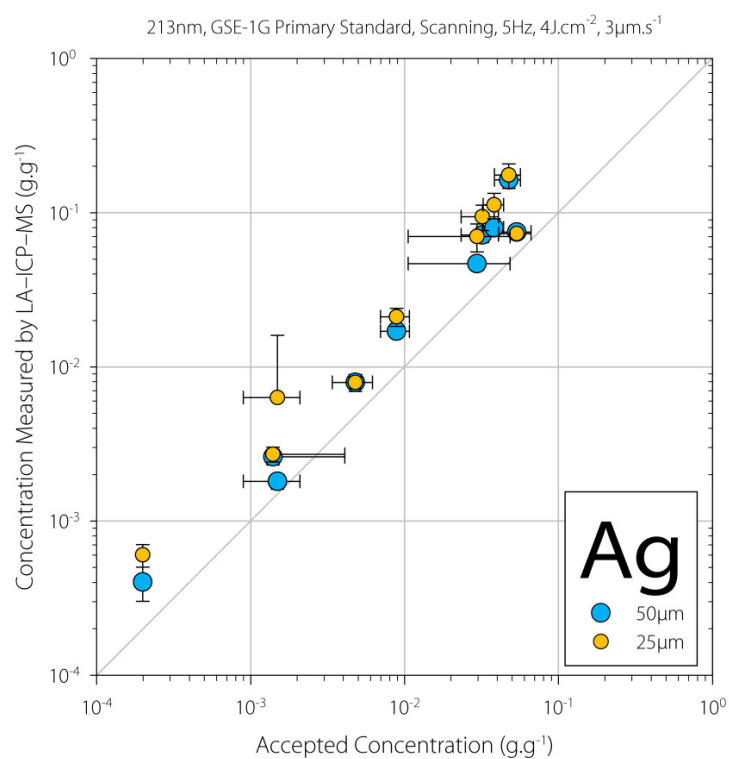


Figure 3.12b—Analytical Accuracy Assessment—Bi

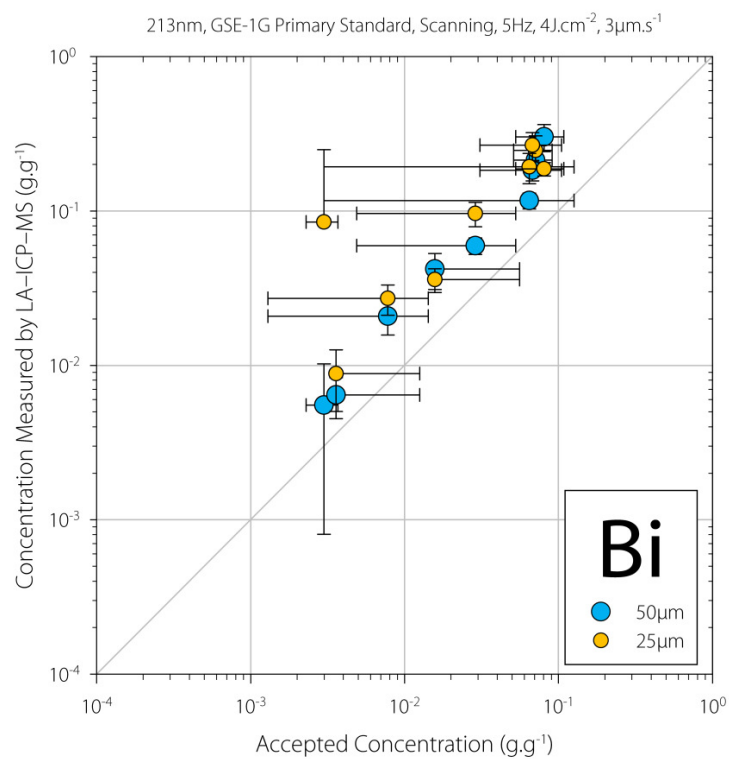




Figure 3.12c—Analytical Accuracy Assessment—Cd

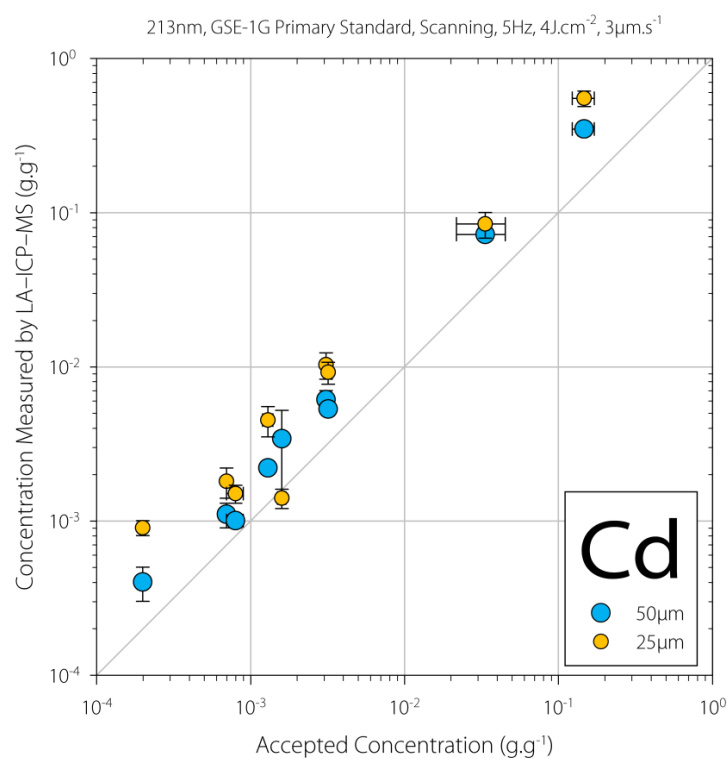


Figure 3.12d—Analytical Accuracy Assessment—Cr

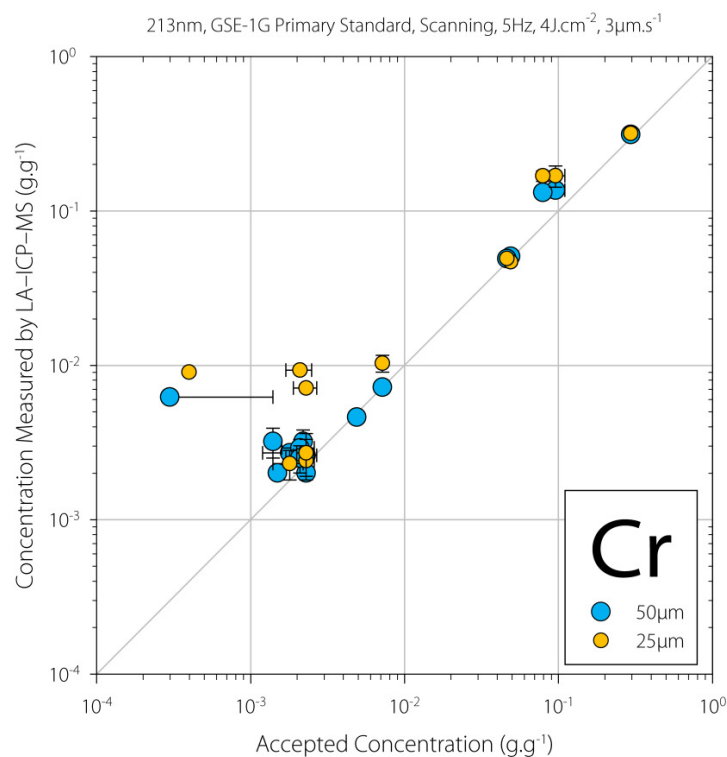


Figure 3.12e—Analytical Accuracy Assessment—Cu

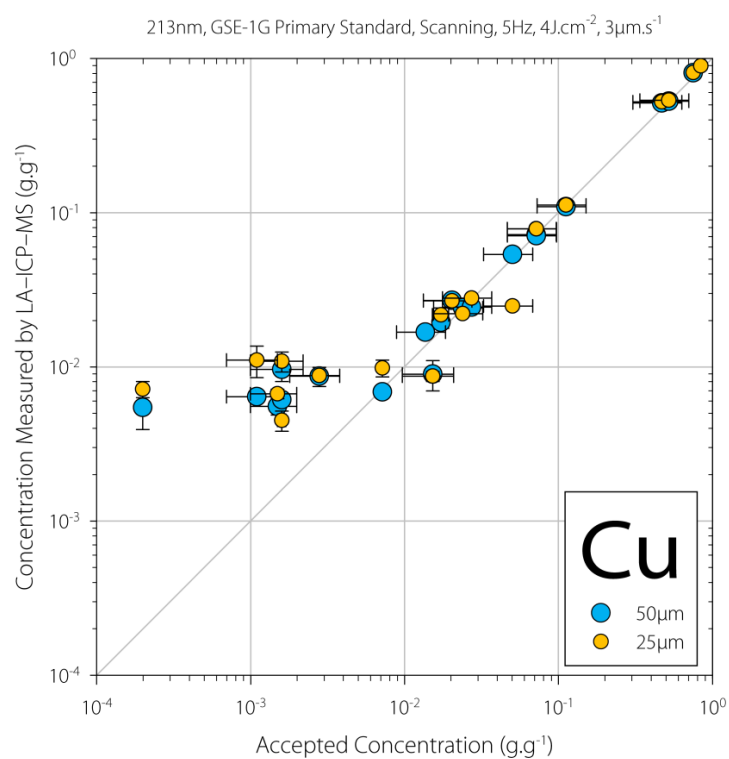


Figure 3.12f—Analytical Accuracy Assessment—Ga

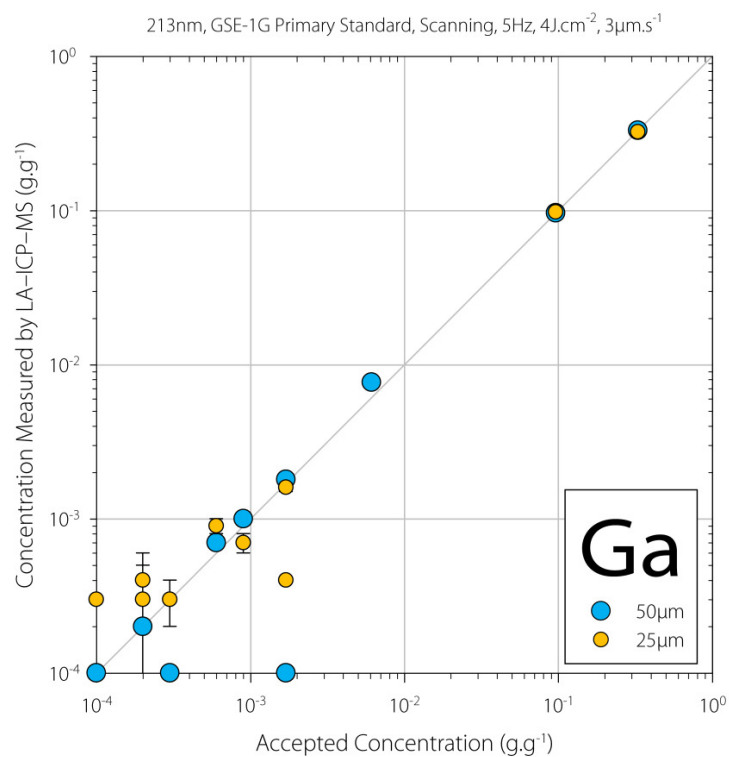


Figure 3.12g—Analytical Accuracy Assessment—Ge

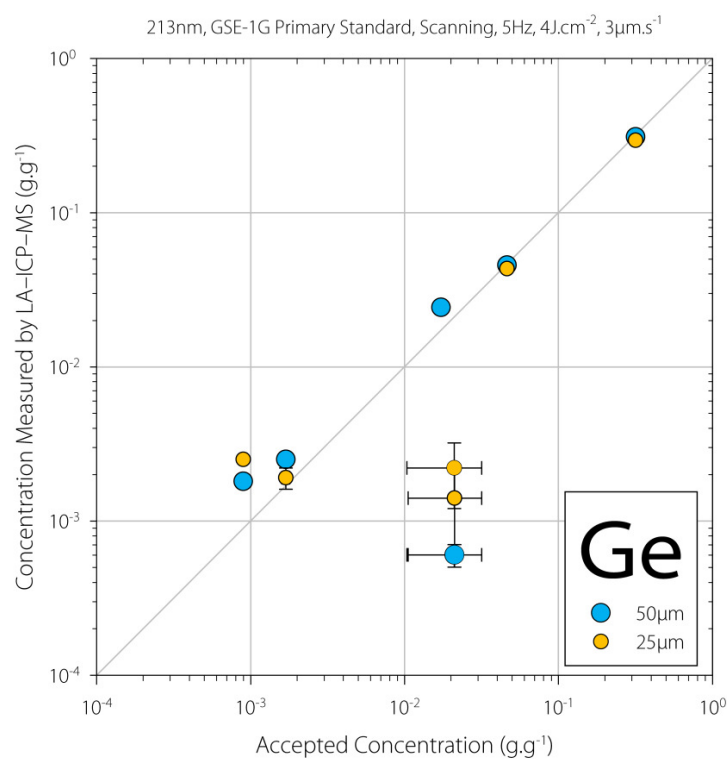


Figure 3.12h—Analytical Accuracy Assessment—In

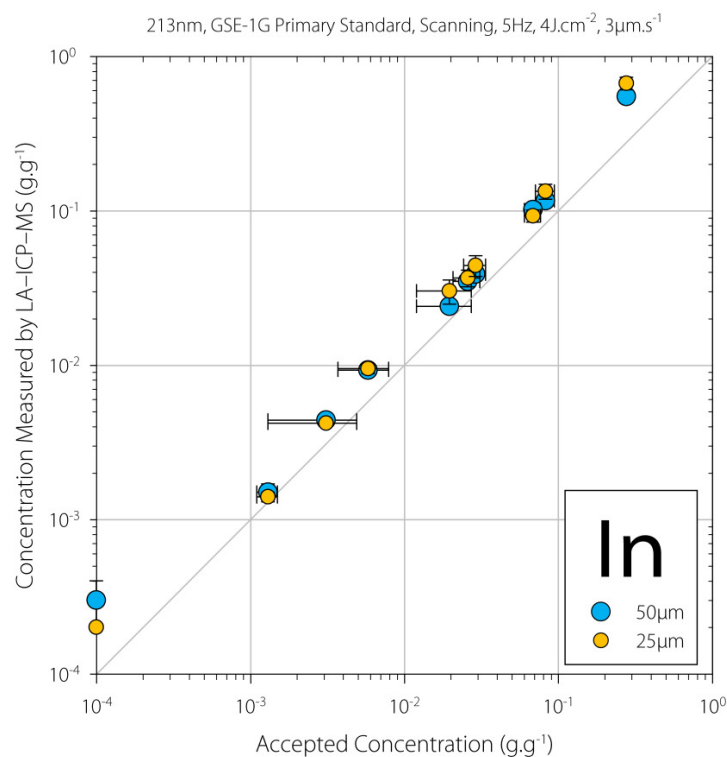


Figure 3.12i—Analytical Accuracy Assessment—Mo

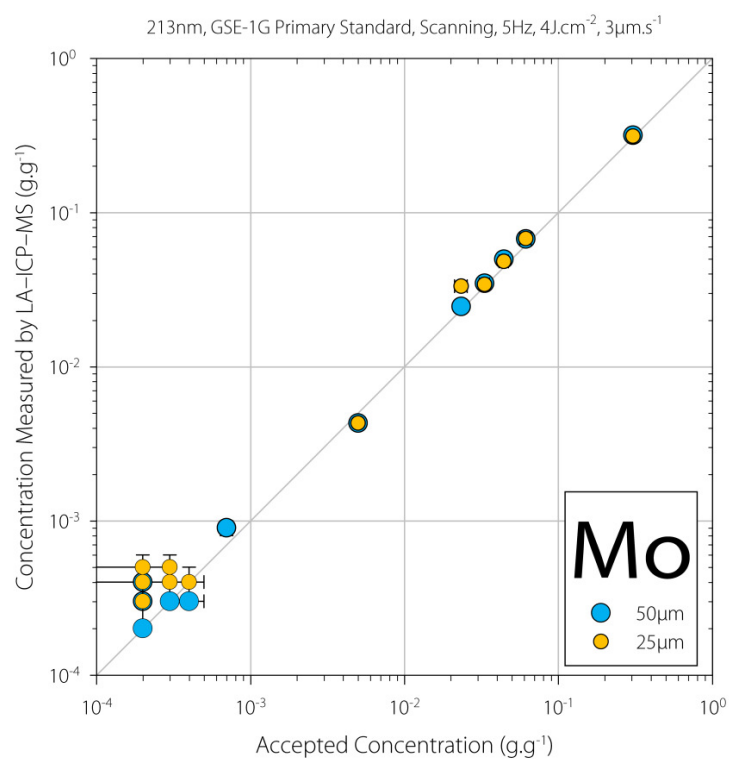


Figure 3.12j—Analytical Accuracy Assessment—Pb

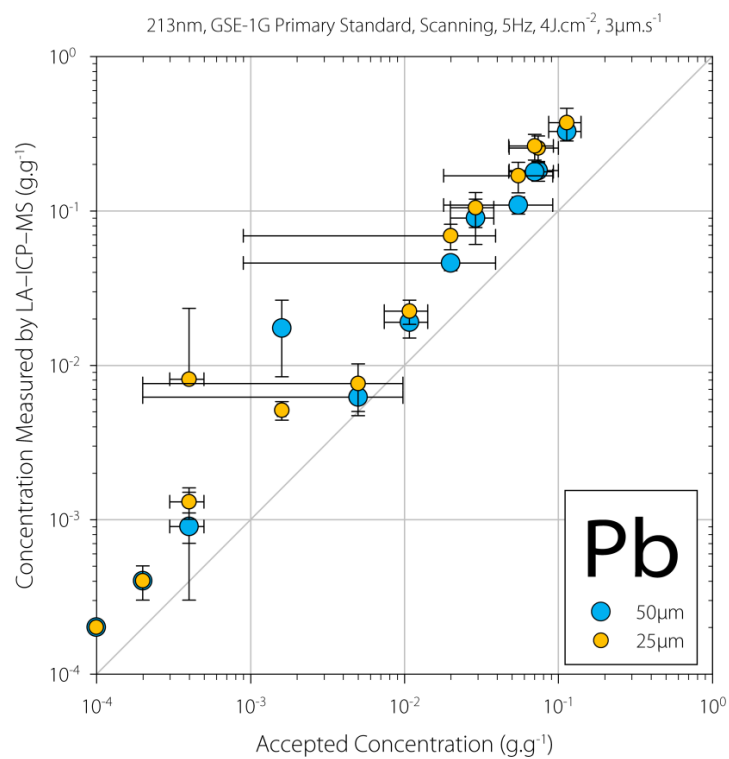


Figure 3.12k—Analytical Accuracy Assessment—Sb

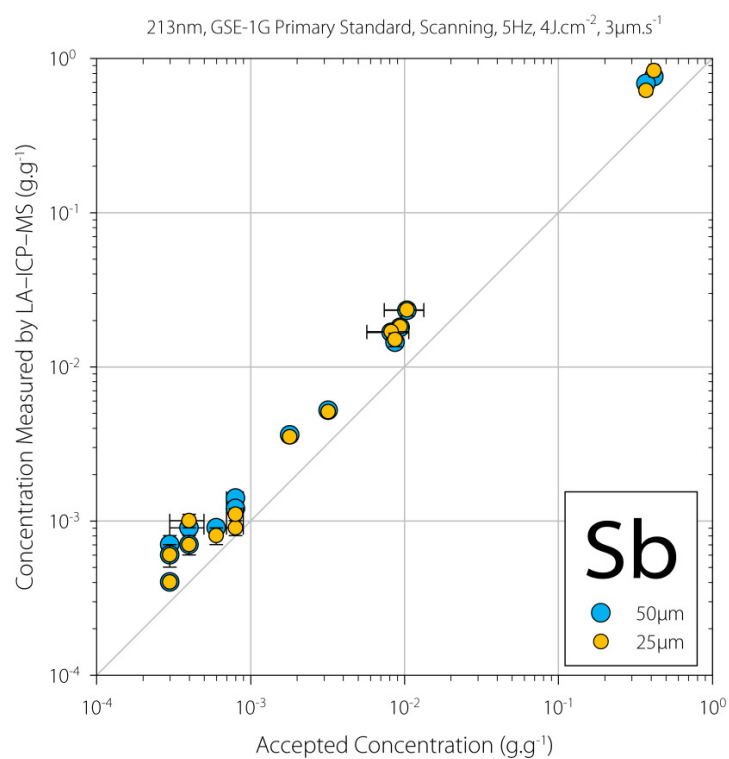


Figure 3.12l—Analytical Accuracy Assessment—Sn

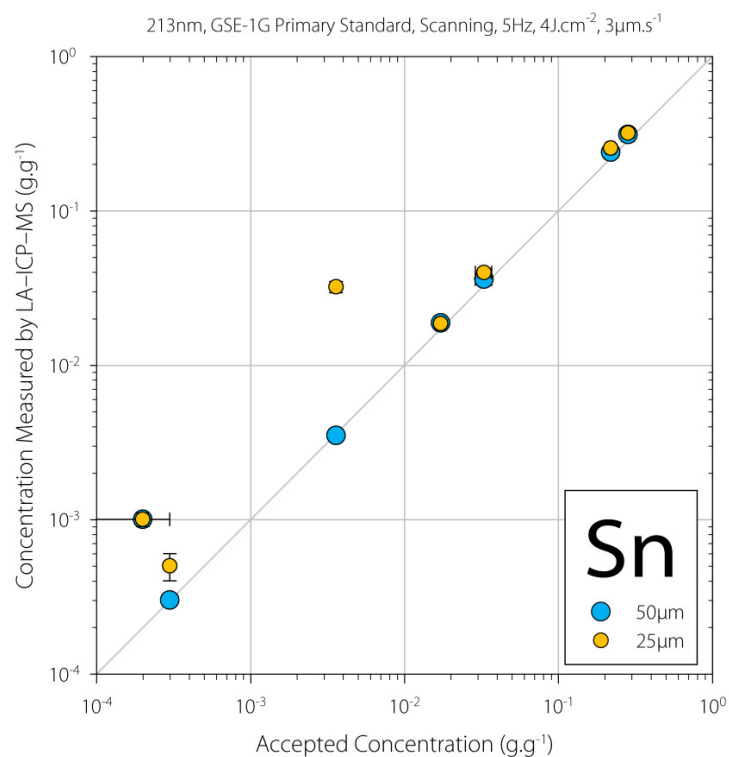


Figure 3.12m—Analytical Accuracy Assessment—Ti

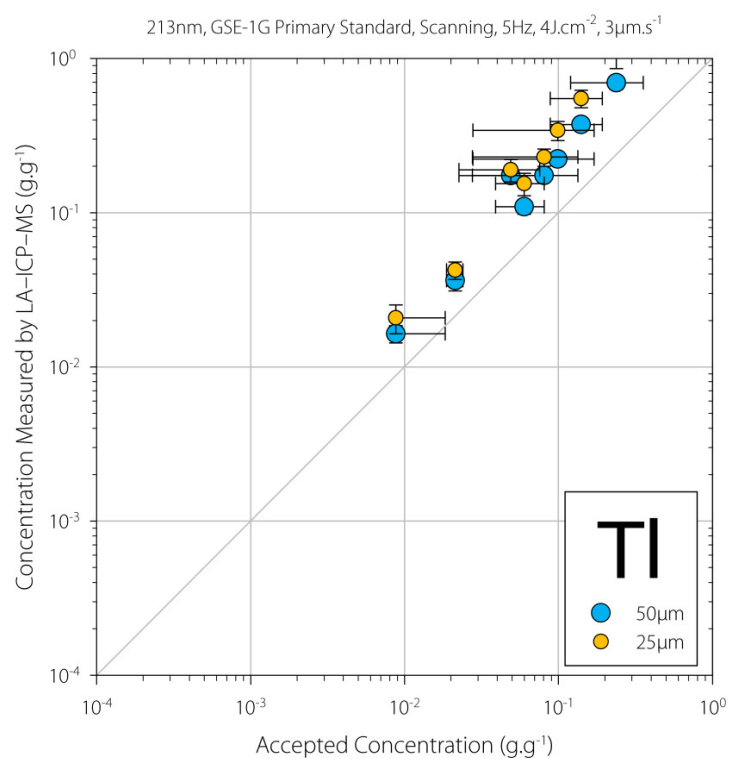


Figure 3.12n—Analytical Accuracy Assessment—V

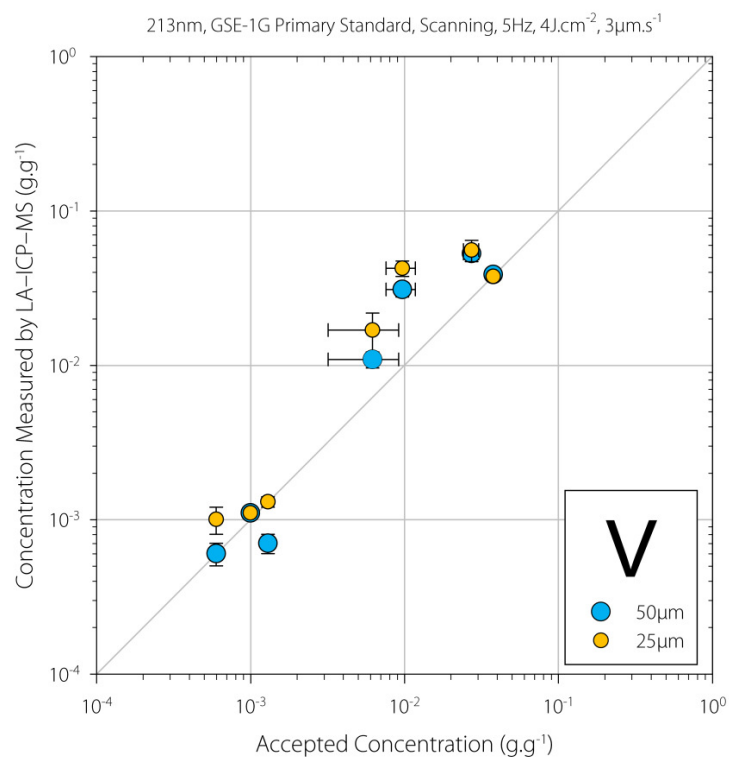


Figure 3.12o—Analytical Accuracy Assessment—W

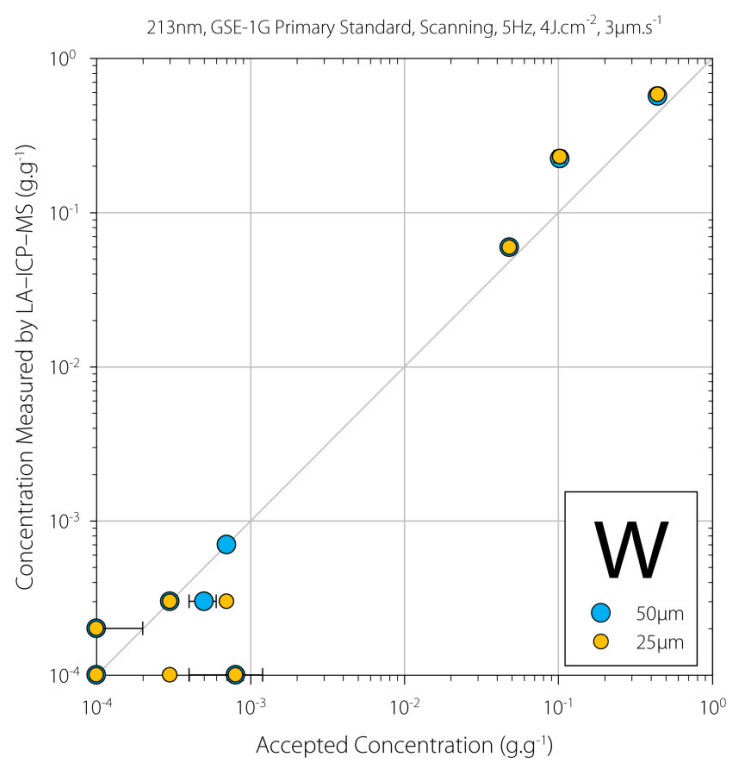
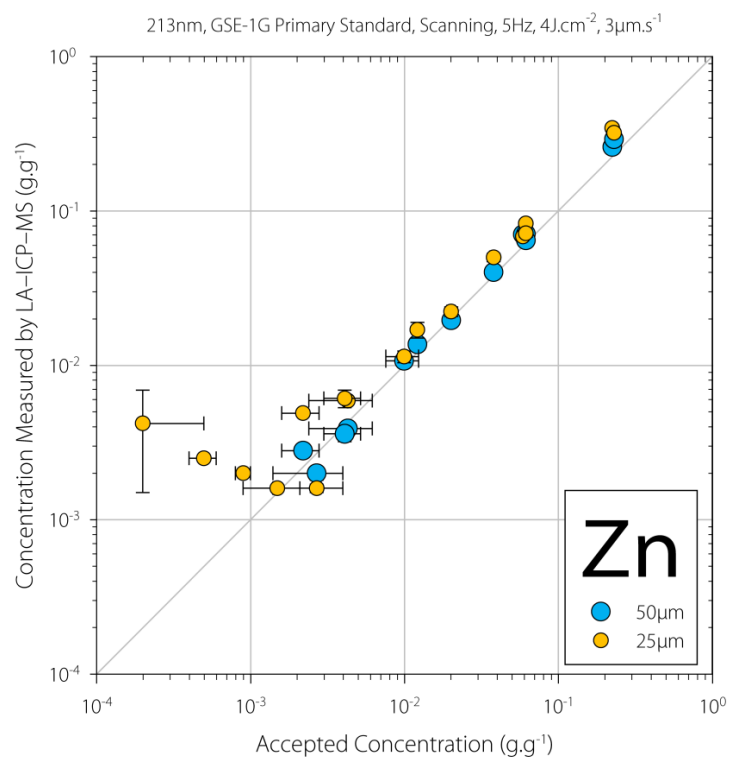


Figure 3.12p—Analytical Accuracy Assessment—Zn



### 3.5.6 Concentration Correction Curves

The measured concentration deviations for the trace elements Ag, Bi, Cd, In, Pb, Sb, and Tl, are all characteristically over-estimated by up to several hundred percent. This discrepancy will affect the metal-silicate partition coefficients (see Chapter 4) by a factor of 2 to 3 which will propagate into the calculated value of activity coefficient for these elements.

To improve the accuracy of LA-ICP-MS analysis for these elements a set of exponential correction curves were regressed on the measured and accepted concentrations. These curves force the laser ablation concentration values to agree with the accepted concentration only over the range 1 to 10,000  $\mu\text{g.g}^{-1}$  and should not be extrapolated in composition space since the wider validity of these curves is unfortunately considerably limited. To effectively make use these curves in this study the laser ablation concentration data were collected the day immediately prior to the analysis session of the metal samples, and the laser, cell, and ICP conditions were maintained consistently between the two sessions. It is expected that any deviation in operating conditions would change the magnitude of the correction curves; however a complete assessment of such effects was beyond the scope of this study.

Most problematic is the exponential increase in the correction factor with trace element concentration. While this is valid over the concentration range of interest to this study, the correction curve should not be extrapolated to higher concentrations. It is the opinion of this author that the correction curves combine numerous separate effects, including oversampling due to element volatility, and oversampling due to a higher ablation rate of blebs rich in trace elements.



### 3.5.7 Discussion and Future Directions of Study

While the iron standards made by piston cylinder in this study ultimately proved to be suitable for their intended application, unfortunately the standard homogeneity was ultimately quite poor, and the volume produced insufficient for wide distribution. Other techniques for manufacturing standards were evaluated as part of this project, and may produce improved reference materials for future work.

#### 3.5.7.1 *Fabricating Iron Standards by Pulsed Laser Deposition*

One method for making metastable solid materials is pulsed laser deposition. This technique is widespread in the photonics, electronics, and nanomaterials industries. A target is mounted inside a vacuum chamber and ablated with a pulsed laser admitted to the chamber via a window. The material is vaporised by the laser and deposits on a nearby substrate. Adjusting the fugacity of various gas components (sulphur or oxygen, for example) as well as the temperature and composition of the substrate, will alter the composition of the deposited layer. If the ablation target comprises separate zones of pure elements, and is rotated rapidly and steadily under the laser beam, then the pure elements will be mixed during ablation and deposited as an effectively homogenous material at the tens of microns length scale. The major drawback of this technique is that the deposited layer grows relatively slowly, and while constraints are not very exact, this author estimated that 24 hours of continual ablation would be required to grow a useful layer tens of microns thick.

This technique has been used by other workers [Neubauer *et al.* 1998; Wodniecki *et al.* 1999] to investigate the iron-indium system, and they report the formation of solid solutions with indium contents up to 15 at.% can be formed in this process, which is 3–4 orders of magnitude higher than those achieved by thermal treatments, and encountered in this study.

It is this author's opinion that pulsed laser deposition may offer a way to consistently fabricate metastable standard materials. While batch to batch compositional homogeneity can only be surmised, the possibility of fabricating materials with trace element concentrations that can be readily analysed by EPMA would enable much utility from a single bespoke standard. And perhaps with appropriate process and quality controls in place then unlimited standards may be fabricated at arbitrary metastable compositions.

#### 3.5.7.2 *Fabricating Iron Standards by High Energy Ball Milling*

Another technique for fabricating metastable materials is physical mixing by a high energy ball mill. Other workers [Nunes *et al.* 2002] report the successful fabrication of an iron-lead alloy containing 0.05 at.% lead. It may be possible to mix other elements and produce a multi-element standard in large quantities, which is a key requirement for certification of reference materials.

#### 3.5.7.3 *Femtosecond Laser Ablation*

As outlined in this chapter, optimising conditions for laser ablation of volatile trace elements in iron metal is problematic. To resolve these difficulties, other workers [Nedialkov *et al.* 2004; Yoichi 2008; Shaheen *et al.* 2013] have suggested that femtosecond laser pulses offer improved ablation of metals with reduced fractionation. The primary mechanism contributing to this improvement is the shorter pulse duration minimising sample heating.

Unfortunately, due to the complexity of implementation, femtosecond laser systems are characteristically expensive and intensive maintenance requirements have limited their use for LA-ICP-MS in the Earth sciences. As such, no published data could be identified that showed clear improvement over the results presented in this study. However, in light of the exciting possibility that a femtosecond laser system would offer superior analytical accuracy then the

iron standards characterised in this study would provide an invaluable set of materials to make an evaluation.

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### **3.6 Conclusion**

Laser ablation ICP–MS has been used to determine the trace element composition of both glass and iron metal experimental run products.

Analysis of the glass samples followed relatively routine practices, and by optimising the laser ablation system, operating conditions, and calibration standard, excellent detection limits and analytical accuracy were achieved.

In contrast, the analysis of iron samples with glass calibration standards resulted in marked deviations in the measured concentrations. To assess and correct for these effects a set of in-house iron standards were fabricated and characterised. These standards allowed the analytical accuracy of glass-calibrated laser ablation to be improved via the generation and application of correction curves for those volatile elements of most interest to this study.



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## **4 Metal–Silicate Partitioning Experiments**

### **4.1 Introduction**

The objective of this project section was to measure the activity coefficients of sixteen trace elements in silicate melts. This will be achieved by measuring the trace element partition coefficients between carbon-saturated iron metal and silicate melt. Starting mixtures comprising a range of CMAS compositions were prepared and doped with trace elements at an abundance of 50 to 5000  $\mu\text{g.g}^{-1}$  per element. The high pressure experiments were conducted in a  $\frac{1}{2}$ " Boyd–England type piston cylinder apparatus operated at 1650°C and a pressure of 1.3 GPa for twenty minutes. At the end of the experiment the samples were quenched by turning off power to the furnace. The samples were analysed by EPMA and LA–ICP–MS. The partition coefficients and available thermochemical data are used to compute the activity coefficients of the trace elements in the silicate melt. Some values for epsilon-carbon have been revised using the results from four experiments conducted in carbon-free capsules. Solubility experiments were performed to ensure that the equilibria of interest were obeying Henry’s law. Absolute values of the activity coefficients have been determined, and those that show a trend with composition have been modelled using linear regression.

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## 4.2 Starting Compositions

Experimental sample compositions were chosen to span the CMAS composition space. Mixtures were prepared from reagent grade oxides, dried in a 400°C furnace, and weighed on the laboratory pan balance<sup>12</sup>. Calcium was added as calcium carbonate, which following weighing was de-carbonated in an alumina crucible by heating from 500°C to 1100°C over a period of one hour before being held at 1100°C for no less than 12 hours. All mixtures were ground and homogenised to an intimate mixture in an agate mortar under acetone. The final compositions were prepared via intermediary end-member compositions (Table 4.1) which were first mixed, pressed into cylindrical pellets (12 x 10mm) and fired in a platinum crucible in air at 1300°C for two hours. The fused pellets were ground back into powder and the process repeated two more times for a total of three firings. In total 8 g of each end member was fabricated.

**Table 4.1—Intermediary End Member Compositions**

| End Member                       | CaO  | MgO  | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Total |
|----------------------------------|------|------|--------------------------------|------------------|-------|
| Diopside                         | 25.9 | 18.6 | 0.0                            | 55.5             | 100.0 |
| Anorthite                        | 20.2 | 0.0  | 36.7                           | 43.2             | 100.0 |
| Forsterite                       | 0.0  | 57.3 | 0.0                            | 42.7             | 100.0 |
| Al <sub>2</sub> SiO <sub>5</sub> | 0.0  | 0.0  | 62.9                           | 37.1             | 100.0 |
| CaSiO <sub>2</sub>               | 48.3 | 0.0  | 0.0                            | 51.7             | 100.0 |

The end member compositions were then combined and homogenised to produce the final starting element compositions (Table 4.2).

These compositions have been projected onto the anorthite–diopside–forsterite (ADF) ternary and shown in Figure 4.1. Additional projection plots, including CMAS tetrahedron views, have been included in the Appendix.

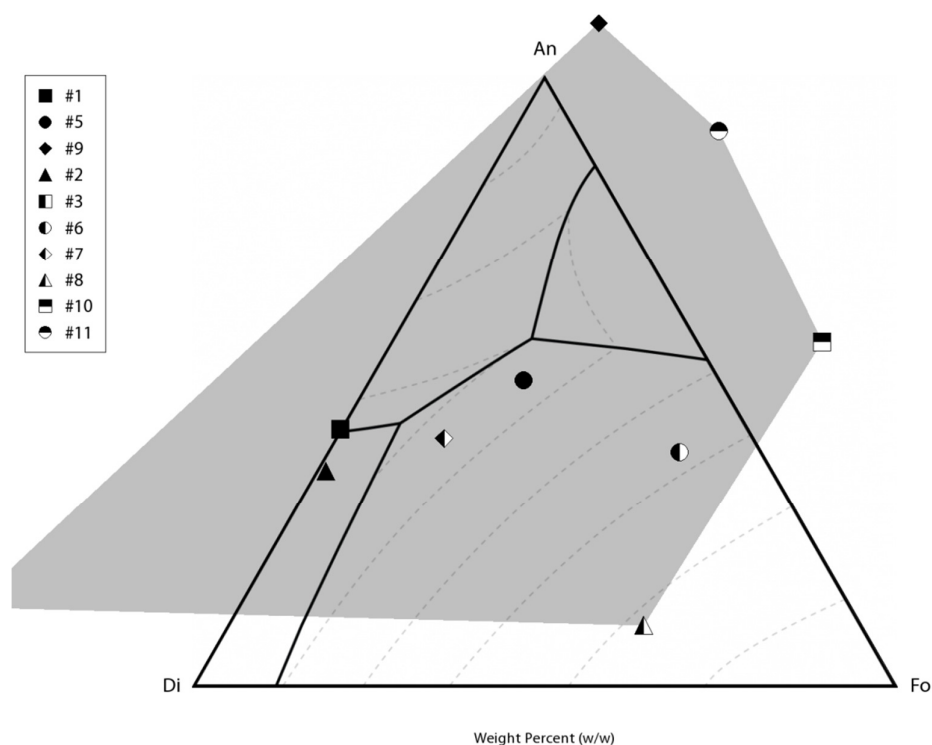
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<sup>12</sup> OHAUS *Explorer Pro* EP64C d=0.1mg

**Table 4.2—Starting Compositions**

| Composition | Alias | CaO  | MgO  | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Total |
|-------------|-------|------|------|--------------------------------|------------------|-------|
| #1          | AD    | 23.5 | 10.8 | 15.4                           | 50.3             | 100.0 |
| #5          | ADF   | 17.3 | 17.8 | 18.3                           | 46.5             | 100.0 |
| #9          | AA    | 19.1 | 0.0  | 39.8                           | 41.0             | 100.0 |
| #2          |       | 15.7 | 7.2  | 10.3                           | 66.7             | 100.0 |
| #3          |       | 38.4 | 4.3  | 6.2                            | 51.2             | 100.0 |
| #4          |       | 32.3 | 0.0  | 0.0                            | 67.7             | 100.0 |
| #6          |       | 14.2 | 32.6 | 15.0                           | 38.2             | 100.0 |
| #7          |       | 11.8 | 12.1 | 12.5                           | 63.6             | 100.0 |
| #8          |       | 0.0  | 35.2 | 0.0                            | 64.8             | 100.0 |
| #10         | SAF   | 0.0  | 28.5 | 19.0                           | 52.5             | 100.0 |
| #11         |       | 16.3 | 15.0 | 33.9                           | 34.9             | 100.0 |

**Figure 4.1—Starting Compositions ADF Projection**



The starting composition mixtures (#1 to #11) expressed as linear combinations of the anorthite–diopside–forsterite (ADF) end members. The range of starting compositions extend well beyond the ADF composition space, resulting in some linear combinations showing “negative” amounts of forsterite and diopside, and those negative compositions plot outside the ADF ternary. The shaded area is the convex hull of the starting compositions in ADF coordinate space.

#### 4.2.1 Trace Elements

Three trace element mixtures were created by weighing reagent grade oxide powders and mixing them under acetone in an agate mortar. The elements were grouped into three groups: “A” contained weakly siderophile elements, “F” contained strongly siderophile elements, and “B” contained more volatile elements. There is some overlap between the groups. The trace element mixes are reported in Tables 4.3a—4.3c.

**Table 4.3a—Trace Element Mixture “A”**

| Element | Added As                       | Oxide Mass (mg) | Element Mass (mg) | Element % (g.g <sup>-1</sup> ) |
|---------|--------------------------------|-----------------|-------------------|--------------------------------|
| Cd      | CdO                            | 50.4            | 44.1              | 8.0                            |
| Cr      | Cr <sub>2</sub> O <sub>3</sub> | 57.4            | 39.3              | 7.1                            |
| Cu      | Cu <sub>2</sub> O              | 100.0           | 88.8              | 16.1                           |
| In      | In <sub>2</sub> O <sub>5</sub> | 49.7            | 36.9              | 6.7                            |
| Pb      | PbO                            | 71.2            | 66.1              | 12.0                           |
| Sn      | SnO <sub>2</sub>               | 50.2            | 39.5              | 7.2                            |
| Tl      | Tl <sub>2</sub> O <sub>3</sub> | 73.1            | 65.4              | 11.8                           |
| V       | V <sub>2</sub> O <sub>5</sub>  | 49.6            | 27.8              | 5.0                            |
| Zn      | ZnO                            | 50.8            | 40.8              | 7.4                            |

**Table 4.3b—Trace Element Mixture “F”**

| Element | Added As                       | Oxide Mass (mg) | Element Mass (mg) | Element % (g.g <sup>-1</sup> ) |
|---------|--------------------------------|-----------------|-------------------|--------------------------------|
| Ag      | Ag <sub>2</sub> O              | 50.0            | 46.5              | 9.8                            |
| Bi      | Bi <sub>2</sub> O <sub>3</sub> | 50.0            | 44.8              | 9.5                            |
| Cu      | Cu <sub>2</sub> O              | 100.3           | 89.1              | 18.8                           |
| Ga      | Ga <sub>2</sub> O <sub>3</sub> | 49.9            | 37.1              | 7.8                            |
| Ge      | GeO <sub>2</sub>               | 50.0            | 34.7              | 7.3                            |
| Mo      | MoO <sub>3</sub>               | 49.7            | 33.1              | 7.0                            |
| Sb      | Sb <sub>2</sub> O <sub>3</sub> | 50.3            | 42.0              | 8.9                            |
| W       | WO <sub>3</sub>                | 73.5            | 58.3              | 12.3                           |

**Table 4.3c—Trace Element Mixture “B”**

| Element | Added As                       | Oxide Mass (mg) | Element Mass (mg) | Element % (g.g <sup>-1</sup> ) |
|---------|--------------------------------|-----------------|-------------------|--------------------------------|
| Ag      | Ag <sub>2</sub> O              | 53.5            | 49.8              | 12.4                           |
| Bi      | Bi <sub>2</sub> O <sub>3</sub> | 55.0            | 49.3              | 12.3                           |
| Cd      | CdO                            | 57.1            | 50.0              | 12.5                           |
| In      | In <sub>2</sub> O <sub>3</sub> | 60.7            | 50.2              | 12.5                           |
| Pb      | PbO                            | 55.0            | 51.1              | 12.8                           |
| Sb      | Sb <sub>2</sub> O <sub>3</sub> | 59.9            | 50.0              | 12.5                           |
| Tl      | Tl <sub>2</sub> O <sub>3</sub> | 55.9            | 50.0              | 12.5                           |
| Zn      | ZnO                            | 61.9            | 49.7              | 12.4                           |



## 4.2.2 Experiment Starting Mixtures

The compositions of each starting mixture are reported in Table 4.4 below. A small amount of FeO was added to the mixture to stabilise the trace element oxide phases, effectively forcing the trace elements to partition more strongly into the silicate melt. This was to ensure the concentration of these elements in the silicate glass could still be analysed by LA-ICP-MS. The more siderophile element mixture (trace F) received a higher amount of FeO to enhance this effect further.

The mixtures were weighed and mixed in a stepwise fashion; first each “OXIDE” mixture was created before being weighed and combined with finely ground (200 mesh, 99% pure) iron metal.

In total 11 major element compositions were combined with three trace element mixtures to prepare 33 experimental compositions.

**Table 4.4—Experiment Starting Mixture Compositions**

| Trace Mix | "OXIDE"    |                  |          | "OXIDE" (mg) | Fe Metal (mg) |
|-----------|------------|------------------|----------|--------------|---------------|
|           | Trace (mg) | Composition (mg) | FeO (mg) |              |               |
| A         | 6.0        | 300              | 6.0      | 150.0        | 150.0         |
| F         | 6.0        | 300              | 45.0     | 150.0        | 150.0         |
| B         | 6.0        | 300              | 6.0      | 150.0        | 150.0         |

*Total Starting Mixture*

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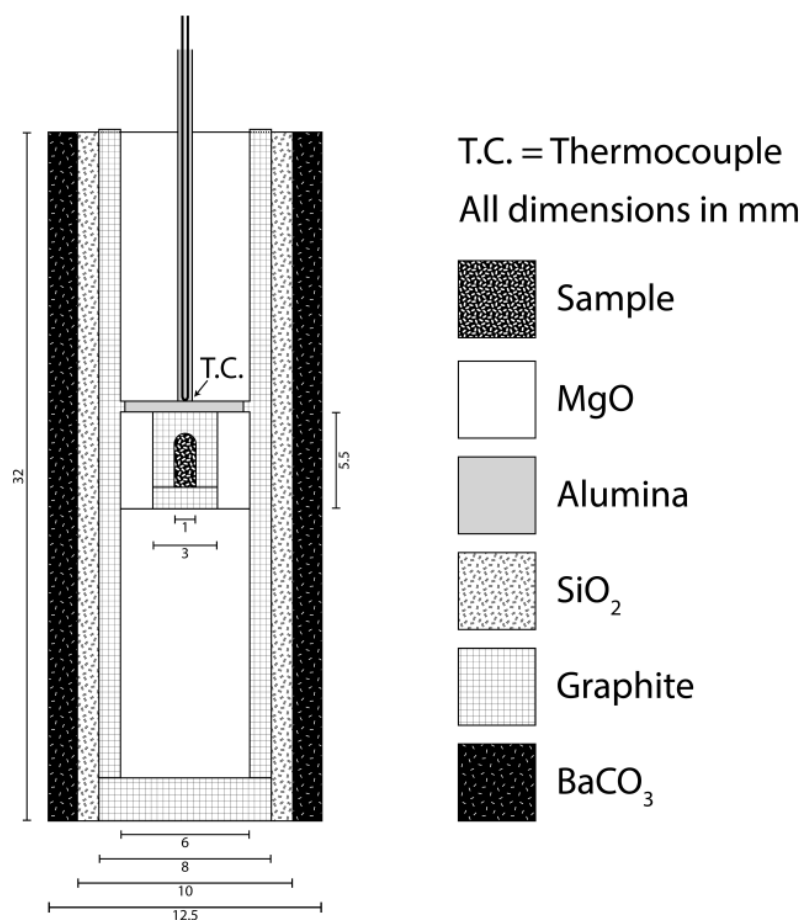
### 4.3 High Pressure Experiments

These experiments were conducted at 1635°C and 1.5 GPa using an end loaded Boyd–England type piston cylinder apparatus. Starting mixture was packed into a graphite capsule surrounded by a polycrystalline MgO sleeve, with MgO spacers above and below, before being placed inside a ½-inch BaCO<sub>3</sub>–SiO<sub>2</sub> glass assembly with a graphite heater [McDade *et al.* 2002]. The assembly construction is shown in Figure 4.2 below.

The experimental temperature of 1650°C was measured using a W<sub>95</sub>Re<sub>5</sub>–W<sub>74</sub>Re<sub>26</sub> thermocouple separated from the capsule by a 0.5 mm alumina disc. Furnace control was achieved via a *Eurotherm 2404* PID temperature controller, running in closed-loop control mode for the experimental duration of 20 minutes. This is considered sufficient to achieve equilibrium, as demonstrated by other [Corgne *et al.* 2008; Thibault and Walker 1995] workers performing similar metal–silicate partitioning experiments.

Due to inhomogeneity in the assembly, the pressure exerted on the sample is less than the pressure applied by the piston. The difference is caused by friction in the piston assembly and the standard approach is to apply extra pressure to compensate. The piston cylinder apparatus used in this study was calibrated for pressure [McDade *et al.* 2002] and a 9% correction applied for thin walled BaCO<sub>3</sub> sleeves, as used in this study.

Figure 4.2—Piston Cylinder Assembly



Vertical section showing the internal arrangement of the piston cylinder apparatus assembly used in this study. The sample is packed into the graphite capsule as a fine powder and each component assembled by hand to the dimensions shown here. The thermocouple is separated from the sample capsule by a protective alumina disc. The outer SiO<sub>2</sub> and BaCO<sub>3</sub> sleeves serve as a pressure medium, and the entire assembly is wrapped in thin lead foil (not shown here) prior to insertion into the high pressure apparatus.

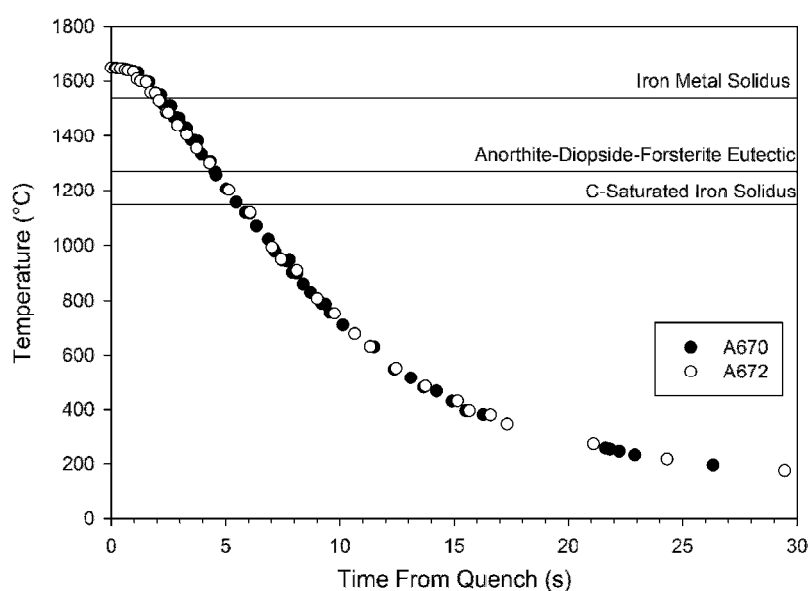
#### 4.3.1 Quench Rate

The samples were quenched by turning off the heater power without adjusting the end load or piston load pressures. The quench rate was recorded for two experiments using a hand-held video camera<sup>13</sup>. The video files were processed frame by frame using the software package *Avidemux* and legible temperatures were plotted over time (Figure 4.3). It is clear that the quench rate is reproducible between the two runs, and that the experiments quench to 1100°C

<sup>13</sup> Samsung Galaxy S2 computer phone, 1920 x 1080 pixels, RGB, 25 fps.

within 5 seconds. The reference lines show relevant solidus temperatures at one atmosphere pressure. At higher pressure the melting point of pure iron is increased by  $2.85 \text{ K.kbar}^{-1}$  [Sterrett *et al.* 1965] and will be elevated by 37 degrees at 1.5 GPa, resulting in a shorter time to quench. The *Eurotherm* 2404 adjusts the thermocouple input using a sliding window filter with a 1.6 s timing constant. As such the quench rate reported here should be regarded as a lower bound.

Figure 4.3—Piston–Cylinder Quench Rate



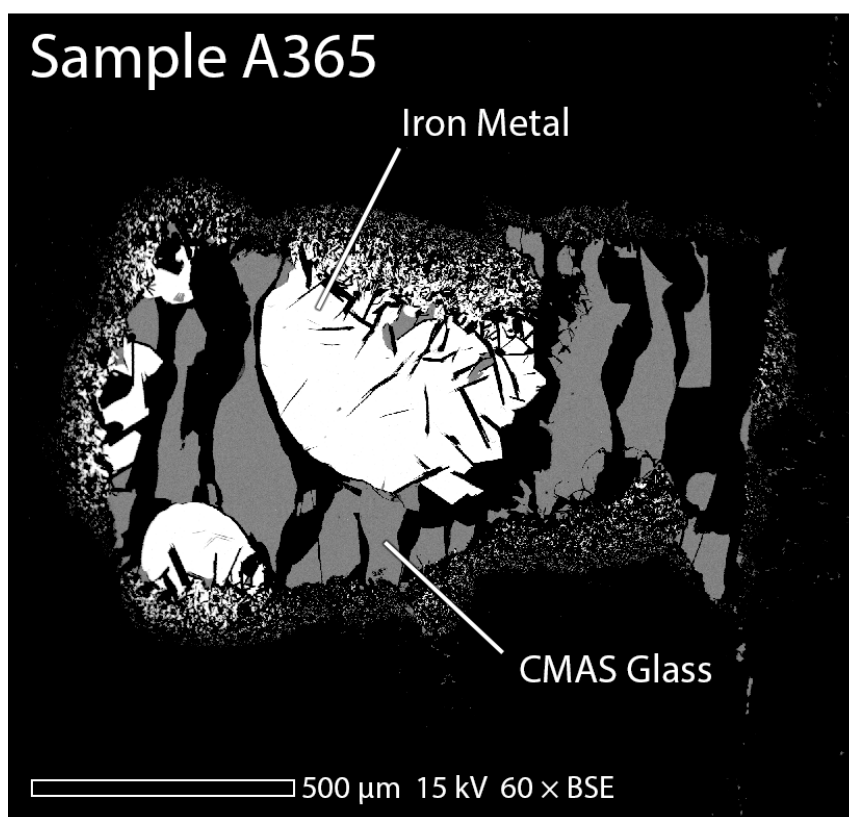
The temperature of the assembly was measured using a W–Re thermocouple which was read and displayed on an LCD panel by a *Eurotherm* 2404 PID controller. A digital video camera was used to record the display during the quench of two experiments. The results are plotted here, along with some helpful reference temperatures. The PID controller was set to use a 1.6 s smoothing constant, and this has resulted in the apparent initial hesitation prior to the rapid drop in temperature. The quench rate is approximately 100 degrees per second.

Samples were extracted from the assembly and mounted in 25 mm acrylic blocks, ground with silicon carbide grinding paper to expose the experimental charge and then polished with first 3 then 1  $\mu\text{m}$  diamond paste.

### 4.3.2 Typical Experimental Charge

During each experiment both the iron metal and silicate phases melt, and the trace elements partition between them. Metal and silicate are immiscible and separate into distinct parts of the capsule (Figure 4.4). Most experiments result in one large metal blob, with 2 or 3 smaller companion blobs sometimes present. The glass is nearly always homogenous, though in some cases primary crystals grew during the experiment, altering the silicate melt composition.

Figure 4.4—Typical Experimental Charge



An SEM BSE image of experiment A365. The CMAS glass and iron metal have separated into distinct parts of the capsule. The glass appears homogenous and has been fractured during decompression of the experiment. The iron is carbon saturated and interspersed with carbon laths.

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## 4.4 Analysis

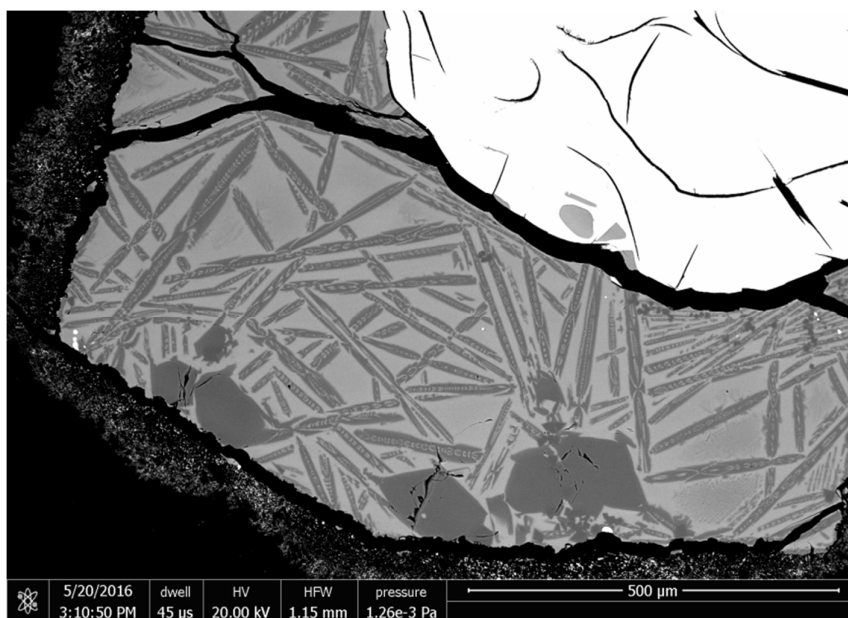
Samples were carbon coated and analysed for major elements using a Jeol JXA-8600 electron microprobe. A thorough description of the EPMA analysis has been presented in Chapter 2.

Trace element compositions were determined using LA-ICP-MS with a NWR 213 nm solid-state laser system connected to a Perkin Elmer 300Q ICP-MS. A thorough description of the LA-ICP-MS analysis has been presented in Chapter 3.

### 4.4.1 Quench Textures in Glass

It should be noted here that in nearly all of the experiments the silicate phase quenched to a homogenous glass. In some of the experiments (Table 4.5) the glass quenched to a finely interlinked network of crystal lamellae (Figure 4.5). To ensure this heterogeneous texture was successfully analysed by EPMA, a modelling project using PENEPMA was conducted. That investigation is documented in Chapter 2.

Figure 4.5—Sample FM1108 Showing Quench Crystal Texture



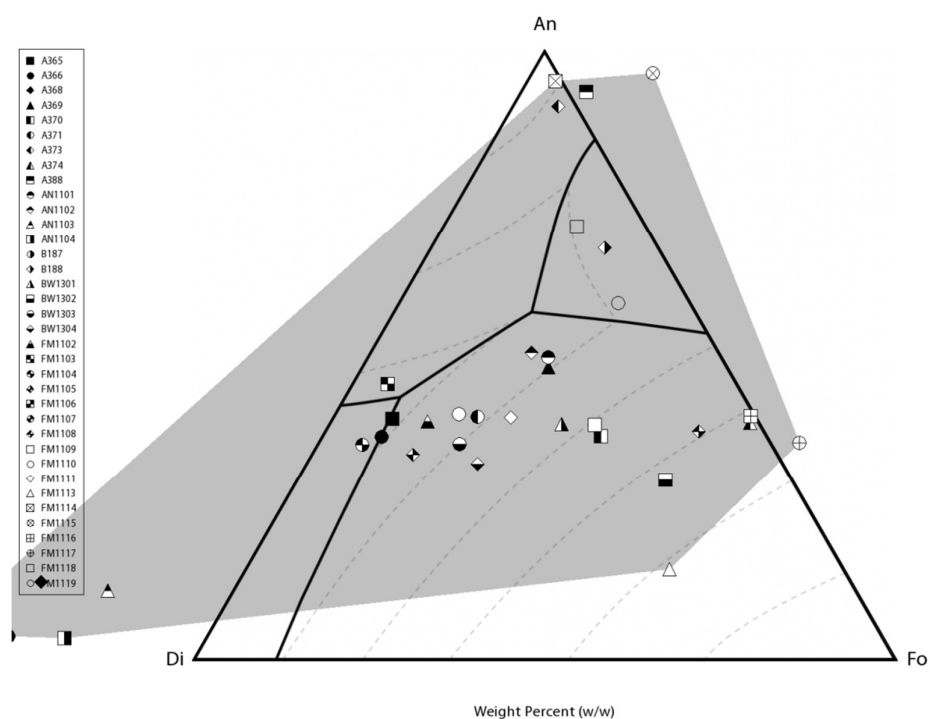
An SEM BSE image of sample FM1108 showing crystal lamellae cross cutting a glass matrix. This texture was formed when the experiment quenched, and the analysis must combine the composition, and

proportions, of each phase so as to reconstruct the composition of the melt prior to quenching. A thorough description and statistical treatment is presented in Chapter 2.

#### 4.4.2 Major Element Compositions

The major element compositions of the silicate melt phase were determined by EPMA and are presented in Table 4.5. In all cases the silicate phase has dissolved some FeO, while only a few have grown primary crystals, which are not included in the analyses. The compositions have also been plotted in the CMAS tetrahedron (FeO content normalised away) and these can be compared to the starting compositions shown previously (Figure 4.1 and the Appendix). Due to the growth of primary crystals the silicate compositions have moved slightly, yet still span a considerable range of the CMAS composition space.

Figure 4.6—Silicate Melt Composition ADF Ternary Diagram



The final silicate compositions as measured by EPMA have been plotted here on the anorthite–diopside–forsterite ternary diagram. The iron content of the silicate has been added to the magnesium content of the forsterite. The shaded region highlights the span of silicate compositions from this study. Forsterite-rich compositions were not attempted since the forsterite end member melts at 1890°C.

The compositions have been plotted here (Figure 4.6) on the anorthite–diopside–forsterite (ADF) ternary. The range of compositions across the ADF ternary are limited by temperature, since these experiments were conducted at 1650°C and the forsterite end member melts at 1890°C.

**Table 4.5—Major Element Silicate Melt Compositions**

| Alias  | Mixture   | Trace | Capsule          | Primary Crystals | Quench Crystals | N  | SiO <sub>2</sub> | 2StdErr | Al <sub>2</sub> O <sub>3</sub> | 2StdErr | FeO | 2StdErr | MgO | 2StdErr | CaO | 2StdErr | Total |
|--------|-----------|-------|------------------|------------------|-----------------|----|------------------|---------|--------------------------------|---------|-----|---------|-----|---------|-----|---------|-------|
| A365   | #1 (AD)   | B     | C                |                  |                 | 7  | 456              | 0.5     | 142                            | 0.3     | 79  | 0.10    | 102 | 0.2     | 214 | 0.14    | 992   |
| A366   | #2        | B     | C                |                  |                 | 7  | 618              | 0.2     | 109                            | 0.08    | 65  | 0.05    | 69  | 0.07    | 144 | 0.04    | 1005  |
| A368   | #3        | B     | C                |                  |                 | 7  | 476              | 0.2     | 60                             | 0.08    | 75  | 0.05    | 39  | 0.03    | 346 | 0.13    | 994   |
| A369   | #5 (ADF)  | B     | C                |                  |                 | 7  | 439              | 0.2     | 171                            | 0.2     | 73  | 0.06    | 156 | 0.12    | 162 | 0.06    | 1001  |
| A370   | #6        | B     | C                | YES              | YES             | 12 | 358              | 1.3     | 142                            | 3.1     | 94  | 0.7     | 231 | 7.1     | 174 | 4.2     | 998   |
| A371   | #7        | B     | C                |                  |                 | 7  | 586              | 0.2     | 118                            | 0.06    | 75  | 0.05    | 99  | 0.07    | 107 | 0.03    | 986   |
| A373   | #9 (AA)   | B     | C                |                  |                 | 5  | 408              | 0.2     | 317                            | 0.3     | 73  | 0.08    | 0.2 | 0.02    | 184 | 0.10    | 985   |
| A374   | #10 (SAF) | B     | C                |                  |                 | 7  | 546              | 0.3     | 115                            | 0.2     | 83  | 0.05    | 251 | 0.3     | 04  | 0.01    | 999   |
| A388   | #9 (AA)   | B     | C                | YES              |                 | 7  | 407              | 0.2     | 329                            | 0.3     | 85  | 0.06    | 0.2 | 0.02    | 178 | 0.08    | 1001  |
| AN1101 | #5 (ADF)  | F     | C                |                  |                 | 10 | 439              | 0.11    | 179                            | 0.09    | 55  | 0.05    | 162 | 0.10    | 166 | 0.07    | 1000  |
| AN1102 | #5 (ADF)  | A     | C                |                  |                 | 19 | 447              | 0.13    | 181                            | 0.2     | 28  | 0.09    | 164 | 0.2     | 170 | 0.06    | 990   |
| AN1103 | #3        | F     | C                |                  |                 | 10 | 426              | 0.2     | 56                             | 0.04    | 157 | 0.13    | 34  | 0.03    | 318 | 0.10    | 992   |
| AN1104 | #4        | F     | C                |                  |                 | 10 | 567              | 0.2     | 05                             | 0.02    | 148 | 0.10    | 01  | 0.02    | 270 | 0.08    | 991   |
| B187   | #4        | B     | C                |                  |                 | 7  | 623              | 0.2     | 03                             | 0.02    | 78  | 0.05    | 05  | 0.02    | 293 | 0.10    | 1001  |
| B188   | #11       | B     | C                | YES              |                 | 7  | 395              | 0.6     | 242                            | 0.7     | 68  | 0.04    | 124 | 0.2     | 167 | 0.2     | 996   |
| BW1301 | #         | A     | MgO              | YES              | YES             | 7  | 484              | 0.8     | 135                            | 1.7     | 34  | 0.2     | 213 | 4.2     | 135 | 1.7     | 1000  |
| BW1302 | #         | F     | MgO              | YES              | YES             | 7  | 425              | 0.9     | 105                            | 0.5     | 96  | 0.9     | 269 | 12.4    | 106 | 5.3     | 1001  |
| BW1303 | #         | F     | SiO <sub>2</sub> |                  |                 | 7  | 641              | 0.2     | 95                             | 0.06    | 91  | 0.09    | 85  | 0.05    | 88  | 0.06    | 1000  |
| BW1304 | #         | A     | SiO <sub>2</sub> |                  |                 | 7  | 666              | 0.2     | 83                             | 0.3     | 42  | 0.13    | 135 | 0.6     | 74  | 0.13    | 999   |
| FM1102 | #1 (AD)   | F     | C                |                  |                 | 10 | 422              | 0.2     | 140                            | 0.08    | 115 | 0.12    | 105 | 0.05    | 207 | 0.07    | 989   |
| FM1103 | #1 (AD)   | A     | C                |                  |                 | 13 | 469              | 0.3     | 163                            | 0.08    | 32  | 0.08    | 105 | 0.12    | 220 | 0.11    | 990   |
| FM1104 | #2        | A     | C                |                  |                 | 9  | 623              | 0.13    | 103                            | 0.11    | 46  | 0.06    | 71  | 0.03    | 148 | 0.03    | 991   |
| FM1105 | #2        | F     | C                |                  |                 | 10 | 569              | 0.2     | 97                             | 0.04    | 133 | 0.13    | 60  | 0.07    | 135 | 0.04    | 994   |
| FM1106 | #3        | A     | C                |                  |                 | 14 | 486              | 0.2     | 64                             | 0.11    | 34  | 0.08    | 41  | 0.07    | 367 | 0.07    | 992   |
| FM1107 | #4        | A     | C                |                  |                 | 14 | 636              | 0.09    | 06                             | 0.02    | 33  | 0.10    | 14  | 0.03    | 304 | 0.04    | 993   |
| FM1108 | #6        | F     | C                | YES              | YES             | 13 | 452              | 0.4     | 125                            | 0.8     | 85  | 0.4     | 251 | 18      | 77  | 0.8     | 990   |
| FM1109 | #6        | A     | C                | YES              | YES             | 24 | 384              | 0.6     | 151                            | 2.8     | 31  | 0.4     | 263 | 64      | 176 | 3.8     | 1005  |
| FM1110 | #7        | A     | C                |                  |                 | 14 | 613              | 0.13    | 121                            | 0.2     | 35  | 0.09    | 110 | 0.08    | 112 | 0.04    | 990   |
| FM1111 | #7        | F     | C                |                  |                 | 11 | 558              | 0.2     | 120                            | 0.09    | 110 | 0.09    | 102 | 0.07    | 102 | 0.04    | 992   |
| FM1113 | #8        | A     | C                |                  |                 | 10 | 615              | 0.2     | 22                             | 0.2     | 30  | 0.06    | 329 | 0.6     | 03  | 0.03    | 999   |
| FM1114 | #9 (AA)   | A     | C                | YES              |                 | 16 | 423              | 0.2     | 341                            | 0.4     | 34  | 0.05    | 07  | 0.10    | 191 | 0.10    | 997   |
| FM1115 | #9 (AA)   | F     | C                |                  |                 | 11 | 366              | 0.11    | 336                            | 0.09    | 124 | 0.04    | 11  | 0.05    | 165 | 0.03    | 1001  |
| FM1116 | #10 (SAF) | A     | C                |                  |                 | 11 | 559              | 0.2     | 120                            | 0.08    | 43  | 0.2     | 272 | 0.2     | 02  | 0.01    | 996   |
| FM1117 | #10 (SAF) | F     | C                |                  |                 | 15 | 490              | 0.13    | 105                            | 0.06    | 160 | 0.10    | 243 | 0.12    | 02  | 0.01    | 1000  |
| FM1118 | #11       | A     | C                | YES              |                 | 9  | 401              | 0.3     | 258                            | 0.4     | 29  | 0.08    | 120 | 0.2     | 182 | 0.2     | 991   |
| FM1119 | #11       | F     | C                | YES              |                 | 15 | 352              | 0.6     | 203                            | 0.8     | 172 | 0.3     | 102 | 0.2     | 161 | 0.3     | 990   |



### Table 4.6—Silicate Melt Trace Element Compositions

| Alias | N | Ag <sub>2</sub> O | 25dEr | B <sub>2</sub> O <sub>3</sub> | 25dEr | Gd <sub>2</sub> O <sub>3</sub> | 25dEr | Cr <sub>2</sub> O <sub>3</sub> | 25dEr | Cu <sub>2</sub> O | 25dEr | Ga <sub>2</sub> O <sub>3</sub> | 25dEr | Gd <sub>2</sub> O <sub>3</sub> | 25dEr | Im <sub>2</sub> O | 25dEr | Mg <sub>2</sub> O | 25dEr | PbO  | 25dEr | Sb <sub>2</sub> O <sub>3</sub> | 25dEr | SnO <sub>2</sub> | 25dEr | VO <sub>2</sub> | 25dEr | WO <sub>3</sub> | 25dEr | ZnO    | 25dEr |      |     |
|-------|---|-------------------|-------|-------------------------------|-------|--------------------------------|-------|--------------------------------|-------|-------------------|-------|--------------------------------|-------|--------------------------------|-------|-------------------|-------|-------------------|-------|------|-------|--------------------------------|-------|------------------|-------|-----------------|-------|-----------------|-------|--------|-------|------|-----|
| A865  | 7 | 32.7              | 1.4   | 1.3                           | 0.1   | 80.7                           | 2.1   | 35.0                           | 5.5   | 16.0              | 184   | 3.6                            | 0.1   | 1063                           | 1.2   | 1043              | 1.2   | 1565              | 2.2   | 0.3  | 0.0   | 345.5                          | 3.9   | 64               | 0.0   | 0.0             | 0.0   | 0.0             | 0.0   | 431.9  | 6.1   |      |     |
| A866  | 7 | 56.0              | 0.9   | 2.8                           | 0.0   | 22.6                           | 8.4   | 59.9                           | 8.2   | 215.3             | 4.5   | 1.7                            | 0.1   | 1668                           | 0.9   | 1668              | 0.9   | 2174              | 2.9   | 0.3  | 0.1   | 0.4                            | 0.0   | 0.4              | 0.0   | 0.0             | 0.0   | 0.0             | 0.0   | 3216   | 12.9  |      |     |
| A867  | 7 | 24.3              | 1.1   | 1.1                           | 0.3   | 20.1                           | 4.1   | 46.2                           | 1.8   | 194.9             | 15.1  | 1.9                            | 0.2   | 82.0                           | 1.1   | 82.0              | 1.1   | 142.2             | 1.3   | 0.2  | 0.2   | 0.0                            | 0.0   | 0.2              | 0.0   | 0.0             | 0.0   | 0.0             | 0.0   | 3266   | 4.8   |      |     |
| A868  | 7 | 25.3              | 0.7   | 1.1                           | 0.1   | 140.3                          | 3.8   | 84.4                           | 18.3  | 179.1             | 3.8   | 0.4                            | 0.2   | 193.1                          | 0.9   | 193.1             | 0.9   | 148.3             | 1.8   | 0.4  | 0.2   | 0.4                            | 0.0   | 0.4              | 0.0   | 0.0             | 0.0   | 0.0             | 0.0   | 341.9  | 8.6   |      |     |
| A869  | 7 | 237.0             | 2     | 21.3                          | 5.1   | 0.2                            | 32.5  | 20.9                           | 13.2  | 60.9              | 23.9  | 1.0                            | 0.1   | 169.8                          | 12.1  | 169.8             | 12.1  | 103.8             | 10.4  | 0.5  | 0.1   | 0.1                            | 0.1   | 0.1              | 0.1   | 0.1             | 0.1   | 0.1             | 0.1   | 267    | 3.1   |      |     |
| A870  | 7 | 16.0              | 0.2   | 0.2                           | 0.2   | 18.2                           | 3.5   | 49.8                           | 1.6   | 292.1             | 1.6   | 0.1                            | 0.1   | 190.4                          | 1.6   | 190.4             | 1.6   | 131.4             | 3.5   | 0.2  | 0.2   | 0.2                            | 0.2   | 0.2              | 0.2   | 0.2             | 0.2   | 0.2             | 0.2   | 324.4  | 15.6  |      |     |
| A871  | 7 | 42.7              | 1.0   | 1.6                           | 0.0   | 19.8                           | 2.7   | 23.2                           | 24.1  | 190.2             | 24.1  | 0.1                            | 0.1   | 140.5                          | 1.6   | 140.5             | 1.6   | 150.7             | 4.4   | 0.4  | 0.3   | 0.3                            | 0.3   | 0.3              | 0.3   | 0.3             | 0.3   | 0.3             | 0.3   | 356.3  | 9.9   |      |     |
| A872  | 7 | 4.6               | 1.4   | 3.2                           | 0.2   | 111.3                          | 3.9   | 19.7                           | 8.9   | 189.2             | 18.9  | 0.1                            | 0.1   | 189.2                          | 18.9  | 189.2             | 18.9  | 233.1             | 4.4   | 0.4  | 0.2   | 0.2                            | 0.2   | 0.2              | 0.2   | 0.2             | 0.2   | 0.2             | 0.2   | 331.2  | 11.2  |      |     |
| A873  | 7 | 53.7              | 1.6   | 0.2                           | 0.2   | 289.4                          | 46.2  | 0.0                            | 0.0   | 255.8             | 35.5  | 275.6                          | 5.6   | 2.4                            | 0.3   | 1528              | 10.2  | 232.0             | 43.0  | 0.3  | 0.0   | 0.6                            | 0.1   | 0.1              | 0.1   | 0.1             | 0.1   | 0.1             | 0.1   | 1878.7 | 70.4  |      |     |
| A874  | 7 | 102.8             | 2.9   | 5.2                           | 0.2   | 55.1                           | 49.5  | 792.0                          | 132.3 | 59.1              | 5.7   | 974.6                          | 5.6   | 8.8                            | 0.2   | 248.5             | 29.4  | 419.2             | 40.7  | 0.0  | 0.0   | 1.4                            | 0.1   | 0.1              | 0.1   | 0.1             | 0.1   | 0.1             | 0.1   | 1878.7 | 70.4  |      |     |
| A875  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A876  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A877  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A878  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A879  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A880  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A881  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A882  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A883  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A884  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A885  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A886  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A887  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A888  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A889  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A890  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A891  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A892  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A893  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A894  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A895  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A896  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A897  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A898  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A899  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A900  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A901  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A902  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A903  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A904  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A905  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A906  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19.9 | 4.6   | 8.3                            | 0.7   | 48.1             | 0.3   | 19.9            | 4.6   | 8.3             | 0.7   | 48.1   | 0.3   | 19.9 | 4.6 |
| A907  | 7 | 19.9              | 4.6   | 8.3                           | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1                           | 0.3   | 19.9                           | 4.6   | 8.3               | 0.7   | 48.1              | 0.3   | 19   |       |                                |       |                  |       |                 |       |                 |       |        |       |      |     |



**Table 4.8—Trace Element Partition Coefficients**

| Alias  | K <sub>D</sub> (Ag) | K <sub>D</sub> (Bi) | K <sub>D</sub> (Cd) | K <sub>D</sub> (Cr) | K <sub>D</sub> (Cu) | K <sub>D</sub> (Ga) | K <sub>D</sub> (Ge) | K <sub>D</sub> (In) | K <sub>D</sub> (Mo) | K <sub>D</sub> (Pb) | K <sub>D</sub> (Sb) | K <sub>D</sub> (Sn) | K <sub>D</sub> (Ti) | K <sub>D</sub> (V) | K <sub>D</sub> (W) | K <sub>D</sub> (Zn) |
|--------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|--------------------|--------------------|---------------------|
| A365   | 1.763               | 1.856               | 0.0234              | 0.0611              | 8.52                | 0.0672              |                     | 0.0418              |                     | 0.033               | 24.1                | 0.0672              | 0.0084              |                    | 0.0793             |                     |
| A366   | 0.708               | 0.431               | 0.0123              | 0.0501              | 4.66                | 0.0796              |                     | 0.0104              | 0.094               | 0.011               | 11.9                | 0.0128              | 0.0019              |                    | 0.0299             |                     |
| A368   | 1.749               | 1.109               | 0.0183              | 0.0560              | 6.83                | 0.0498              |                     | 0.0423              | 0.204               | 0.032               | 25.1                | 0.0339              | 0.0083              |                    | 0.0510             |                     |
| A369   | 1.746               | 1.757               | 0.0216              | 0.0639              | 7.06                | 0.0587              |                     | 0.0403              |                     | 0.032               | 11.4                | 0.0288              | 0.0139              | 0.0102             | 0.0295             | 0.0384              |
| A370   | 4.519               | 4.458               | 0.0559              |                     | 9.74                |                     |                     | 0.083               |                     | 0.109               | 14.8                |                     | 0.0578              |                    |                    |                     |
| A371   | 0.780               | 0.438               | 0.0166              |                     | 5.61                |                     |                     | 0.0152              |                     | 0.012               | 29.2                |                     | 0.0019              |                    |                    |                     |
| A373   | 0.744               | 0.676               | 0.0176              |                     | 5.14                |                     |                     | 0.0214              |                     | 0.013               | 16.0                |                     | 0.0040              |                    |                    |                     |
| A374   | 1.012               | 0.471               | 0.0232              |                     | 6.94                |                     |                     | 0.0223              |                     | 0.016               | 16.7                |                     | 0.0043              |                    |                    |                     |
| A388   | 0.810               | 0.427               | 0.0169              |                     | 4.66                |                     |                     |                     |                     | 0.010               | 16.3                |                     | 0.0020              |                    |                    |                     |
| AN1101 | 0.571               | 0.914               |                     |                     | 7.12                | 0.0639              | 1.7707              |                     | 9.321               |                     | 32.4                |                     |                     |                    | 0.2135             |                     |
| AN1102 |                     |                     | 0.0128              | 0.0759              | 8.78                |                     |                     | 0.0177              |                     | 0.021               |                     | 0.0469              | 0.0088              | 0.0067             |                    | 0.0408              |
| AN1103 | 0.733               | 0.696               |                     |                     | 6.87                | 0.0483              | 4.7121              |                     | 42.214              |                     | 59.6                |                     |                     |                    | 0.0527             |                     |
| AN1104 | 0.901               | 2.186               |                     |                     | 6.64                | 0.0986              | 6.3980              |                     | 4.038               |                     | 32.9                |                     |                     |                    | 1.3201             |                     |
| B187   | 1.256               | 0.864               | 0.0166              | 0.0647              | 5.84                | 0.0858              |                     | 0.0257              |                     | 0.022               | 20.1                | 0.0387              | 0.0034              |                    | 0.0611             |                     |
| B188   | 1.482               | 0.878               | 0.0188              |                     | 7.12                |                     |                     | 0.0332              |                     | 0.026               | 1.4                 |                     | 0.0098              |                    |                    |                     |
| BW1301 |                     |                     | 0.1386              | 0.0256              | 23.27               |                     |                     | 0.0922              |                     | 0.266               |                     | 0.4116              | 0.0811              | 0.0020             |                    | 0.0125              |
| BW1302 | 2.587               | 5.149               |                     |                     | 20.42               | 0.4655              | 6.3647              |                     | 14.732              |                     | 66.8                |                     |                     |                    | 0.0723             |                     |
| BW1303 | 0.838               | 1.282               |                     |                     | 16.08               | 0.6203              | 14.6384             |                     | 18.359              |                     | 126.5               |                     |                     |                    | 0.1765             |                     |
| BW1304 |                     |                     | 0.0513              | 0.0240              | 13.78               |                     |                     | 0.0139              |                     | 0.061               |                     | 0.1572              | 0.0070              | 0.0035             |                    | 0.0196              |
| FM1102 | 1.032               | 3.385               |                     |                     | 6.87                | 0.0505              | 4.3209              |                     | 84.892              |                     | 73.1                |                     |                     |                    | 0.1282             |                     |
| FM1103 |                     |                     | 0.0137              | 0.0515              | 6.98                |                     |                     | 0.0154              |                     | 0.020               |                     | 0.0434              | 0.0076              | 0.0058             |                    | 0.0323              |
| FM1104 |                     |                     | 0.0873              | 0.0645              | 6.42                |                     |                     | 0.0164              |                     | 0.092               |                     | 0.0569              | 0.0156              | 0.0135             |                    | 0.0619              |
| FM1105 | 0.481               | 1.013               |                     |                     | 5.52                | 0.1098              | 6.5583              |                     | 17.997              |                     | 74.2                |                     |                     |                    | 2.5635             |                     |
| FM1106 |                     |                     | 0.0361              | 0.0310              | 5.22                |                     |                     | 0.0089              |                     | 0.004               |                     | 0.0301              | 0.0066              | 0.0031             |                    | 0.0165              |
| FM1107 |                     |                     | 0.0212              | 0.0742              | 6.22                |                     |                     | 0.0145              |                     | 0.034               |                     | 0.0450              | 0.0095              | 0.0107             |                    | 0.0578              |
| FM1108 | 1.092               | 0.565               |                     |                     | 6.53                | 0.0128              | 0.6064              |                     | 9.990               |                     | 16.1                |                     |                     |                    | 0.0047             |                     |
| FM1109 |                     |                     | 0.0412              | 0.0472              | 8.26                |                     |                     | 0.0256              |                     | 0.093               |                     | 0.0370              | 0.0582              | 0.0045             |                    | 0.0270              |
| FM1110 |                     |                     | 0.0244              | 0.0680              | 5.80                |                     |                     | 0.0075              |                     | 0.026               |                     | 0.0335              | 0.0051              | 0.0143             |                    | 0.0768              |
| FM1111 | 2.216               | 4.542               |                     |                     | 12.39               | 0.2337              | 7.4934              |                     | 26.759              |                     | 227.7               |                     |                     |                    | 1.9782             |                     |
| FM1113 |                     |                     | 0.0609              | 0.0893              | 7.99                |                     |                     | 0.0153              |                     | 0.065               |                     | 0.0436              | 0.0179              | 0.0192             |                    | 0.1153              |
| FM1114 |                     |                     | 0.0125              | 0.0586              | 5.70                |                     |                     | 0.0088              |                     | 0.016               |                     | 0.0373              | 0.0038              | 0.0100             |                    | 0.0541              |
| FM1115 | 0.379               | 0.651               |                     |                     | 6.40                | 0.0790              | 5.6712              |                     | 100.489             |                     | 64.3                |                     |                     |                    | 0.6209             |                     |
| FM1116 |                     |                     | 0.0126              | 0.0637              | 6.61                |                     |                     | 0.0121              |                     | 0.013               |                     | 0.0498              | 0.0031              | 0.0136             |                    | 0.0681              |
| FM1117 | 0.369               | 0.853               |                     |                     | 7.92                | 0.1341              | 10.4586             |                     | 60.549              |                     | 89.6                |                     |                     |                    | 2.3335             |                     |
| FM1118 |                     |                     | 0.0445              | 0.0695              | 6.96                |                     |                     | 0.0212              |                     | 0.057               |                     | 0.0262              | 0.0221              | 0.0074             |                    | 0.0442              |
| FM1119 | 0.743               | 1.408               |                     |                     | 7.26                | 0.0438              | 4.4590              |                     | 21.369              |                     | 30.5                |                     |                     |                    | 0.0940             |                     |
| TT1    | 1.656               | 2.447               | 0.0668              | 0.0876              | 10.28               | 0.0787              |                     | 0.0684              | 9.056               | 0.049               | 52.9                | 0.0798              | 0.0207              | 0.0000             | 0.0565             | 0.0000              |
| TT2    | 1.930               | 2.825               | 0.0463              | 0.0939              | 9.00                | 0.0650              | 0.0052              | 0.0602              | 0.784               | 0.044               | 34.4                | 0.0224              | 0.0143              | 0.0168             | 0.0476             | 0.0538              |
| TT3    | 2.573               | 8.503               | 0.2079              | 0.1507              | 13.46               | 0.0725              |                     | 0.0953              | 7.467               | 0.213               | 70.0                |                     | 0.0639              | 0.0213             | 0.1985             | 0.0504              |

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## 4.5 Calculating Activity Coefficients

This section introduces the general method of calculating the activity coefficients of trace elements in silicate melt. This approach is then applied to each of the trace elements, which are presented sequentially in the following sections. Throughout this work the symbol  $M$  will be used to represent an arbitrary trace element that forms an oxide of the general form  $MO_{n/2}$ . The values for  $n$  are given in Table 4.9 below and are used consistently throughout this work.

**Table 4.9—Oxidation States of Trace Elements in Silicate Melts**

| Element | n | n/2 | Reference                 |
|---------|---|-----|---------------------------|
| Ag      | 1 | 0.5 |                           |
| Bi      | 3 | 1.5 |                           |
| Cd      | 2 | 1   |                           |
| Cr      | 2 | 1   | Wade <i>et al.</i> 2012   |
| Cu      | 1 | 0.5 | Holzheid and Lodders 2001 |
| Fe      | 2 | 1   |                           |
| Ga      | 3 | 1.5 |                           |
| Ge      | 4 | 2   |                           |
| In      | 3 | 1.5 |                           |
| Mo      | 4 | 2   | O'Neill and Eggins 2002   |
| Pb      | 2 | 1   |                           |
| Sb      | 3 | 1.5 |                           |
| Sn      | 4 | 2   |                           |
| Tl      | 1 | 0.5 |                           |
| V       | 3 | 1.5 |                           |
| W       | 6 | 3   | Wade <i>et al.</i> 2013   |
| Zn      | 2 | 1   |                           |

Consider the following expression for the liquid phases of interest in equilibrium at high temperature ( $T > T_{\text{melt}}$ ):



Let  $X_M$  represent the mole-fraction of component  $M$ . For this reaction we can define the partition coefficient  $D$  and the equilibrium constant  $K_D$  to be:

$$D = \frac{X_M^{\text{metal}}}{X_{MO_{\frac{n}{2}}}^{\text{silicate}}}$$

$$K_D = \frac{X_M^{\text{metal}} \left( X_{\text{FeO}}^{\text{silicate}} \right)^{\frac{n}{2}}}{X_{MO_{\frac{n}{2}}}^{\text{silicate}} \left( X_{\text{Fe}}^{\text{metal}} \right)^{\frac{n}{2}}}$$

$$K_D = D \left( \frac{X_{\text{FeO}}^{\text{silicate}}}{X_{\text{Fe}}^{\text{metal}}} \right)^{\frac{n}{2}}$$

Since we do not wish to assume ideal behaviour the activity is used instead of the concentration.

Substituting for activity (  $a_M = \gamma_M X_M$  ) gives this expression for  $K_f$  :

$$K_f = \frac{a_M^{\text{metal}} \left( a_{\text{FeO}}^{\text{silicate}} \right)^{\frac{n}{2}}}{a_{MO_{\frac{n}{2}}}^{\text{silicate}} \left( a_{\text{Fe}}^{\text{metal}} \right)^{\frac{n}{2}}} = \frac{\gamma_M^{\text{metal}} X_M^{\text{metal}} \left( \gamma_{\text{FeO}}^{\text{silicate}} X_{\text{FeO}}^{\text{silicate}} \right)^{\frac{n}{2}}}{\gamma_{MO_{\frac{n}{2}}}^{\text{silicate}} X_{MO_{\frac{n}{2}}}^{\text{silicate}} \left( \gamma_{\text{Fe}}^{\text{metal}} X_{\text{Fe}}^{\text{metal}} \right)^{\frac{n}{2}}}$$

Taking the expression of Gibbs [Gibbs 1878] for the free energy of this reaction at equilibrium,

we start with:

$$\Delta G^\circ = -RT \ln K_f$$

And substituting with our equilibrium expression for  $K_f$  we trivially arrive at:

$$\Delta G^\circ = -RT \left[ \frac{n}{2} \ln \left( a_{\text{FeO}}^{\text{silicate}} \right) + \ln \left( a_M^{\text{metal}} \right) - \ln \left( a_{MO_{\frac{n}{2}}}^{\text{silicate}} \right) - \frac{n}{2} \ln \left( a_{\text{Fe}}^{\text{metal}} \right) \right]$$

$$\Delta G^\circ = -RT \left[ \frac{n}{2} \ln \left( \gamma_{\text{FeO}}^{\text{silicate}} X_{\text{FeO}}^{\text{silicate}} \right) + \ln \left( \gamma_M^{\text{metal}} X_M^{\text{metal}} \right) - \ln \left( \gamma_{MO_{\frac{n}{2}}}^{\text{silicate}} X_{MO_{\frac{n}{2}}}^{\text{silicate}} \right) - \frac{n}{2} \ln \left( \gamma_{\text{Fe}}^{\text{metal}} X_{\text{Fe}}^{\text{metal}} \right) \right]$$

To solve this expression for  $\gamma_{MO_{\frac{n}{2}}}^{\text{silicate}}$  we need to determine the value of  $\Delta G^\circ$  for each reaction.

This can be computed using the equilibrium constants of formation of the individual

components, which are tabulated in thermochemical data references [e.g. Barin 1997] or in the literature. Specific references for these values are provided for each trace element in the relevant sections.

To compute the free energy of formation using thermochemical data we again start with the expression:

$$\Delta G^\circ = -RT \ln K_f$$

Where the equilibrium constant is the sum of the natural logarithm of the equilibrium constants of formation of the separate components:

$$\ln K_f = \frac{n}{2} \ln K_{f,\text{FeO}}^{\text{liquid}} + \ln K_{f,M}^{\text{liquid}} - \ln K_{f,\text{MO}_{n/2}}^{\text{liquid}} - \frac{n}{2} \ln K_{f,\text{Fe}}^{\text{liquid}}$$

Setting  $\Delta G^\circ$  equal to  $\Delta G^\circ$  gives the following relationship:

$$\begin{aligned} \ln K_f &= \\ \frac{n}{2} \ln K_{f,\text{FeO}}^{\text{liquid}} + \ln K_{f,M}^{\text{liquid}} - \ln K_{f,\text{MO}_{n/2}}^{\text{liquid}} - \frac{n}{2} \ln K_{f,\text{Fe}}^{\text{liquid}} &= \\ \frac{n}{2} \ln \left( \gamma_{\text{FeO}}^{\text{silicate}} X_{\text{FeO}}^{\text{silicate}} \right) + \ln \left( \gamma_M^{\text{metal}} X_M^{\text{metal}} \right) - \ln \left( \gamma_{\text{MO}_{n/2}}^{\text{silicate}} X_{\text{MO}_{n/2}}^{\text{silicate}} \right) - \frac{n}{2} \ln \left( \gamma_{\text{Fe}}^{\text{metal}} X_{\text{Fe}}^{\text{metal}} \right) \end{aligned}$$

Which can be manipulated into a simpler form and rearranged to solve for  $\gamma_{\text{MO}_{n/2}}^{\text{silicate}}$  to yield:

$$\ln \left( \gamma_{\text{MO}_{n/2}}^{\text{silicate}} X_{\text{MO}_{n/2}}^{\text{silicate}} \right) = \frac{n}{2} \ln \left( \frac{a_{\text{FeO}}^{\text{silicate}}}{a_{\text{Fe}}^{\text{metal}}} \right) + \ln a_M^{\text{metal}} - \ln K_f$$

$$\gamma_{\text{MO}_{n/2}}^{\text{silicate}} = \frac{e^{\left[ \frac{n}{2} \ln \left( \frac{a_{\text{FeO}}^{\text{silicate}}}{a_{\text{Fe}}^{\text{metal}}} \right) + \ln a_M^{\text{metal}} - \ln K_f \right]}}{X_{\text{MO}_{n/2}}^{\text{silicate}}}$$

The final expression with all terms explicitly expanded gives us the following:

$$\gamma_{MO_{n/2}}^{\text{silicate}} = \frac{e^{\left[ \frac{n}{2} \ln \left( \frac{\gamma_{\text{FeO}}^{\text{silicate}} X_{\text{FeO}}^{\text{silicate}}}{\gamma_{\text{Fe}}^{\text{metal}} X_{\text{Fe}}^{\text{metal}}} \right) + \ln \left( \gamma_M^{\text{metal}} X_M^{\text{metal}} \right) - \left( \frac{n}{2} \ln K_{f,\text{FeO}}^{\text{liquid}} + \ln K_{f,M}^{\text{liquid}} - \ln K_{f,MO_{n/2}}^{\text{liquid}} - \frac{n}{2} \ln K_{f,\text{Fe}}^{\text{liquid}} \right) \right]}}{X_{MO_{n/2}}^{\text{silicate}}} \quad (\text{Equation 4.1})$$

#### 4.5.1 Determining Common Thermochemical Terms

The terms common to all trace element partition coefficients are determined as follows:

##### 4.5.1.1 Activity Coefficient of FeO in Silicate Melt

Previous work [Wood and Wade 2013] provides an effective ( $N=83$ , standard error of 1740 J) model for the activity coefficient of FeO in anhydrous silicate melts at 1 atmosphere pressure.

$$RT \ln \gamma_{\text{FeO}}^{\text{silicate}} = -18994 + 99579 X_{\text{NaO}_{0.5}} + 192553 X_{\text{AlO}_{1.5}} X_{\text{SiO}_2} + 282789 X_{\text{CaO}} X_{\text{MgO}} + 79492 X_{\text{CaO}}^2 + 120972 X_{\text{FeO}}^2$$

This model results in variation of  $\gamma_{\text{FeO}}$  from 0.5 to 2.5 across the ADF basaltic ternary. This is plotted in Figure 4.7, after Figure 2 in Wood and Wade 2013.

Figure 4.7—Wood and Wade 2013:  $\gamma_{\text{FeO}}$  Contours on the ADF Ternary

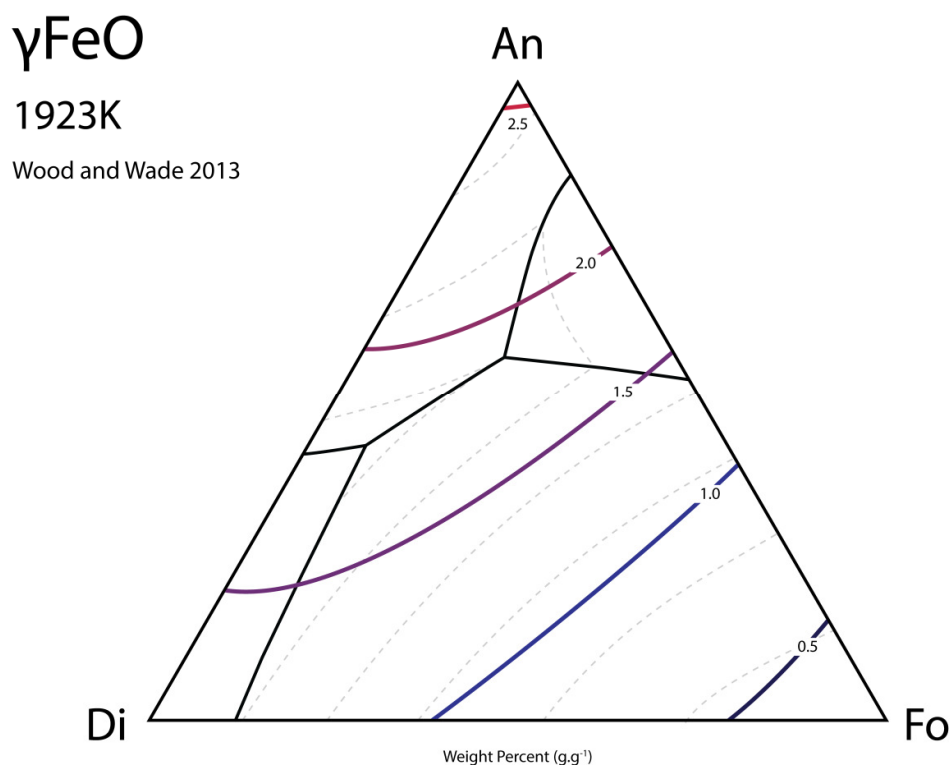


Figure 2 from Wood and Wade 2013 has been reproduced here and shows contours of FeO activity coefficients model on the ADF ternary at 1923 K.

The computed activity coefficients of FeO in the experimental liquid silicate melts are tabulated below in Table 4.10.

#### 4.5.1.2 Uncertainty of FeO Activity Coefficients

The uncertainty in the concentration of each element comes from the EPMA analysis and is approximately 2%. Combining these uncertainties gives an average relative uncertainty of 13% on the modelled values of  $\gamma_{\text{FeO}}$ . The uncertainty of the fit in the model is larger, with an average relative uncertainty of  $\approx 30\%$ . For the purposes of this work, the larger uncertainty of 30% has been applied to the activity coefficients of FeO in the silicate melt.



**Table 4.10—Activity Coefficients of FeO in Silicate Melt Compositions at 1923 K**

| Alias  | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | FeO  | MgO  | CaO  | RTln $\gamma_{\text{FeO}}$ | $\gamma_{\text{FeO}}$ | ( $\gamma_{\text{FeO}}$ ) |
|--------|------------------|--------------------------------|------|------|------|----------------------------|-----------------------|---------------------------|
| A365   | 45.6             | 14.2                           | 7.9  | 10.2 | 21.4 | 6484.8                     | 1.50                  | 0.45                      |
| A366   | 61.8             | 10.9                           | 6.4  | 6.9  | 14.4 | 676.7                      | 1.04                  | 0.31                      |
| A368   | 47.6             | 5.9                            | 7.5  | 3.8  | 34.6 | 3135.3                     | 1.22                  | 0.36                      |
| A369   | 43.9             | 17.1                           | 7.3  | 15.6 | 16.2 | 6501.4                     | 1.50                  | 0.45                      |
| A370   | 35.8             | 14.2                           | 9.4  | 23.1 | 17.4 | 6754.7                     | 1.53                  | 0.46                      |
| A371   | 58.6             | 11.8                           | 7.5  | 9.9  | 10.7 | 935.3                      | 1.06                  | 0.32                      |
| A373   | 40.8             | 31.7                           | 7.3  | 0.2  | 18.4 | 11362.7                    | 2.04                  | 0.61                      |
| A374   | 54.6             | 11.5                           | 8.3  | 25.1 | 0.4  | -6982.7                    | 0.65                  | 0.19                      |
| A388   | 40.7             | 32.9                           | 8.5  | 0.2  | 17.8 | 11289.4                    | 2.03                  | 0.61                      |
| AN1101 | 43.9             | 17.9                           | 5.5  | 16.2 | 16.6 | 7320.9                     | 1.58                  | 0.47                      |
| AN1102 | 44.6             | 18.1                           | 2.8  | 16.4 | 17.0 | 8176.1                     | 1.67                  | 0.50                      |
| AN1103 | 42.6             | 5.6                            | 15.7 | 3.4  | 31.8 | 1974.5                     | 1.13                  | 0.34                      |
| AN1104 | 56.7             | 0.5                            | 14.8 | 0.0  | 27.0 | -9536.3                    | 0.55                  | 0.17                      |
| B187   | 62.3             | 0.2                            | 7.8  | 0.5  | 29.3 | -9915.0                    | 0.54                  | 0.16                      |
| B188   | 39.5             | 24.2                           | 6.8  | 12.4 | 16.7 | 9035.9                     | 1.76                  | 0.53                      |
| BW1301 | 48.4             | 13.5                           | 3.4  | 21.3 | 13.5 | 3985.6                     | 1.28                  | 0.38                      |
| BW1302 | 42.5             | 10.5                           | 9.5  | 26.9 | 10.6 | -11.4                      | 1.00                  | 0.30                      |
| BW1303 | 64.1             | 9.5                            | 9.1  | 8.5  | 8.8  | -2100.1                    | 0.88                  | 0.26                      |
| BW1304 | 66.6             | 8.3                            | 4.2  | 13.4 | 7.4  | -3897.2                    | 0.78                  | 0.24                      |
| FM1102 | 42.2             | 14.0                           | 11.5 | 10.5 | 20.7 | 6069.3                     | 1.46                  | 0.44                      |
| FM1103 | 46.9             | 16.3                           | 3.2  | 10.5 | 22.0 | 8509.7                     | 1.70                  | 0.51                      |
| FM1104 | 62.3             | 10.3                           | 4.6  | 7.1  | 14.8 | 461.5                      | 1.03                  | 0.31                      |
| FM1105 | 56.9             | 9.7                            | 13.3 | 6.0  | 13.5 | -704.3                     | 0.96                  | 0.29                      |
| FM1106 | 48.6             | 6.4                            | 3.4  | 4.1  | 36.7 | 4963.6                     | 1.36                  | 0.41                      |
| FM1107 | 63.6             | 0.6                            | 3.3  | 1.4  | 30.4 | -8087.6                    | 0.60                  | 0.18                      |
| FM1108 | 45.2             | 12.5                           | 8.5  | 25.1 | 7.7  | -1092.1                    | 0.93                  | 0.28                      |
| FM1109 | 38.4             | 15.1                           | 3.1  | 26.3 | 17.6 | 7986.4                     | 1.65                  | 0.49                      |
| FM1110 | 61.3             | 12.1                           | 3.5  | 11.0 | 11.2 | 1599.5                     | 1.11                  | 0.33                      |
| FM1111 | 55.8             | 12.0                           | 11.0 | 10.2 | 10.2 | 687.2                      | 1.04                  | 0.31                      |
| FM1113 | 61.5             | 2.2                            | 3.0  | 32.9 | 0.3  | -16353.7                   | 0.36                  | 0.11                      |
| FM1114 | 42.3             | 34.2                           | 3.4  | 0.7  | 19.1 | 12948.9                    | 2.25                  | 0.67                      |
| FM1115 | 36.6             | 33.6                           | 12.4 | 1.1  | 16.5 | 9940.9                     | 1.86                  | 0.56                      |
| FM1116 | 55.9             | 12.0                           | 4.3  | 27.2 | 0.2  | -7151.9                    | 0.64                  | 0.19                      |
| FM1117 | 49.0             | 10.5                           | 16.0 | 24.3 | 0.2  | -7654.3                    | 0.62                  | 0.19                      |
| FM1118 | 40.1             | 25.8                           | 2.9  | 12.0 | 18.2 | 10751.5                    | 1.96                  | 0.59                      |
| FM1119 | 35.2             | 20.3                           | 17.2 | 10.2 | 16.1 | 6319.7                     | 1.48                  | 0.45                      |
| TT1    | 41.2             | 16.9                           | 9.3  | 15.9 | 15.8 | 5979.6                     | 1.45                  | 0.44                      |
| TT2    | 41.2             | 17.0                           | 10.1 | 15.7 | 15.8 | 5935.6                     | 1.45                  | 0.43                      |
| TT3    | 36.3             | 14.9                           | 17.3 | 13.8 | 14.1 | 3530.0                     | 1.25                  | 0.37                      |

Silicate composition is shown as weight percent (g.g<sup>-1</sup>) oxide.

#### 4.5.1.3 Activity Coefficient of Fe in Iron Metal

By definition the activity coefficient of iron in pure liquid iron metal is 1. For these experiments the iron metal was saturated with 5.5% (g.g<sup>-1</sup>) carbon and this will change the activity of the iron. Using the epsilon model [Zhongting 2001; Wade and Wood 2005; *MetalAct* Website] at

the temperature of interest, the activity coefficient for Fe in carbon-saturated iron metal is computed to be:  $\gamma_{\text{Fe}}^{\text{metal}}(1923 \text{ K}) = 0.7157$ .

#### 4.5.1.4 Equilibrium Constant of Formation of Liquid FeO at 1923 K

The equilibrium constant of formation of liquid FeO is tabulated in Barin 1973, p561, and can be used to interpolate the value at 1923 K. To improve the interpolation corrections were applied to account for the change in state of the reference state of pure iron. The reference state changes over the temperature range of interest: at  $T < T_{\text{F1}}$  (1665 K) it is “SOL-C” and from 1665 K to  $T_{\text{F2}}$  (1809 K) it is “SOL-D”. To correct for this Equation 4.6 was used, resulting in the following expressions for the double-correction:

$$\ln K_{f,\text{FeO}}^{\text{liquid-Fe}}(T < 1665 \text{ K}) = \ln K_{f,\text{FeO}}^{\text{solid-Fe}}(T) - \frac{\Delta S(T_{\text{F1}} - T)}{RT} - \frac{\Delta S(T_{\text{F2}} - T)}{RT}$$

$$\ln K_{f,\text{FeO}}^{\text{liquid-Fe}}(T < 1665 \text{ K}) = \ln K_{f,\text{FeO}}^{\text{solid-Fe}}(T) - \frac{0.503(1665 - T) - 7.632(1809 - T)}{RT}$$

And for the single correction at the higher temperature range:

$$\ln K_{f,\text{FeO}}^{\text{liquid-Fe}}(1665 \text{ K} < T < 1809 \text{ K}) = \ln K_{f,\text{FeO}}^{\text{solid-Fe}}(T) - \frac{\Delta S(T_{\text{F2}} - T)}{RT}$$

$$\ln K_{f,\text{FeO}}^{\text{liquid-Fe}}(1665 \text{ K} < T < 1809 \text{ K}) = \ln K_{f,\text{FeO}}^{\text{solid-Fe}}(T) - \frac{7.632(1809 - T)}{RT}$$

A least-squares regression ( $R^2=1.000$ ,  $N=10$ ,  $1650 \text{ K} \leq T \leq 2500 \text{ K}$ ) resulted in the following expression for the equilibrium constant of formation for liquid FeO relative to the standard state of liquid iron over the temperatures shown:

$$\ln K_{f,\text{FeO}}^{\text{liquid-Fe}}(1650\text{ K} \leq T \leq 2500\text{ K}) = \frac{31217}{T} - 6.6503$$

Evaluation at the experimental temperature of 1923 K gives:

$$\ln K_{f,\text{FeO}}^{\text{liquid-Fe}}(1923\text{ K}) = 9.583$$

#### 4.5.1.5 *Energy of Formation of Liquid Fe at 1923 K*

The stable state of iron at 1923 K is liquid molten iron. As such the energy of formation is equal to zero [Barin 1973, p536].

$$\ln K_{f,\text{Fe}}^{\text{liquid}}(1923\text{ K}) = 0$$

---

## 4.6 Calculating Revised Epsilons and Gamma-Zeros

An epsilon model [Zhongting 2001; Wade and Wood 2005; *MetalAct* Website] was implemented in PHP (see Chapter 1 for details) and used to compute the activity coefficients of the trace elements in carbon-saturated iron metal. This model is based on two main parameters for each element: gamma-zero, the activity coefficient of the trace element at infinite dilution in pure iron, and epsilon-carbon, a term that describes the effect of carbon on the activity of the trace element. Where literature data were unavailable, some values have been computed using phase diagrams (e.g. In, Ag, Pb), others have been estimated from unpublished values (e.g. Ga), and the rest are based on thermodynamic modelling (e.g. Bi, Cd, Tl).

**Table 4.11—Values and References for Gamma-Zero and Epsilon-Carbon**

| Element | Gamma Zero ( $\gamma^0$ ) 1873K | Reference                                       | Initial Epsilon-Carbon ( $\epsilon_M^C$ ) 1873K | Reference                 |
|---------|---------------------------------|-------------------------------------------------|-------------------------------------------------|---------------------------|
| Ag      | 319                             | This Study, Computed, Swartzendruber 1984       | 11.69                                           | Gordon and Breach 1984    |
| Bi      | 11792                           | This Study, Computed, Boom <i>et al.</i> 1983   | 1                                               | This Study, Estimate      |
| Cd      | 132                             | This Study, Computed, Boom <i>et al.</i> 1983   | 1                                               | This Study, Estimate      |
| Cr      | 1                               | Tuff <i>et al.</i> 2011                         | -4.86                                           | Gordon and Breach 1984    |
| Cu      | 8.58                            | Gordon and Breach 1984                          | 3.97                                            | Gordon and Breach 1984    |
| Ga      | 0.6                             | This Study, Computed, Boom <i>et al.</i> 1983   | 2.63                                            | BJ Wood, Unpublished Data |
| Ge      | 0.02                            | Nunoue and Kato 1988                            | 2.27                                            | Gordon and Breach 1984    |
| In      | 27.4                            | This Study, Computed, Okamoto 1990              | 0                                               | This Study, Estimate      |
| Mo      | 1                               | Tuff <i>et al.</i> 2011                         | -6.02                                           | Gordon and Breach 1984    |
| Pb      | 1107                            | This Study, Computed, Vaajamo and Taskinen 2011 | 5.59                                            | Gordon and Breach 1984    |
| Sb      | 0.41                            | Voisin <i>et al.</i> 2005                       | 14.63                                           | Voisin <i>et al.</i> 2005 |
| Sn      | 2.58                            | Gordon and Breach 1984                          | 9.45                                            | Gordon and Breach 1984    |
| Tl      | 25483                           | This Study, Computed, Boom <i>et al.</i> 1983   | 1                                               | This Study, Estimate      |
| V       | 0.08                            | Tuff <i>et al.</i> 2011                         | -5.99                                           | Gordon and Breach 1984    |
| W       | 3                               | Tuff <i>et al.</i> 2011                         | -6.51                                           | Gordon and Breach 1984    |
| Zn      | 2.31                            | This Study, Computed, Su <i>et al.</i> 2001     | 1                                               | This Study, Estimate      |

The major element composition of the metal phase in these experiments will be 5.5% (g / g) carbon (saturation at 1923K) in an iron matrix. Based on solubility data, some silicon may dissolve into the iron, but X-Ray analyses by EDS shows it to never exceed c.a. 0.1% (g / g) in these run products. Likewise, there may be some oxygen dissolved in the iron phase, but at the oxygen fugacity of these experiments (unconstrained, but believed to be close to the Fe:FeO buffer due to presence of elemental Fe and FeO in silicate) the concentration must be very low and no more than a few hundred parts per million. Furthermore, the interaction parameters of most of these trace elements for oxygen in iron are currently unknown.

#### 4.6.1 Calculation of Gamma-Zero Values from Binary Phase Diagrams

For some systems gamma-zero can be computed from the binary phase diagram. One such approach is possible when the phase diagram shows a large miscibility gap. This is represented in general by Figure 4.8 below. Consider the two points P1, P2 at the same temperature  $T$ . At equilibrium the activity has to be the same on each side of the miscibility gap, so we can start with the following expression:

$$RT \ln X_{A,1} + RT \ln \gamma_{A,1} = RT \ln X_{A,2} + RT \ln \gamma_{A,2}$$

Define the term  $W$  to be:

$$RT \ln \gamma_i = W (1 - X_i)^2$$

Substitute  $W$  into the starting expression:

$$RT \ln \frac{X_{A,1}}{X_{A,2}} = W \left( (1 - X_{A,1})^2 - (1 - X_{A,2})^2 \right)$$

And solve for the  $W$  term:

$$W = \frac{RT \ln \frac{X_{A,1}}{X_{A,2}}}{(1 - X_{A,1})^2 - (1 - X_{A,2})^2}$$

By definition, at the reference temperature of 1893 K,  $\gamma_A \rightarrow \gamma_A^0$  as  $X_A \rightarrow 0$  resulting in:

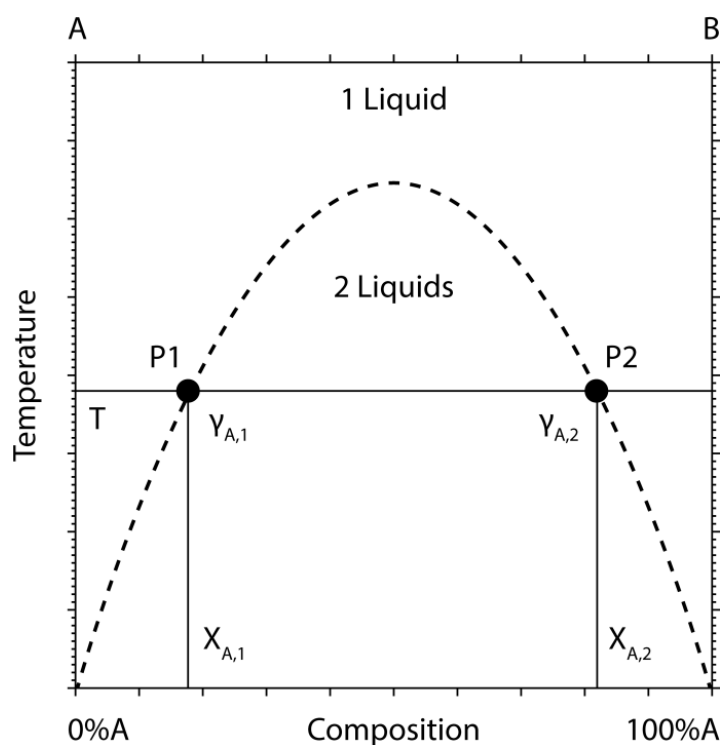
$$RT \ln \gamma_A^0 = W$$

Writing this out explicitly gives the following expression for computing the gamma-zero from the miscibility gap on the phase diagram:

$$\gamma_A^0 = e^{\left(\frac{W}{RT_{ref}}\right)} = e^{\left(\frac{T \ln \frac{X_{A,1}}{X_{A,2}}}{T_{ref} \left((1-X_{A,1})^2 - (1-X_{A,2})^2\right)}\right)} \quad (\text{Equation 4.2})$$

This expression allows us to compute gamma zero at our reference temperature of 1873 K and will be used to compute values for the elements Ag, In, and Pb.

Figure 4.8—Computing Gamma Zero from a Miscibility Gap



A generalised binary phase diagram showing a large miscibility gap between components A and B. The concentration of component A on each side of the gap at the same temperature (point P1 and P2) can be used to compute the activity coefficient of component A in B at infinite dilution (i.e. gamma-zero). See text for derivation.

#### 4.6.2 Computing Gamma-Zero with the Miedema Thermodynamic Model

The semi-empirical thermodynamic model of Miedema [Miedema *et al.* 1980] has been applied to liquid iron alloys [Boom *et al.* 1983] and offers an opportunity to compute gamma-zero values for elements that would otherwise be inaccessible by experimental means. In particular,

this model can provide values for Bi, Cd, and Tl, which in addition to being elements of interest to this study, are rather toxic, volatile, and mostly insoluble in iron. The Miedema model provides tabulated estimates of the partial molar enthalpies of solution for various elements and compares them to experimental data where available.

To compute gamma zero from the partial molar enthalpy of solution (presented as  $\Delta\bar{H}_M^0$  in table Fe-IV of Boom *et al.* 1983) start by assuming the entropy of mixing is ideal:

$$\Delta S_M^{XS} \equiv 0$$

Leading to:

$$\Delta\bar{G}_M^{XS} = \Delta\bar{H}_M^{XS}$$

Since:

$$\Delta\bar{G}_M^{XS} = RT \ln \gamma_M^0$$

Thus we can compute the gamma zero values using the simple relation:

$$RT \ln \gamma_M^0 = \Delta\bar{H}_M^0$$

Writing this out explicitly for  $\gamma_M^0$  gives:

$$\gamma_M^0 = e^{\left(\frac{\Delta\bar{H}_M^0}{RT}\right)} \quad \text{(Equation 4.3)}$$

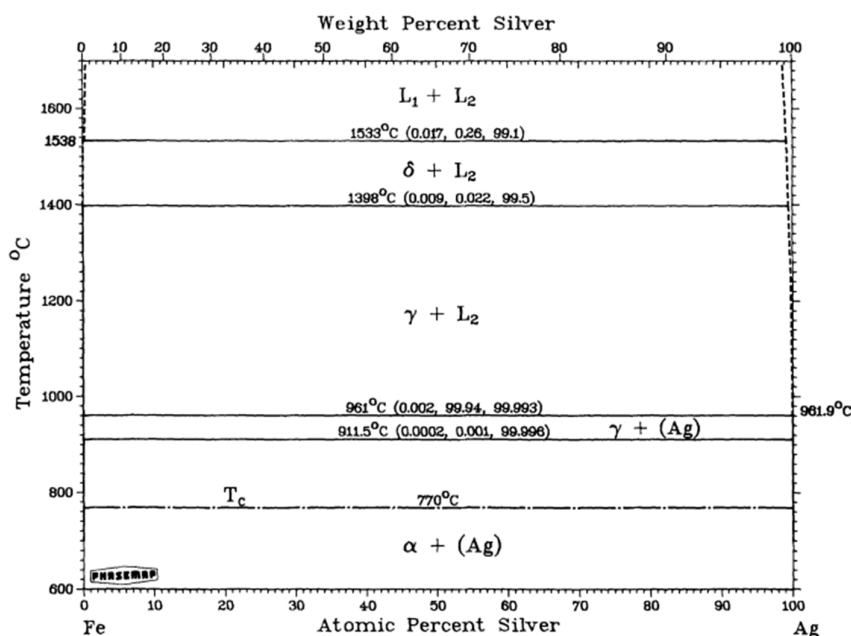
This expression will be used to compute some gamma-zero values in the subsequent sections.

## 4.6.3 Calculated Gamma Zero Values

### 4.6.3.1 Silver (Ag)

The iron–silver system [Swartzendruber 1984] shows a large miscibility gap and is reproduced here in Figure 4.9 below. Using the compositions at  $T = 1806\text{ K}$  gives  $X_{\text{Ag},1} = 0.00259$  and  $X_{\text{Ag},2} = 0.991$ . Substituting into equation 4.2 gives  $W = 89772\text{ J.mol}^{-1}$  and at  $1873\text{ K}$  this result in  $\gamma_{\text{In}}^0 = 318.8$  for the gamma-zero of indium in iron.

Figure 4.9—Iron–Silver Phase Diagram



L.J. Swartzendruber evaluation on p 560 in this issue.  
L.J. Swartzendruber is Category Editor for binary iron alloys.

Bulletin of Alloy Phase Diagrams Vol. 5 No. 6 1984 621

The iron–silver phase diagram from Swartzendruber 1984. The two phases exhibit a large miscibility gap above  $1538^\circ\text{C}$  and has been used to compute an estimate for gamma-zero value for silver in iron.

### 4.6.3.2 Bismuth (Bi)

The literature does contain some experimental values [Chang and Schlesinger 1998; Boa *et al.* 2008] for the solubility of bismuth in solid iron. The model of Miedema [Boom *et al.* 1983] provides an estimation of the partial molar enthalpy of solution of liquid bismuth in liquid iron



( $\Delta\bar{H}_{\text{Bi}}^0 = 146 \text{ kJ.mol}^{-1}$ ) which is substituted into Equation 4.3 to compute a gamma-zero at 1873 K of:  $\gamma_{\text{Bi}}^0 = 11792$ .

#### 4.6.3.3 Cadmium (Cd)

A thorough literature search found no useful data describing the solubility of cadmium in liquid iron. The model of Miedema [Boom *et al.* 1983] provides an estimation of the partial molar enthalpy of solution of liquid cadmium in liquid iron ( $\Delta\bar{H}_{\text{Cd}}^0 = 76 \text{ kJ.mol}^{-1}$ ) which is substituted into Equation 4.3 to compute a gamma-zero at 1873 K of  $\gamma_{\text{Cd}}^0 = 132$ .

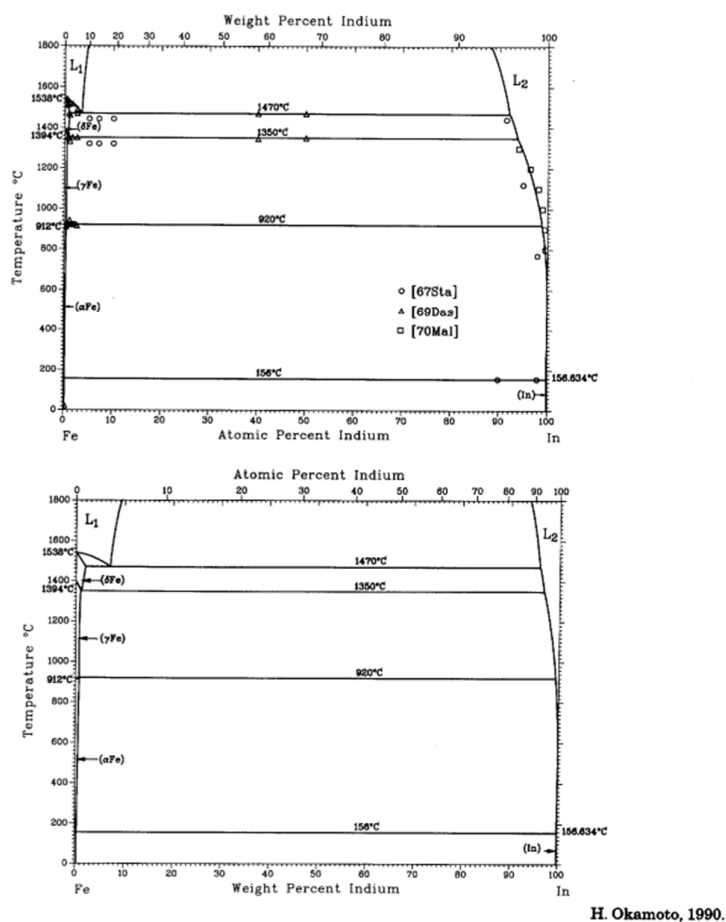
#### 4.6.3.4 Gallium (Ga)

While the iron–gallium system is well described [Dasarathy and Hume-Rothery 1965; Dryś *et al.* 1979] there exist no data on the thermochemical properties of the liquid phase. The model of Miedema [Boom *et al.* 1983] provides an estimate of the partial molar enthalpy of solution of liquid gallium in liquid iron ( $\Delta\bar{H}_{\text{Ga}}^0 = -8 \text{ kJ.mol}^{-1}$ ) which is substituted into Equation 4.3 to compute the gamma zero value of  $\gamma_{\text{Ga}}^0 = 0.38$  at the reference temperature 1873 K.

#### 4.6.3.5 Indium (In)

Indium shows little solubility in iron [Wodniecki *et al.* 1999]. At temperatures above 1470 K the iron–indium phase diagram [Dasarathy 1974; Okamoto 1990] shows a large miscibility gap and is reproduced here in Figure 4.10 below. Reading from the phase diagram at  $T = 1743 \text{ K}$  the compositions  $X_{\text{In},1} = 0.034$  and  $X_{\text{In},2} = 0.915$  can be substituted into Equation 4.2 to compute  $\gamma_{\text{In}}^0 = 27.4$  at 1873 K.

Figure 4.10—Iron–Indium Phase Diagram

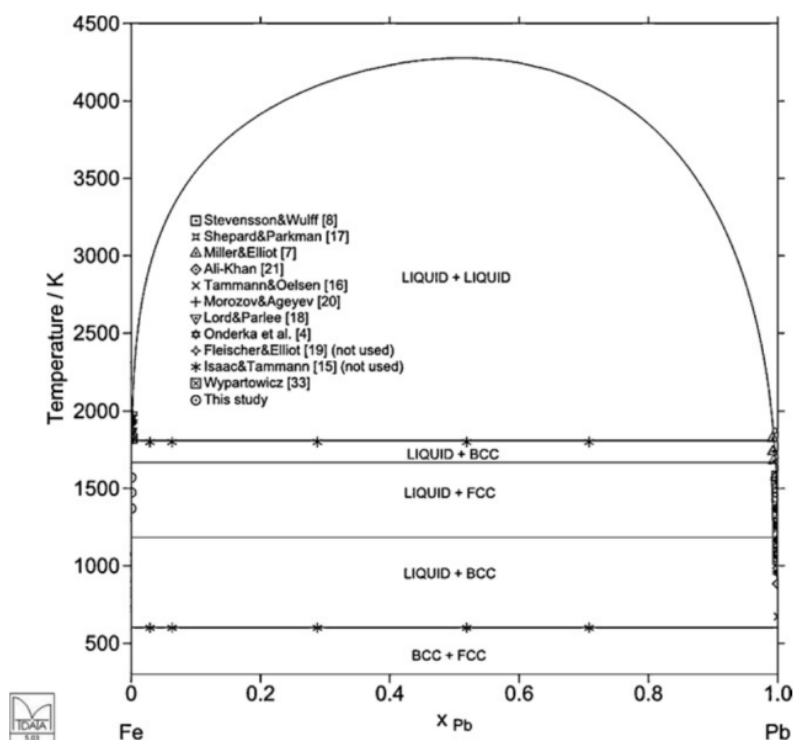


The iron–indium phase diagram from Okamoto 1990. The two components show a large miscibility gap above 1470°C and this has been used to compute an estimate of gamma-zero of indium in iron.

#### 4.6.3.6 Lead (Pb)

Lead is almost total insolubility in iron, yet despite this difficulty some workers have managed to assess the iron–lead system using experimental means [Vaajamo and Taskinen 2011]. At temperatures above 1809.6 K the iron–lead phase diagram shows a large miscibility gap and is reproduced here in Figure 4.11 below. Reading from the phase diagram at  $T = 1809.6 \text{ K}$  gives the compositions  $X_{\text{Pb},1} = 0.00071$  and  $X_{\text{Pb},2} = 0.9943$  which are substituted into Equation 4.2 to give  $\gamma_{\text{Pb}}^0 = 1107$  at 1873 K.

Figure 4.11—Iron–Lead Phase Diagram



The iron–lead phase diagram from [Vaajamo and Taskinen 2011]. The large miscibility gap above 1809.6 K has been used to estimate the gamma-zero of lead in iron.

#### 4.6.3.7 Antimony (Sb)

The iron–antimony system has been well characterised [Hino *et al.* 1994; Pei *et al.* 1995; Voisin *et al.* 2005] and the gamma-zero of antimony in liquid iron is provided by Voisin *et al.* 2005.

Those authors state that  $\gamma_{\text{Sb}}^0(1473\text{ K}) = 0.32$  and this value can be converted to the reference

temperature of 1873 K via the relationship  $\ln \gamma_M^0(T) = \left(\frac{T'}{T}\right) \ln \gamma_M^0(T')$  [Gordon and Breach

1988, p275] resulting in:  $\gamma_{\text{Sb}}^0(1873\text{ K}) = 0.41$ .

#### 4.6.3.8 Thallium (Tl)

A thorough literature search resulted in no useful data describing the solubility of thallium in liquid iron. The model of Miedema [Boom *et al.* 1983] provides an estimation of the partial

molar enthalpy of solution of liquid thallium in liquid iron ( $\Delta\bar{H}_{\text{Tl}}^0 = 158 \text{ kJ.mol}^{-1}$ ) which is used to compute the gamma zero value of  $\gamma_{\text{Tl}}^0 = 25483$  at the reference temperature 1873 K.

#### 4.6.3.9 Zinc (Zn)

The solubility of zinc in iron has been assessed by other workers [Su *et al.* 2001] who presented their results using CALPHAD models. The model parameters of Su *et al.* 2001 have been manipulated to provide a gamma-zero value for zinc in iron by the following approach.

Start with the chemical potential expression of Gibbs:

$$\mu_{\text{Zn}} = G + (1 - X_{\text{Zn}}) \frac{\partial G}{\partial X_{\text{Zn}}}$$

Substituting Equation 2 from Su *et al.* 2001 for the Gibbs energy:

$$G_m^\phi = X_{\text{Fe}} {}^0G_{\text{Fe}}^\phi + X_{\text{Zn}} {}^0G_{\text{Zn}}^\phi + RT (X_{\text{Fe}} \ln X_{\text{Fe}} + X_{\text{Zn}} \ln X_{\text{Zn}}) + {}^E G_m^\phi + {}^{mg} G_m^\phi$$

Note that the magnetic term  ${}^{mg} G_m^\phi$  can be ignored when considering the liquid phases.

Resulting in:

$$\mu_{\text{Zn}} = G_{\text{Zn}}^\circ + RT \ln X_{\text{Zn}} + {}^E G_m^\phi + (1 - X_{\text{Zn}}) \frac{\partial {}^E G_m^\phi}{\partial X_{\text{Zn}}}$$

Which can be rearranged to give:

$$RT \ln \gamma_{\text{Zn}} = {}^E G_m^\phi + (1 - X_{\text{Zn}}) \frac{\partial {}^E G_m^\phi}{\partial X_{\text{Zn}}}$$

Now write out Equation 3 from Su *et al.* 2001 explicitly:

$${}^E G_m^\phi = X_{\text{Fe}} X_{\text{Zn}} \left[ {}^0 L_{\text{Fe,Zn}}^{\text{liq}} + {}^1 L_{\text{Fe,Zn}}^{\text{liq}} (X_{\text{Fe}} - X_{\text{Zn}}) + {}^2 L_{\text{Fe,Zn}}^{\text{liq}} (X_{\text{Fe}} - X_{\text{Zn}})^2 \right]$$

To make differentiation simpler substitute:  $X_{\text{Fe}} = 1 - X_{\text{Zn}}$

$${}^E G_m^\phi = X_{\text{Zn}} (1 - X_{\text{Zn}}) \left[ {}^0 L_{\text{Fe,Zn}}^{\text{liq}} + {}^1 L_{\text{Fe,Zn}}^{\text{liq}} (1 - 2X_{\text{Zn}}) + {}^2 L_{\text{Fe,Zn}}^{\text{liq}} (1 - 2X_{\text{Zn}})^2 \right]$$

$${}^E G_m^\phi =$$

$${}^0 L_{\text{Fe,Zn}}^{\text{liq}} (X_{\text{Zn}} - X_{\text{Zn}}^2) + {}^1 L_{\text{Fe,Zn}}^{\text{liq}} (X_{\text{Zn}} - 3X_{\text{Zn}}^2 + 2X_{\text{Zn}}^3) + {}^2 L_{\text{Fe,Zn}}^{\text{liq}} (X_{\text{Zn}} - 5X_{\text{Zn}}^2 + 8X_{\text{Zn}}^3 - 4X_{\text{Zn}}^4)$$

Now differentiate with respect to  $X_{\text{Zn}}$  to give:

$$\frac{\partial {}^E G_m^\phi}{\partial X_{\text{Zn}}} = {}^0 L_{\text{Fe,Zn}}^{\text{liq}} (1 - 2X_{\text{Zn}}) + {}^1 L_{\text{Fe,Zn}}^{\text{liq}} (1 - 6X_{\text{Zn}} + 6X_{\text{Zn}}^2) + {}^2 L_{\text{Fe,Zn}}^{\text{liq}} (1 - 10X_{\text{Zn}} + 24X_{\text{Zn}}^2 - 16X_{\text{Zn}}^3)$$

This expression appears to be rather involved, but it is noted that upon inspection:

As  $X_{\text{Zn}} \rightarrow 0$ :

$$\frac{\partial {}^E G_m^\phi}{\partial X_{\text{Zn}}} \rightarrow {}^0 L_{\text{Fe,Zn}}^{\text{liq}} + {}^1 L_{\text{Fe,Zn}}^{\text{liq}} + {}^2 L_{\text{Fe,Zn}}^{\text{liq}}$$

$$(1 - X_{\text{Zn}}) \rightarrow 1$$

$${}^E G_m^\phi \rightarrow 0$$

Therefore the gamma-zero value is given at the limit of infinite dilution by the expression:

$$RT \ln \gamma_{\text{Zn}}^0 = {}^0 L_{\text{Fe,Zn}}^{\text{liq}} + {}^1 L_{\text{Fe,Zn}}^{\text{liq}} + {}^2 L_{\text{Fe,Zn}}^{\text{liq}}$$

Where the polynomial expressions ( ${}^nL$ ) from Su *et al.* 2001 are:

$${}^0L_{\text{Fe,Zn}}^{\text{liq}} = 65056.7 - 28.9522T$$

$${}^1L_{\text{Fe,Zn}}^{\text{liq}} = 102244.1 - 60.5058T$$

$${}^2L_{\text{Fe,Zn}}^{\text{liq}} = 20809.4 - 4.0235T$$

Evaluating and substituting give the final expression for gamma-zero:

$$\gamma_{\text{Zn}}^0 = e^{\left(\frac{188110.2 - 93.4815T}{RT}\right)}$$

Which at 1873 K is computed to equal  $\gamma_{\text{Zn}}^0(1873 \text{ K}) = 2.307$ .

#### 4.6.4 Revising Epsilon-Carbon Values

Because the partitioning experiments were performed with carbon-saturated iron, the epsilon model has been used to compute the activity coefficients in the iron metal. To assess the accuracy of the computed activity coefficients, four high pressure experiments were performed with MgO and SiO<sub>2</sub> capsules and the metal in these experiments was carbon-free. To compare the carbon-saturated experiments with the carbon-free experiments the Gibbs free energy values have been modelled in the carbon-saturated experiments using parameters derived from the silicate melt composition. In each case where a model could be regressed, it was then used to compute the free energy value at the same compositions as the carbon-free experiments. A direct comparison is thus possible and any difference has been utilised to revise the epsilon-carbon value for that element.

First, a check was performed to assess whether the activity coefficients are able to correct the effect of the carbon on the trace element activity in the iron metal. To do this, start with the now-familiar expression:

$$K_M = \frac{X_M^{\text{metal}} \left( X_{\text{FeO}}^{\text{silicate}} \right)^{\frac{n}{2}}}{X_{\text{MO}_{n/2}}^{\text{silicate}} \left( X_{\text{Fe}}^{\text{metal}} \right)^{\frac{n}{2}}}$$

$$K_M^{\text{Ideal}} = \frac{\gamma_M^{\text{C-Sat}} X_M^{\text{metal}} \left( X_{\text{FeO}}^{\text{silicate}} \right)^{\frac{n}{2}}}{X_{\text{MO}_{n/2}}^{\text{silicate}} \left( \gamma_{\text{Fe}}^{\text{C-Sat}} X_{\text{Fe}}^{\text{metal}} \right)^{\frac{n}{2}}} = K_M^{\text{C-Sat}} \frac{\gamma_M^{\text{C-Sat}}}{\left( \gamma_{\text{Fe}}^{\text{C-Sat}} \right)^{\frac{n}{2}}}$$

$$K_M^{\text{Ideal}} = \frac{\gamma_M^{\text{C-Free}} X_M^{\text{metal}} \left( X_{\text{FeO}}^{\text{silicate}} \right)^{\frac{n}{2}}}{X_{\text{MO}_{n/2}}^{\text{silicate}} \left( \gamma_{\text{Fe}}^{\text{C-Free}} X_{\text{Fe}}^{\text{metal}} \right)^{\frac{n}{2}}} = K_M^{\text{C-Free}} \frac{\gamma_M^{\text{C-Free}}}{\left( \gamma_{\text{Fe}}^{\text{C-Free}} \right)^{\frac{n}{2}}}$$

Since we have both modelled and measured values, the explicit comparison should be performed using:

$$\frac{\text{modelled}}{K_M^{\text{Ideal}}} = K_M^{\text{C-Sat}} \frac{\gamma_M^{\text{C-Sat}}}{\left( \gamma_{\text{Fe}}^{\text{C-Sat}} \right)^{\frac{n}{2}}}$$

$$\frac{\text{measured}}{K_M^{\text{Ideal}}} = K_M^{\text{C-Free}} \frac{\gamma_M^{\text{C-Free}}}{\left( \gamma_{\text{Fe}}^{\text{C-Free}} \right)^{\frac{n}{2}}}$$

If the activity coefficients are correct then:  $\frac{\text{modelled}}{K_M^{\text{Ideal}}} \stackrel{\text{should}}{=} \frac{\text{measured}}{K_M^{\text{Ideal}}}$

If they vary by more than the estimated uncertainty then a revised epsilon-carbon value can be computed using:

$$\textcircled{1} RT \ln K_M^{\text{C-Sat}} - RT \ln K_M^{\text{C-Free}} = RT \ln \gamma_M^{\text{C-Free}} - RT \ln \gamma_M^{\text{C-Sat}}$$

$$\textcircled{2} \quad RT \ln \gamma_M^{C\text{-Sat}} = RT \ln \gamma_{\text{Fe}}^{C\text{-Sat}} + RT \ln \gamma_M^{C\text{-Free}} - RT \epsilon_M^C \ln(1 - X_C^{\text{metal}})$$

Substitute:  $\textcircled{2} \rightarrow \textcircled{1}$

$$RT \ln K_M^{C\text{-Sat}} - RT \ln K_M^{C\text{-Free}} = -RT \ln \gamma_{\text{Fe}}^{C\text{-Sat}} - RT \epsilon_M^C \ln(1 - X_C^{\text{metal}})$$

Define  $\Delta K \equiv RT \ln K_M^{C\text{-Sat}} - RT \ln K_M^{C\text{-Free}}$  and substitute:

$$\Delta K = -RT \ln \gamma_{\text{Fe}}^{C\text{-Sat}} - RT \epsilon_M^C \ln(1 - X_C^{\text{metal}})$$

$$\epsilon_M^C = \frac{\Delta K + RT \ln \gamma_{\text{Fe}}^{C\text{-Sat}}}{RT \ln(1 - X_C^{\text{metal}})} \quad (\text{Equation 4.4})$$

Where possible, Equation 4.4 is now used to revise values of epsilon-carbon. However, it must be noted that it should only be used when there is reasonable confidence that gamma-zero for the trace element is correct.

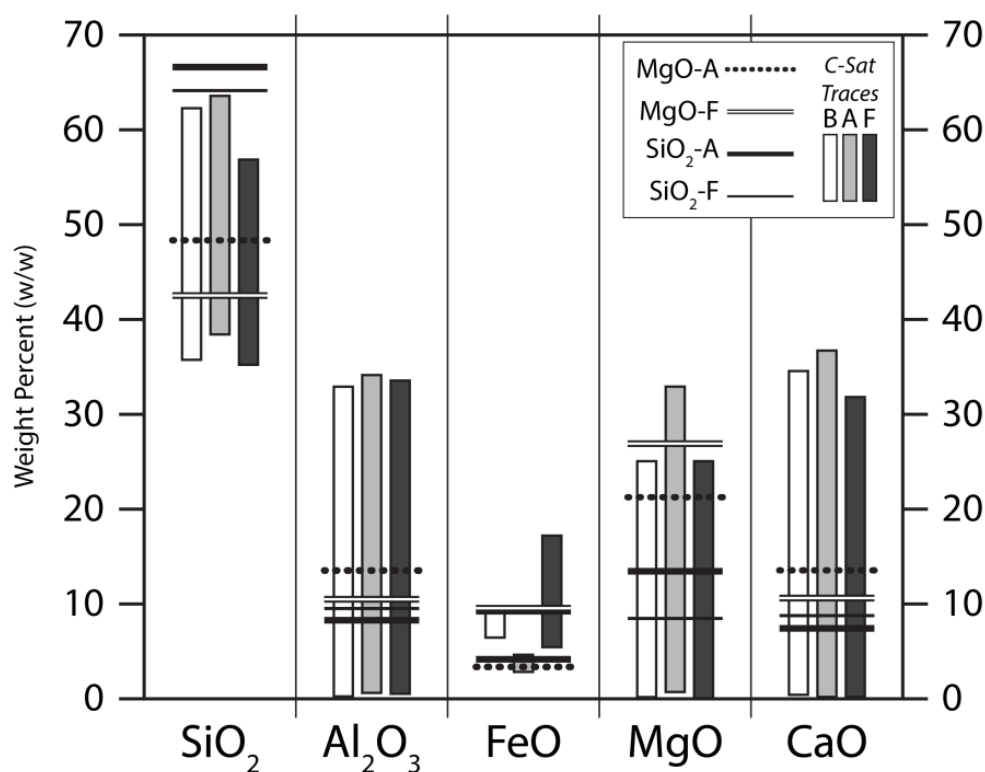
#### 4.6.5 Revise Epsilon-Carbon Values by Modelling Free Energy

The composition of both the metal and silicate phases from each experiment have been converted to mole fraction and the Gibbs free energy ( $RT \ln K_D$ ) of each equilibrium computed. To produce a model capable of interpolating a reasonable free energy value at the compositions of the carbon-free experiments it is important that the carbon-free experiment compositions are do not lie too far beyond the range of compositions from the carbon-saturated experiments. Figure 4.12 shows the range of major element components for each set of trace elements compared to the compositions of the four carbon-free experiments. As expected, the experiments performed in  $\text{SiO}_2$  and  $\text{MgO}$  capsules have dissolved capsule material which has altered the composition of the silicate melt.



The melt composition of the carbon-free experiments suggests that no significant extrapolation is required. While the two experiments performed in SiO<sub>2</sub> capsules sit slightly (no more than 5% relative) above the composition range for all trace mixes, that extrapolation is regarded to be insignificant.

Figure 4.12—Major Oxide Composition Ranges



The concentration ranges of each major element component have been illustrated along with the four carbon-free experiments. For most elements there is no extrapolation to the carbon-free experiments, while the 5% extrapolation in SiO<sub>2</sub> content is regarded to be insignificant.

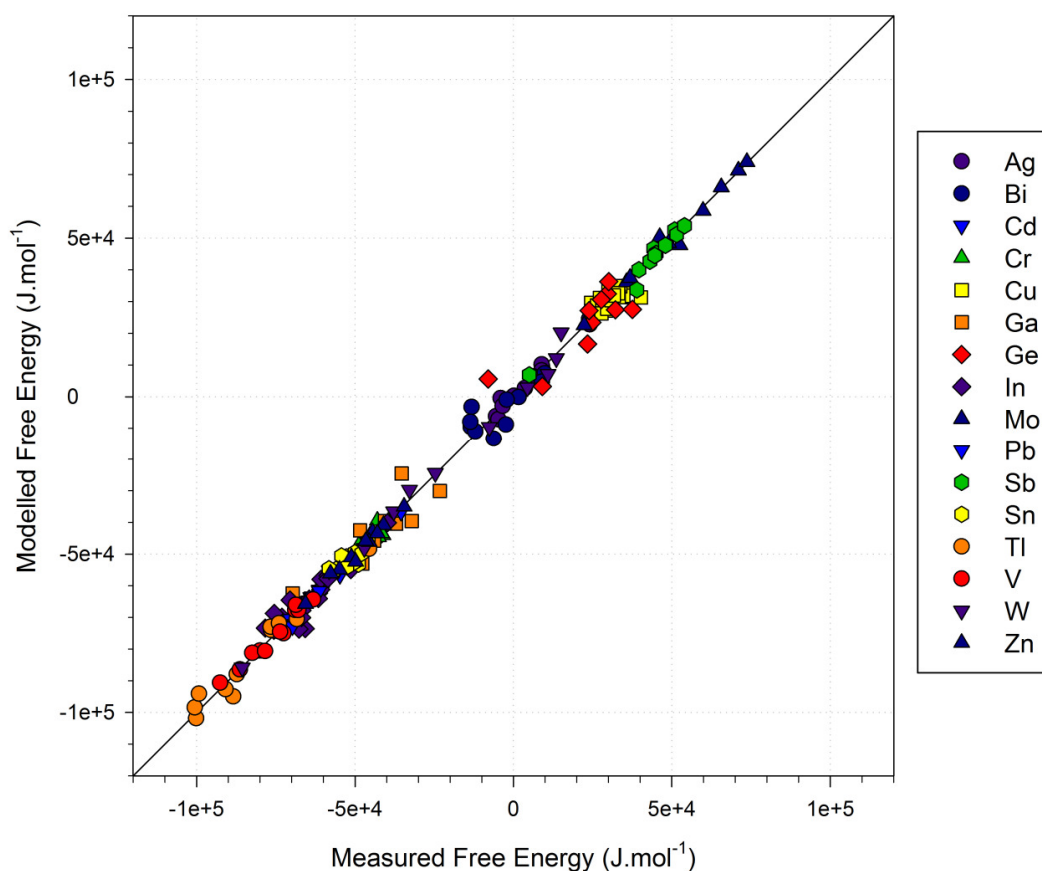
Modelling was performed with the software package SPSS (SPSS, I. "IBM SPSS statistics version 21." Boston, Mass: International Business Machines Corp, 2012) using stepwise linear regression. The independent variable terms comprised the composition of the melt expressed as single-cation oxide mole fraction; cross terms and square terms were also included. The significance of the fitting was adjusted element by element, since the objective of this modelling

effort is to produce robust models to interpolate the free energy values. Nearly all elements produced significant models with a reasonable goodness of fit (judged by  $R^2$ ) based on relatively restrictive (F-enter = 0.2 F-leave = 0.21) significance rules. The models produced are summarised in Table 4.12 below. The input and output variables of all models have also been plotted in Figure 4.13. That figure shows the range of free energies measured for each trace element and also shows the scatter for each model.

**Table 4.12—Summary of Models of Free Energy by Melt Composition**

| Element | Procedure | F - Params               | Experiments | R <sup>2</sup> | Std Error (mJ) | # Terms | Terms (Plus a Constant)                                       |
|---------|-----------|--------------------------|-------------|----------------|----------------|---------|---------------------------------------------------------------|
| Ag      | Stepwise  | Entry: 0.2 Remove: 0.21  | B           | 0.970          | 1988.9         | 4       | AlMg, Ca <sup>2</sup> , CaMg, Fe                              |
| Bi      | Stepwise  | Entry: 0.2 Remove: 0.21  | B           | 0.816          | 5787.9         | 2       | CaMg, Fe                                                      |
| Cd      | Stepwise  | Entry: 0.1 Remove: 0.11  | B           | 0.997          | 435.5          | 4       | Fe, Fe <sup>2</sup> , FeMg, MgSi                              |
| Cr      | Stepwise  | Entry: 0.2 Remove: 0.21  | A           | 0.825          | 2468.8         | 4       | Al <sup>3</sup> , Ca <sup>2</sup> , Fe, Si <sup>2</sup>       |
| Cu      | Stepwise  | Entry: 0.2 Remove: 0.21  | B+A+F       | 0.428          | 2620.6         | 3       | CaMg, FeSi, Mg                                                |
| Ga      | Stepwise  | Entry: 0.3 Remove: 0.31  | F           | 0.755          | 8343.9         | 4       | AlFe, AlSi, Fe <sup>2</sup> , Si <sup>2</sup>                 |
| Ge      | Stepwise  | Entry: 0.2 Remove: 0.21  | F           | 0.711          | 8056.7         | 2       | AlSi, FeSi                                                    |
| In      | Stepwise  | Entry: 0.2 Remove: 0.21  | B+A         | 0.859          | 4081.0         | 5       | AlMg, CaFe, Fe <sup>2</sup> , FeSi, Mg <sup>2</sup>           |
| Mo      | Stepwise  | Entry: 0.5 Remove: 0.51  | F           | 0.983          | 3264.9         | 5       | Al, AlCa, AlMg, Fe <sup>2</sup> , FeMg                        |
| Pb      | Stepwise  | Entry: 0.2 Remove: 0.21  | B           | 0.979          | 2092.8         | 4       | AlSi, CaMg, Si, Si <sup>2</sup>                               |
| Sb      | Stepwise  | Entry: 0.21 Remove: 0.31 | B           | 0.977          | 3183.4         | 6       | Ca <sup>2</sup> , CaSi, Fe, Fe <sup>2</sup> , FeSi, Si        |
| Sn      | Stepwise  | Entry: 0.6 Remove: 0.61  | A           | 0.537          | 3225.7         | 4       | Ca, Ca <sup>2</sup> , FeSi, Mg <sup>2</sup>                   |
| Tl      | Stepwise  | Entry: 0.2 Remove: 0.21  | B           | 0.958          | 4084.5         | 3       | AlSi, CaMg, Si                                                |
| V       | Stepwise  | Entry: 0.05 Remove: 0.1  | A           | 0.966          | 1964.8         | 3       | Ca <sup>2</sup> , CaMg, Si <sup>2</sup>                       |
| W       | Stepwise  | Entry: 0.45 Remove: 0.5  | F           | 0.994          | 5529.5         | 7       | AlFe, CaFe, Fe <sup>2</sup> , FeMg, FeSi, Mg, Si <sup>2</sup> |
| Zn      | Stepwise  | Entry: 0.2 Remove: 0.21  | A           | 0.983          | 1456.8         | 4       | Ca, CaSi, FeMg, Mg <sup>2</sup>                               |

Figure 4.13—Gibbs Free Energy of Metal–Silicate Partitioning at 1923 K—Measured vs Modelled Values



Linear models for free energy were regressed using SPSS. These models are primarily used to interpolate values at the carbon-free experimental major element compositions. This plot shows good agreement between measured and modelled values, which illustrates that the models are effective but may be slightly over fitted. As outlined in the text, for the application of these models this is not a great concern.

The epsilon-carbon revision models are useful, but not especially meaningful beyond interpolating the free energies at the carbon-free experiment compositions. For the interested reader the complete model terms have been included in the Appendix for completeness.

#### 4.6.5.1 Henry's Law Assessment

It is important for partitioning experiments to be conducted using low-levels of trace elements to be certain that they obey Henry's law [Schmidt *et al.* 1989]. The partitioning experiments in this study were doped with different abundances of trace elements: "Trace B" is the lowest, with

less than 500  $\mu\text{g.g}^{-1}$ ; “Trace A” and “Trace F” are the highest, with up to 5000  $\mu\text{g.g}^{-1}$ ; while the carbon-free experiments were doped at an intermediate level.

To ensure these experiments were performed in the *Henrian* region, a set of three experiments (TT1, TT2, TT3) were conducted using the same silicate melt composition (#5 “ADF”) but with trace element concentrations spanning two orders of magnitude: 50–5000  $\mu\text{g.g}^{-1}$ . These results were combined with other experiments (A369, AN1101, and AN1102) that had also been performed with the same silicate melt composition. The activity coefficient for each trace element in each experimental melt was computed to verify that they remained constant with doping level.

Four elements (Bi, Cd, Pb, Tl, and W) were identified that showed a significant change in melt activity at high concentration. They have been processed using one of the methods outlined here:

#### 4.6.5.2 Cadmium (Cd)

Trace mixture B provides meaningful partition coefficients, and the carbon-free experiments are low enough to provide a reasonable estimate for epsilon-carbon.

#### 4.6.5.3 Bismuth (Bi) and Thallium (Tl)

Trace mixture B provides meaningful partition coefficients. The abundance in the carbon-free experiments is too high to give the true epsilon-carbon value, but is used because no other estimate for epsilon-carbon has been previously determined.

#### 4.6.5.4 Lead (Pb)

Trace mixture B provides meaningful partition coefficients, however the carbon-free experiments are too high in abundance to be used. Since epsilon-carbon has been determined

by previous work, the carbon-free experiments will not be used to revise the epsilon-carbon values.

#### 4.6.5.5 Tungsten (W)

Same as for Pb, however this element was not added to trace mixture B and the experiments using trace mixture F will be used for this element.

**Table 4.13—Revised Epsilon-Carbon Values**

| Element | Initial Epsilon-Carbon ( $\epsilon_M^C$ ) 1873 K | Revised Epsilon-Carbon ( $\epsilon_M^C$ ) 1873 K |
|---------|--------------------------------------------------|--------------------------------------------------|
| Ag      | 11.69                                            |                                                  |
| Bi      | 1                                                | 3.06                                             |
| Cd      | 1                                                | 18.83                                            |
| Cr      | -4.86                                            | -2.89                                            |
| Cu      | 3.97                                             | 4.99                                             |
| Ga      | 2.63                                             | 11.56                                            |
| Ge      | 2.27                                             | 7.1                                              |
| In      | 0                                                | 5.49                                             |
| Mo      | -6.02                                            |                                                  |
| Pb      | 5.59                                             |                                                  |
| Sb      | 14.63                                            | 17.57                                            |
| Sn      | 9.45                                             | 8.37                                             |
| Tl      | 1                                                | 8.24                                             |
| V       | -5.99                                            | -4.72                                            |
| W       | -6.51                                            |                                                  |
| Zn      | 1                                                | -3.94                                            |

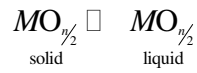
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## 4.7 Computing Thermochemical Data

### 4.7.1 Computing $\log K_f(\text{liquid})$ from $\log K_f(\text{solid})$

If the thermochemical data tables do not include equilibrium constant values for the liquid state then we can apply the following correction to convert from solid to liquid.

First, consider the equilibrium:



From Gibbs we have  $\Delta G^\circ = -RT \ln \frac{K_f^{\text{liquid}}}{K_f^{\text{solid}}}$  and  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ .

At the temperature of melting ( $T_M$ ) we can write  $\Delta G_{T_M}^\circ = 0$  while at any other temperature:

$$\Delta G_T^\circ = \Delta G_{T_M}^\circ + \int_{T_M}^T \frac{\partial \Delta G^\circ}{\partial T} dT$$

Since  $\frac{\partial \Delta G^\circ}{\partial T} = \Delta S^\circ$  and  $\Delta G_{T_M}^\circ = 0$  this expression can be written out in full as:

$$\Delta G_T^\circ = (T - T_M) \Delta S^\circ$$

Combining the two expressions for  $\Delta G_T^\circ$  we finally get:

$$-RT \ln \frac{K_f^{\text{liquid}}}{K_f^{\text{solid}}} = (T - T_M) \Delta S^\circ$$

Which can be trivially simplified to:

$$\ln K_f^{\text{liquid}} = \ln K_f^{\text{solid}} - \frac{(T - T_M) \Delta S^\circ}{RT} \quad (\text{Equation 4.5})$$

This expression will be used in the subsequent sections to compute the equilibrium constant of formation for the liquid state.

#### 4.7.2 Computing $\log K_f(\text{liquid})$ From Vapour Data

If the thermochemical data tables only show data for the vapour phase then the following computation can be used to estimate the equilibrium constant for the formation of the liquid.

To start, consider the equilibrium:



At temperatures above the boiling temperature ( $T_B$ ) we can apply Gibbs  $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

and  $\Delta C_p = C_p^{\text{gas}} - C_p^{\text{liquid}}$  to write:

$$\Delta G_T^\circ = \Delta H_{T_B}^\circ + \int_{T_B}^T \Delta C_p dT - T \left( \Delta S_{T_B}^\circ + \int_{T_B}^T \frac{\Delta C_p}{T} dT \right)$$

Writing out the exact integrals gives the cumbersome but perfectly tractable expression:

$$\Delta G_T^\circ = \Delta H_{T_B}^\circ - T \Delta S_{T_B}^\circ + \Delta C_p (T - T_B) - \Delta C_p \ln \frac{T}{T_B}$$

The requisite thermochemical quantities can be found in the thermochemical tables and substituted accordingly. Setting this equal to  $\Delta G^\circ = RT \ln K_f^{\text{liquid}}$  and simplifying slightly gives the final expression for the equilibrium constant:

$$\ln K_f^{\text{liquid}} = \frac{\Delta H_{T_B}^\circ - T \Delta S_{T_B}^\circ + \Delta C_P \left( T - T_B - \ln \frac{T}{T_B} \right)}{RT} \quad (\text{Equation 4.6})$$

This expression will be used as required in the subsequent sections to compute the equilibrium of formation for the liquid state.



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## 4.8 Thermochemical Data Summary

Now we collate the natural logarithm of the equilibrium constants of formation for the pure elements and the element oxides, all in liquid form, with liquid reference states, at the experiment temperature of 1923 K. The treatment of data each trace element is presented here somewhat laboriously but this is absolutely essential, since data for each element has originated from a different thermodynamic data source, calculation, or estimate. A summary of all values is provided in Table 4.14 below.

**Table 4.14—Summary of Thermodynamic Values**

| Element | C-Sat Iron Gamma ( $\gamma_M$ ) 1923 K | Pure Iron Gamma ( $\gamma_M$ ) 1923 K | $\ln K_f$ (M) 1923 K | $\ln K_f$ ( $\text{MO}_{0.5}$ ) 1923 K |
|---------|----------------------------------------|---------------------------------------|----------------------|----------------------------------------|
| Fe      | 0.716                                  | 1.0                                   | 0                    | 9.553                                  |
| Ag      | 3029                                   | 274                                   | 0                    | -6.49                                  |
| Bi      | 13309                                  | 9124                                  | 0                    | 2.807                                  |
| Cd      | 6809                                   | 116                                   | -5.68                | 4.8                                    |
| Cr      | 0.364                                  | 1.0                                   | -0.103               | 13.342                                 |
| Cu      | 18.7                                   | 8.11                                  | 0                    | 1.194                                  |
| Ga      | 6.539                                  | 0.608                                 | 0                    | 14.317                                 |
| Ge      | 0.0837                                 | 0.0222                                | 0                    | 13.367                                 |
| In      | 65.2                                   | 25.1                                  | 0                    | 9.365                                  |
| Mo      | 0.175                                  | 1.0                                   | -0.822               | 14.455                                 |
| Pb      | 2439                                   | 702                                   | 0                    | 3.155                                  |
| Sb      | 18.463                                 | 0.420                                 | -0.047               | 7.481                                  |
| Sn      | 12.8                                   | 2.52                                  | 0                    | 11.775                                 |
| Tl      | 89379                                  | 19093                                 | -1.14                | 1.67                                   |
| V       | 0.0202                                 | 0.0854                                | -0.152               | 22.66                                  |
| W       | 0.454                                  | 2.92                                  | -1.057               | 24.546                                 |
| Zn      | 0.64                                   | 2.26                                  | -5.04                | 4.671                                  |

### 4.8.1 Silver (Ag)

#### 4.8.1.1 *Equilibrium Constant of Formation of Liquid Ag*

The stable state of pure silver at 1923 K is liquid molten silver. As such the energy of formation is equal to zero [Barin 1973, p1].

#### 4.8.1.2 *Equilibrium Constant of Formation of Liquid $\text{AgO}_{0.5}$*

Measuring the thermochemical properties of the silver–oxygen system is complicated by the decomposition of pure  $\text{Ag}_2\text{O}$  in one-atmosphere of air pressure at 420 K. Despite this difficulty some workers [Assal *et al.* 1997] have characterised the system. The model in Assal *et al.* 1997

for the molar Gibbs energy of the liquid was used and the natural logarithm of the equilibrium constant of formation at 1923 K has been computed to be  $-6.493$ .

## 4.8.2 Bismuth (Bi)

### 4.8.2.1 *Equilibrium Constant of Formation of Liquid Bi*

The stable state of pure bismuth at 1923 K is liquid molten bismuth. As such the energy of formation is equal to zero [Barin 1973, p190].

### 4.8.2.2 *Equilibrium Constant of Formation of Liquid BiO<sub>1.5</sub>*

The available data table [Barin 1973, p202] only lists thermochemical data for liquid Bi<sub>2</sub>O<sub>3</sub> up to 1800 K. The boiling point of liquid Bi<sub>2</sub>O<sub>3</sub> at one-atmosphere pressure is 2163 K so an extrapolation to 1923 K was considered valid. To perform the extrapolation, the energy of formation was converted from the log base-ten to the natural log prior to being charted against inverse temperature. A linear regression ( $R^2=1.000$ ,  $N=8$ ,  $1100\text{ K} \leq T \leq 1800\text{ K}$ ) gave the following relationship:

$$\ln K_{f, \text{Bi}_2\text{O}_3, \text{liquid}}(1100 \leq T \leq 2163\text{ K}) = \frac{61188}{T} - 26.2$$

This expression was used to compute the natural logarithm of the equilibrium constant of formation of liquid Bi<sub>2</sub>O<sub>3</sub> at 1923 K to be 5.613 and liquid BiO<sub>1.5</sub> at the same temperature to be 2.807.

## 4.8.3 Cadmium (Cd)

### 4.8.3.1 *Equilibrium Constant of Formation of Liquid Cd*

The stable state of pure cadmium at 1923 K is monoatomic cadmium gas [Barin 1973, p357]. To compute the equilibrium constant of formation for the liquid phase Equation 4.6 was used with

the following parameters:  $T_{\text{vap}} = 1039 \text{ K}$ ,  $\Delta H(T_{\text{vap}}) = 97.4 \text{ kJ.mol}^{-1}$ ,  $\Delta C_p(T_{\text{vap}}) = -8.92$ ,  $\Delta S(T_{\text{vap}}) = 93.7 \text{ J.mol}^{-1}$ . The natural logarithm of the equilibrium constant of formation was computed to be  $-5.68$ .

#### 4.8.3.2 Equilibrium Constant of Formation of Liquid CdO

The stable state of pure CdO at 1923 K is solid CdO [Barin 1923, p362]. Pure cadmium metal is solid up to 594K and liquid to 1039 K. As such the equilibrium constant of formation of solid CdO was first corrected for the change in reference states of pure cadmium over the temperature range 300 to 1500 K. A linear regression ( $R^2=1.000$ ,  $N=13$ ,  $300 \text{ K} \leq T \leq 1500 \text{ K}$ )

gave the expression  $\ln K_{f,\text{CdO}}^{\text{solid}} = \frac{30895}{T} - 11.938$  and this was extrapolated up to the

experimental temperature:  $\ln K_{f,\text{CdO}}^{\text{solid}}(1923 \text{ K}) = 4.128$ . To then use Equation 4.5 to correct

for the entropy of the phase change between the solid and liquid states, the temperature of melting was estimated to be 1500 K and the entropy change estimated to be similar to the elements Ca, Mg, and Ba, at  $25 \text{ J.K}^{-1}.\text{mol}^{-1}$ . These estimates are in agreement with those of other workers [Behrens and Mason 1981]. As such the natural logarithm of the equilibrium constant of formation of liquid CdO at 1923 K has been estimated to be 4.8.

#### 4.8.4 Chromium (Cr)

##### 4.8.4.1 Equilibrium Constant of Formation of Liquid Cr

The stable state of chromium at 1923 K is solid chromium metal. To apply the entropy of melting to the solid state data Equation 4.5 was used with  $T_m=2130 \text{ K}$  and  $\Delta S=7.95 \text{ J.K}^{-1}.\text{mol}^{-1}$  [Barin 1973, p418] and the natural logarithm of the equilibrium constant computed to be:

$$\ln K_{f,\text{Cr}}^{\text{liquid}}(1923 \text{ K}) = -0.103.$$

#### 4.8.4.2 Equilibrium Constant of Formation of Liquid CrO

Other workers [Okabe *et al.* 1996] have provided the expression for the Gibbs energy of formation of liquid CrO to be:  $\Delta G^\circ = -334,000 + 63.8T$  J.mol<sup>-1</sup>. This expression is relative to pure chromium in the solid state. By applying Equation 4.5 to change the reference state to liquid chromium and fitting a linear regression ( $R^2=1.000$ ,  $N=10$ ,  $1500 \text{ K} \leq T \leq 2400 \text{ K}$ ) to interpolate gave the relationship:  $\ln K_{f,\text{CrO}}^{\text{liquid}} (1500 \text{ K} \leq T \leq 2400 \text{ K}) = \frac{41891}{T} - 8.44$  .

Evaluating at 1923 K gave the natural logarithm of the equilibrium constant for liquid chromium oxide to be:  $\ln K_{f,\text{CrO}}^{\text{liquid}} (1923 \text{ K}) = 13.342$  .

#### 4.8.5 Copper (Cu)

##### 4.8.5.1 Equilibrium Constant of Formation of Liquid Cu

The stable state of copper at 1923 K is liquid molten copper. As such the energy of formation is equal to zero [Barin 1973, p465].

##### 4.8.5.2 Equilibrium Constant of Formation of Liquid CuO<sub>0.5</sub>

The energy of formation of liquid Cu<sub>2</sub>O is tabulated in Barin 1973, p485, and was interpolated using a linear regression ( $R^2=1.000$ ,  $N=6$ ,  $1517 \text{ K} \leq T \leq 2000 \text{ K}$ ) to give this relationship for the natural logarithm of the equilibrium constant:

$$\ln K_{f,\text{Cu}_2\text{O}}^{\text{liquid}} (1517 \leq T \leq 2000 \text{ K}) = \frac{14645}{T} - 5.227 \quad . \quad \text{Evaluating at } 1923 \text{ K gave}$$

$$\ln K_{f,\text{CuO}_{0.5}}^{\text{liquid}} (1923 \text{ K}) = 1.194 \quad .$$

## 4.8.6 Gallium (Ga)

### 4.8.6.1 Equilibrium Constant of Formation of Liquid Ga

The stable state of pure gallium at 1923 K is liquid molten gallium. As such the energy of formation is equal to zero [Barin 1973, p586].

### 4.8.6.2 Equilibrium Constant of Formation of Liquid $GaO_{1.5}$

The energy of formation of solid  $Ga_2O_3$  is tabulated in Barin 1973, p600, and was interpolated using a linear regression ( $R^2=1.000$ ,  $N=10$ ,  $1200\text{ K} \leq T \leq 2073\text{ K}$ ) to give this relationship for the natural logarithm of the equilibrium constant:

$$\ln K_{f,Ga_2O_3}^{\text{solid}} (1200 \leq T \leq 2073\text{ K}) = \frac{129722}{T} - 38.318. \text{ This expression was evaluated at } 1923\text{ K}$$

to give  $\ln K_{f,Ga_2O_3}^{\text{solid}} (1923\text{ K}) = 29.127$  which was then corrected using Equation 4.5 to give

this value of the natural logarithm of the equilibrium constant:  $\ln K_{f,GaO_{1.5}}^{\text{liquid}} (1923\text{ K}) = 14.317.$

## 4.8.7 Germanium (Ge)

### 4.8.7.1 Equilibrium Constant of Formation of Liquid Ge

The stable state of pure gallium at 1923 K is liquid molten germanium. As such the energy of formation is equal to zero [Barin 1973, p618].

### 4.8.7.2 Equilibrium Constant of Formation of Liquid $GeO_2$

The equilibrium constant of formation of liquid  $GeO_2$  is tabulated in Barin 1973, p631, and was interpolated using a linear regression ( $R^2=1.000$ ,  $N=6$ ,  $1500\text{ K} \leq T \leq 2000\text{ K}$ ) to give this relationship for the natural logarithm of the equilibrium constant:

$\ln K_{f,\text{GeO}_2}^{\text{liquid}} (1500 \leq T \leq 2000 \text{ K}) = \frac{67976}{T} - 21.982$ . Evaluating this expression at 1923 K gave

the following value:  $\ln K_{f,\text{GeO}_2}^{\text{liquid}} (1923 \text{ K}) = 13.367$ .

#### 4.8.8 Indium (In)

##### 4.8.8.1 *Equilibrium Constant of Formation of Liquid In*

The stable state of pure indium at 1923 K is liquid molten indium. As such the energy of formation is equal to zero [Barin 1973, p700].

##### 4.8.8.2 *Equilibrium Constant of Formation of Liquid InO<sub>1.5</sub> at 1923 K*

The energy of formation of solid In<sub>2</sub>O<sub>3</sub> is tabulated in Barin 1973, p717, and a linear regression ( $R^2=1.000$ ,  $N=7$ ,  $1000 \text{ K} \leq T \leq 1600 \text{ K}$ ) was applied to find this relationship for the natural

logarithm of the equilibrium constant:  $\ln K_{f,\text{In}_2\text{O}_3}^{\text{solid}} (1000 \leq T \leq 2183 \text{ K}) = \frac{110368}{T} - 37.81$ .

This was used to extrapolate up to 1923 K (which is considered valid since the temperature of melting of In<sub>2</sub>O<sub>3</sub> is 2183 K) which gave:  $\ln K_{f,\text{In}_2\text{O}_3}^{\text{solid}} (1923 \text{ K}) = 19.584$ . This value was then

corrected using Equation 4.5 ( $\Delta S$  of melting taken from Wood and Wade 2013) to give the value of the natural logarithm of the equilibrium constant of indium oxide as:

$\ln K_{f,\text{InO}_{1.5}}^{\text{liquid}} (1923 \text{ K}) = 9.365$ .

#### 4.8.9 Molybdenum (Mo)

##### 4.8.9.1 *Equilibrium Constant of Formation of Liquid Mo*

The stable state of molybdenum at 1923 K is solid molybdenum metal. To apply the entropy change to the liquid state Equation 4.5 was used with  $T_m=2897 \text{ K}$  and  $\Delta S=13.496 \text{ J.K}^{-1}.\text{mol}^{-1}$

[Barin 1973, p917] and the natural logarithm of the equilibrium constant computed to be:

$$\ln K_{f,\text{Mo}}^{\text{liquid}}(1923\text{ K}) = -0.822.$$

#### 4.8.9.2 Equilibrium Constant of Formation of Liquid MoO<sub>2</sub>

The equilibrium constant of formation of solid MoO<sub>2</sub> is tabulated in Barin 1973, p924, with the reference state for pure Mo to be solid Mo. Equation 4.5 was used to change the reference state to liquid Mo and then a linear regression ( $R^2=1.000$ ,  $N=9$ ,  $1200\text{ K} \leq T \leq 2000\text{ K}$ ) applied to find this relationship for the natural logarithm of the equilibrium constant:

$$\ln K_{f,\text{MoO}_2}^{\text{solid}}(1200 \leq T \leq 2200\text{ K}) = \frac{63630}{T} - 18.091.$$

This expression was used to interpolate

the value at 1923 K as:  $\ln K_{f,\text{MoO}_2}^{\text{solid}}(1923\text{ K}) = 14.999$ . This value was then corrected using

Equation 4.5 ( $T_m$  of 2200K and  $\Delta S=31.4\text{ J}\cdot\text{mol}^{-1}$  taken from O'Neill and Eggins 2002, where they approximate these values as being the same as for TiO<sub>2</sub>) to give the estimate of the natural logarithm of the equilibrium constant of molybdenum oxide to be:

$$\ln K_{f,\text{MoO}_2}^{\text{liquid}}(1923\text{ K}) = 14.455.$$

### 4.8.10 Lead (Pb)

#### 4.8.10.1 Equilibrium Constant of Formation of Liquid Pb

The stable state of lead at 1923 K is liquid molten lead. As such the natural logarithm of the equilibrium constant of formation is equal to zero [Barin 1973, p1127].

#### 4.8.10.2 Equilibrium Constant of Formation of Liquid PbO

The equilibrium constant of formation of liquid PbO is tabulated in Barin 1973, p1148, and a linear regression ( $\Delta T=1500\text{ K}-2000\text{ K}$ ,  $N=6$ ,  $R^2=1.000$ ) was applied to give the expression:

$\ln K_{f,\text{PbO}}^{\text{liquid}}(1500 \leq T \leq 2000 \text{ K}) = \frac{21666}{T} - 8.112$ . This was evaluated at the experimental

temperature of 1923 K to give:  $\ln K_{f,\text{PbO}}^{\text{liquid}}(1923 \text{ K}) = 3.155$ .

#### 4.8.11 Antimony (Sb)

##### 4.8.11.1 Equilibrium Constant of Formation of Liquid Sb

The stable state of pure antimony at 1923 K is diatomic antimony gas [Barin 1973, p1287]. To compute the equilibrium constant of formation for the liquid phase Equation 4.6 was used with the following parameters:  $T_{\text{vap}} = 1891 \text{ K}$ ,  $\Delta H(T_{\text{vap}}) = 77.75 \text{ kJ.mol}^{-1}$ ,  $\Delta C_p(T_{\text{vap}}) = -6.01$ ,  $\Delta S(T_{\text{vap}}) = 41.116 \text{ J.mol}^{-1}$ . The natural logarithm of the equilibrium constant of formation was computed to be  $-0.047$  for each atom in the gas.

##### 4.8.11.2 Equilibrium Constant of Formation of Liquid $\text{SbO}_{1.5}$

The equilibrium constant of formation of liquid  $\text{Sb}_2\text{O}_3$  is tabulated in Barin 1973, p1297. A linear regression ( $R^2=1.000$ ,  $N=10$ ,  $928 \text{ K} \leq T \leq 1729 \text{ K}$ ) was applied to find the following expression for the natural logarithm of the equilibrium constant:

$\ln K_{f,\text{Sb}_2\text{O}_3}^{\text{liquid}}(928 \text{ K} \leq T \leq 1729 \text{ K}) = \frac{80352}{T} - 26.823$ . The boiling temperature of  $\text{Sb}_2\text{O}_3$  at one

atmosphere of pressure is 1729 K. While this is below the experimental temperature, in this instance it was considered appropriate to extrapolate the liquid data up to 1923 K so as to provide a useful estimate of the equilibrium constant of formation at that temperature. The

extrapolated value is:  $\ln K_{f,\text{SbO}_{1.5}}^{\text{liquid}}(1923 \text{ K}) = 7.481$ .



## 4.8.12 Tin (Sn)

### 4.8.12.1 Equilibrium Constant of Formation of Liquid Sn

The stable state of tin at 1923 K is liquid molten tin. As such the natural logarithm of the equilibrium constant of formation is equal to zero [Barin 1973, p1392].

### 4.8.12.2 Equilibrium Constant of Formation of Liquid SnO<sub>2</sub>

The equilibrium constant of formation of solid SnO<sub>2</sub> is tabulated in Barin 1973, p1404. A linear regression ( $R^2=1.000$ ,  $N=6$ ,  $1300\text{ K} \leq T \leq 1800\text{ K}$ ) was applied to give this relationship for the natural logarithm of the equilibrium constant:

$$\ln K_{f,\text{SnO}_2}^{\text{solid}}(1300 \leq T \leq 1800\text{ K}) = \frac{68377}{T} - 23.795.$$
 This expression is used to extrapolate the

value up to 1923 K giving:  $\ln K_{f,\text{SnO}_2}^{\text{solid}}(1923\text{ K}) = 11.762$ . This temperature is slightly above the

melting point ( $T_m=1900\text{K}$ , Weast *et al.* 1988) and a small correction using Equation 4.5 ( $\Delta S=9.04\text{ J.mol}^{-1}$  is the same value for GeO<sub>2</sub>, which is used here as an approximation for SnO<sub>2</sub>)

was applied to account for the entropy of melting. This gave the value of the natural logarithm

of the equilibrium constant of tin oxide as:  $\ln K_{f,\text{SnO}_2}^{\text{liquid}}(1923\text{ K}) = 11.775$ .

## 4.8.13 Thallium (Tl)

### 4.8.13.1 Equilibrium Constant of Formation of Liquid Tl

The stable state of pure thallium at 1923 K is monoatomic thallium gas [Barin 1973, p1558]. To compute the equilibrium constant of formation for the liquid phase Equation 4.6 was used with the following parameters:  $T_{\text{vap}} = 1744\text{K}$ ,  $\Delta H(T_{\text{vap}}) = 164.08\text{ kJ.mol}^{-1}$ ,  $\Delta C_p(T_{\text{vap}}) = -7.651$ ,  $\Delta S(T_{\text{vap}}) = 93.7\text{ J.mol}^{-1}$ . The natural logarithm of the equilibrium constant of formation was computed to be  $-1.14$ .

#### 4.8.13.2 Equilibrium Constant of Formation of Liquid $TlO_{0.5}$

The thermodynamic properties of the thallium–oxygen system has been assessed by Lamoreaux *et al.* 1987 and their model for the Gibbs energy of formation of liquid  $Tl_2O$  (relative to pure thallium in the liquid state) over the temperature range of interest was applied. The modelled energies of formation have been converted to the natural logarithm of the equilibrium constant and at 1923 K this was computed to be 1.67.

#### 4.8.14 Vanadium (V)

##### 4.8.14.1 Equilibrium Constant of Formation of Liquid V

The stable state of vanadium at 1923 K is solid vanadium metal. To apply the entropy of melting to reach the liquid reference state Equation 4.5 was used with  $T_m=2175K$  and  $\Delta S=9.62 J.K^{-1}.mol^{-1}$  [Barin 1973, p1613] and the natural logarithm of the equilibrium constant was computed to be:  $\ln K_{f,V}^{liquid}(1923 K) = -0.152$ .

##### 4.8.14.2 Equilibrium Constant of Formation of Liquid $VO_{1.5}$

The equilibrium constant of formation of solid  $V_2O_3$  is tabulated in Barin 1973, p1632, with the reference state for pure vanadium at the temperatures of interest as solid vanadium metal. Equation 4.5 was used to change the reference state to liquid vanadium and then a linear regression ( $R^2=1.000$ ,  $N=6$ ,  $1600 K \leq T \leq 2100 K$ ) applied to give this relationship for the natural

logarithm of the equilibrium constant:  $\ln K_{f,V_2O_3}^{solid}(1600 \leq T \leq 2100 K) = \frac{139663}{T} - 26.011$ .

This expression was used to interpolate the value at 1923 K as:  $\ln K_{f,V_2O_3}^{solid}(1923 K) = 46.617$ .

This value was then corrected using Equation 4.5 ( $T_m$  of 2340 K and  $\Delta S=50.065 J.mol^{-1}$  taken

from Barin 1973 p1632) to compute the value of the natural logarithm of the equilibrium constant of vanadium oxide as:  $\ln K_{f, \text{VO}_{1.5}}^{\text{liquid}}(1923 \text{ K}) = 22.66$ .

#### 4.8.15 Tungsten (W)

##### 4.8.15.1 Equilibrium Constant of Formation of Liquid W

The stable state of tungsten at 1923 K is solid tungsten metal. To apply the entropy change to the liquid state Equation 4.5 was used with  $T_m = 3680 \text{ K}$  and  $\Delta S = 9.62 \text{ J.K}^{-1}.\text{mol}^{-1}$  [Barin 1973, p1636] and the natural logarithm of the equilibrium constant was computed to be:

$$\ln K_{f, \text{W}}^{\text{liquid}}(1923 \text{ K}) = -1.057.$$

##### 4.8.15.2 Equilibrium Constant of Formation of Liquid $\text{WO}_3$

The equilibrium constant of formation of solid  $\text{WO}_3$  is tabulated in Barin 1973, p1660, with the reference state for pure tungsten as solid tungsten metal. Equation 4.5 was used to change the reference state to liquid tungsten and then a linear regression ( $R^2 = 1.000$ ,  $N = 6$ ,  $1745 \text{ K} \leq T \leq 2110 \text{ K}$ ) applied to determine this relationship for the natural logarithm of the equilibrium

constant:  $\ln K_{f, \text{WO}_3}^{\text{liquid}}(1745 \text{ K} \leq T \leq 2110 \text{ K}) = \frac{92371}{T} - 23.489$ . This expression was used to

interpolate the value at 1923 K as:  $\ln K_{f, \text{WO}_3}^{\text{liquid}}(1923 \text{ K}) = 24.546$ .

#### 4.8.16 Zinc (Zn)

##### 4.8.16.1 Equilibrium Constant of Formation of Liquid Zn

The stable state of pure zinc at 1923 K is monoatomic zinc gas [Barin 1973, p1682]. To compute the equilibrium constant of formation for the liquid phase Equation 4.6 was used with the following parameters:  $T_{\text{vap}} = 1179 \text{ K}$ ,  $\Delta H(T_{\text{vap}}) = 115.33 \text{ kJ.mol}^{-1}$ ,  $\Delta C_p(T_{\text{vap}}) = -10.594$ ,

$\Delta S(T_{\text{vap}}) = 97.82 \text{ J}\cdot\text{mol}^{-1}$ . The natural logarithm of the equilibrium constant of formation has been computed to be  $-5.04$ .

#### 4.8.16.2 Equilibrium Constant of Formation of Liquid ZnO

The equilibrium constant of formation of solid ZnO is tabulated in Barin 1973, p1690. The reference state of pure zinc at the temperatures of interest is monatomic zinc gas. Equation 4.5 was used to change the reference state from gaseous zinc to liquid zinc. A linear regression ( $R^2=1.000$ ,  $N=9$ ,  $1500 \text{ K} \leq T \leq 2248 \text{ K}$ ) was applied to find this relationship for the natural

logarithm of the equilibrium constant:  $\ln K_{f,\text{ZnO}}^{\text{solid}}(1500 \leq T \leq 2248 \text{ K}) = \frac{57656}{T} - 24.82$ . This

expression was used to extrapolate the value up to 1923 K as:  $\ln K_{f,\text{ZnO}}^{\text{solid}}(1923 \text{ K}) = 5.162$ . A

correction using Equation 4.5 ( $T_m=2248\text{K}$ ,  $\Delta S=24.169 \text{ J}\cdot\text{mol}^{-1}$ , Barin 1973 p1690) was applied to account for the entropy of melting. This gave the value of the natural logarithm of the

equilibrium constant of zinc oxide at 1923 K as:  $\ln K_{f,\text{ZnO}}^{\text{liquid}}(1923 \text{ K}) = 4.671$ .

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## 4.9 Silicate Melt Activity Coefficients and Composition Models

The activity coefficients of the liquid trace element oxides in the silicate melt can now be computed using Equation 4. The activity coefficient values are presented in Table 4.15 and a summary of these values is shown in Table 4.16. Next, we consider the range of trace element activity coefficients in turn and evaluate the composition dependence, if any, by linear regression modelling. As presented previously, modelling was performed with the SPSS software package using stepwise linear regression. The independent variable terms were: composition of the melt as single-cation oxide mole fraction; cross terms; square terms; the natural logarithm of the single-cation oxide mole fraction terms; and the computed values for optical basicity ( $\Lambda$ ) and non-bridging-oxygen over total oxygen (NBO/T) from Mills 1993. The dependant term in each case was the computed activity coefficient for the liquid oxide in the silicate melt (from Table 4.15).

The regression was limited to significant terms with the significance assessed by F-test and the probability threshold set to  $F > 0.05$ . The model terms, goodness of fit values, and standard errors are presented in Table 4.17. The model coefficients and ADF ternary plots are now presented element-by-element in the following sections.

**Table 4.15—Activity Coefficients of Liquid Oxides in Silicate Melts at 1923 K**

| Alias  | $\gamma_{\text{AgO}_{1.5}}$ | $\gamma_{\text{BiO}_{1.5}}$ | $\gamma_{\text{CdO}}$ | $\gamma_{\text{CrO}}$ | $\gamma_{\text{CuO}_{0.5}}$ | $\gamma_{\text{GaO}_{1.5}}$ | $\gamma_{\text{GeO}_2}$ | $\gamma_{\text{InO}_{1.5}}$ | $\gamma_{\text{MoO}_2}$ | $\gamma_{\text{PbO}}$ | $\gamma_{\text{SbO}_{1.5}}$ | $\gamma_{\text{SnO}_2}$ | $\gamma_{\text{TiO}_{0.5}}$ | $\gamma_{\text{VO}_{1.5}}$ | $\gamma_{\text{WO}_3}$ | $\gamma_{\text{ZnO}}$ |
|--------|-----------------------------|-----------------------------|-----------------------|-----------------------|-----------------------------|-----------------------------|-------------------------|-----------------------------|-------------------------|-----------------------|-----------------------------|-------------------------|-----------------------------|----------------------------|------------------------|-----------------------|
| A365   | 0.099                       | 0.742                       | 833                   |                       | 6.4                         |                             |                         | 0.058                       |                         | 0.28                  | 1.50                        |                         | 151                         |                            |                        |                       |
| A366   | 0.033                       | 0.100                       | 305                   |                       | 2.9                         |                             |                         | 0.008                       |                         | 0.07                  | 0.43                        |                         | 29                          |                            |                        |                       |
| A368   | 0.088                       | 0.324                       | 528                   |                       | 4.6                         |                             |                         | 0.043                       |                         | 0.22                  | 1.14                        |                         | 135                         |                            |                        |                       |
| A369   | 0.098                       | 0.704                       | 768                   |                       | 5.3                         |                             |                         | 0.056                       |                         | 0.27                  | 0.71                        |                         | 250                         |                            |                        |                       |
| A370   | 0.255                       | 1.828                       | 2021                  |                       | 7.4                         |                             |                         | 0.118                       |                         | 0.94                  | 0.95                        |                         | 1053                        |                            |                        |                       |
| A371   | 0.037                       | 0.104                       | 416                   |                       | 3.6                         |                             |                         | 0.012                       |                         | 0.07                  | 1.08                        |                         | 28                          |                            |                        |                       |
| A373   | 0.049                       | 0.427                       | 850                   |                       | 4.5                         |                             |                         | 0.047                       |                         | 0.15                  | 1.57                        |                         | 83                          |                            |                        |                       |
| A374   | 0.037                       | 0.053                       | 356                   |                       | 3.4                         |                             |                         | 0.009                       |                         | 0.06                  | 0.29                        |                         | 50                          |                            |                        |                       |
| A388   | 0.053                       | 0.268                       | 812                   |                       | 4.1                         |                             |                         | 0.048                       |                         | 0.11                  | 1.60                        |                         | 42                          |                            |                        |                       |
| AN1101 |                             |                             |                       |                       | 5.5                         | 1.35                        | 0.0023                  |                             | 0.172                   |                       | 2.18                        |                         |                             |                            | 0.0492                 |                       |
| AN1102 |                             |                             |                       | 3.6                   | 7.0                         |                             |                         | 0.029                       |                         |                       |                             | 0.00214                 |                             | 2.3                        |                        | 0.072                 |
| AN1103 |                             |                             |                       |                       | 4.5                         | 0.62                        | 0.0032                  |                             | 0.400                   |                       | 2.43                        |                         |                             |                            | 0.0044                 |                       |
| AN1104 |                             |                             |                       |                       | 3.0                         | 0.43                        | 0.0010                  |                             | 0.009                   |                       | 0.46                        |                         |                             |                            | 0.0129                 |                       |
| B187   | 0.042                       | 0.074                       | 211                   | 1.0                   | 2.6                         | 0.36                        |                         | 0.008                       |                         | 0.07                  | 0.27                        |                         | 37                          |                            | 0.0006                 |                       |
| B188   | 0.090                       | 0.446                       | 784                   |                       | 5.8                         |                             |                         | 0.058                       |                         | 0.26                  | 0.11                        |                         | 191                         |                            |                        |                       |
| FM1102 |                             |                             |                       |                       | 5.1                         | 0.95                        | 0.0049                  |                             | 1.343                   |                       | 4.38                        |                         |                             |                            | 0.0233                 |                       |
| FM1103 |                             |                             |                       | 2.5                   | 5.6                         |                             |                         | 0.026                       |                         |                       |                             | 0.00206                 |                             | 2.1                        |                        | 0.058                 |
| FM1104 |                             |                             |                       | 1.9                   | 4.0                         |                             |                         | 0.013                       |                         |                       |                             | 0.00099                 |                             | 2.3                        |                        | 0.067                 |
| FM1105 |                             |                             |                       |                       | 3.3                         | 1.10                        | 0.0032                  |                             | 0.122                   |                       | 2.36                        |                         |                             |                            | 0.1310                 |                       |
| FM1106 |                             |                             |                       | 1.2                   | 3.7                         |                             |                         | 0.011                       |                         |                       |                             | 0.00092                 |                             | 0.8                        |                        | 0.024                 |
| FM1107 |                             |                             |                       | 1.3                   | 3.0                         |                             |                         | 0.005                       |                         |                       |                             | 0.00027                 |                             | 0.8                        |                        | 0.037                 |
| FM1108 |                             |                             |                       |                       | 3.9                         | 0.12                        | 0.0003                  |                             | 0.065                   |                       | 0.49                        |                         |                             |                            | 0.0002                 |                       |
| FM1109 |                             |                             |                       | 2.2                   | 6.5                         |                             |                         | 0.041                       |                         |                       |                             | 0.00165                 |                             | 1.5                        |                        | 0.047                 |
| FM1110 |                             |                             |                       | 2.1                   | 3.7                         |                             |                         | 0.007                       |                         |                       |                             | 0.00067                 |                             | 2.7                        |                        | 0.090                 |
| FM1111 |                             |                             |                       |                       | 7.8                         | 2.66                        | 0.0043                  |                             | 0.216                   |                       | 8.24                        |                         |                             |                            | 0.1312                 |                       |
| FM1113 |                             |                             |                       | 0.9                   | 2.9                         |                             |                         | 0.002                       |                         |                       |                             | 0.00009                 |                             | 0.7                        |                        | 0.044                 |
| FM1114 |                             |                             |                       | 3.8                   | 5.3                         |                             |                         | 0.022                       |                         |                       |                             | 0.00309                 |                             | 5.4                        |                        | 0.128                 |
| FM1115 |                             |                             |                       |                       | 5.4                         | 2.14                        | 0.0103                  |                             | 2.581                   |                       | 5.54                        |                         |                             |                            | 0.2338                 |                       |
| FM1116 |                             |                             |                       | 1.2                   | 3.3                         |                             |                         | 0.005                       |                         |                       |                             | 0.00033                 |                             | 1.1                        |                        | 0.046                 |
| FM1117 |                             |                             |                       |                       | 3.8                         | 0.70                        | 0.0021                  |                             | 0.172                   |                       | 1.48                        |                         |                             |                            | 0.0324                 |                       |
| FM1118 |                             |                             |                       | 3.9                   | 6.0                         |                             |                         | 0.044                       |                         |                       |                             | 0.00165                 |                             | 3.3                        |                        | 0.091                 |
| FM1119 |                             |                             |                       |                       | 5.4                         | 0.85                        | 0.0052                  |                             | 0.349                   |                       | 1.87                        |                         |                             |                            | 0.0179                 |                       |
| TT1    | 0.091                       | 0.933                       | 2302                  | 3.6                   | 7.6                         | 1.47                        |                         | 0.090                       |                         | 0.41                  | 3.14                        |                         | 368                         |                            |                        |                       |
| TT2    | 0.106                       | 1.073                       | 1589                  | 3.9                   | 6.7                         | 1.21                        |                         | 0.079                       |                         | 0.36                  | 2.04                        |                         | 254                         | 4.7                        |                        |                       |
| TT3    | 0.131                       | 2.577                       | 6142                  | 5.3                   | 9.2                         | 1.08                        |                         | 0.100                       |                         | 1.50                  | 3.30                        |                         | 1052                        | 4.8                        |                        |                       |

**Table 4.16—Summary of Computed Activity Coefficients of Liquid Oxides in Silicate Melts at 1923 K**

| $\gamma$ Oxide     | Trace Set | $\gamma$ N | $\gamma$ Minimum | $\gamma$ Maximum | $\gamma$ Mean | $\gamma$ $\sigma$ | $\gamma$ Std Error |
|--------------------|-----------|------------|------------------|------------------|---------------|-------------------|--------------------|
| $\text{AgO}_{1.5}$ | B         | 11         | 0.033            | 0.26             | 0.080         | 0.064             | 0.019              |
| $\text{BiO}_{1.5}$ | B         | 11         | 0.053            | 1.8              | 0.46          | 0.51              | 0.15               |
| $\text{CdO}$       | B         | 11         | 211              | 2021             | 717           | 493               | 149                |
| $\text{CrO}$       | A         | 11         | 0.91             | 3.9              | 2.2           | 1.1               | 0.33               |
| $\text{CuO}_{0.5}$ | B+A+F     | 32         | 2.6              | 7.8              | 4.7           | 1.4               | 0.25               |
| $\text{GaO}_{1.5}$ | F         | 10         | 0.12             | 2.7              | 1.1           | 0.78              | 0.25               |
| $\text{GeO}_2$     | F         | 10         | 0.00028          | 0.010            | 0.0037        | 0.0028            | 0.00089            |
| $\text{InO}_{1.5}$ | B+A       | 22         | 0.0025           | 0.12             | 0.030         | 0.028             | 0.0059             |
| $\text{MoO}_2$     | F         | 10         | 0.0091           | 2.6              | 0.54          | 0.81              | 0.26               |
| $\text{PbO}$       | B         | 11         | 0.059            | 0.94             | 0.23          | 0.25              | 0.076              |
| $\text{SbO}_{1.5}$ | B+F       | 21         | 0.11             | 8.2              | 1.9           | 2.0               | 0.43               |
| $\text{SnO}_2$     | A         | 11         | 0.000093         | 0.0031           | 0.0013        | 0.00094           | 0.00028            |
| $\text{TiO}_{0.5}$ | B         | 11         | 28               | 1053             | 186           | 297               | 89                 |
| $\text{VO}_{1.5}$  | A         | 11         | 0.66             | 5.4              | 2.1           | 1.4               | 0.42               |
| $\text{WO}_3$      | F         | 10         | 0.00022          | 0.23             | 0.064         | 0.077             | 0.024              |
| $\text{ZnO}$       | A         | 11         | 0.024            | 0.13             | 0.064         | 0.030             | 0.0091             |

**Table 4.17—Models of Trace Element Activity Coefficients in Silicate Melts**

| $\gamma$ Oxide              | Procedure | F - Params               | Trace Set | $R^2$                    | Std Error | # Terms | Terms (Plus a Constant)        |
|-----------------------------|-----------|--------------------------|-----------|--------------------------|-----------|---------|--------------------------------|
| $\gamma_{\text{AgO}_{1.5}}$ | Stepwise  | Entry: 0.05 Remove: 0.10 | B         | 0.900                    | 0.02      | 2       | CaMg, Fe <sup>2</sup>          |
| $\gamma_{\text{BiO}_{1.5}}$ | Stepwise  | Entry: 0.05 Remove: 0.10 | B         | 0.915                    | 0.18      | 3       | CaMg, Fe <sup>2</sup> , ln(Si) |
| $\gamma_{\text{CdO}}$       | Stepwise  | Entry: 0.05 Remove: 0.10 | B         | 0.861                    | 205.82    | 2       | ln(Si), Si                     |
| $\gamma_{\text{CrO}}$       | Stepwise  | Entry: 0.05 Remove: 0.10 | A         | 0.958                    | 0.27      | 3       | Al, AlFe, FeSi                 |
| $\gamma_{\text{CuO}_{0.5}}$ | Stepwise  | Entry: 0.05 Remove: 0.10 | B+A+F     | 0.652                    | 0.86      | 2       | CaMg, Al                       |
| $\gamma_{\text{GaO}_{1.5}}$ | Stepwise  | Entry: 0.05 Remove: 0.10 | F         | 0.594                    | 0.53      | 1       | NBO/T                          |
| $\gamma_{\text{GeO}_2}$     | Stepwise  | Entry: 0.05 Remove: 0.10 | F         | 0.904                    | 0.00      | 2       | AlCa, CaMg                     |
| $\gamma_{\text{InO}_{1.5}}$ | Stepwise  | Entry: 0.05 Remove: 0.10 | B+A       | 0.919                    | 0.01      | 3       | Fe <sup>2</sup> , CaMg, FeSi   |
| $\gamma_{\text{MoO}_2}$     | Stepwise  | Entry: 0.05 Remove: 0.10 | F         | 0.740                    | 0.44      | 1       | Al <sup>2</sup>                |
| $\gamma_{\text{PbO}}$       | Stepwise  | Entry: 0.05 Remove: 0.10 | B         | 0.861                    | 0.11      | 2       | CaMg, Fe <sup>2</sup>          |
| $\gamma_{\text{SbO}_{1.5}}$ | Stepwise  | Entry: 0.05 Remove: 0.10 | B         | Regression Failed F-Test |           |         |                                |
| $\gamma_{\text{SnO}_2}$     | Stepwise  | Entry: 0.05 Remove: 0.10 | A         | 0.867                    | 0.00      | 1       | AlCa                           |
| $\gamma_{\text{TlO}_{0.5}}$ | Stepwise  | Entry: 0.05 Remove: 0.10 | B         | 0.807                    | 145.70    | 2       | CaMg, Fe <sup>2</sup>          |
| $\gamma_{\text{VO}_{1.5}}$  | Stepwise  | Entry: 0.05 Remove: 0.10 | A         | 0.961                    | 0.32      | 3       | AlSi, ln(Al), AlFe             |
| $\gamma_{\text{WO}_3}$      | Stepwise  | Entry: 0.05 Remove: 0.10 | F         | 0.836                    | 0.03      | 1       | NBO/T                          |
| $\gamma_{\text{ZnO}}$       | Stepwise  | Entry: 0.05 Remove: 0.10 | A         | 0.898                    | 0.01      | 2       | AlSi, ln(Al)                   |

#### 4.9.1 Silver ( $\gamma_{\text{AgO}_{0.5}}$ )

The average value of the activity coefficient of liquid silver oxide in silicate melt was computed to be  $0.080 \pm 0.019$  while spanning the range 0.033 to 0.26. A meaningful ( $F > 0.05$ ) model was found by stepwise linear regression with a standard error of 0.02 and the following terms:

$$\gamma_{\text{AgO}_{0.5}}(1923\text{ K}) = 3.282 X_{\text{CaO}} X_{\text{MgO}} + 37.789 X_{\text{FeO}}^2 - 0.115$$

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.14 below.

All of the compositions plotted on this ternary have 7.7% ( $\text{g.g}^{-1}$ ) FeO, which for plotting purposes is added to the MgO content of the forsterite. The positive coefficient for the squared FeO term limits the validity of extrapolation using this model, however this model should be considered as valid over the range 6.5 to 9.4% ( $\text{g.g}^{-1}$ ) FeO (see Figure 4.12).

#### 4.9.2 Bismuth ( $\gamma_{\text{BiO}_{1.5}}$ )

The average value of the activity coefficient of liquid bismuth oxide in silicate melt was computed to be  $0.46 \pm 0.51$  while spanning the range 0.053 to 1.8. A meaningful ( $F > 0.05$ ) model was found by stepwise linear regression with a standard error of 0.18 and the following terms:

$$\gamma_{\text{BiO}_{1.5}}(1923\text{ K}) = 234X_{\text{FeO}}^2 + 20.6X_{\text{CaO}}X_{\text{MgO}} + -0.769\ln(X_{\text{SiO}_2}) - 1.38$$

The inclusion of the natural logarithm term may appear unfortunate since it limits the applicability of this model to melts with no SiO<sub>2</sub> content, if indeed they would still be called a *silicate* melt. However, semantic issues, if attempting to apply this model to other melts and slags would be reasonable to drop the logarithm term for those with SiO<sub>2</sub> content below 0.1% (g.g<sup>-1</sup>).

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.15 below. All of the compositions plotted on this ternary have 7.7% (g.g<sup>-1</sup>) FeO, which for plotting purposes is added to the MgO content of the forsterite. The positive coefficient for the squared FeO term limits the validity of extrapolation using this model, however this model should be considered as valid over the range 6.5 to 9.4% (g.g<sup>-1</sup>) FeO (see Figure 4.12).

#### 4.9.3 Cadmium (γCdO)

The average value of the activity coefficient of liquid cadmium oxide in silicate melt was computed to be 717±493 while spanning the range 211 to 2021. A meaningful (F > 0.05) model was found by stepwise linear regression with a standard error of 206 and the following terms:

$$\gamma_{\text{CdO}}(1923\text{ K}) = 21190X_{\text{SiO}_2} - 11604\ln(X_{\text{SiO}_2}) - 18320$$

The inclusion of the natural logarithm term may appear unfortunate since it limits the applicability of this model to melts with no SiO<sub>2</sub> content, if indeed they would still be called a *silicate* melt. However, semantic issues, if attempting to apply this model to other melts and slags would be reasonable to drop the logarithm term for those with SiO<sub>2</sub> content below 0.1% (g.g<sup>-1</sup>).



Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.16 below.

#### 4.9.4 Chromium ( $\gamma_{\text{CrO}}$ )

The average value of the activity coefficient of liquid chromium oxide in silicate melt was computed to be  $2.2 \pm 1.1$  while spanning the range 0.91 to 3.9. A meaningful ( $F > 0.05$ ) model was found by stepwise linear regression with a standard error of 0.27 and the following terms:

$$\gamma_{\text{CrO}}(1923\text{ K}) = 45.3X_{\text{Al}_2\text{O}_3} - 1357X_{\text{AlO}_{1.5}}X_{\text{FeO}} + 162X_{\text{FeO}}X_{\text{SiO}_2} - 1.37$$

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.17 below.

#### 4.9.5 Copper ( $\gamma_{\text{CuO}_{0.5}}$ )

The average value of the activity coefficient of liquid copper oxide in silicate melt was computed to be  $4.7 \pm 1.4$  while spanning the range 2.6 to 7.8. A meaningful ( $F > 0.05$ ) model was found by stepwise linear regression with a standard error of 0.86 and the following terms:

$$\gamma_{\text{CuO}_{0.5}}(1923\text{ K}) = 5.71X_{\text{AlO}_{1.5}} + 64.2X_{\text{CaO}}X_{\text{MgO}} + 2.60$$

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.18 below.

#### 4.9.6 Gallium ( $\gamma_{\text{GaO}_{1.5}}$ )

The average value of the activity coefficient of liquid gallium oxide in silicate melt was computed to be  $1.1 \pm 0.78$  while spanning the range 0.12 to 2.7. A meaningful ( $F > 0.05$ ) model was found by stepwise linear regression with a standard error of 0.5 and based entirely on the computed NBO/T [Mills 1993] value:

$$\gamma_{\text{GaO}_{1.5}}(1923\text{ K}) = -1.270\text{NBO/T} + 2.60$$

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.19 below.

Note, this is one of only two elements (the other is W) to show a significant correlation between activity coefficient and the value of NBO/T.

#### 4.9.7 Germanium ( $\gamma_{\text{GeO}_2}$ )

The average value of the activity coefficient of liquid germanium oxide in silicate melt was computed to be  $0.0037 \pm 0.0028$  while spanning the range 0.00028 to 0.010. A meaningful ( $F > 0.05$ ) model was found by stepwise linear regression with a standard error of 0.0010 and the following terms:

$$\gamma_{\text{GeO}_2} (1923 \text{ K}) = 0.145 X_{\text{AlO}_{1.5}} X_{\text{CaO}} - 0.083 X_{\text{CaO}} X_{\text{MgO}} + 0.0020$$

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.20 below.

#### 4.9.8 Indium ( $\gamma_{\text{InO}_{1.5}}$ )

The average value of the activity coefficient of liquid indium oxide in silicate melt was computed to be  $0.0037 \pm 0.0028$  while spanning the range 0.0025 to 0.12. A meaningful ( $F > 0.05$ ) model was found by stepwise linear regression with a standard error of 0.008 and the following terms:

$$\gamma_{\text{InO}_{1.5}} (1923 \text{ K}) = 24.7 X_{\text{FeO}}^2 + 0.612 X_{\text{CaO}} X_{\text{MgO}} - 3.287 X_{\text{FeO}} X_{\text{SiO}_2} + 0.030$$

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.21 below.

#### 4.9.9 Molybdenum ( $\gamma_{\text{MoO}_2}$ )

The average value of the activity coefficient of liquid germanium oxide in silicate melt was computed to be  $0.54 \pm 0.81$  while spanning the range 0.0091 to 2.6. A meaningful ( $F > 0.05$ )

model was found by stepwise linear regression with a standard error of 0.44 and the following terms:

$$\gamma_{\text{MoO}_2}(1923\text{ K}) = 17.128X_{\text{AlO}_{1.5}}^2 - 0.004$$

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.22 below.

#### 4.9.10 Lead ( $\gamma_{\text{PbO}}$ )

The average value of the activity coefficient of liquid lead oxide in silicate melt was computed to be  $0.23 \pm 0.25$  while spanning the range 0.059 to 0.94. A meaningful ( $F > 0.05$ ) model was found by stepwise linear regression with a standard error of 0.1 and the following terms:

$$\gamma_{\text{PbO}}(1923\text{ K}) = 148.0X_{\text{FeO}}^2 + 12.67X_{\text{CaO}}X_{\text{MgO}} - 0.535$$

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.23 below.

All of the compositions plotted on this ternary have 7.7% ( $\text{g.g}^{-1}$ ) FeO, which for plotting purposes is added to the MgO content of the forsterite. The positive coefficient for the squared FeO term limits the validity of extrapolation using this model, however, this model should be considered as valid over the range 6.5 to 9.4% ( $\text{g.g}^{-1}$ ) FeO (see Figure 4.12).

#### 4.9.11 Antimony ( $\gamma_{\text{SbO}_{1.5}}$ )

The average value of the activity coefficient of liquid antimony oxide in silicate melt was computed to be  $1.9 \pm 2.0$  while spanning the range 0.11 to 8.2. It was not possible to fit a significant ( $F > 0.05$ ) model to these data.

#### 4.9.12 Tin ( $\gamma_{\text{SnO}_2}$ )

The average value of the activity coefficient of liquid tin oxide in silicate melt was computed to be  $0.0013 \pm 0.00094$  while spanning the range 0.000093 to 0.0031. A meaningful ( $F > 0.05$ ) model

was found by stepwise linear regression with a standard error of 0.00036 and the following terms:

$$\gamma_{\text{SnO}_2}(1923\text{ K}) = 0.040 X_{\text{AlO}_{1.5}} X_{\text{CaO}}$$

This model is unique due to the dependence on a single term, with no constant value. This is limiting since it invalidates the model for compositions that do not contain both  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$ . In addition these activity coefficients for tin oxide are the lowest of all the trace elements measured.

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.24 below.

#### 4.9.13 Thallium ( $\gamma_{\text{TlO}_{0.5}}$ )

The average value of the activity coefficient of liquid thallium oxide in silicate melt was computed to be  $186 \pm 297$  while spanning the range 28 to 1053. A meaningful ( $F > 0.05$ ) model was found by stepwise linear regression with a standard error of 146 and the following terms:

$$\gamma_{\text{TlO}_{0.5}}(1923\text{ K}) = 181511 X_{\text{FeO}} + 14133 X_{\text{CaO}} X_{\text{MgO}} - 724$$

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.25 below.

All of the compositions plotted on this ternary have 7.7% ( $\text{g.g}^{-1}$ )  $\text{FeO}$ , which for plotting purposes is added to the  $\text{MgO}$  content of the forsterite. The positive coefficient for the squared  $\text{FeO}$  term limits the validity of extrapolation using this model, however, this model should be considered as valid over the range 6.5 to 9.4% ( $\text{g.g}^{-1}$ )  $\text{FeO}$  (see Figure 4.12). In addition, all values in the anorthite-rich area of the figure are within the standard error of ideal behaviour and have been set to 1 in this region accordingly.

#### 4.9.14 Vanadium ( $\gamma_{\text{VO}_{1.5}}$ )

The average value of the activity coefficient of liquid vanadium oxide in silicate melt was computed to be  $2.1 \pm 1.4$  while spanning the range 0.66 to 5.4. A meaningful ( $F > 0.05$ ) model was found by stepwise linear regression with a standard error of 0.32 and the following terms:

$$\gamma_{\text{VO}_{1.5}}(1923 \text{ K}) = 38.48 X_{\text{AlO}_{1.5}} X_{\text{SiO}_2} + 145.2 X_{\text{AlO}_{1.5}} X_{\text{FeO}} - 0.597 \ln(X_{\text{AlO}_{1.5}}) - 2.301$$

The inclusion of the natural logarithm term is unfortunate since it limits the applicability of this model to melts with no  $\text{Al}_2\text{O}_3$  content. However, while applying this model it would be reasonable to drop the logarithm term for melts with  $\text{Al}_2\text{O}_3$  content below 0.1% ( $\text{g.g}^{-1}$ ).

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.26 below.

#### 4.9.15 Tungsten ( $\gamma_{\text{WO}_3}$ )

The average value of the activity coefficient of liquid tungsten oxide in silicate melt was computed to be  $0.064 \pm 0.077$  while spanning the range 0.00022 to 0.23. A meaningful ( $F > 0.05$ ) model was found by stepwise linear regression with a standard error of 0.033 and based entirely on the computed NBO/T [Mills 1993] value:

$$\gamma_{\text{WO}_3}(1923 \text{ K}) = -0.149 \text{NBO/T} + 0.24$$

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.27 below.

Note, this is one of only two elements (the other is Ga) to show a significant correlation between activity coefficient and the value of NBO/T.

#### 4.9.16 Zinc ( $\gamma_{\text{ZnO}}$ )

The average value of the activity coefficient of liquid zinc oxide in silicate melt was computed to be  $0.064 \pm 0.030$  while spanning the range 0.024 to 0.13. A meaningful ( $F > 0.05$ )

model was found by stepwise linear regression with a standard error of 0.01 and the following terms:

$$\gamma_{\text{ZnO}}(1923\text{ K}) = 1.068 X_{\text{AlO}_{1.5}} X_{\text{SiO}_2} - 0.016 \ln(X_{\text{AlO}_{1.5}}) - 0.04$$

The inclusion of the natural logarithm term is unfortunate since it limits the applicability of this model to melts with no  $\text{Al}_2\text{O}_3$  content. However, while applying this model it would be reasonable to drop the logarithm term for melts with  $\text{Al}_2\text{O}_3$  content below 0.1% ( $\text{g.g}^{-1}$ ).

Plotting this model across the ADF ternary gives the contour plot shown in Figure 4.28 below.

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#### 4.10 Trace Element Activity Figures

Figure 4.14—Model of  $\text{AgO}_{0.5}$  Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

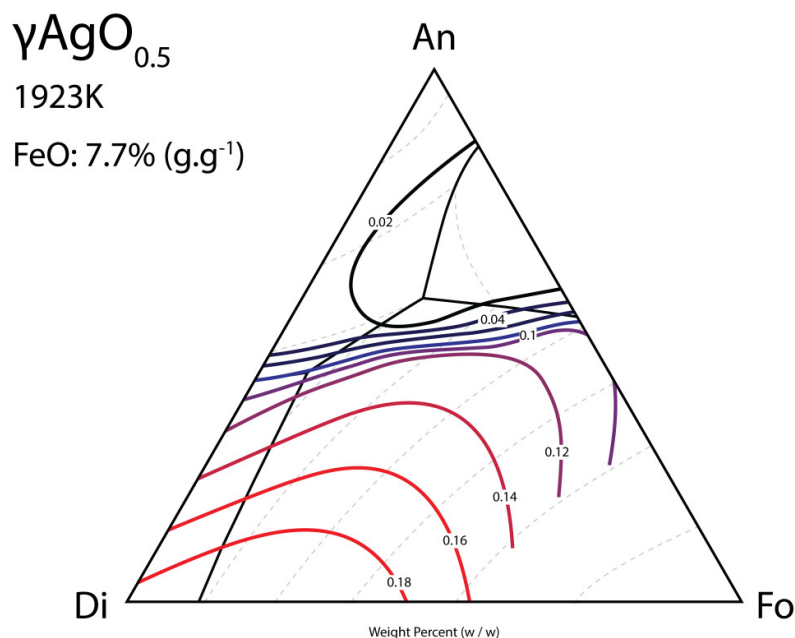


Figure 4.15—Model of  $\text{BiO}_{1.5}$  Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

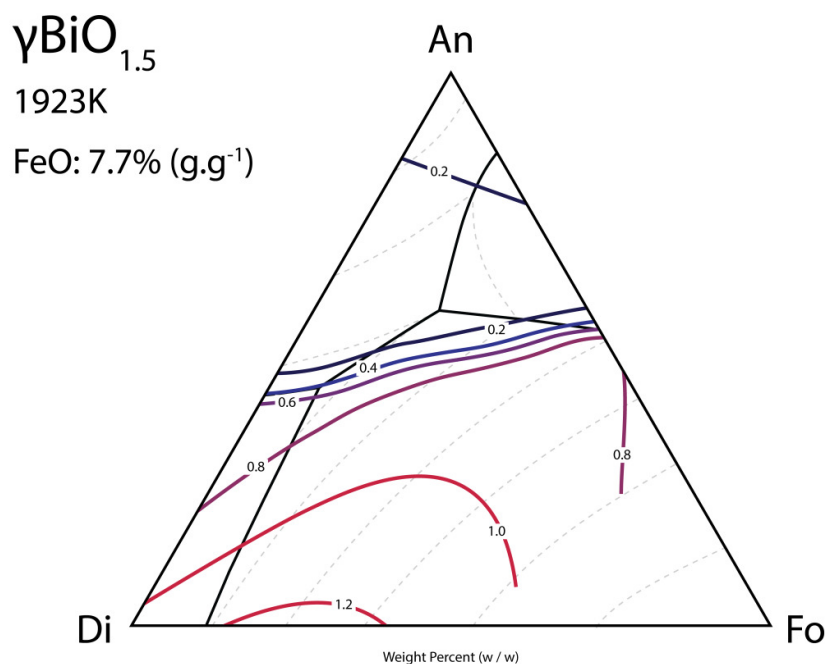


Figure 4.16—Model of CdO Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

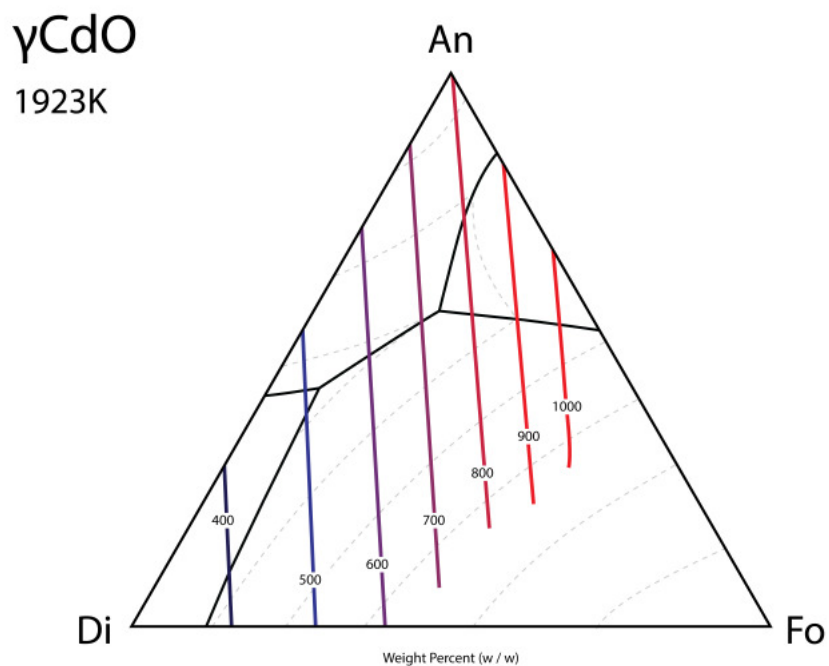


Figure 4.17—Model of  $\text{CuO}_{0.5}$  Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

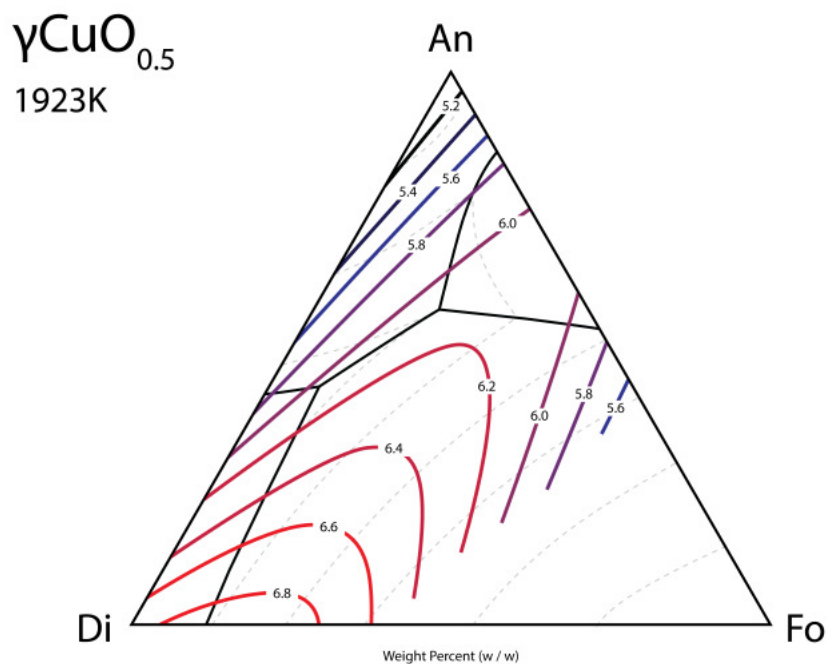




Figure 4.18—Model of CrO Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

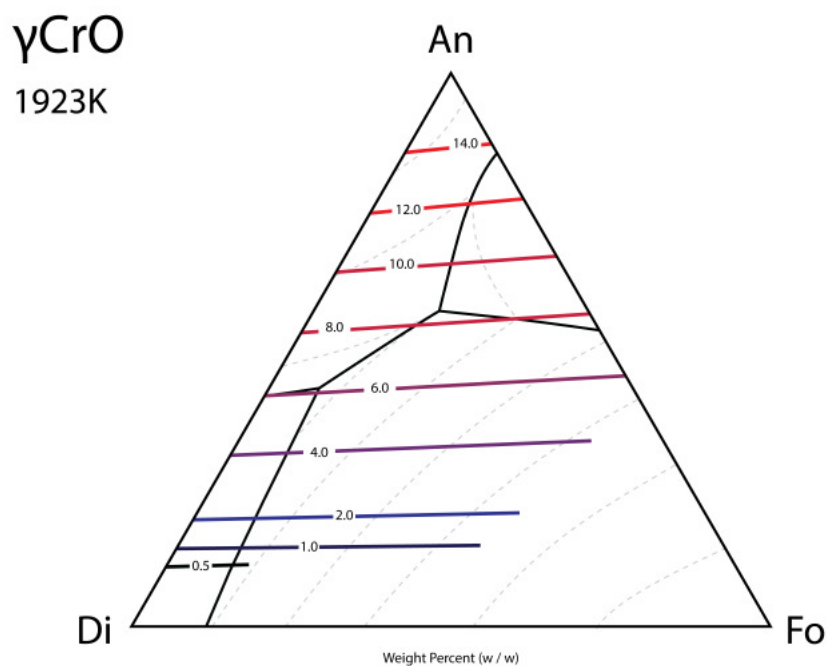


Figure 4.19—Model of  $\text{GaO}_{1.5}$  Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

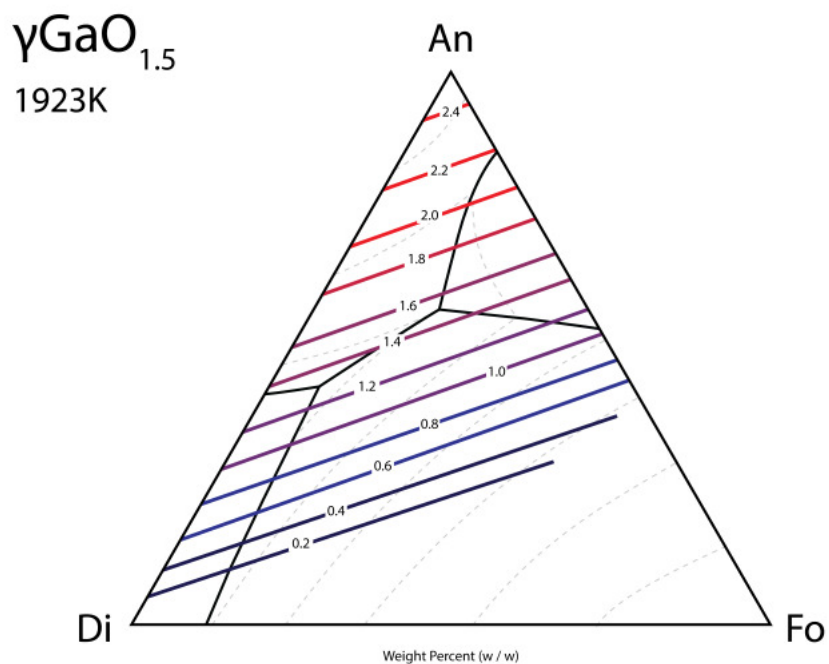


Figure 4.20—Model of  $\text{GeO}_2$  Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

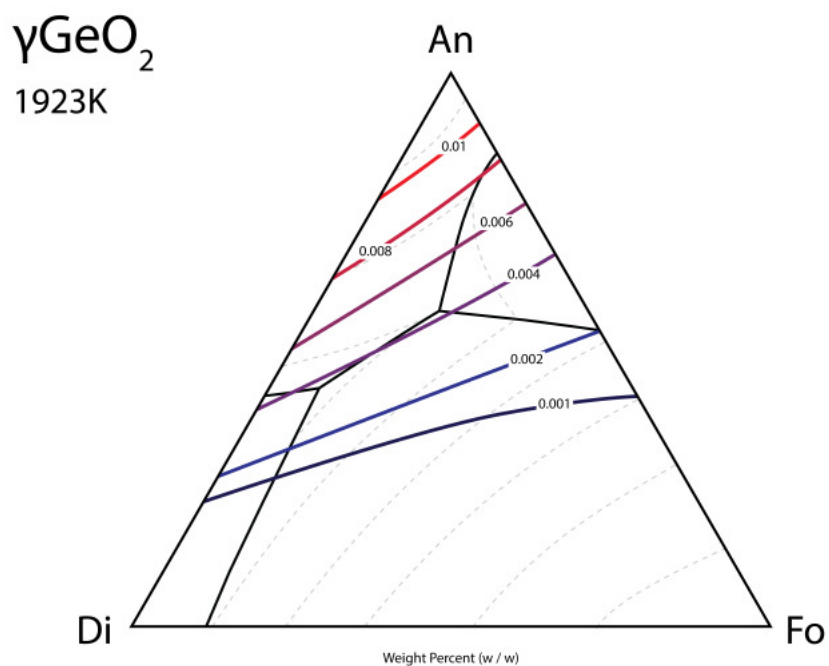


Figure 4.21—Model of  $\text{InO}_{1.5}$  Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

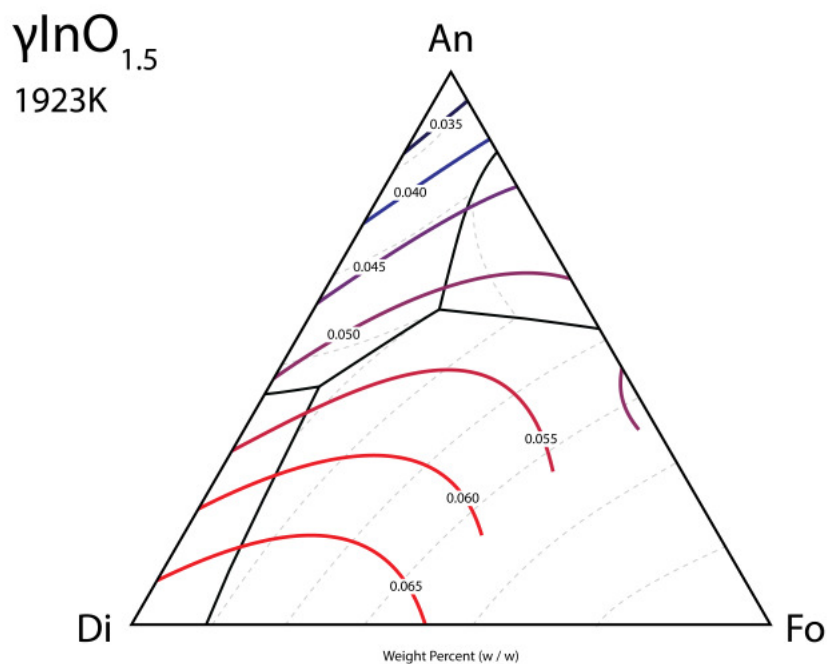


Figure 4.22—Model of  $\text{MoO}_2$  Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

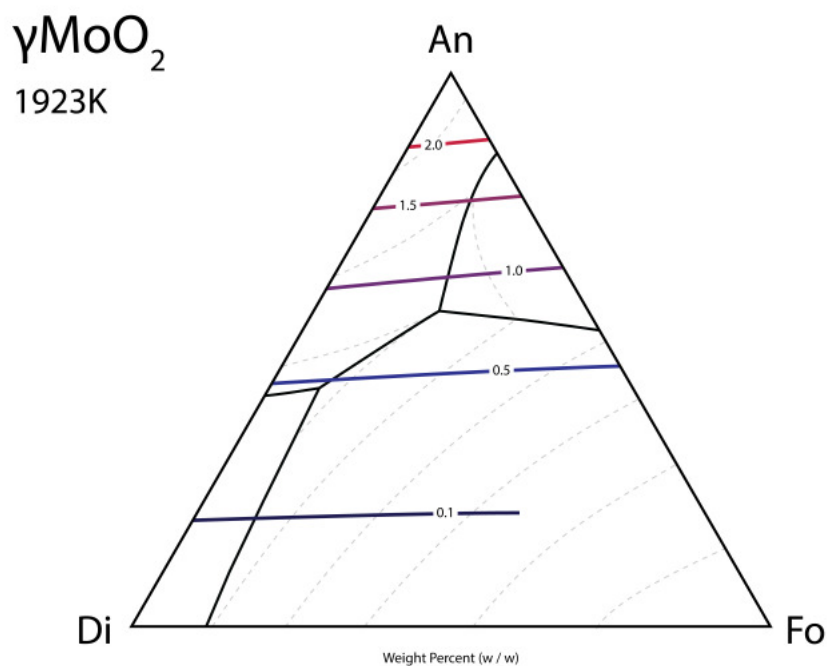


Figure 4.23—Model of  $\text{PbO}$  Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

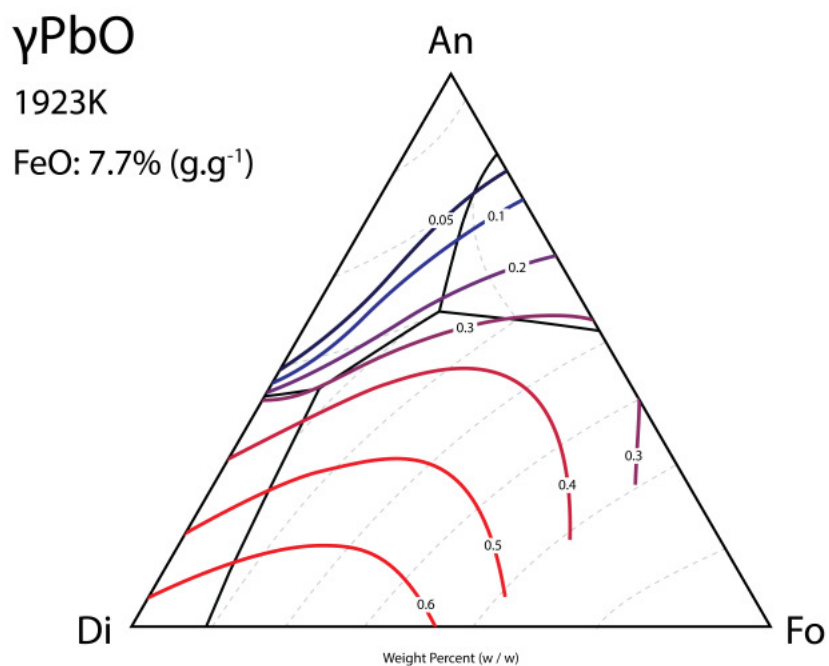


Figure 4.24—Model of  $\text{SnO}_2$  Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

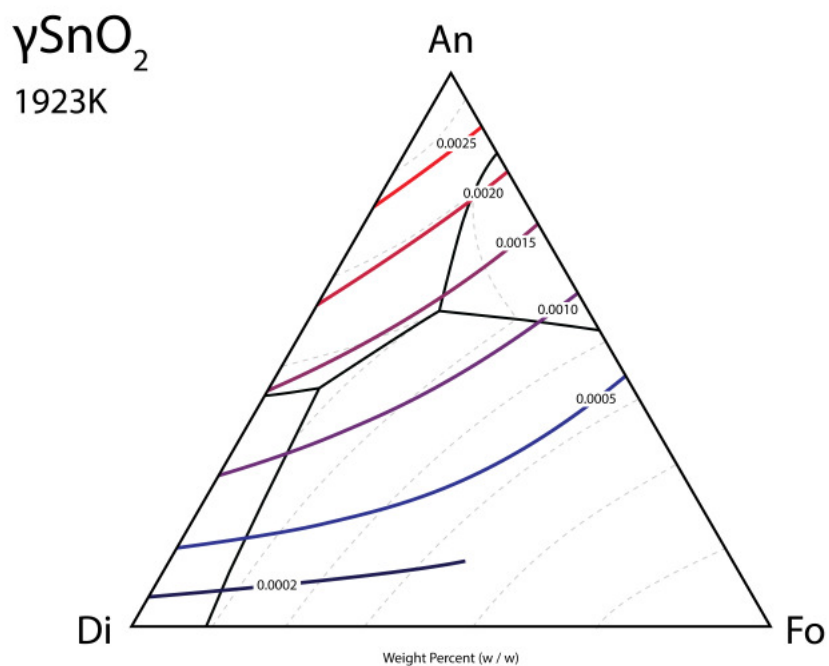


Figure 4.25—Model of  $\text{TiO}_{0.5}$  Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

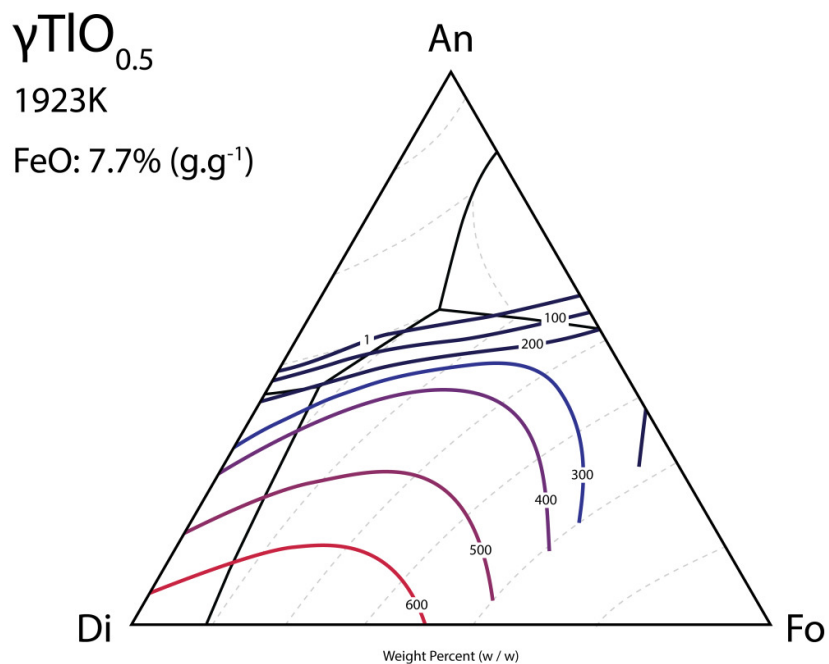


Figure 4.26—Model of  $\text{VO}_{1.5}$  Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

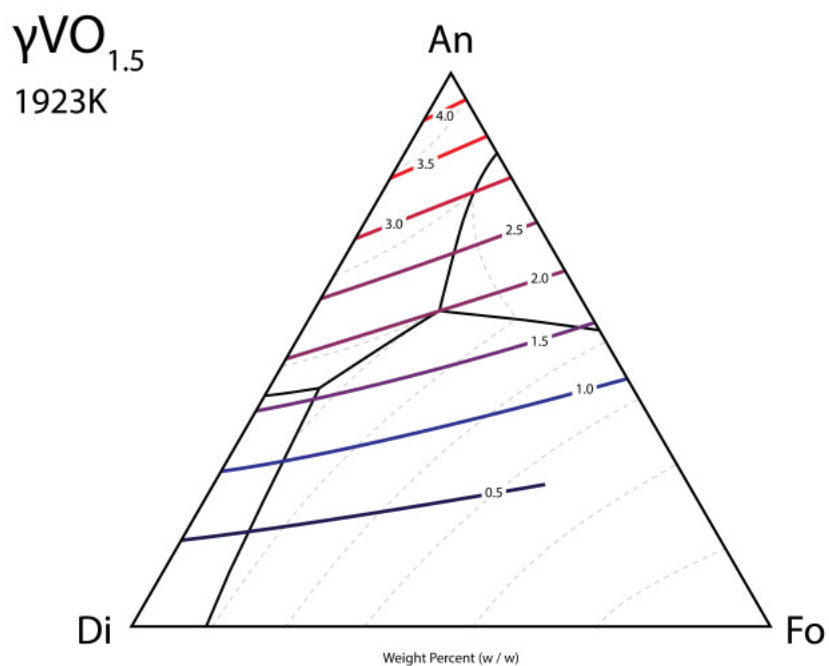


Figure 4.27—Model of  $\text{WO}_3$  Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary

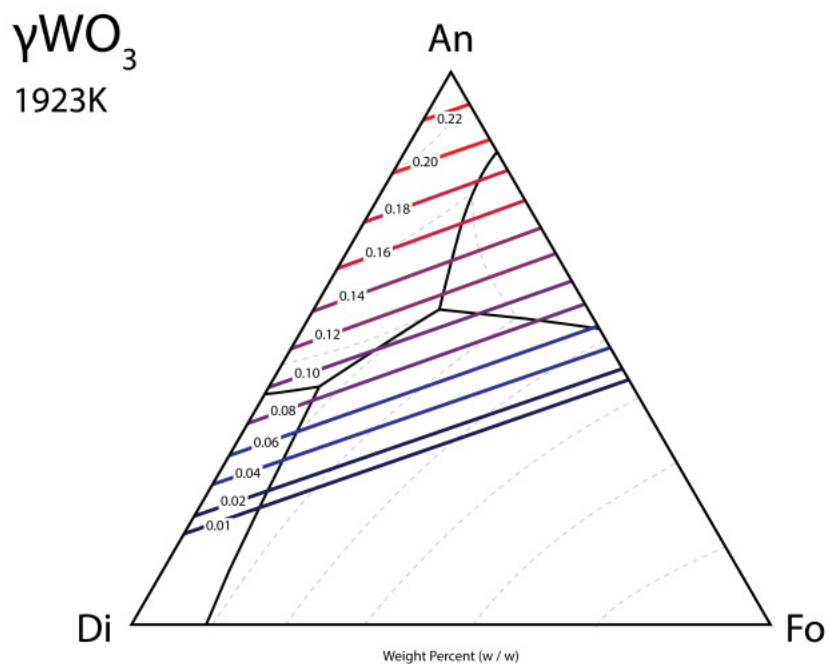
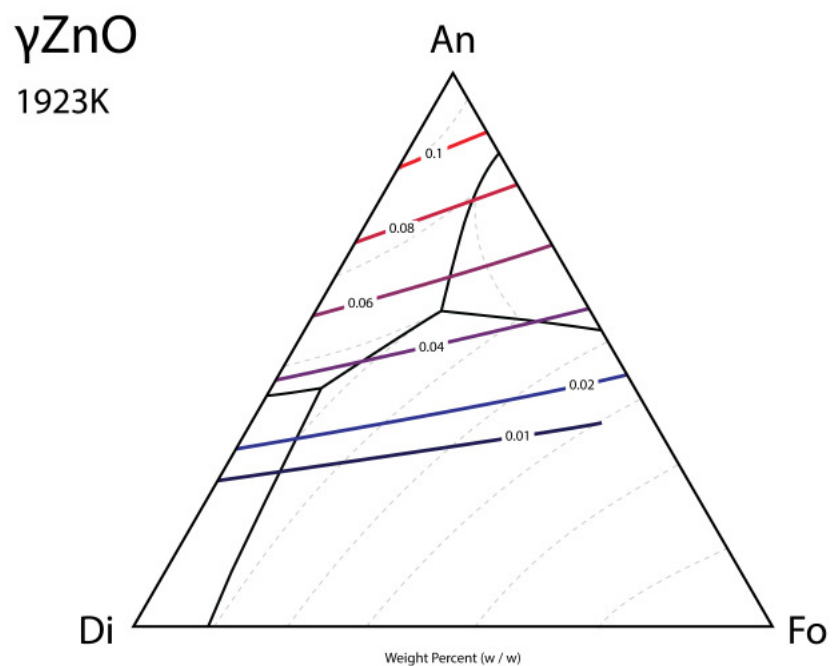


Figure 4.28—Model of ZnO Activity Coefficient in Silicate Melt at 1923 K on ADF Ternary



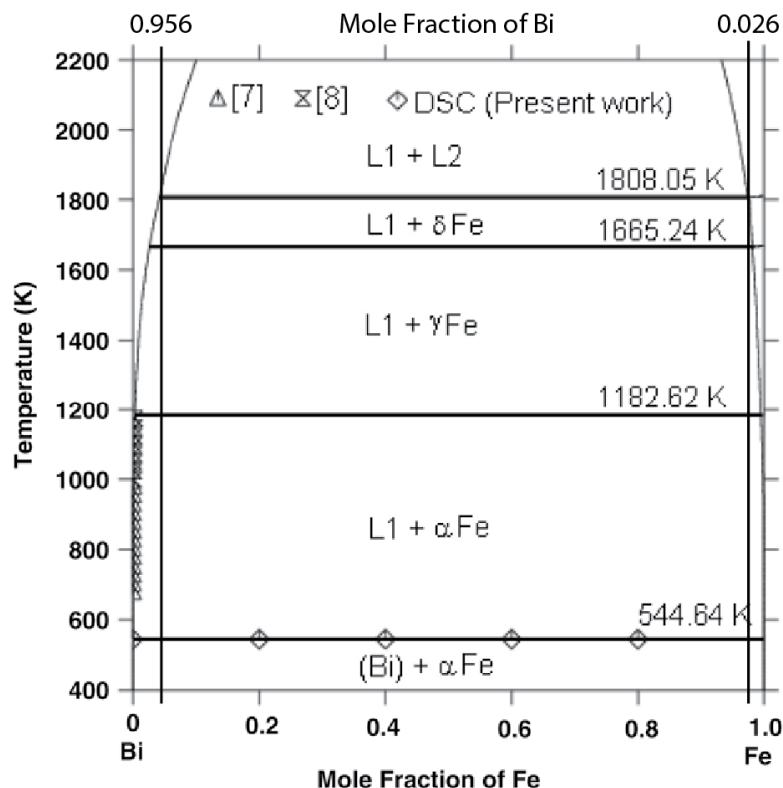
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## 4.11 Discussion

### 4.11.1 Computed Values of Gamma-Zero

The Miedema model [Miedema *et al.* 1980; Boom *et al.* 1983] provides the only estimate of gamma-zero in iron for the trace elements bismuth, cadmium, and thallium. To assess whether the values for these elements are reasonable the value of gamma-zero for lead is compared to existing literature data [Gordon and Breach 1988]. The Miedema model predicts a gamma-zero of 20,000 (all gamma-zeros stated in this section are for the trace element in liquid iron at the reference temperature of 1873 K) for lead, while the Gordon and Breach reference provides a value of 800. This suggests that the Miedema model may overestimate the gamma-zero value for bismuth, cadmium, and thallium. To make a further comparison for bismuth, the Miedema model gives a very large value for gamma-zero of 11,800. The work of Chang and Schlesinger [Chang and Schlesinger 1998] measured the solubility of bismuth in solid gamma-iron up to the melting temperature of 1665 K. If this solubility is regarded to be a lower limit to the solubility of bismuth in liquid iron (which is assumed to be greater) then we can compute a value of 4000 for gamma-zero in liquid iron, which is significantly lower. This also suggests that the Miedema model over predicts values for gamma-zero in iron. The work of Boa *et al.* [Boa *et al.* 2008] published a CALPHID model which shows a large miscibility gap in the bismuth-iron system above temperatures of 1808 K. While exact solubility values are not provided in that publication, reading bismuth saturation from the phase diagram (see Figure 4.29) results in a computed value of 39 for gamma-zero of bismuth in iron. While this value should not be regarded as superior to that of the Miedema model, it does suggest that the Miedema model has overestimated the value for gamma-zero of bismuth in iron.

Figure 4.29—Iron–Bismuth Phase Diagram



Modified iron–bismuth phase diagram after Fig10 in Boa *et al.* 2008. The annotated mole fractions have been read from the figure and are potentially incorrect in case of plotting discrepancies.

For indium, the Miedema model of 446 can be compared to the value computed from the miscibility gap of the phase diagram of Okamoto [Okamoto 1990] which is 27.4. While these values are substantially different, it is the author’s opinion that the computed value is more reliable as the phase diagram is based on a more recent thermodynamic assessment than that of Miedema. It should be noted that again, the Miedema model has overestimated the gamma-zero of indium in liquid iron.

The iron-tin system [Nüssler *et al.* 1979] features a miscibility gap which can be used to compute an estimate of gamma-zero for tin in iron as 4.9. This value should be compared to the Gordon and Breach literature value of 2.58. In comparison, Boom *et al.* 1983 provide an



experimental value of 1.73 and the Miedema model of 36.5. Again, as for the other trace elements discussed in this section, the Miedema model over estimates the gamma-zero value for tin in iron.

In conclusion, experimental thermochemical data for trace element solubility in liquid iron should always be used when they are available. Where the Miedema model has been used in this study (for bismuth, cadmium, and thallium) then those values should be regarded as upper estimates to the true value.

#### 4.11.2 Activity Uncertainties

Uncertainty in the activity coefficient values comes from the analytical uncertainty of the EPMA and LA-ICP-MS analysis as well as the thermochemical data.

The electron microprobe can typically achieve 2% relative uncertainty for both accuracy and precision. The PENEPMA modelling work (see Chapter 2) showed that while the observed variance of analysis of the quench textures will be high, the standard error on the mean provides a reasonable uncertainty estimate of the bulk composition of the two phases.

In contrast, LA-ICP-MS can achieve 10-20% relative precision, the accuracy of the LA-ICP-MS analysis was assessed and found for some of these trace elements to be overestimated by up to 500% (see Chapter 3). The correction curves based on fabricated iron standards allows the accuracy to be improved to match the precision, which should be regarded as no better than 20% relative for these samples.

Analytical errors that contribute to uncertainty in the partition coefficient are represented by the standard error of the fit in the linear regression models (see Table 4.17). Where a model could not be determined (such as for antimony) or a model showed a poor goodness of fit due

to a small range of activity coefficient values (such as for copper) then the standard error of the activity coefficient can be taken directly from the experimental data, as summarised in Table 4.16.

The uncertainty of the thermochemical data is significantly more varied, especially considering that some properties have been estimated or modelled from first principles, or experimental data exhibit a wide range of values (see previous discussion section). It is the author's opinion that all activity coefficient values presented in this work are correct to within an order of magnitude, which while large is still significant considering the range of activity coefficients measured (compare  $\text{SnO}_2$  to  $\text{Tl}_2\text{O}$ ) and the strong dependence on silicate melt composition for some elements (such as  $\text{MoO}_2$  or  $\text{PbO}$ ). As shown in Chapter 5 the activity coefficients measured here, despite a large uncertainty, are still of use in understanding the volatility of trace elements in silicate melts.

#### 4.11.3 Comparison to Previous Work

As outlined in the introduction, measuring the activity of trace elements in silicate melts has been difficult and only limited data are available. Using a similar methodology as this work, the workers Wood and Wade 2013 collated published values to present silicate melt models for  $\gamma\text{MoO}_2$  and  $\gamma\text{WO}_3$  which agree quite well with the models from this study. The Wood and Wade model for  $\gamma\text{MoO}_2$  on the ADF ternary spans from 5.0 in the anorthite-poor region to as high as 100 in the anorthite-rich corner. This general shape, and factor of 20, is reassuringly reproduced in this study, where  $\gamma\text{MoO}_2$  varies from 0.1 to 2.5 across the same composition range. The Wood and Wade model for  $\gamma\text{WO}_3$  shows a variation from 0.001 in the forsterite-rich corner up to 0.05 in the forsterite-poor region. This is also well reproduced in this study, with commensurate values modelled with just the NBO/T term.

The value of  $\gamma_{\text{Cu}_2\text{O}}$  was measured by Holzheid and Lodders [Holzheid and Lodders 2000] by partitioning with iron and sulphide. They determined an activity coefficient of  $10 \pm 1$  in silicate melts at  $1300^\circ\text{C}$  with a composition dependence on the  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  content of the melt. This agrees very well with the results of this study, in both the absolute value of the activity coefficient and the trend with silicate melt composition.

It is challenging to assess the magnitude and trends in the activity coefficients of the other trace elements since there are no published data to compare to.

#### 4.11.4 Trends and Patterns

All of the activity models show two main patterns: silver, bismuth, lead, thallium, copper, and indium, exhibit a maximum in the diopside-rich compositions, with activity decreasing towards the anorthite-rich compositions, while in contrast: zinc, tungsten vanadium, tin, molybdenum, germanium, gallium, and chromium, all show the opposite trend, with their maxima coinciding with the anorthite-rich compositions, and minima towards the anorthite-poor compositions. The variation of activity for cadmium looks entirely different.

Various elemental parameters have been evaluated in an attempt to understand these elemental groupings. Valence state is inadequate, as are traditional ideas of “volatility” with zinc, tin and gallium being grouped with molybdenum, vanadium and tungsten.

The trends may come from affinity with the iron metal imprinting on the activity in the melt. If this was the case then one would expect the two groupings to correlate with the free energy in the iron metal. A comparison with the Miedema model (offering consistent treatment for all elements) shows that in order of affinity with iron metal the elements are (from most to least, with the marker | placed at  $\Delta\bar{H}_M^0 = 0$ ): V, Ge, Mo, Ga, Cr, W | Zn, Cu, Sn, Sb, Cd, In, Ag, Bi,

Tl, Pb. It would be possible to roughly align the observed groupings with the iron-affinity, yet there remain clear outliers (such as Cd) and some “reshuffling” in the central region between Cu and In.

#### 4.11.5 Physical Melt Models

Previous work (Mills 1993) has presented physical melt models for silicate slags, namely the “Optical Basicity” and the “Non-Bridging Oxygen / Total Oxygen” abbreviated by  $\Lambda$  and NBO/T respectively. To determine whether either of these models aligned with the observed trend in activity coefficients, both  $\Lambda$  and NBO/T were used as independent variables for the linear regression. For all elements  $\Lambda$  failed to be included in any of the models as a significant ( $F > 0.05$ ) predictor of activity coefficient. For two trace elements (gallium and tungsten) the NBO/T term was found to be the solely significant predictor for the activity coefficient. It must be noted that the valence states of gallium and tungsten in silicate melts are 3+ and 6+ respectively. This is interesting because while valence is a major factor in silicate melt models, this study failed to determine any clear trend in activity coefficients based on valence.

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## 4.12 Summary

This chapter has outlined the methods and results from an experimental campaign to measure metal–silicate partition coefficients.

In combination with thermochemical data the partition coefficients have been used to compute the activity coefficients of the trace elements in the silicate melt.

The values of the activity coefficients for most of the trace elements in silicate melts show a significant dependence on melt composition. This compositional dependence has been modelled for each element. Plotting the models as contours in the ADF ternary system reveals two major groups of behaviour which this author is unable to explain.

Comparison with literature data, where available, shows fair agreement with both the absolute magnitude and the composition trends. However, it must be noted that for most of these trace elements this is the first time these activity coefficients in silicate melt have been measured.



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## 5 Design, Construction and Application of a One Atmosphere Gas Mixing Furnace

### 5.1 Introduction

The objective of this section of the project was to design and build a one-atmosphere gas mixing furnace capable of stirring a crucible of silicate melt at high temperatures up to 1700°C. By measuring the loss of volatile elements to the vapour phase this apparatus will provide direct measurement of trace element volatility, or effusion rate, from silicate melts. Previous workers [Dingwell *et al.* 1994] have built *in situ* stirring mechanisms integrated into gas-mixing furnaces, but the design presented here offers a number of advantages and improvements, such as: an entirely gas-tight assembly to maintain  $f\text{O}_2$  as well as facilitate working with toxic or reactive gases (e.g.  $\text{H}_2$ ,  $\text{SO}_4$ ); a rapid-quenching mechanism; low-cost of consumables; and strongly-supported end caps that can be adapted to a wide range of experiments.

Volatile loss experiments will be performed at 1300°C and a range of  $\log(f\text{O}_2)$  values from  $-7$  to  $-13$ . The volatile loss results will be compared to vapour pressure values predicted using thermochemical data, while assuming ideal trace element activities in the silicate melt.

Then, the trace element activity coefficients determined in Chapter 4 will be applied to assess whether the partial vapour pressures are able to predict the rates of volatile loss from the silicate melt.

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## 5.2 Furnace Design

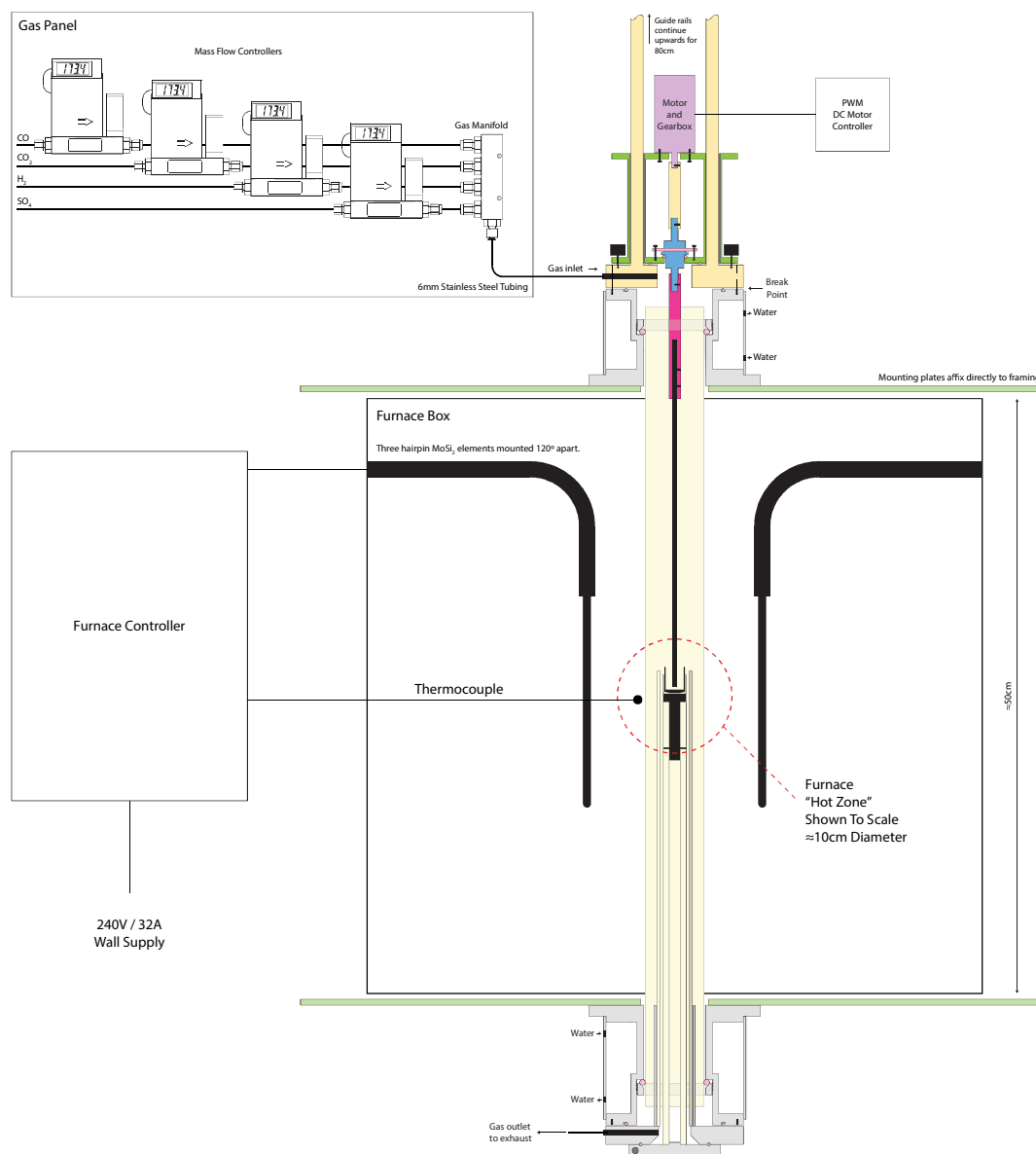
The design objective was to assemble a gas-mixing furnace that can actively stir molten materials. It will: operate at one-atmosphere; be capable of working at temperatures up to 1700°C; mix up to four different working gases; remain air tight during operation; quench the experiment as rapidly as possible; and, be economical with disposable components.

The design presented in this study was constructed and utilised for a series of experiments to measure volatile loss of trace elements from silicate melts. The apparatus successfully addressed all of the design objectives and is currently used by the University of Oxford Experimental Petrology research group for ongoing research into volatile elements and planetary formation.

Please refer to Figures 5.1 to 5.4 for equipment dimensions and experimental layout.

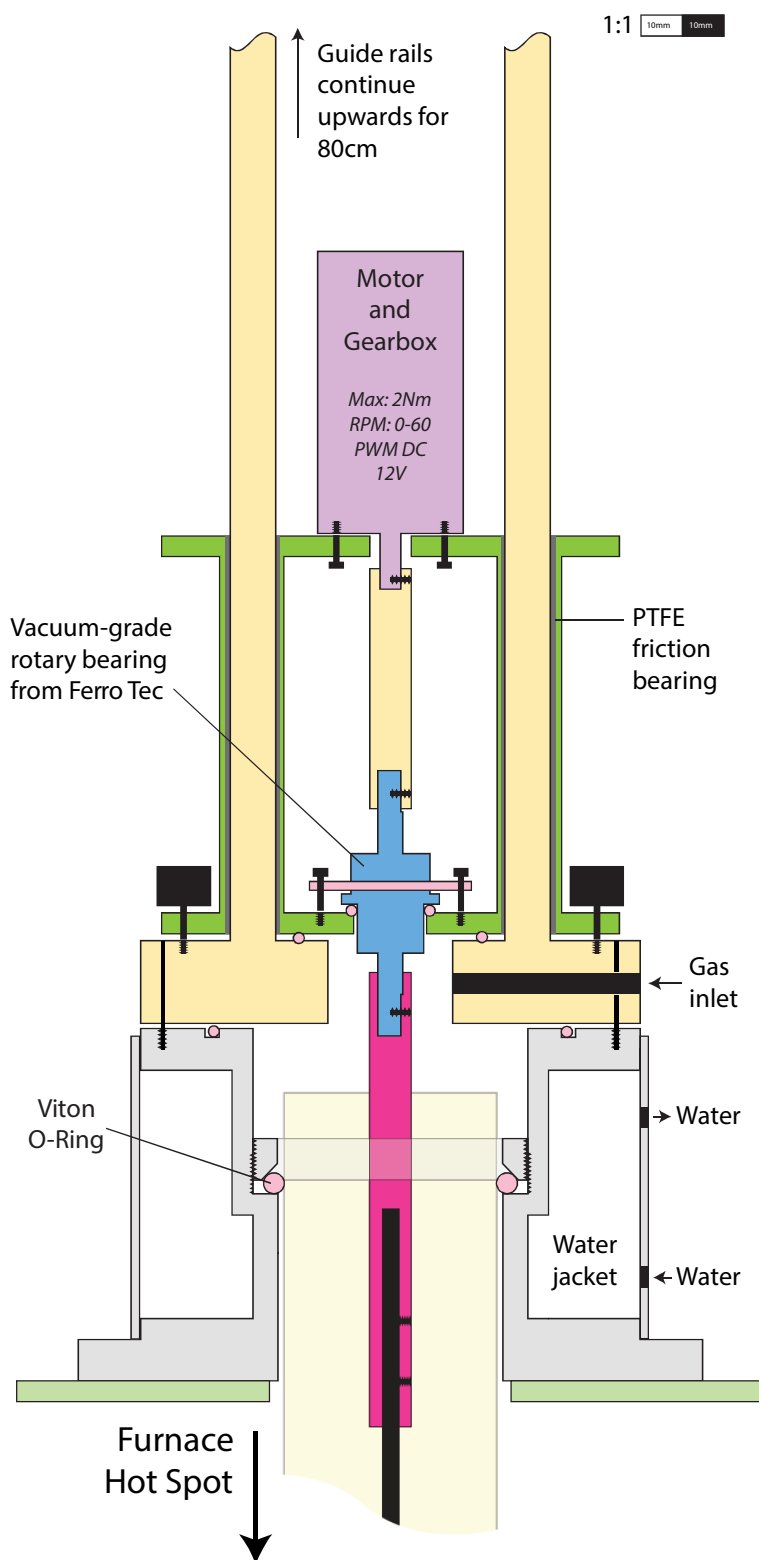


Figure 5.1—Stirring Furnace Overview



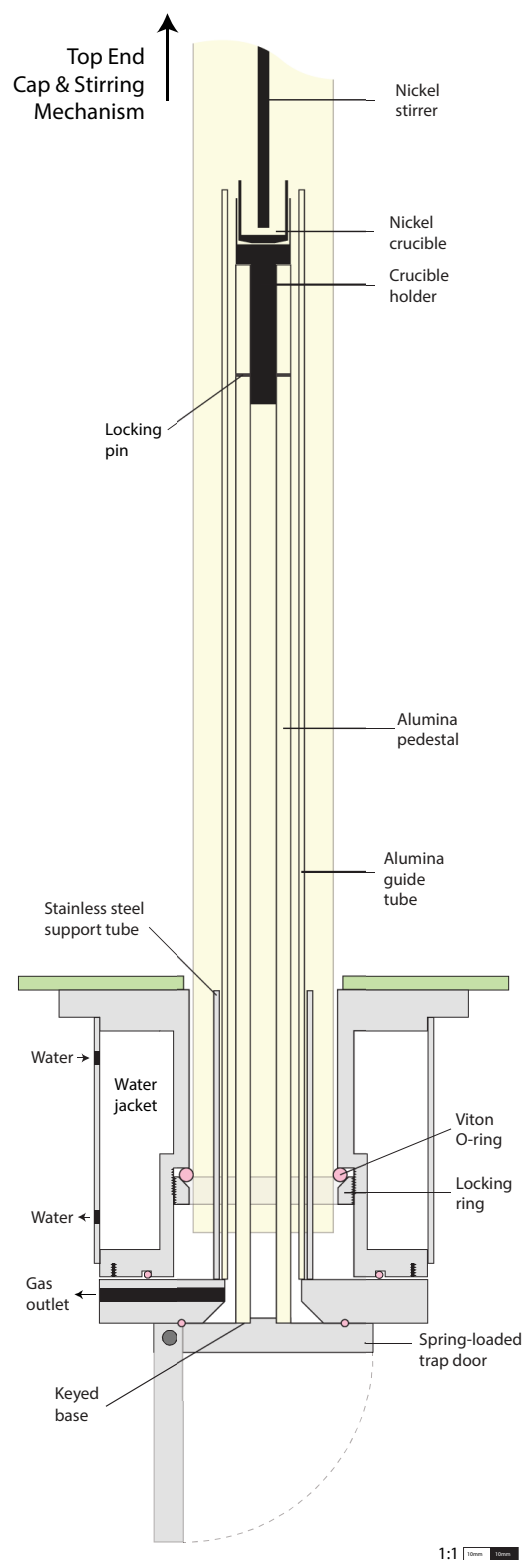
An overview of the stirring furnace design. The furnace tube and end caps are positions approximately to scale, while the other components are not. The trap door in the bottom end cap allows the experimental charge, nickel crucible, and alumina pedestal to fall out of the furnace to quench in a waiting bucket of water (not shown).

Figure 5.2—Furnace Top End Cap and Stirring Mechanism



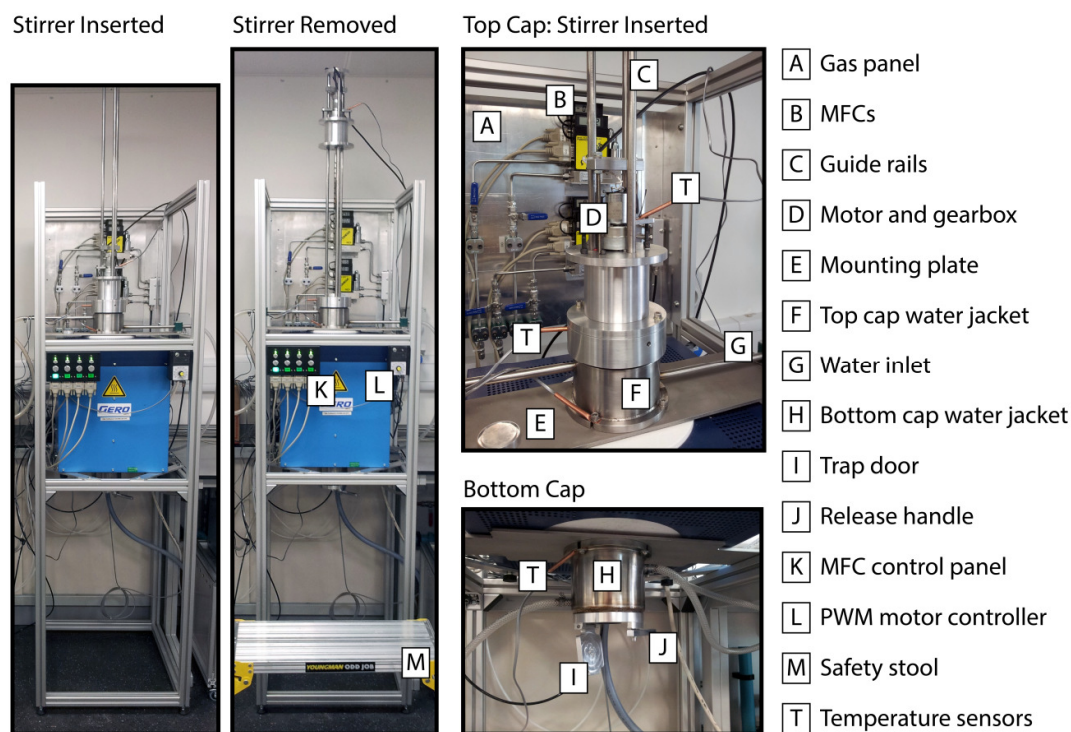
Detailed view of the furnace top cap and stirring mechanism. The stirring mechanism detaches from the top cap and slides on the guide rails to remove the stirrer entirely from the furnace tube. The design ensures the stirrer remains concentric to the centre line of the apparatus and that the stirrer enters the crucible when inserted at the beginning of the experiment.

Figure 5.3—Furnace Bottom End Cap and Quench Mechanism



Detailed view of the furnace bottom cap and the pedestal and crucible. The pedestal is keyed to the base to ensure the crucible is able to counter the rotational moment of the stirrer. At the end of the experiment the trap door is opened and the pedestal, crucible, and experimental charge, all fall free of the furnace and into a waiting bucket of water for quenching.

Figure 5.4—Furnace Photographs



Labelled components of the stirring furnace in four panels: stirrer inserted, stirrer removed, top cap with stirrer inserted, and bottom cap with trap door open.

### 5.2.1 Tube Furnace

The furnace is a vertical tube furnace supplied by Gero<sup>14</sup> and equipped with “Kanthal Super”<sup>15</sup> molybdenum disilicide ( $\text{MoSi}_2$ ) elements. The furnace model number is “HTRV 70-250/18” and is rated for operation up to 1800°C in ambient air. The furnace tube is high-purity alumina, 5 mm wall thickness, with an outside diameter of 5 cm. The top-to-bottom distance of the furnace body is 58 cm, the distance from end cap to end cap is 73 cm, and the recommended length of furnace tube to work with these end caps is 72 cm.

### 5.2.2 Furnace Controller

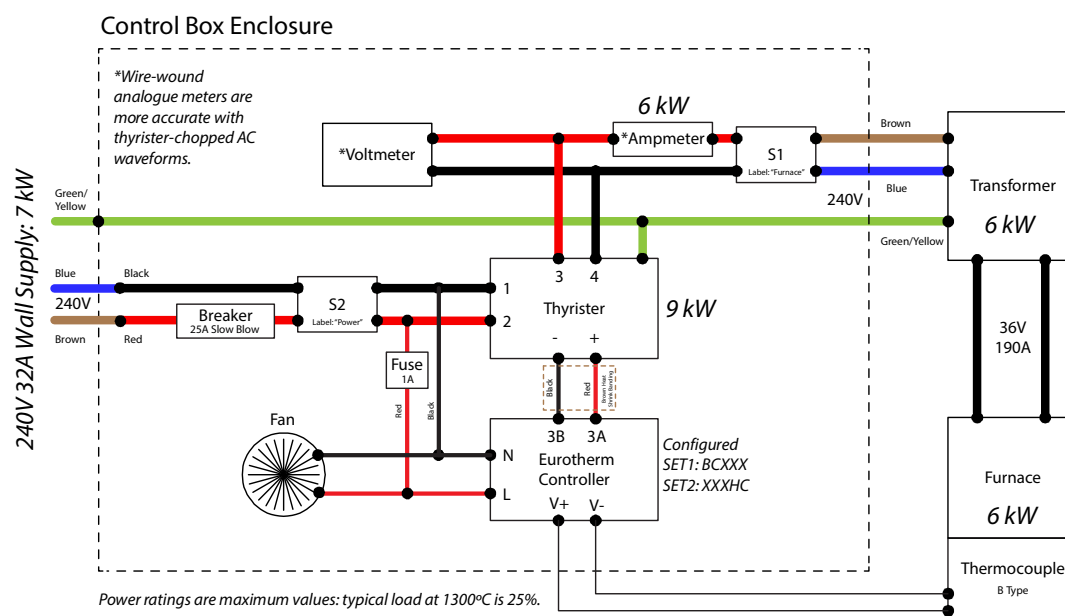
The three furnace elements are driven in series by low voltage (36 V) AC running at up to 190 A. The entire power train is rated for the maximum element load of 6 kW. A control circuit

<sup>14</sup> Carbolite Gero Germany, <http://www.carbolite-gero.com>, 2016

<sup>15</sup> Kanthal Sweden, <http://www.kanthal.com>, 2016

was built around a *Eurotherm*<sup>16</sup> 3204 PID controller driving a single phase thyristor (TE10A, also from *Eurotherm*) feeding into a 240 V to 35 V step-down transformer<sup>17</sup>. The PID controller reads process temperature from a type B thermocouple mounted outside but next to the centre of the furnace tube and drives the thyristor via a 4 to 20 mA signal. A wire-wound voltmeter and ammeter are connected to the output stage, as this type of meter shows a more accurate reading once the AC waveform has been chopped by the thyristor. The entire control circuit is mounted in a sturdy metal box with a cooling fan for ventilation. The transformer is passively air cooled, weighs approximately 50 kg, and is mounted on a rolling castor frame.

Figure 5.5—Furnace Controller Circuit Diagram



### 5.2.3 Furnace Tube End Caps

The furnace end caps must provide adequate cooling to the primary O-ring seals as well as a stable base for the stirring and quenching mechanisms. There is an end cap at the top and bottom of the furnace tube. Each end cap was assembled from two parts of 316 stainless steel,

<sup>16</sup> Eurotherm by Schneider Electric, <http://www.eurotherm.com/>, 2016

<sup>17</sup> Supplier: Claude Lyons, <http://www.teccoltd.com/>, 2016

milled separately, TIG welded together and pressure tested prior to use. Spigots for circulation of the cooling fluid were welded to openings vertically offset on opposite sides of the cooling jacket. The cooling spigots extend for 5 cm beyond the edge of the furnace box to ensure that any leak from the hose connections will not run directly into the furnace. A recess in the end cap retains a 2 mm Viton<sup>18</sup> O-ring that can seal against a range of accessories, including: a blanking plate for testing the furnace, a trap-door for quenching experiments, a gas-tight bearing and stirring mechanism for stirring the experiments, as well as an adapter set that accepts fittings from the other working furnaces used in this laboratory.

To provide a gas-tight seal a 50 x 5 mm Viton O-ring is pressed against the outside of the furnace tube using a screw-down compression clamp. A special tool was fabricated to adjust the compression clamp. Since the furnace tube will expand at high temperature it is important that the tube be able to move against the O-ring as an expansion joint. For this reason, the bottom O-ring was secured tightly (wound until resistance was felt, then an entire turn added) relative to the top O-ring, which was left relatively loose (wound until resistance, then a quarter turn added). After a year of operation dark witness marks were observed on the furnace tube exterior over a range of 5 mm past the top O-ring suggesting that the tube expansion joint was working and moving as expected.

The flash point and failure temperature of Viton is 200°C<sup>19</sup> so that permanent cooling must be provided to the end caps. The end caps were connected in series (top-caps first in the loop) to the building chiller supply via ½" reinforced nylon hose. The building supply delivers water (some glycol and algae inhibitors are added periodically) at approximately 6°C at a flow rate of

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<sup>18</sup> Viton is a common trade name, the actual product is a fluorinated elastomer.

<sup>19</sup> Viton product information, <http://o-ring.info/en/downloads/material-safety-datasheets/>, accessed 2016-09-08

3 to 4 L.s<sup>-1</sup>. Via the temperature monitoring system it was found that the end cap surfaces always stayed within the temperature range of 20 to 35°C.

The end caps were mounted on a transverse 5 mm steel plate secured to the framing. This ensured that no loading was ever applied to the furnace box itself and the furnace tube was supported entirely by the primary O-ring contact points. Any thermal movement of the furnace box was completely separated from the end caps, and since the framing members are well removed from the furnace itself, there was no measurable change in the end cap separation, even when operating at high temperature.

#### 5.2.4 Stirring Mechanism

The stirring mechanism is driven by a PWM DC motor connected to a 185:1 gearbox<sup>20</sup> capable of free-running up to 27 RPM. The maximum output torque is 2 Nm. The rotational moment is delivered via a gas-tight ferrofluidic feed-through supplied by Ferro Tec<sup>21</sup>.

##### 5.2.4.1 Length Extension

Two designs were used for the stirring arm with negligible operating differences between them. The first comprised a 10 mm diameter nickel rod. The large diameter was chosen to ensure the mechanism remained concentric during operation. Large 8 mm transverse holes were cut at alternating perpendicular angles to minimise thermal conductivity of the rod, while still retaining mechanical integrity. The second design used a solid 4 mm nickel rod and a coupling secured with grub screws. The steel coupling was placed well outside the furnace hot-zone and showed little oxidation even after repetitive use.

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<sup>20</sup> Crouzet, Part Number 82869007

<sup>21</sup> Ferrofluidic Seals, <https://seals.ferrotec.com/>, 2016

### 5.2.5 Crucible

The crucibles used for these experiments were made from 98% purity nickel, 20 mm in height, 19 mm outside diameter, with 1 mm wall thickness. The base was bevelled at 45 degrees to prevent the crucible from jamming in the holder. The crucible holder was also fashioned from nickel of commensurate purity and was 8 cm long. The holder was bored axially with a 6 mm channel. This reduced the thermal mass of the holder, and also allowed a steel rod to be inserted to assist with extracting the crucible from the holder.

A new crucible was used for each experiment. When preparing for an experiment the crucible was cleaned, inserted into the holder, and then the holder was given a sharp transverse tap from a hammer. This deformed the holder slightly, retained the crucible, and most importantly prevented the crucible from rotating freely inside the holder.

The holder was supported on a 35 cm pedestal made of low-purity alumina. The pedestal was drilled transverse, 5 cm from the top end, with a 3 mm diamond tipped auger. These holes aligned with matching holes in the crucible holder, and a loop of nickel (99.9%) wire wound through to tie the two parts together. A recess groove was ground with a diamond wheel in the outside of the pedestal to ensure that the exterior surface of the pedestal was smooth and uninterrupted so as to avoid catching or jamming during the quench. The thin wire proved sufficient for these experiments, but it should be noted that if more torque was required (i.e. if mixing rhyolitic glasses) then the wire could be replaced with a nickel pin, peened gently at each end on an appropriate anvil.

The bottom of the pedestal was notched ( $3 \times 3$  mm) in a crossways pattern to match a keyed surface raised in the topmost surface of the trapdoor. During these experiments this keying provided an adequate moment to prevent the assembly from rotating. If more torque was to be



required for future work then the keying could be made longer, but would ultimately be limited by the shear modulus of low-purity alumina.

### 5.2.6 Quenching Mechanism

To quench the experiment a spring-loaded trap door was mounted to the bottom end cap. At the end of the experiment the trap door was opened and the low-purity alumina pedestal, nickel crucible, and experimental charge, would leave the furnace under the assistance of gravity. These components then plunged into a metal bucket holding 10 to 15 L of water at ambient laboratory temperature. The completion of quenching was identified once visible signs of boiling from the crucible and holder had ended. Such quenching always occurred within tens of seconds so no effort was made to cool the water bath to a lower temperature. It should be noted that there may be some merit in replacing the quenching water with mineral oil, as this will exhibit less of water's propensity for the Leidenfrost effect [Leidenfrost 1756; Gottfried *et al.* 1966] resulting in slightly faster quench rates, but there would be a clear safety risk associated with doing so and it was not attempted during this project.

### 5.2.7 Temperature Monitoring System

#### 5.2.7.1 Overview

The one-atmosphere gas-mixing furnace described in the previous section operates at temperatures up to 1700°C. The internal temperature of the furnace is controlled via a *Eurotherm* PID controller that reads the process temperature via a type-B thermocouple mounted outside, but within a few cm of the furnace tube. The end caps are actively cooled with circulating coolant supplied to the laboratory at a nominal 6°C. The outside surfaces of the furnace are passively air cooled. There is a risk of temperature damage to the primary O-ring seals, the motors, the gear box, and the vacuum bearing.

Over the course of a typical experiment component temperatures should remain stable. To ensure that no part of the furnace exceeded its design limits, it was desirable to monitor the outside temperature of the equipment. In addition to monitoring the components, it was also advantageous to monitor the stability of the gas flows reported by the MFCs (0 to 5 V signal representing the range from no-flow to full-flow).

Several commercially available units were considered, but unfortunately, while a range of units did meet these operating requirements they were all characterised by a relatively high price. As an example, at the time of writing the Omega Instruments RDXL8 8-channel temperature logger is priced at £1365<sup>22</sup> not counting the cost of the thermocouple probes, and foregoing the monitoring of the MFC gas flows.

Advances in modern computing have produced a wide range of microcontrollers that are both powerful enough to perform many useful tasks while available for purchase at low cost. Unlike previous generations of microcontrollers, contemporary boards are often equipped with flexible networking features. The availability of low-cost networked devices has encouraged many to declare that our society is currently entering the age of the “Internet of Things”, also called the “IoT” [Xia *et al.* 2012; Gubbi *et al.* 2013].

Despite the budgetary constraints this flexible monitoring system was designed and implemented for less than £50 in parts.

### 5.2.7.2 Design

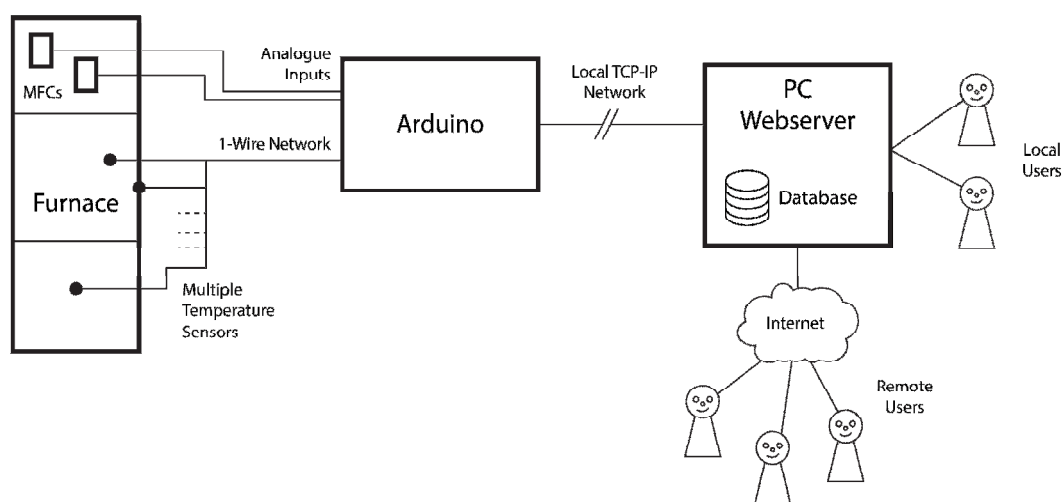
The block diagram in Figure 5.6 illustrates operation of the monitoring system. At the front-end an *Arduino* [Barret 2010] microcontroller hosts a one-wire bus [Awtrey 1997] that

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<sup>22</sup> “8 Input Portable Thermometer-Data Logger”, <http://www.omega.co.uk/pptst/RDXL8.html>, retrieved 2016-08-21

communicates with multiple DS18B20<sup>23</sup> temperature sensors mounted to the furnace exterior. The microcontroller uploads sensor readings at regular intervals to the back-end server running on the same local network. As well as logging the readings to a database, the server also hosts a web server that allows local users to access the readings, and if the external firewall is configured appropriately, this access can be securely extended to remote users.

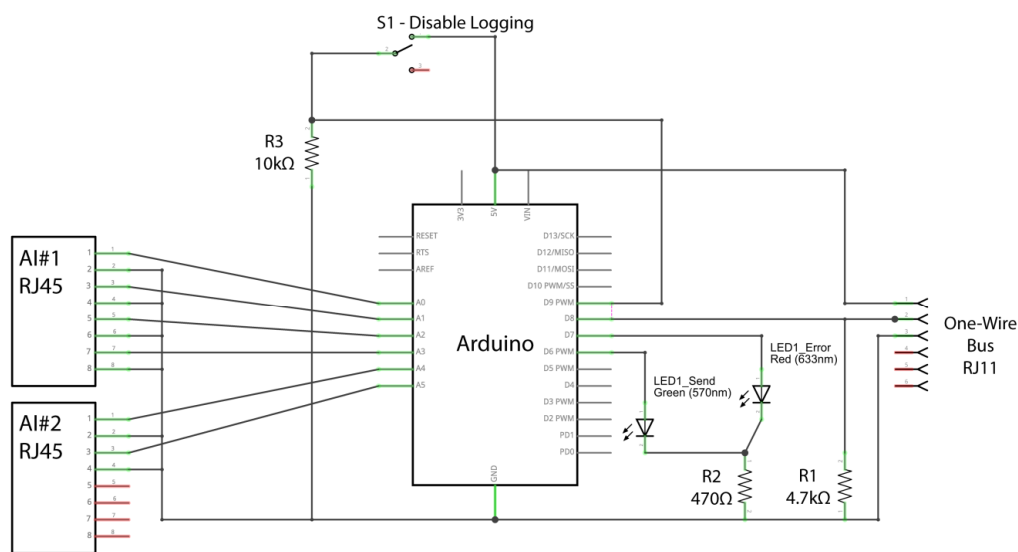
Figure 5.6—Temperature Monitor Block Diagram



Block diagram showing the various parts of the temperature monitoring system. The Arduino is located in the laboratory close to the furnace, yet the PC Webserver can be located anywhere in the building. Local users can access the temperature information via the local network, and if the external firewall is configured appropriately this access can also be extended to remove users.

<sup>23</sup> “DS18S20 High-Precision 1-Wire Digital Thermometer”, <http://datasheets.maximintegrated.com/en/ds/DS18S20.pdf>, retrieved 2016-08-22

Figure 5.7—Monitor Box Circuit Diagram

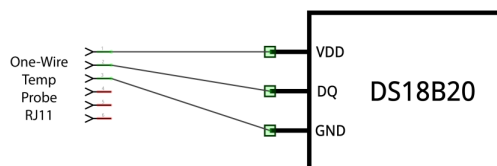


Circuit diagram of the monitor box. Most of the circuit comprises the Arduino microcontroller. The circuit is simple enough that it can be wired point-to-point without a PCB.

Multiple temperature probes were assembled using salvaged 4-core RJ11 telephone leads. The DS18S20 sensor was wired to the lead using a three-trace separate power (VDD) configuration and embedded inside a 10 cm length of 6 mm diameter copper tube. The end located closest to the sensor was crimped flat, leaving a 1 cm tag that was drilled with a 4 mm diameter hole to allow convenient screw mounting to the furnace. The tube was filled with *Epothin* epoxy resin and allowed to cure. The resin provides strain relief to the soldered leads and ensures the temperature sensor is unable to be dislodged from the tubing. The final package is very robust, easy to mount, thermally conductive, and can be made with convenient lengths of cabling. If required, RJ11 extension cables and joiners can be used to provide additional flexibility. The one-wire bus can be arranged in a range of convenient topologies, including linear bus, stubbed bus, or star<sup>24</sup>.

<sup>24</sup> Guidelines for Reliable 1-Wire Networks, [http://neutrino.phys.ksu.edu/~gahs/doublechooz/DC\\_SlowMRS/AN148.pdf](http://neutrino.phys.ksu.edu/~gahs/doublechooz/DC_SlowMRS/AN148.pdf), retrieved 2016-08-27

Figure 5.8—Temperature Probe Circuit Diagram



The DS18B20 temperature sensor is wired directly to the one wire bus. The bus was implemented using RJ11 connectors and second-hand 4-core telephone cable.

The PC server was a regular desktop PC fulfilling mixed roles such as daily computing tasks, web browsing, and email, as well as writing and typesetting this manuscript. Apart from the operating system (Windows 7 x64) all of the software stack was free open-source software: the webserver software was Apache<sup>25</sup>; the database software was MySQL Community Edition<sup>26</sup>; the scripting language for dynamic website content was PHP<sup>27</sup>. Colloqually in the web-server community this would be referred to as a “WAMP stack”.

To simplify the software and minimise memory requirements, the program running on the microcontroller uploads each sensor reading sequentially using a separate HTTP GET request for each one. From the microcontroller’s perspective it makes the reading, opens a TCP connection to the web server, sends the minimum headers to identify the GET request, and then passes a well-formed URL containing the parameters to submit. The URL contains four pieces of information: a string identifying the monitoring device (allowing multiple devices to report to a single server), a string identifying the name of the sensor reading, an integer value for the reading itself, and a pre-shared secret token string. On the server the Apache web server passes the request to the PHP script engine, which parses the GET request for completeness and

<sup>25</sup> The Apache Team, “Apache HTTP server project.”, <http://www.apache.org/>, 2016

<sup>26</sup> MySQL, A. B. “MySQL database server.”, <http://www.mysql.com>, 2016

<sup>27</sup> PHP Group. “PHP: Hypertext preprocessor.”, <http://www.php.net/>, 2016

saves the reading to the local database. If the URL is complete and the database accepts the new value, then the web server responds with the short string “OK” to inform the *Arduino* that the upload has been accepted. Upon receipt of the “OK” string the *Arduino* then flashes a green LED to inform nearby workers that the logging is working correctly, and in case any other string is received the red LED is flashed instead. The operation is fast (approximately 1s per reading) and relatively efficient (200-300 bytes per upload). Following the upload cycle the *Arduino* sleeps until the next set of readings are required.

The *Arduino* reports the 0 to 5 V analogue input voltages using an integer scale from 0 to 1024, giving an effective resolution of 5 mV. The temperature sensor readings are reported to the nearest 0.01°C as an integer without the decimal place, i.e. integers from –5500 to +12500.

Calibration of the readings against their physical interpretation is performed on the web server using a configuration file. This allows various sensors to be assigned to different scales, and most importantly, the 0 to 5 V analogue signals can be correctly assigned to different MFC units calibrated for different flow scales.

When a user accesses the monitoring web page the server generates a table of current readings, and also creates dynamic charts showing how the readings have changed over time. All readings are archived indefinitely.

#### 5.2.7.3 *Assessment*

The system has provided continuous service for three years, requiring little to no maintenance during this time. For three weeks it was trivially relocated to provide temporary temperature monitoring in an adjacent laboratory.

The monitoring features proved to be extremely useful for optimising the flow of cooling fluid to the end caps. It also identified periodic temperature cycling of the building chiller circuit

During all experiments the gas flows were recorded as constant and within tolerance, offering assurance that the oxygen fugacity remained stable for the duration of the experiments.

It is the author's opinion that similar systems may be of benefit to other laboratories and the enthusiastic reader is encouraged to implement a similar design of their own.

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## 5.3 Furnace Characterisation

### 5.3.1 Furnace Temperature

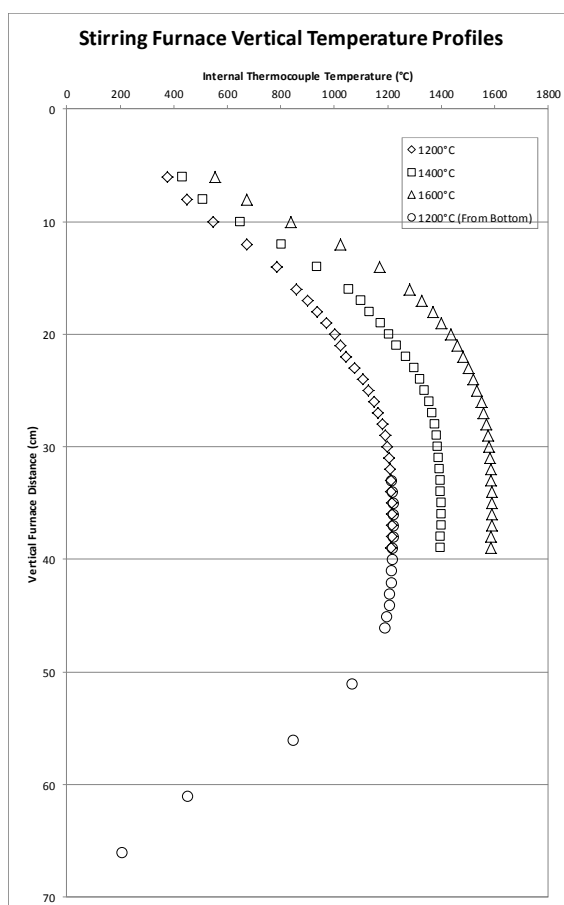
To measure the temperature inside the furnace tube a Type B thermocouple ( $\text{Pt}_{70}\text{Rh}_{30}$ — $\text{Pt}_{94}\text{Rh}_6$ , 0 to 1700°C) was spot-welded between the two thermocouple wires at the end of a 45 cm × 4 mm diameter 2-bore pure alumina rod. The thermocouple wires ran through the bores in the rod and out the far end where the openings were sealed with a dab of high temperature silicone sealant. The rod passed through a blanking cap covering the furnace end cap and the space around the rod was sealed by a small (5 × 2 mm) Viton O-ring compressed by a cover plate tightened by three bolts. The length of the rod from the blanking cap could be adjusted by releasing pressure on the cover plate and sliding the rod in either direction. The assembly was inserted from either the top or bottom of the furnace and bolted securely in place to the end cap.

### 5.3.2 Vertical Temperature Profile

While the furnace was held stable at a constant temperature the thermocouple was gradually inserted into the furnace in 2 cm increments and the temperature recorded after 5 minutes of stabilisation time. Within 20 cm of the “hot spot” the thermocouple was adjusted in 1 cm increments. For all measurements the ends of the furnace were closed to ensure convection currents were minimised. Vertical profiles were recorded at three temperatures, 1200, 1400, and 1600°C. At 1200°C the profile was also recorded from the bottom end of the furnace and aligns nicely with the one taken from the top. The profiles at all three temperatures show a wide “hot spot” at least 10 cm in height, becoming broader (up to 15 cm) at higher temperatures. For all experiments performed with this furnace the length of the crucible pedestal was chosen to ensure the crucible was held in the middle of this “hot spot”.



Figure 5.10—Stirring Furnace Vertical Temperature Profiles



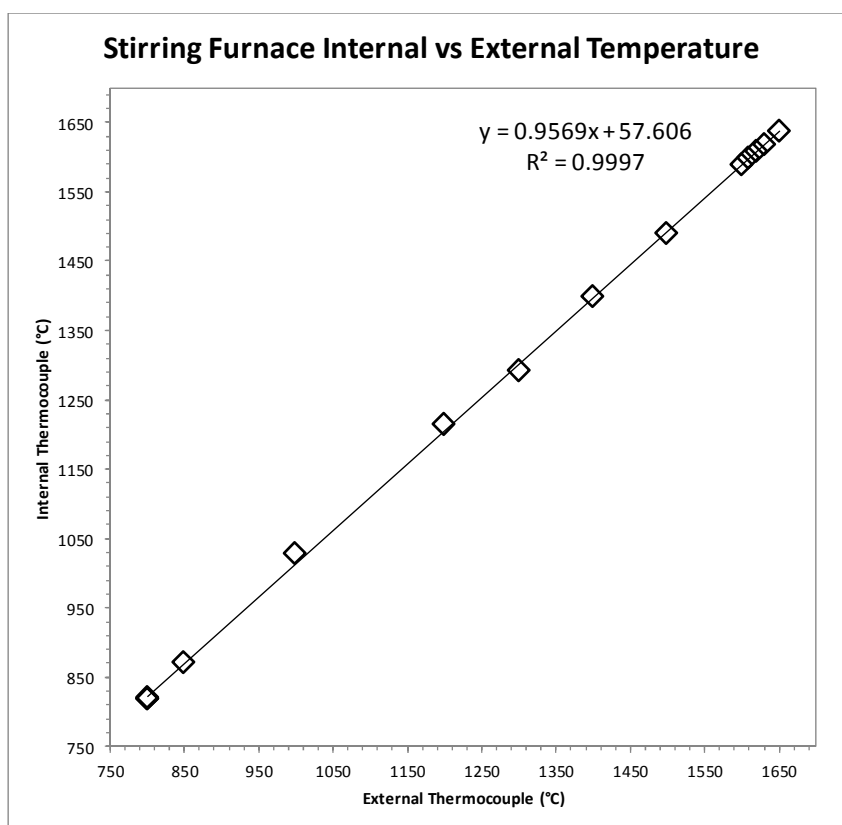
The vertical temperature profile inside the furnace tube was measured using a Type-B thermocouple at three separate temperatures. A profile was also taken from below at one temperature. All temperatures show a broad zone of constant temperature approximately 10 cm in height. All stirring furnace experiments were designed to place the crucible in the middle of this hot spot.

### 5.3.3 External Thermocouple Calibration

The internal thermocouple was positioned in centre of the furnace “hot spot” while the furnace temperature was incrementally taken from 800°C to 1650°C and back to 800°C again. At intermediate values the temperature was left to stabilise for five minutes and then the readings from the internal and external thermocouples compared. The results are shown in Figure 5.11 below and show extremely good agreement over this substantial temperature range. At lower temperatures the internal thermocouple would tend to over-read and at higher temperatures it would under read. This may have been caused by increased convection through the furnace

body at the higher temperature or a slight difference to the calibration of each thermocouple. To reconcile the difference a linear least-squares regression was performed and a line of best fit determined to have an  $R^2 = 0.9997$ . The crossover temperature was found to be 1337°C. Each of the volatile loss experiments described in the next section were performed at 1300°C and the external thermocouple reading is deemed to be satisfactory and reliable at this temperature.

Figure 5.11—Stirring Furnace Internal Thermocouple vs External Thermocouple



Calibration between the external thermocouple connected to the PID controller, and an independent Type-B thermocouple held inside the furnace hot spot. The two sensors show excellent agreement over the temperature range of interest and the linear regression shows that the two readings are exactly equal at a temperature of 1337°C.

### 5.3.4 Stirrer Length Extension

The vertical distance between the end cap flanges is temperature independent and over the course of an experiment remains constant at 73 cm. Both the stirring rod and the low-purity alumina pedestal experience a significant thermal gradient and will expand towards the centre

of the furnace. Here I estimate the magnitude of the expansion as we wish to maintain only a small 1 to 2mm gap between the inside of the crucible and the bottom of the stirring rod.

The linear expansion coefficient of nickel varies with temperature [Kollie 1977] and shows a steep non-linear increase around the Curie temperature of 628.2 K. For the sake of estimating the expansion of the stirring rod the Curie effect has been ignored and a linear regression ( $N=14$ ,  $R^2=0.98$ ) applied to find an approximation of the expansion coefficient. Based on data from the range 300 to 1473 K the coefficient can be estimated by the expression  $\alpha_{Ni} \approx (0.008T + 10.963) \times 10^{-6} \cdot K^{-1}$  which has been extrapolated here up to 1873 K. A single-pass numerical integration (variable step size 1 to 2 cm) was applied to the top vertical furnace profile at the three temperatures where profiles have been measured. Relative to STP a 39 mm stirrer will expand by 6.0, 7.6, and 9.6 mm at 1200, 1400, and 1600°C, respectively. It is not expected that the expansion will be universally linear with temperature, however a linear regression ( $N=3$ ,  $R^2=0.995$ ) was applied over this narrow temperature range and the length expansion can be reasonably approximated by:

$$\Delta L(1473 \text{ K} \leq T \leq 1873 \text{ K}) = (0.009T - 4.938) \text{ mm.}$$

At 1300°C it has been estimated that the 39 mm nickel stirrer will expand by 6.8 mm relative to STP. This value has been used to plan the experiments in this study.

The linear expansion coefficient of pure alumina is  $7.2 \times 10^{-6} \cdot K^{-1}$ . If we take the temperature profile from the bottom half of the furnace and apply this to a single-pass numerical integration (variable step size 1 to 5 cm) of the expansion coefficient then relative to STP (1 bar, 25°C) a 375 mm pedestal will have expanded by 2.5 mm at 1300°C. This is regarded to be an upper bound since the low purity alumina used for these pedestals is only 60% alumina with the rest assumed to be mullite. The linear expansion coefficient of pure mullite is  $5 \times 10^{-6} \cdot K^{-1}$  which

results in a 375 mm pedestal expanding by 1.7 mm at 1300°C. In practice the true expansion will lie somewhere between these two values and for these experiments a 2 mm expansion of the pedestal has been assumed.

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## 5.4 Volatile Loss Experiments

### 5.4.1 Source Material

A natural basalt (named “EB” in this study) dredged from Reykjanes Ridge, south of Iceland, was crushed in a Fritsch steel-jaw rock crusher before being ground to a fine grey powder using a Tema agate disc mill, both located at the University of Oxford Earth Sciences Department. To ensure a sufficient supply of material for the experiments approximately 500 g of material was crushed. A trace element mixture was designed to target a final composition of  $500 \mu\text{g.g}^{-1}$  per element and was weighed out from reaction grade oxide powders. The trace element mixture was first homogenised with a quarter of the powdered basalt, followed by the remaining quarters in three stages, being thoroughly homogenised under acetone in a large agate mortar following each addition. In total 60 g of the crushed basalt was mixed with 625.5 mg of trace elements. The crushed and doped powder has been named EBT1 in this study.

Figure 5.12—Starting Material “EB”



Natural basalt specimen “EB” dredged from Reykjanes Ridge, south of Iceland. Approximately 500 g of material was crushed, powdered, and doped with trace elements for use as starting mixture “EBT1” in this study.

To determine the major element composition of basalt specimen EB an  $\approx 8 \text{ mm}^3$  chip was held in a platinum wire loop and suspended in a one-atmosphere gas mixing furnace for 30 minutes at 1200, 1225, and 1250°C. The oxygen fugacity was held stable at  $\log(f\text{O}_2) = -10.4$  (approximately FMQ) by a CO–CO<sub>2</sub> mixture of 66 and 134 ml.min<sup>-1</sup> respectively. On removal from the furnace the sample was quenched in ambient air and mounted in acrylic resin, ground and polished using 3 $\mu\text{m}$  and 1 $\mu\text{m}$  diamond paste, and subsequently carbon-coated. They were imaged with an FEI Quanta FEG 650 SEM and analysed using on Oxford X–Max<sup>N</sup> standard-less EDS from Oxford Instruments, located in the Oxford University department of Earth Sciences. All standard-less analysis of basaltic glass material presented in this study has been checked for accuracy against the secondary glass standards GSE–1G, GSD–1G, and GSC–1G [Jochum *et al.* 2005]. Some scattered crystals of olivine and pyroxene are present in the samples melted at 1200°C and 1225°C while none are observed in the 1250°C sample.

**Table 5.1—EB Major Element Composition**

| Temperature                    | 1200°C |       |       | 1225°C |       |       | 1250°C |
|--------------------------------|--------|-------|-------|--------|-------|-------|--------|
| Phase                          | Glass  | Xtal1 | Xtal2 | Glass  | Xtal1 | Xtal2 | Glass  |
| Na <sub>2</sub> O              | 2.01   | 0.00  | 3.01  | 1.97   | 2.79  | 0.00  | 1.98   |
| MgO                            | 9.09   | 45.99 | 0.83  | 9.19   | 0.32  | 45.22 | 8.89   |
| Al <sub>2</sub> O <sub>3</sub> | 15.32  | 0.00  | 29.55 | 15.34  | 31.46 | 0.21  | 15.01  |
| SiO <sub>2</sub>               | 50.73  | 39.99 | 51.39 | 50.39  | 49.66 | 39.56 | 50.45  |
| CaO                            | 12.26  | 0.34  | 14.10 | 12.42  | 15.13 | 0.39  | 12.27  |
| TiO <sub>2</sub>               | 1.02   | 0.00  | 0.00  | 1.00   | 0.00  | 0.00  | 1.08   |
| MnO                            | 0.00   | 0.26  | 0.00  | 0.21   | 0.00  | 0.21  | 0.27   |
| FeOT                           | 9.61   | 13.46 | 1.12  | 9.49   | 0.67  | 14.43 | 10.14  |
| Total                          | 100.0  | 100.0 | 100.0 | 100.0  | 100.0 | 100.0 | 100.1  |

An attempt was made to measure the composition of EBT1 by melting small (0.5 g) piles of EBT1 powder on iron foil in an air filled box furnace at 1300°C. The samples were inserted, left for 3 minutes to flash melt and then removed and quenched in a water bath. This procedure failed to produce a homogenous glass suitable for analysis and was abandoned.

To successfully measure the trace element composition of the mixture EBT1 a portion of sample was melted and quenched to a glass in a high pressure piston cylinder experiment: BaCO<sub>3</sub> sleeve, 1.5GPa, 1500°C, graphite capsule, 5 minute run time. The sample was mounted in acrylic, ground to expose the sample and polished to a fine sheen using 3 and 1µm diamond paste. After carbon coating the sample was analysed for major elements by SEM EDS (as described above) and for trace elements by LA-ICP-MS (see Chapter 3 for an outline of the glass analysis method). The results are presented in Table 5.2 below. This composition is regarded to be a reasonable assessment of the starting composition of this doped basalt.

**Table 5.2—Starting Material EBT1 Composition**

| Oxide                          | Technique | Units              | Composition | $\sigma$ |
|--------------------------------|-----------|--------------------|-------------|----------|
| SiO <sub>2</sub>               | SEM-EDS   | g.g <sup>-1</sup>  | 50.66       | 0.04     |
| TiO <sub>2</sub>               | SEM-EDS   | g.g <sup>-1</sup>  | 0.96        | 0.02     |
| Al <sub>2</sub> O <sub>3</sub> | SEM-EDS   | g.g <sup>-1</sup>  | 15.11       | 0.02     |
| FeO                            | SEM-EDS   | g.g <sup>-1</sup>  | 9.69        | 0.08     |
| MnO                            | SEM-EDS   | g.g <sup>-1</sup>  | 0.20        | 0.02     |
| MgO                            | SEM-EDS   | g.g <sup>-1</sup>  | 8.90        | 0.05     |
| CaO                            | SEM-EDS   | g.g <sup>-1</sup>  | 12.28       | 0.04     |
| Na <sub>2</sub> O              | SEM-EDS   | g.g <sup>-1</sup>  | 1.96        | 0.06     |
| K <sub>2</sub> O               | SEM-EDS   | g.g <sup>-1</sup>  | 0.07        | 0.01     |
| Ag <sub>2</sub> O              | LA-ICP-MS | μg.g <sup>-1</sup> | 353         | 11       |
| Bi <sub>2</sub> O <sub>3</sub> | LA-ICP-MS | μg.g <sup>-1</sup> | 226         | 19       |
| CdO                            | LA-ICP-MS | μg.g <sup>-1</sup> | 405         | 50       |
| Cr <sub>2</sub> O <sub>3</sub> | LA-ICP-MS | μg.g <sup>-1</sup> | 878         | 129      |
| Cu <sub>2</sub> O              | LA-ICP-MS | μg.g <sup>-1</sup> | 349         | 26       |
| Ga <sub>2</sub> O <sub>3</sub> | LA-ICP-MS | μg.g <sup>-1</sup> | 424         | 125      |
| GeO <sub>2</sub>               | LA-ICP-MS | μg.g <sup>-1</sup> | 643         | 176      |
| In <sub>2</sub> O <sub>3</sub> | LA-ICP-MS | μg.g <sup>-1</sup> | 457         | 48       |
| MoO <sub>2</sub>               | LA-ICP-MS | μg.g <sup>-1</sup> | 526         | 54       |
| Ni <sub>2</sub> O              | LA-ICP-MS | μg.g <sup>-1</sup> | 98          | 7        |
| PbO                            | LA-ICP-MS | μg.g <sup>-1</sup> | 489         | 22       |
| Sb <sub>2</sub> O <sub>3</sub> | LA-ICP-MS | μg.g <sup>-1</sup> | 578         | 21       |
| SnO <sub>2</sub>               | LA-ICP-MS | μg.g <sup>-1</sup> | 424         | 8        |
| Tl <sub>2</sub> O              | LA-ICP-MS | μg.g <sup>-1</sup> | 430         | 14       |
| V <sub>2</sub> O <sub>3</sub>  | LA-ICP-MS | μg.g <sup>-1</sup> | 1019        | 113      |
| WO <sub>3</sub>                | LA-ICP-MS | μg.g <sup>-1</sup> | 406         | 65       |
| ZnO                            | LA-ICP-MS | μg.g <sup>-1</sup> | 666         | 16       |
| Total                          |           | g.g <sup>-1</sup>  | 100.66      | 0.43     |

#### 5.4.2 Experiment Preparation

The nickel crucibles were manufactured in-house at the Earth Sciences workshop, and were cleaned with three ultrasonic rinses in deionised (DI) water, clean ethanol, and finally DI water again. They were dried thoroughly and stored in a clean container until use. Two crucibles were analysed for trace elements by LA-ICP-MS (internal standard <sup>61</sup>Ni, 40 μm spot, 10 Hz, 180 μm



scan,  $N=12$ , GSE-1G primary calibration standard) and the composition is shown in Table 5.3 below. All trace elements of interest are at least two orders of magnitude lower in the crucible material than they are in the starting mixture (see Table 5.2). The only exception is Cu which is one order of magnitude less abundant in the crucible than in the starting mixture.

**Table 5.3—Nickel Crucible Trace Element Composition**

| Element | $\mu\text{g.g}^{-1}$ | $\sigma$ |
|---------|----------------------|----------|
| Al      | 32                   | 8.0      |
| Ag      | 0.36                 | 0.18     |
| Bi      | 1.3                  | 0.69     |
| Ca      | < 1913               |          |
| Cd      | < 1.4                |          |
| Cr      | < 16                 |          |
| Cu      | 33                   | 2.8      |
| Fe      | 723                  | 244      |
| Ga      | 0.92                 | 0.45     |
| Ge      | < 6.8                |          |
| In      | 0.45                 | 0.24     |
| Mo      | 1.9                  | 0.2      |
| Pb      | 2.6                  | 0.15     |
| Sb      | 1.2                  | 0.13     |
| Si      | < 1652               |          |
| Sn      | 0.56                 | 0.16     |
| Tl      | 0.14                 | 0.15     |
| V       | < 1.14               |          |
| W       | 0.37                 | 0.15     |
| Zn      | < 3.5                |          |

*Plus nickel to 100% (w/w)*

The powdered starting mixture EBT1 was stored in a vacuum desiccator throughout the project. To prepare an experiment 3g of material was weighed out and pressed into a 1cm diameter pellet with 10 ton of force ( $9.8 \times 10^4 \text{ N}$ ) on a workshop press. The crucible was inserted into the crucible holder and the holder deformed with a hammer to secure the crucible. The crucible and holder were then wired to a low-purity alumina pedestal using nickel wire. The pedestal was inserted slowly into the furnace from below and then keyed onto the trap door

as the trap door was closed and secured. The stirrer was inserted into the melt over a 60 s timespan and the experimental run-time commenced with the sealing of the furnace that this afforded. The stirring mechanism was brought up to speed over 60 s and left at constant RPM for the duration of the experiment. The CO–CO<sub>2</sub> gas flows were held constant throughout the experiment.

### 5.4.3 Quenching

To quench, the stirring mechanism was first stopped, the MFCs turned off and the trap door opened. The pedestal, crucible holder, and crucible would then fall freely out of the furnace and into a metal bucket of water.

The low-purity alumina pedestal would break on quenching and was discarded after each run. The pedestal tubing cost less than £10 per experiment. The crucible was easily recovered and after mounting in epoxy resin a transverse section was made by sectioning the sample with a diamond-tipped saw. One half of the sample was re-mounted, ground, and polished flat using first 3 then 1µm diamond paste. Due to the large volume of sample and prevalence of cracks and voids, some backfilling with epoxy was required.

### 5.4.4 Oxygen Fugacity

The oxygen fugacity ( $f_{\text{O}_2}$ ) of the experiments was controlled using a constant CO–CO<sub>2</sub> gas mixture, apportioned according to the table in Deines *et al.* 1976. Verification of the oxygen fugacity was performed before and after each experiment using a solid zirconia potentiometric oxygen sensor [Ramamoorthy *et al.* 2003]. The zirconia electrochemical cell produces a voltage proportional to the difference in the chemical potential of oxygen on either side of the sensor. Measuring this voltage allows the oxygen fugacity to be computed with the expression (from the

Nernst equation, where:  $E$  = emf,  $R$  = gas constant,  $T$  = temperature,  $n$  = number of charges per reactant species,  $F$  = Faraday's constant,  $p$  = partial pressure):

$$E = \frac{RT}{nF} \ln \left( \frac{pO_2}{pO'_2} \right)$$

When using clean dry air as the reference gas then this equation simplifies to:

$$pO_2 = -0.209e^{\left(-46.421\frac{E}{T}\right)}$$

The sensor voltage (typically 0 to 1200 mV) was measured using a high-precision digital voltmeter<sup>28</sup>. No experiments were conducted where the fugacity measurements varied significantly from the expected values, indicating that the MFCs were functioning correctly and there were no leaks in the furnace.

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<sup>28</sup> Tektronix DMM4020, 10  $\mu$ V resolution, 0.015% accuracy (1 yr.)  
<http://www.tek.com/datasheet/dmm4020-digital-multimeter/> (2016)

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## 5.5 Results

Experiments were performed at 1300°C and a range of oxygen fugacity values from  $\log(f\text{O}_2)$  of  $-7$  to  $-13$ . The experiment temperature was chosen as an approximate lower bound to the melting temperature of basalt at one atmosphere pressure. It is expected that higher temperatures would result in faster volatile loss. The oxygen fugacity range was chosen to cover a range of conditions relevant to planetary formation [Richter and Drake 1996; Wade and Wood 2005], from just below the Ni–NiO buffer, characteristic of the modern mantle [Wood *et al.* 1990] down to a value 2.3 log units below the Fe–FeO buffer. The latter value corresponds to the case of molten peridotitic mantle in equilibrium with Fe and hence simulates conditions during core formation.

In total 19 stirring furnace experiments were attempted, while ten ran to completion and quenched successfully. Not counting the initial five experiments which were required for furnace commissioning, the experimental success rate was 70%. The successful experiments are listed here in Table 5.4, while a complete list of experiments and outcomes has been included in the Appendix.

**Table 5.4—Stirring Furnace Experiment List**

| Experiment | Date       | Sample | Wetted Material | Temp (°C) | Run Time (min) | $\log(f\text{O}_2)$ |
|------------|------------|--------|-----------------|-----------|----------------|---------------------|
| F006       | 10/11/2015 | EBT1   | nickel          | 1300      | 10             | $-7$                |
| F007       | 11/11/2015 | EBT1   | nickel          | 1300      | 30             | $-7$                |
| F008       | 13/11/2015 | EBT1   | nickel          | 1300      | 60             | $-7$                |
| F010       | 24/01/2015 | EBT1   | nickel          | 1300      | 180            | $-7$                |
| F012       | 26/11/2015 | EBT1   | nickel          | 1300      | 5              | $-9$                |
| F013       | 26/11/2015 | EBT1   | nickel          | 1300      | 30             | $-9$                |
| F014       | 27/11/2015 | EBT1   | nickel          | 1300      | 60             | $-9$                |
| F015       | 11/12/2015 | EBT1   | nickel          | 1300      | 30             | $-11$               |
| F018       | 23/12/2015 | EBT1   | nickel          | 1300      | 60             | $-11$               |
| F019       | 04/02/2015 | EBT1   | nickel          | 1300      | 60             | $-13$               |

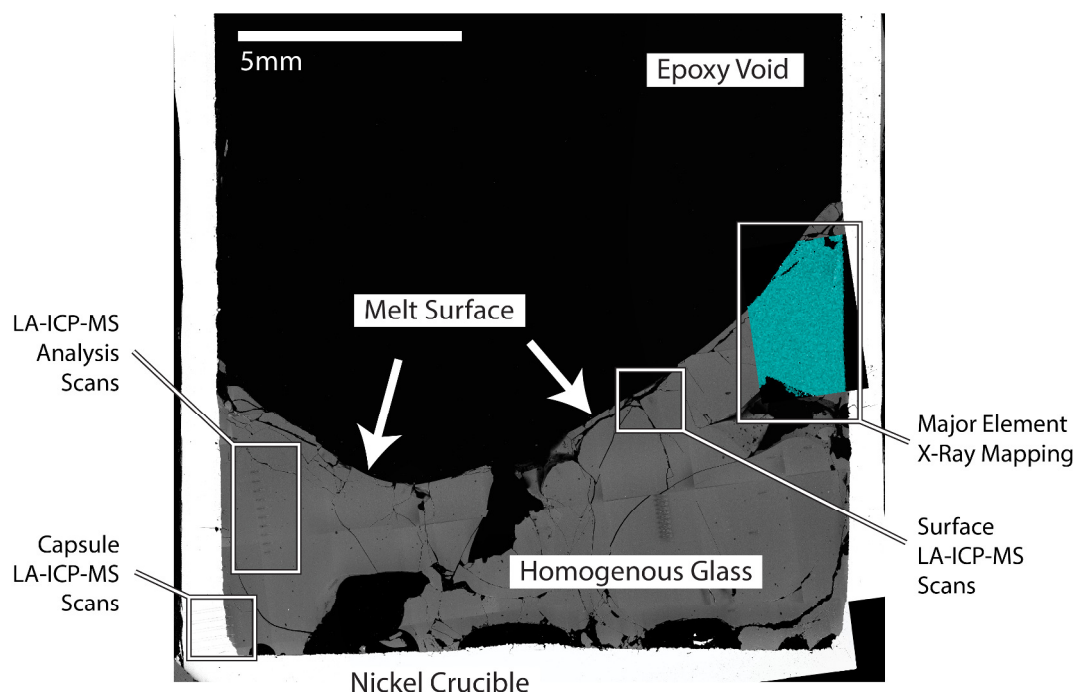
### 5.5.1 Analysis and Homogeneity Assessment

All experiments presented as a mass of homogenous black glass containing no observable gas bubbles. The volume of glass remaining in each crucible did vary, most likely due to variable

degrees of splashing and wetting between the melt and the nickel stirrer and crucible. Despite this, all experiments produced a copious volume of glass for analysis.

Figure 5.13—Typical Volatile Loss Experiment Sample

F008, EBT1, 1hr, 1573K,  $\log(fO_2) = -7$ , BSE Mosaic Image



A composite mosaic of SEM BSE images showing the quenched run product from experiment F008 in its entirety. The bright material around the sides and bottom of the Figure is the nickel capsule. The sample was investigated using both SEM and LA-ICP-MS for homogeneity as well as depletion profiles at the surface of the glass, and between the glass and the nickel crucible. Major Element Homogeneity

Samples were imaged and analysed by SEM to determine the major element homogeneity. All experiments showed uniform major element composition to within the limits of the standard-less SEM EDS. Across all stirring furnace experiments the only change in major element composition was a variation in nickel saturation of the melt, ranging from 0.2 to 2.3 g.g<sup>-1</sup> Ni<sub>2</sub>O. By normalising away the variable Ni<sub>2</sub>O content of the melt the average composition and variance of all the experiment compositions could be compared. As expected very little variation was observed, and the results are shown in Table 5.5 below.

**Table 5.5—Major Element Composition of all Volatile Loss Experimental Glasses**

| Element                        | Mean   | $\sigma$ | RSD% |
|--------------------------------|--------|----------|------|
| SiO <sub>2</sub>               | 51.00  | 0.25     | 1.0  |
| TiO <sub>2</sub>               | 0.99   | 0.03     | 5.1  |
| Al <sub>2</sub> O <sub>3</sub> | 15.32  | 0.10     | 1.3  |
| FeO                            | 9.35   | 0.22     | 4.6  |
| MnO                            | 0.26   | 0.05     | 39.1 |
| MgO                            | 8.71   | 0.12     | 2.8  |
| CaO                            | 12.41  | 0.13     | 2.1  |
| Na <sub>2</sub> O              | 1.83   | 0.11     | 12.1 |
| K <sub>2</sub> O               | 0.12   | 0.02     | 32.3 |
| Total                          | 100.08 | 1.02     | 2.0  |

Variable Ni<sub>2</sub>O content has been normalised away;  
Num. Points=106; Num. Experiments=9

### 5.5.2 Trace Element Homogeneity

To measure the trace element composition of the melt, LA-ICP-MS was used to sample the exposed glass surface. The LA-ICP-MS analytical method has been outlined in Chapter 2. Scans were made at random locations scattered across the exposed surface of the glass and the results show excellent trace element homogeneity. For some experiments nickel blebs had formed and were inadvertently sampled by the laser. Any signals from nickel blebs were discarded in the analysis.

Trace element compositions are shown in Table 5.6 below.

**Table 5.6—Volatile Loss Experiments Trace Element Compositions**

| Experiment | Ag  | Ag (o) | Bi  | Bi (o) | Cd  | Cd (o) | Cr  | Cr (o) | Cu  | Cu (o) | Ga  | Ga (o) | Ge  | Ge (o) | In  | In (o) |
|------------|-----|--------|-----|--------|-----|--------|-----|--------|-----|--------|-----|--------|-----|--------|-----|--------|
| F006       | 304 | 46     | 107 | 14     | 158 | 36     | 492 | 57     | 288 | 32     | 419 | 15     | 241 | 26     | 338 | 11     |
| F007       | 223 | 54     | 49  | 21     | 91  | 41     | 539 | 60     | 242 | 48     | 414 | 15     | 145 | 51     | 302 | 18     |
| F008       | 210 | 38     | 46  | 16     | 80  | 17     | 606 | 58     | 189 | 17     | 453 | 19     | 139 | 12     | 305 | 15     |
| F010       | 13  | 1.2    | 2.3 | 0.3    | 0.8 | 0.1    | 698 | 27     | 31  | 3.4    | 431 | 21     | 11  | 3.5    | 183 | 7.4    |
| F012       | 298 | 9      | 48  | 4      | 91  | 4.0    | 446 | 14     | 339 | 11     | 380 | 41     | 147 | 24     | 385 | 12     |
| F013       | 247 | 17     | 71  | 19     | 134 | 12     | 574 | 23     | 257 | 16     | 427 | 10     | 226 | 14     | 307 | 11     |
| F014       | 65  | 5.0    | 34  | 15     | 25  | 4.0    | 711 | 20     | 102 | 5.3    | 381 | 15     | 74  | 8.5    | 234 | 13     |
| F015       | 163 | 61     | 73  | 31     | 96  | 26     | 591 | 49     | 192 | 63     | 355 | 108    | 189 | 41     | 238 | 23     |
| F018       | 41  | 2.0    | 15  | 0.8    | 6.5 | 0.5    | 589 | 18     | 112 | 3.7    | 407 | 11     | 20  | 1.9    | 231 | 7.2    |
| F019       | 13  | 1.4    | 2.9 | 0.7    | 7.7 | 1.0    | 600 | 31     | 95  | 5.1    | 308 | 19     | 6.1 | 1.6    | 123 | 6.5    |

| Experiment | Mo  | Mo (o) | Pb  | Pb (o) | Sb  | Sb (o) | Sn  | Sn (o) | Tl  | Tl (o) | V   | V (o) | W   | W (o) | Zn  | Zn (o) |
|------------|-----|--------|-----|--------|-----|--------|-----|--------|-----|--------|-----|-------|-----|-------|-----|--------|
| F006       | 478 | 13     | 486 | 23     | 333 | 30     | 216 | 11     | 261 | 18     | 804 | 26    | 711 | 28    | 555 | 23     |
| F007       | 481 | 15     | 441 | 71     | 223 | 85     | 164 | 25     | 185 | 50     | 805 | 18    | 724 | 25    | 511 | 55     |
| F008       | 491 | 25     | 462 | 33     | 218 | 39     | 155 | 10     | 215 | 20     | 834 | 29    | 797 | 35    | 549 | 34     |
| F010       | 568 | 26     | 150 | 18     | 11  | 6.7    | 57  | 6.4    | 27  | 3.6    | 931 | 24    | 968 | 31    | 308 | 23     |
| F012       | 477 | 27     | 896 | 36     | 255 | 34     | 111 | 12     | 360 | 8.3    | 747 | 45    | 455 | 53    | 759 | 37     |
| F013       | 509 | 17     | 477 | 20     | 305 | 33     | 166 | 8.2    | 277 | 12     | 859 | 20    | 778 | 23    | 605 | 32     |
| F014       | 457 | 14     | 291 | 28     | 101 | 34     | 64  | 5.5    | 163 | 15     | 843 | 21    | 749 | 24    | 328 | 27     |
| F015       | 441 | 113    | 426 | 55     | 206 | 95     | 113 | 11     | 237 | 63     | 788 | 255   | 793 | 69    | 454 | 50     |
| F018       | 438 | 12     | 163 | 6.7    | 5.7 | 0.4    | 66  | 2.7    | 51  | 2.1    | 803 | 21    | 703 | 25    | 257 | 9.2    |
| F019       | 372 | 11     | 96  | 8.9    | 1.2 | 0.3    | 24  | 2.6    | 51  | 4.3    | 776 | 13    | 693 | 17    | 105 | 11     |

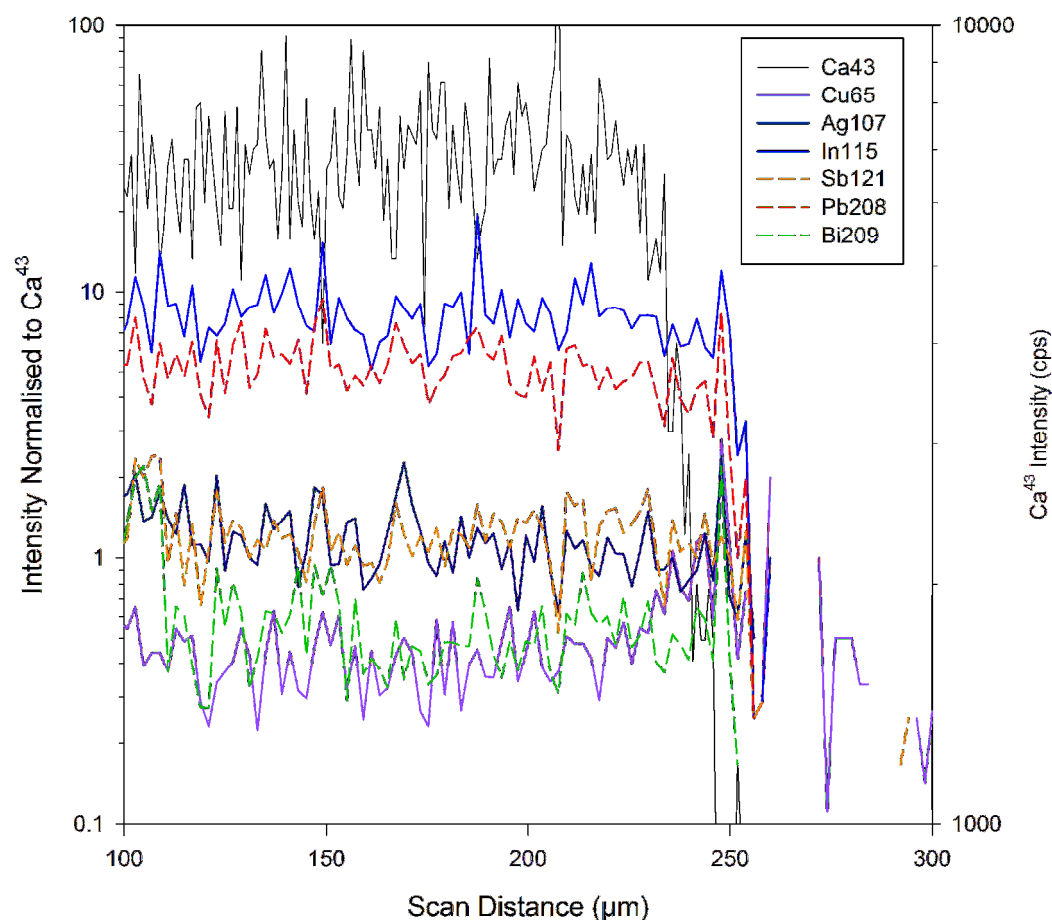
All concentrations in  $\mu\text{g.g}^{-1}$ 

### 5.5.3 Surface Scans

Using scanning mode LA-ICP-MS tracks were ablated perpendicular to the accessible surface of the glass. With a 40  $\mu\text{m}$  spot and scanning over 200  $\mu\text{m}$  it was possible to detect qualitative changes to the trace element composition. While masses for all elements were collected, a scan of the most volatile elements is shown in Figure 5.14 below. There is no observable change in the composition of any trace elements at the surface of the melt, suggesting that the stirring mechanism worked as designed and provided a continual turnover of material throughout the experiment.

Figure 5.14—Typical Laser Ablation Scan at Glass Surface

213nm, 5Hz, 40 $\mu$ m Spot, 3 $\mu$ m/s, 4J/cm<sup>2</sup>



A LA-ICP-MS scan on sample F008 perpendicular to the exposed surface of the glass. The signals shown are for the most volatile elements in this study, none of which show a diffusion profile. This suggests that the stirring mechanism worked as expected and maintained a continual turnover of material during the experiment.

#### 5.5.4 Capsule Scans

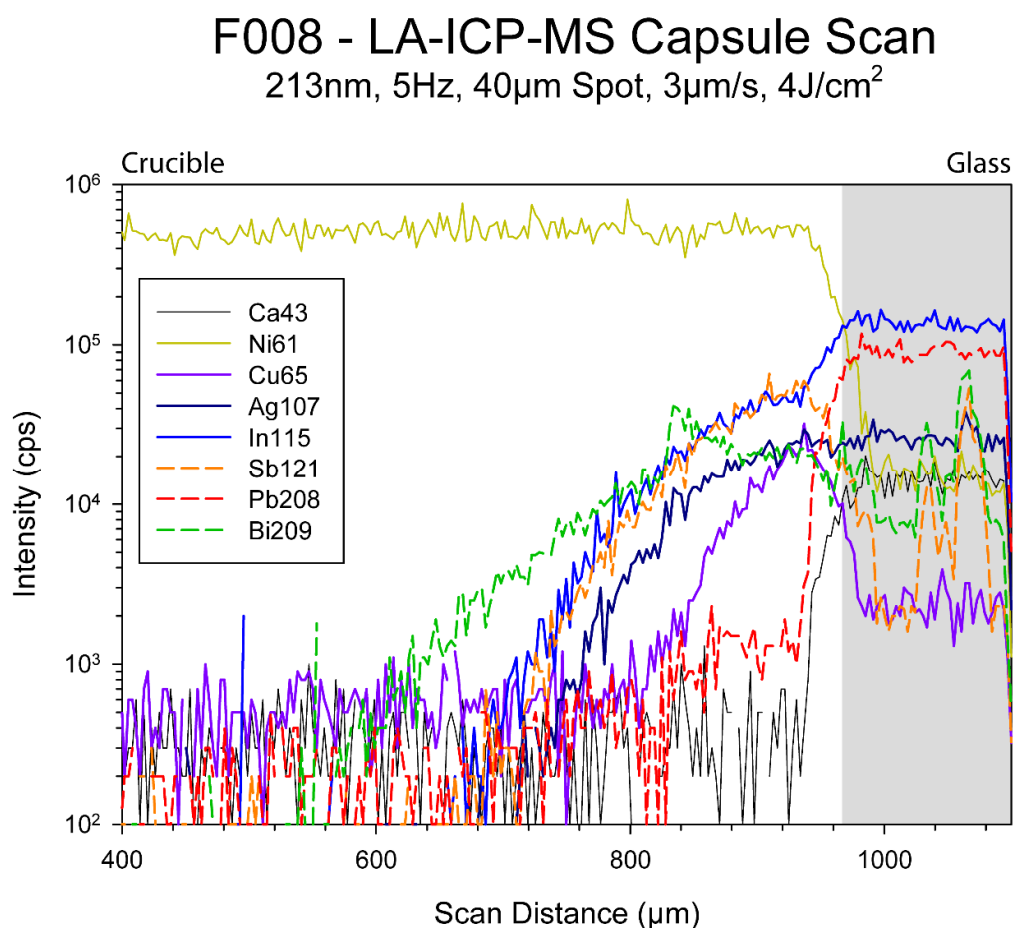
As well as migrating into the melt, the capsule material dissolved some elements. To assess the magnitude of this loss a number of LA-ICP-MS scans were performed from the glass into the neighbouring crucible. These scans show a small diffusion profile for some elements, extending up to a maximum distance of 200  $\mu$ m into the crucible. A representative scan is shown in Figure 5.15 below. The effect of this diffusion will be to artificially enhance the perceived volatile loss of those elements. An estimate has been made to gauge the scale of this effect: a 200  $\mu$ m “rind”



on the inside of the crucible can only equate to no more than 5% of the volume of the melt. As such diffusion into the capsule material can be neglected in these experiments.

The capsule trace element composition is shown in Table 5.3 above and all trace elements are significantly less abundant in the capsule than they are in the melt.

Figure 5.15—Typical Laser Ablation Scan at Glass–Crucible Interface



A LA–ICP–MS scan on sample F008 perpendicular to interface between the crucible and the quenched glass. Some elements have formed a thin diffusion profile into the crucible material. The estimated volume of this *ring* is no more than 5% of the melt volume and has not significantly affected the results from this study.

### 5.5.5 Time Series Results

Over the duration of each experiment volatile elements partition into the gas phase and are flushed from the furnace by the constant stream of CO and CO<sub>2</sub> gas. In this environment a

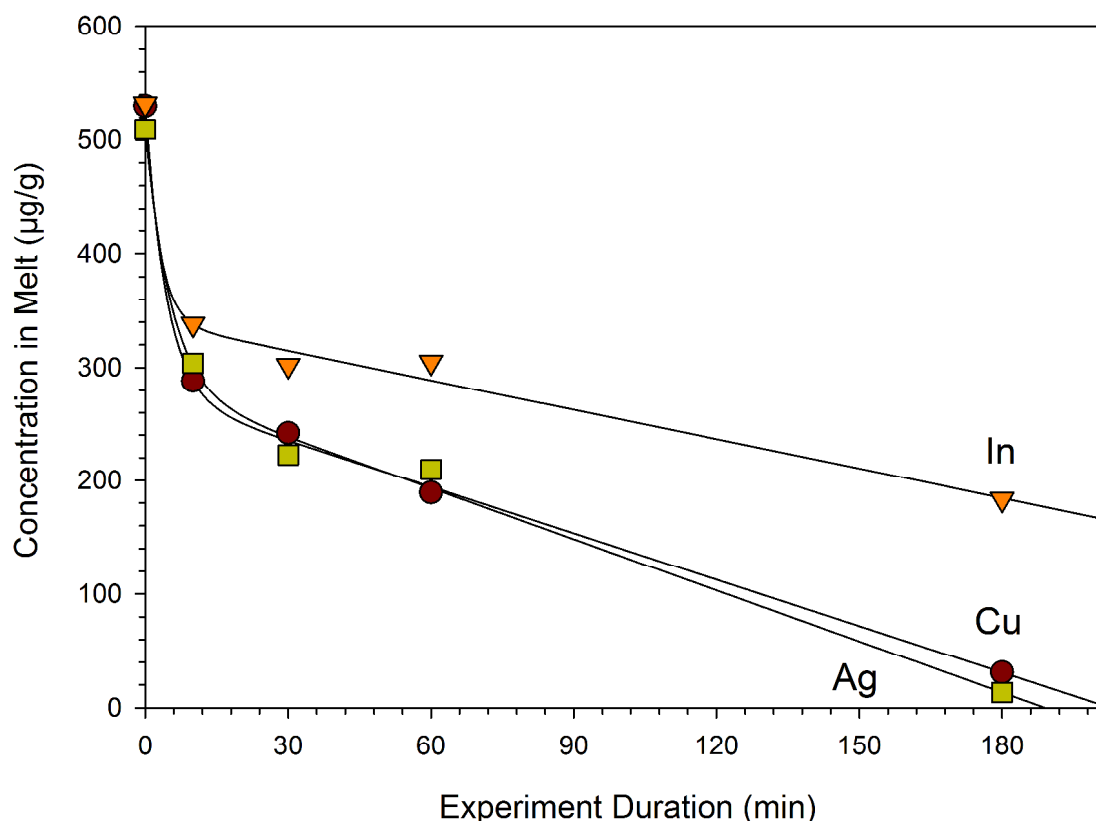
crucible of static viscous melt would form a diffusion profile at the melt surface, as volatile elements transition into the gas phase, and most significantly different elements will show different rates of diffusion from the melt. As such, measuring volatile loss from a static crucible results in a combined measurement of volatility and diffusion rates, which was not the purpose of this study.

For these volatile loss experiments the surface of the melt is continuously replenished by the stirring mechanism and the diffusion of the element can be neglected. The longer the duration of the experiment the more of each element that is lost to the vapour phase. As can be seen in Figure 5.16 the relative orders of the loss do not change significantly over the range of experiment durations assessed. In addition, the stirring mechanism has resulted in the formation of extremely (to within the limit of LA-ICP-MS analysis, approximately 10%) homogenous glasses.

The rapid loss of some elements in the first 5-10 minutes of the experiment is believed to be due to the initially unconstrained oxygen fugacity inside the furnace. The furnace only becomes sealed once the stirrer is inserted. With a total gas flow of  $300 \text{ mL}\cdot\text{min}^{-1}$  it will take five minutes for the initial purge of the 1.5 L furnace tube

Figure 5.16—Time Series of Volatile Loss: Ag, Cu, and In

Trace Mixture EBT1, 1573K, Stirred Crucible, Water Quench



Results from four volatile loss experiments, all performed at  $\log(fO_2)=-7$  for the three trace elements In, Cu, and Ag. The lines are not considered to follow any physical law, and comprise a combined exponential and linear curve regressed to the points so as to guide the eye. Significantly: the relative degrees of volatile loss for Cu and In do not alter over time; In is less volatile than Cu; and, Cu and Ag show a similar degree of volatility. Analysis 1-sigma error bars are smaller than the markers, while total relative uncertainty is regarded to be 10%.

## 5.5.6 Introducing the Volatility Factor

To quantify the volatile loss from the silicate melt we define the “volatility factor” ( $F_M$ ) of trace element  $M$  to be the final concentration of the trace element divided by the initial concentration in the starting mixture. All volatility factor values presented in this study will be based on experiments of 60 minute duration. Smaller values of the volatility factor equate to greater volatility of that trace element.

$$F_M = \frac{X_{MO_{\eta/2}}^{\text{final}}}{X_{MO_{\eta/2}}^{\text{initial}}} \quad (\text{Equation 5.1})$$

The volatility factor defined by Equation 5.1 is used throughout this study. Note that the concentration values are expressed as mole fraction single cation oxide so as to evaluate the number of atoms lost to the vapour phase. Tabulated volatility factor values for the experiments of 60 minute duration are presented in Table 5.7 below.

**Table 5.7—Computed Volatility Factors (60 Minute Experiments)**

| log( <i>f</i> O <sub>2</sub> ) | Ag    | σ     | Bi    | σ     | Cd    | σ     | Cr    | σ     | Cu    | σ     | Ga    | σ     | Ge    | σ     | In    | σ     |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| -7                             | 0.646 | 0.117 | 0.227 | 0.080 | 0.228 | 0.057 | 1.021 | 0.179 | 0.618 | 0.072 | 1.454 | 0.432 | 0.315 | 0.090 | 0.816 | 0.095 |
| -9                             | 0.198 | 0.017 | 0.170 | 0.078 | 0.071 | 0.014 | 1.192 | 0.179 | 0.331 | 0.030 | 1.217 | 0.361 | 0.168 | 0.050 | 0.622 | 0.074 |
| -11                            | 0.127 | 0.007 | 0.074 | 0.007 | 0.019 | 0.003 | 0.998 | 0.150 | 0.367 | 0.030 | 1.314 | 0.388 | 0.045 | 0.013 | 0.621 | 0.068 |
| -13                            | 0.022 | 0.019 | 0.008 | 0.007 | 0.019 | 0.009 | 1.171 | 0.265 | 0.176 | 0.138 | 0.669 | 0.380 | 0.014 | 0.005 | 0.192 | 0.142 |

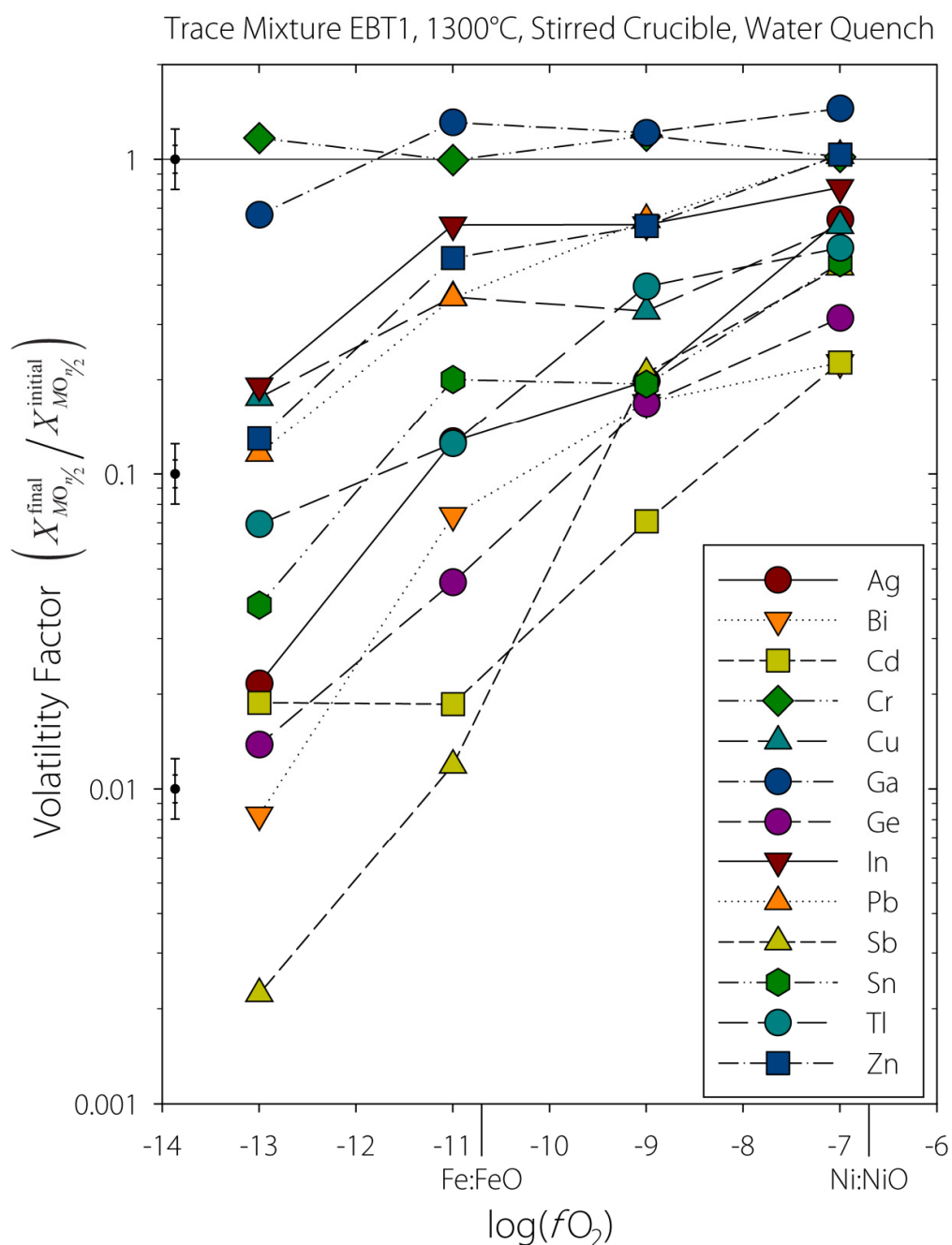
  

| log( <i>f</i> O <sub>2</sub> ) | Mo    | σ     | Pb    | σ     | Sb    | σ     | Sn    | σ     | Tl    | σ     | V     | σ     | W     | σ     | Zn    | σ     |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| -7                             | 1.260 | 0.144 | 1.030 | 0.087 | 0.457 | 0.084 | 0.471 | 0.031 | 0.525 | 0.052 | 1.219 | 0.141 | 2.508 | 0.416 | 1.038 | 0.069 |
| -9                             | 1.168 | 0.125 | 0.646 | 0.069 | 0.210 | 0.071 | 0.194 | 0.017 | 0.397 | 0.040 | 1.226 | 0.139 | 2.347 | 0.383 | 0.617 | 0.053 |
| -11                            | 1.130 | 0.120 | 0.365 | 0.022 | 0.012 | 0.001 | 0.201 | 0.009 | 0.125 | 0.007 | 1.179 | 0.134 | 2.223 | 0.365 | 0.488 | 0.021 |
| -13                            | 0.624 | 0.349 | 0.116 | 0.099 | 0.002 | 0.001 | 0.038 | 0.035 | 0.069 | 0.057 | 1.112 | 0.125 | 1.975 | 0.405 | 0.130 | 0.087 |

### 5.5.7 Variation in Volatility Factor with Oxygen Fugacity

The volatility factors of each trace element have been plotted against the oxygen fugacity of the experiment, as shown in Figure 5.17 below. There is a clear increase in volatility across all masses with decreasing oxygen fugacity. Some of the refractory elements have plotted above a value of 1, which is clearly non-physical based on the definition of the volatility factor. Careful review shows that the refractory elements chromium, vanadium, and molybdenum have mostly remained at constant composition and are actually all within error of the starting composition. The elevated value for tungsten is most likely due to contamination from the tungsten-rich tool steel used to machine the nickel crucibles. Most intriguing is the result for gallium which essentially shows no volatile loss, placing it at a similar level of volatility as the refractory metals.

Figure 5.17—Volatility Factor vs Oxygen Fugacity



Volatility factors (taken at 60 minutes) for all elements plotted over the range of oxygen fugacity values from this study. All of the elements show increased volatility at lower oxygen fugacity, but the relative order of the elements changes, as illustrated by Cd and Sb. Analytical errors (1SD) are less than 10% (inner mark of representative error bars, drawn at LHS) but some elements show variation up to 20% (total mark), especially at lower abundance.

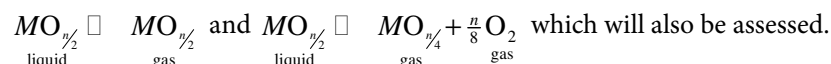
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## 5.6 Calculating Volatile Element Vapour Pressure

Consider a liquid trace element oxide in equilibrium with a gaseous phase at some oxygen fugacity:



It is possible to write  $K_f$  for this expression and to use known thermochemical data to compute the partial pressure of the elemental gas phase in equilibrium with the molten oxide phase. Some elements also form additional stable gaseous oxides with equilibria such as



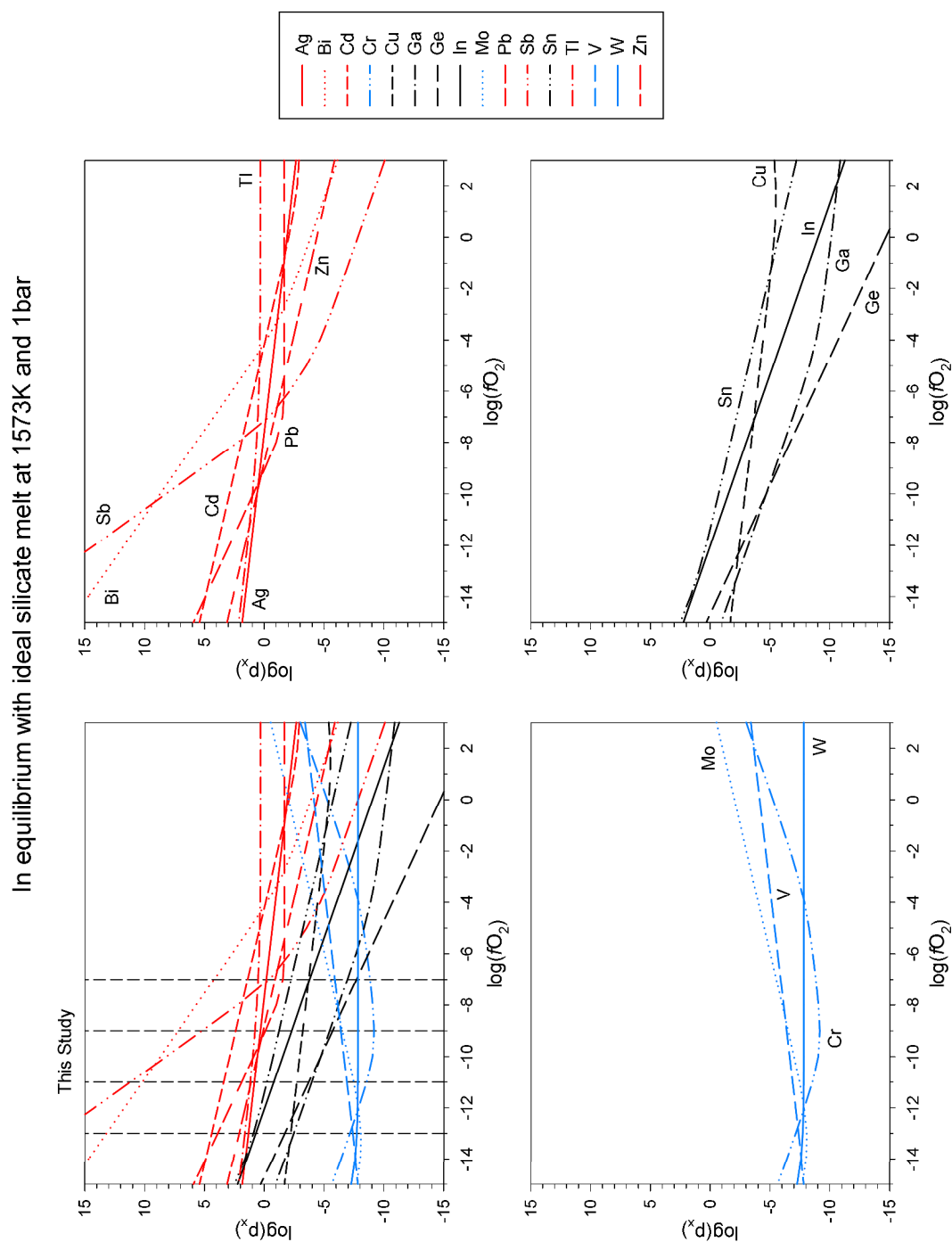
All initial calculations assume ideal behaviour in the molten liquid phase. The computed partial pressures of all gas phases for each trace element have been plotted against oxygen fugacity in Figure 5.18 below. This figure shows, for each element of interest, the total number of atoms in all gas species relative to each atom in the liquid state. Some elements, such as antimony, form many stable gas species (such as Sb, Sb<sub>2</sub>, Sb<sub>4</sub>,) and in this case the gas pressure is the sum of the partial pressures of all stable gas phases. The gas species considered in this study are shown in Table 5.8.

Visible kinks in pressure, seen in some of the plots in Figure 5.18, reflect the changing stabilisation of various gas species with respect to the change in oxygen fugacity. It is common for most of these trace elements to form stable oxide gases at high oxygen fugacity values, and it must be noted that the upper limit to these charts is an entirely unreasonable pressure of three atmospheres of oxygen.

**Table 5.8—Gas Species Present in Computed Total Pressures**

| Element | Elemental Gas Species                 | Oxide Gas Species                        |
|---------|---------------------------------------|------------------------------------------|
| Ag      | Ag                                    |                                          |
| Bi      | Bi, Bi <sub>2</sub>                   |                                          |
| Cd      | Cd                                    | CdO                                      |
| Cr      | Cr                                    | CrO, CrO <sub>2</sub> , CrO <sub>3</sub> |
| Cu      | Cu                                    | CuO                                      |
| Ga      | Ga                                    | GaO                                      |
| Ge      | Ge                                    | GeO                                      |
| In      | In                                    |                                          |
| Mo      | Mo                                    | MoO, MoO <sub>2</sub> , MoO <sub>3</sub> |
| Pb      | Pb, Pb <sub>2</sub>                   | PbO                                      |
| Sb      | Sb, Sb <sub>2</sub> , Sb <sub>4</sub> |                                          |
| Sn      | Sn                                    | SnO                                      |
| Tl      | Tl                                    | Tl <sub>2</sub> O, TlO                   |
| V       | V                                     | VO, VO <sub>2</sub>                      |
| W       | W                                     | WO, WO <sub>2</sub> , WO <sub>3</sub>    |
| Zn      | Zn                                    |                                          |

Figure 5.18—Total Partial Pressure of Trace Element Gases



The total number of atoms in all gas species in equilibrium with ideal silicate melt, plotted at a range of oxygen fugacity values. The total pressure is considered to be a proxy for volatile loss. The elements have been divided into three groups that approximately align with the degree of their volatility.



### 5.6.1 Correction for Non-Ideality Using Activity Coefficients

The previous calculations of gas partial pressure are based on the assumption of ideal behaviour in the silicate melt. Applying the activity coefficient models from Chapter 4 to the major element composition of starting mixture EB gives the activity coefficients tabulated in Table 5.9 below.

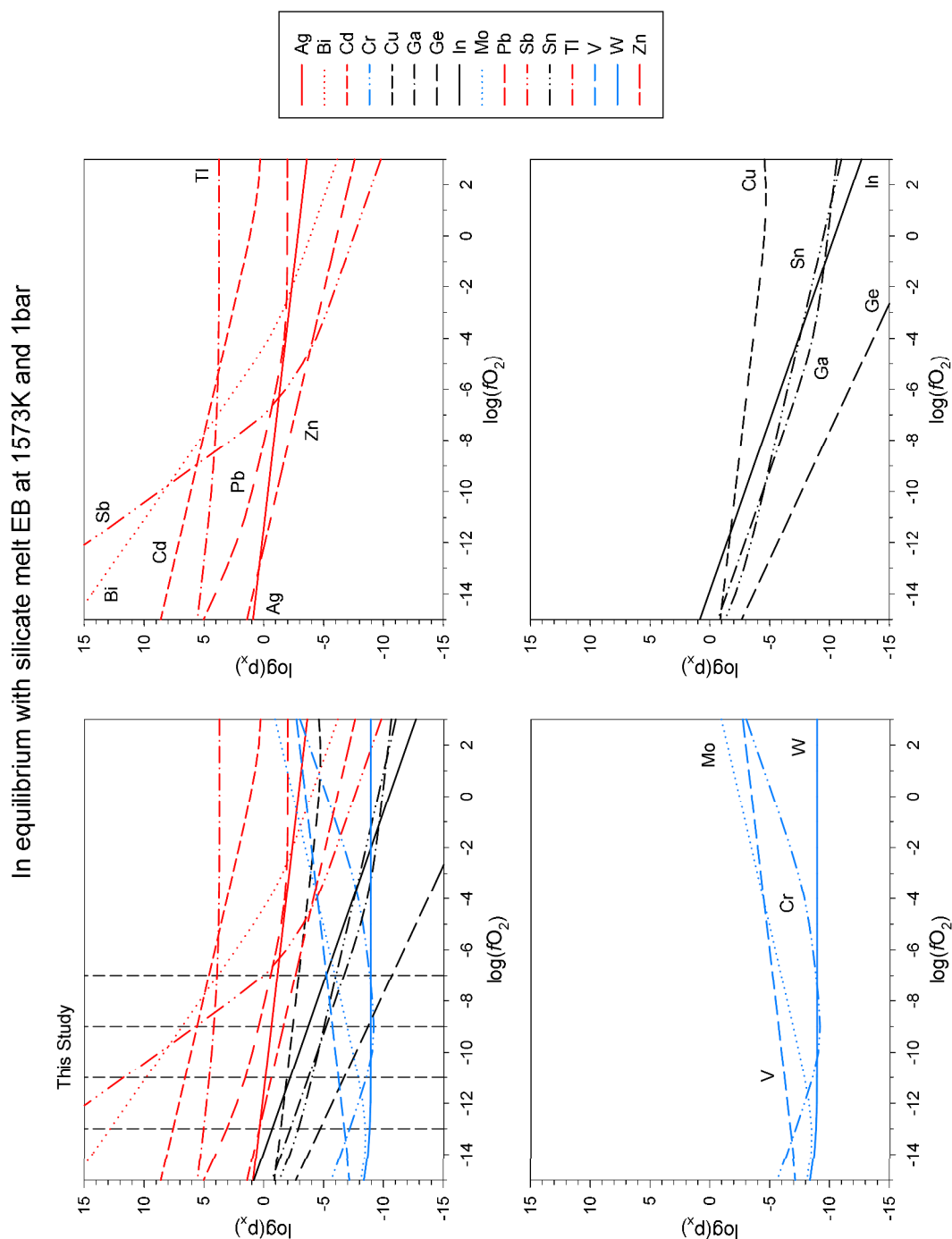
**Table 5.9—Activity Coefficients from Models at EB Composition**

| Element         | $\gamma$ | StdErr  |
|-----------------|----------|---------|
| Ag              | 0.11     | 0.023   |
| Bi              | 0.95     | 0.18    |
| Cd              | 1561     | 206     |
| Cr <sup>a</sup> | 1        |         |
| Cu              | 6.33     | 0.86    |
| Ga              | 1.82     | 0.53    |
| Ge              | 0.0010   | 0.0010  |
| In              | 0.039    | 0.0085  |
| Mo              | 0.39     | 0.44    |
| Pb              | 0.50     | 0.11    |
| Sb <sup>b</sup> | 1.90     | 0.43    |
| Sn              | 0.00016  | 0.00036 |
| Tl              | 2535     | 146     |
| V               | 4.8      | 0.32    |
| W               | 0.080    | 0.033   |
| Zn              | 0.019    | 0.010   |

<sup>a</sup>The model for chromium is not valid for this composition. <sup>b</sup>No model for antimony was found, the value here is the mean of all measured values.

Applying the activity coefficients from Table 5.8 to the liquid–gas equilibria introduced in the previous section results in adjusted partial pressures for each gas. These are then plotted for all elements in Figure 5.19 below.

Figure 5.19—Total Partial Pressure for Trace Element Gases

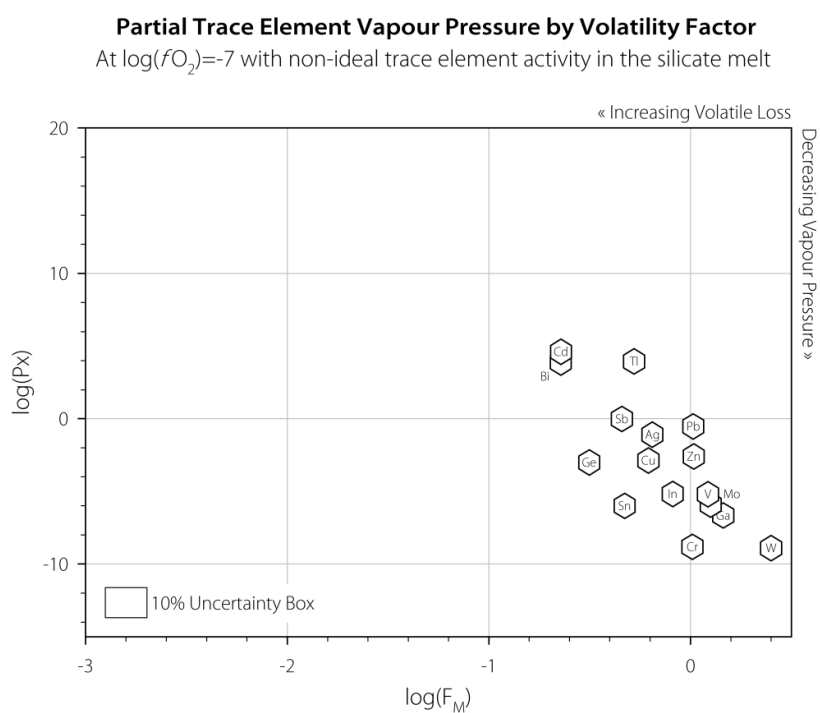
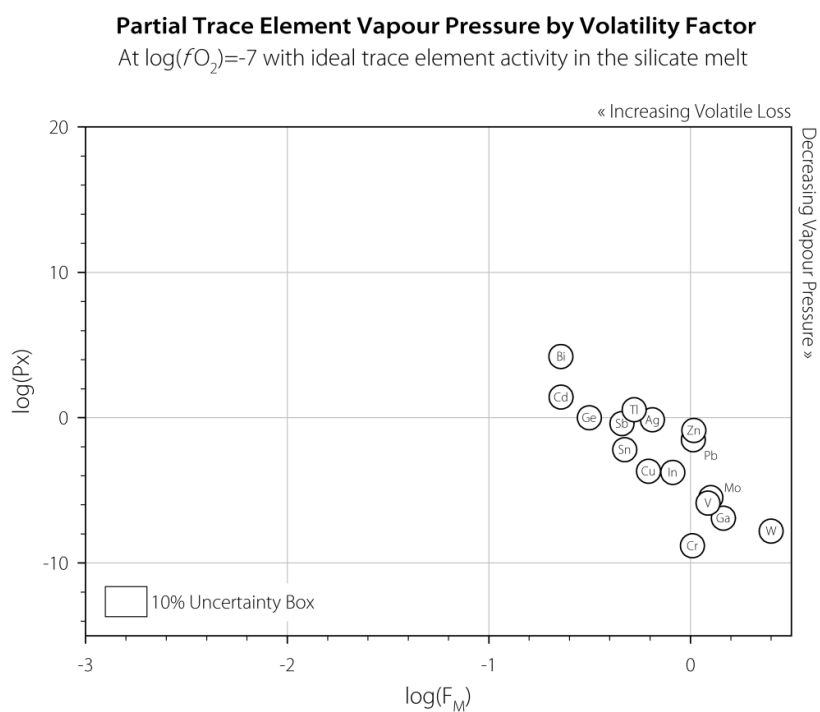


The total number of atoms in all gas species in equilibrium with non-ideal silicate melt, plotted at a range of oxygen fugacity values. The activity coefficients for the trace elements in the melt come from the metal–silicate partitioning experiments performed in Chapter 4. The correction for non-ideality is sufficient to change the relative volatilities of most elements. For clarity, the elements have been divided into three groups that approximately align with the degree of their volatility.

While Figure 5.19 is complete, it can be difficult to interpret. An alternative visualisation of volatile loss is presented in Figures 5.20 to 5.23. There, the volatility factor is plotted against the

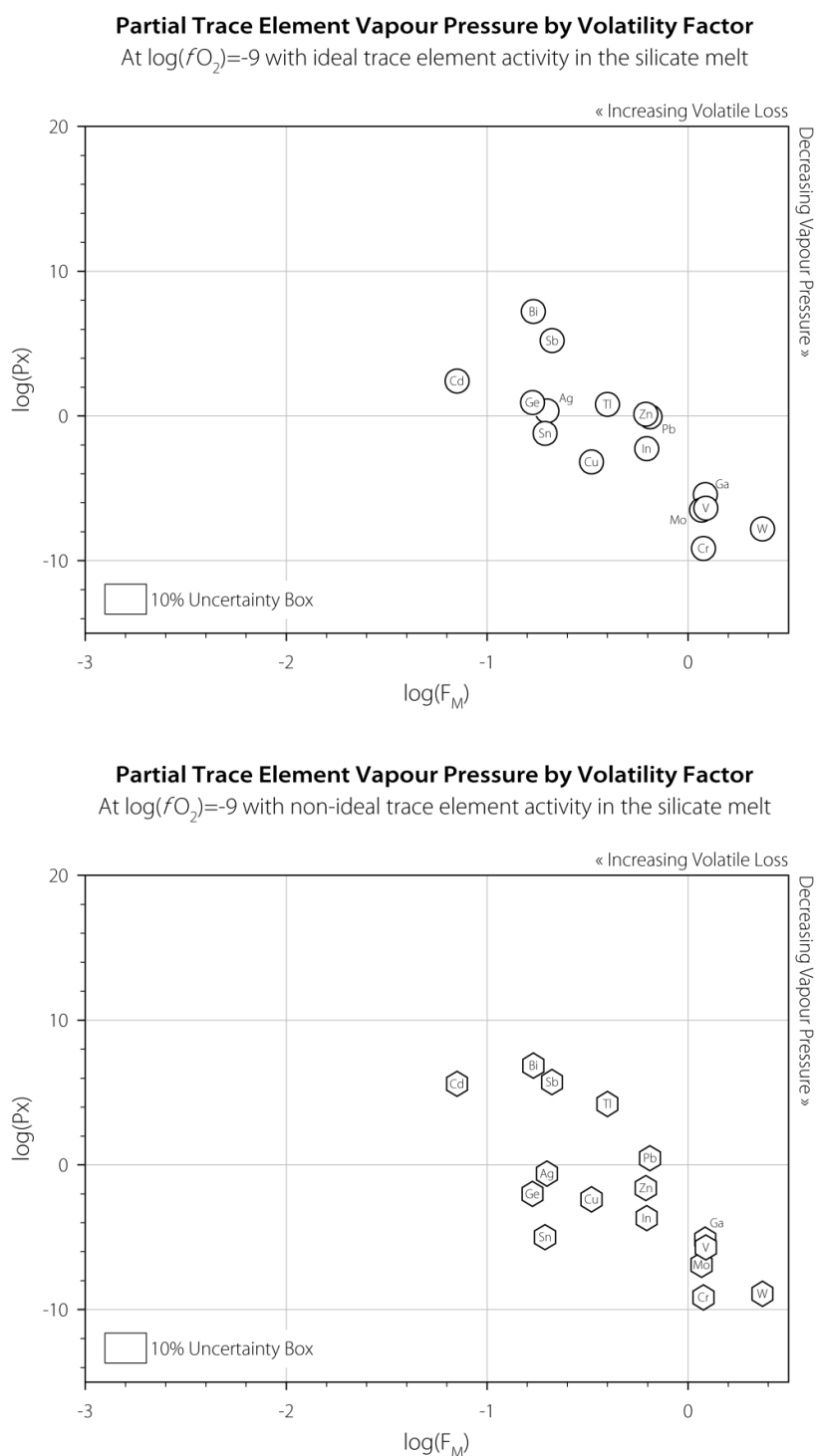
vapour pressure for each trace element. It is expected that elements with low vapour pressures would exhibit low levels of volatile loss, and while no claim is made that the relationship between them should be linear, we see on these figures a relatively clear linear relationship in log-log space.

Figure 5.20—Vapour Pressure vs Volatile Loss:  $\log(f\text{O}_2)=-7$



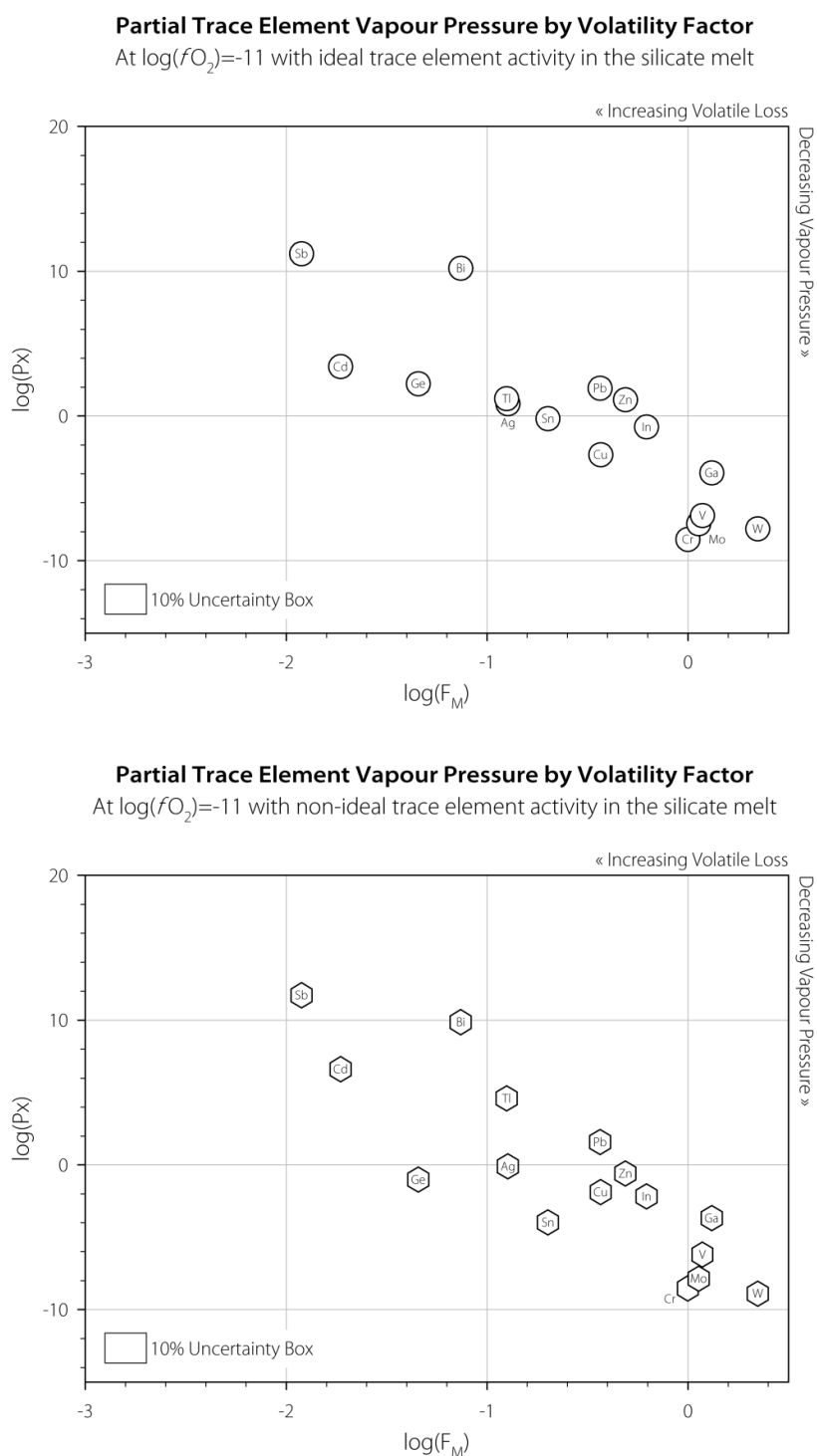
Vapour pressures calculated from thermodynamic equilibrium with silicate melt plotted against the measured volatility factors. Two charts are shown, one assuming ideality in the melt, and the other using the activity coefficients measured in Chapter 4. The relationship between them is not expected to be linear.

Figure 5.21—Vapour Pressure vs Volatile Loss:  $\log(fO_2)=-9$



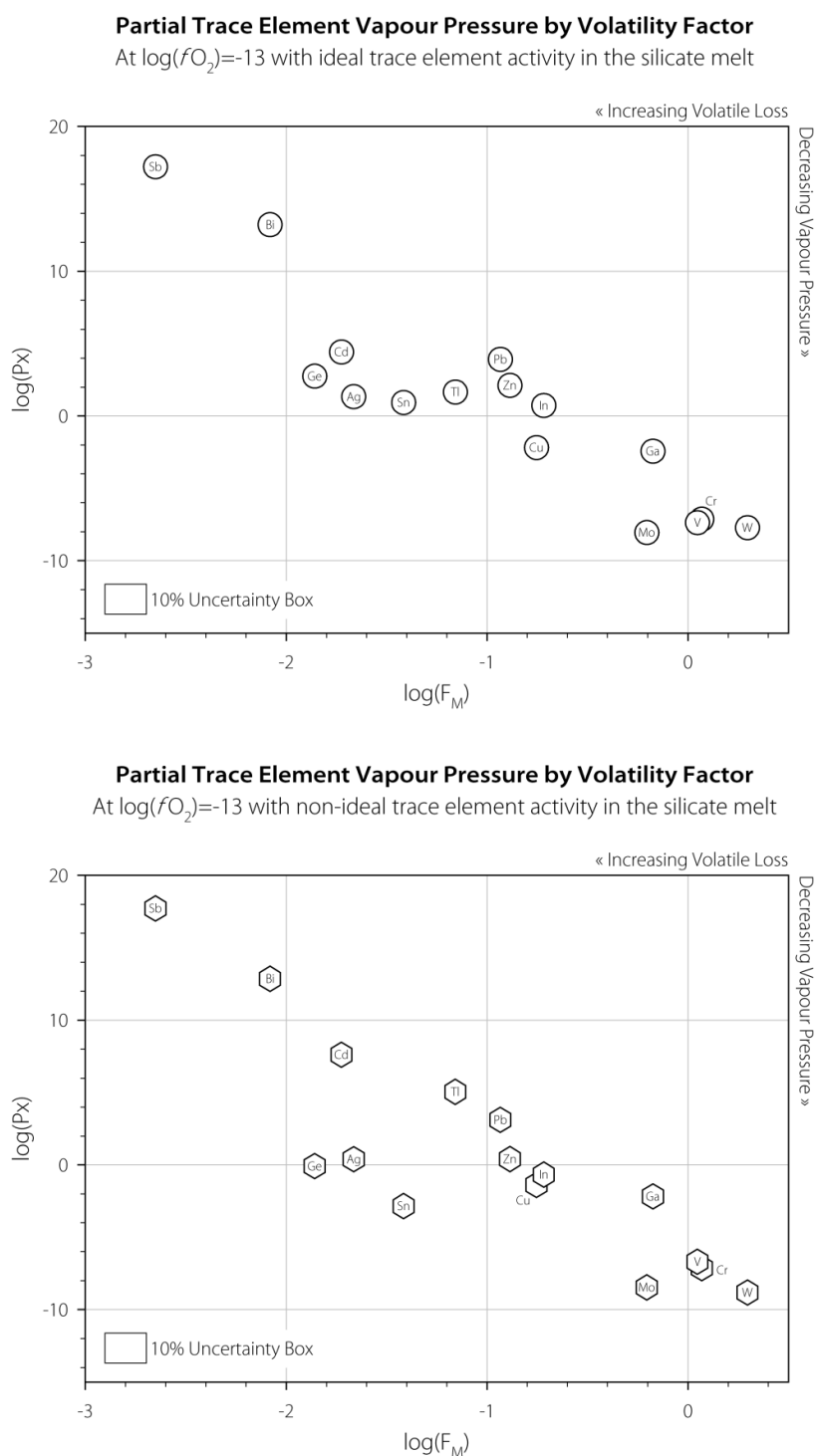
Vapour pressures calculated from thermodynamic equilibrium with silicate melt plotted against the measured volatility factors. Two charts are shown, one assuming ideality in the melt, and the other using the activity coefficients measured in Chapter 4. The relationship between them is not expected to be linear.

Figure 5.22—Vapour Pressure vs Volatile Loss:  $\log(fO_2)=-11$



Vapour pressures calculated from thermodynamic equilibrium with silicate melt plotted against the measured volatility factors. Two charts are shown, one assuming ideality in the melt, and the other using the activity coefficients measured in Chapter 4. The relationship between them is not expected to be linear.

Figure 5.23—Vapour Pressure vs Volatile Loss:  $\log(fO_2)=-13$



Vapour pressures calculated from thermodynamic equilibrium with silicate melt plotted against the measured volatility factors. Two charts are shown, one assuming ideality in the melt, and the other using the activity coefficients measured in Chapter 4. The relationship between them is not expected to be linear.

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## 5.7 Discussion

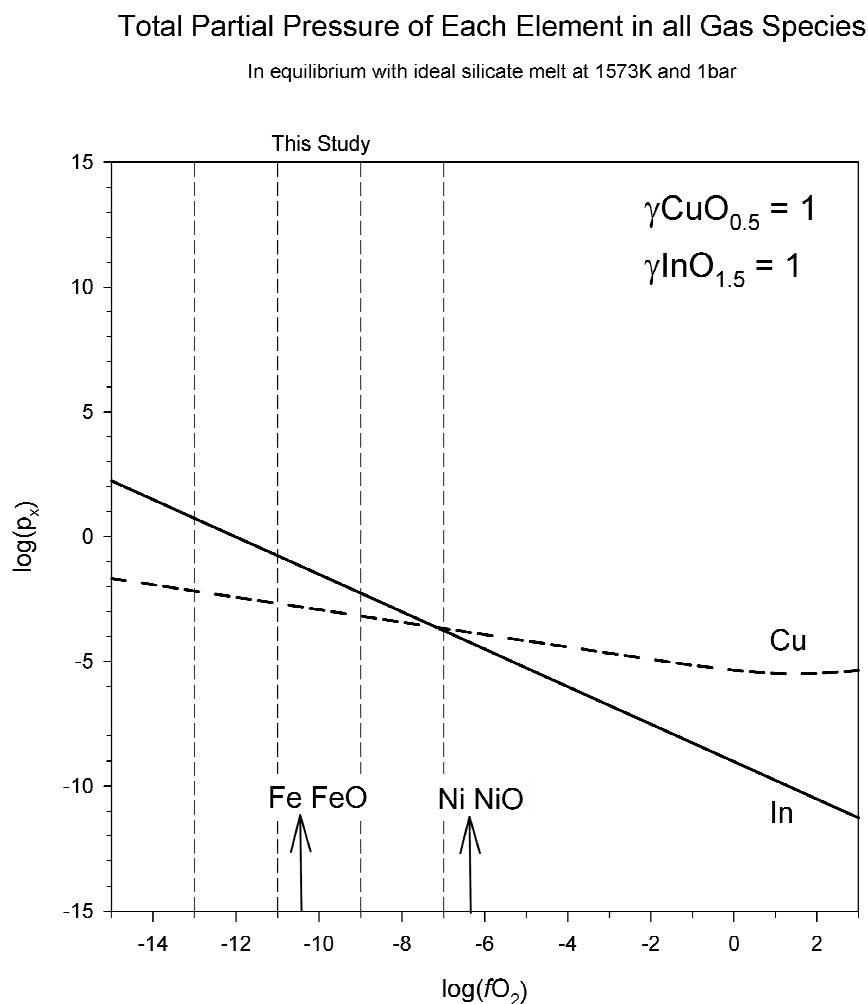
There is no physical reason why equilibrium vapour pressure would be correlated with volatile loss, since in general Gibbs does not tell us how quickly the equilibrium will be reached. However, inspection of figures 5.20 to 5.23 shows very reasonable agreement between the two parameters. As such, in these experiments with a constant gas flow, and constant turnover from the stirring mechanism, each gas phase is forming at a similar rate and complex kinetic effects at the surface interface are of minor importance. The scatter seen in the vapour pressure vs volatility factor plots is most likely caused by a combination of uncertainty in the computed vapour pressures (and activity coefficients used in the “non-ideal” plots) as well as differences in the rate of each reaction.

### 5.7.1 Copper and Indium

The volatility factors plotted in Figure 5.17 show that indium is clearly less volatile than copper. This is in contradiction of the computed gas pressures based on ideal behaviour in the silicate melt, as shown in Figure 5.24 below, as well as in Figures 5.19 to 5.23.



Figure 5.24—Copper and Indium Ideal Behaviour

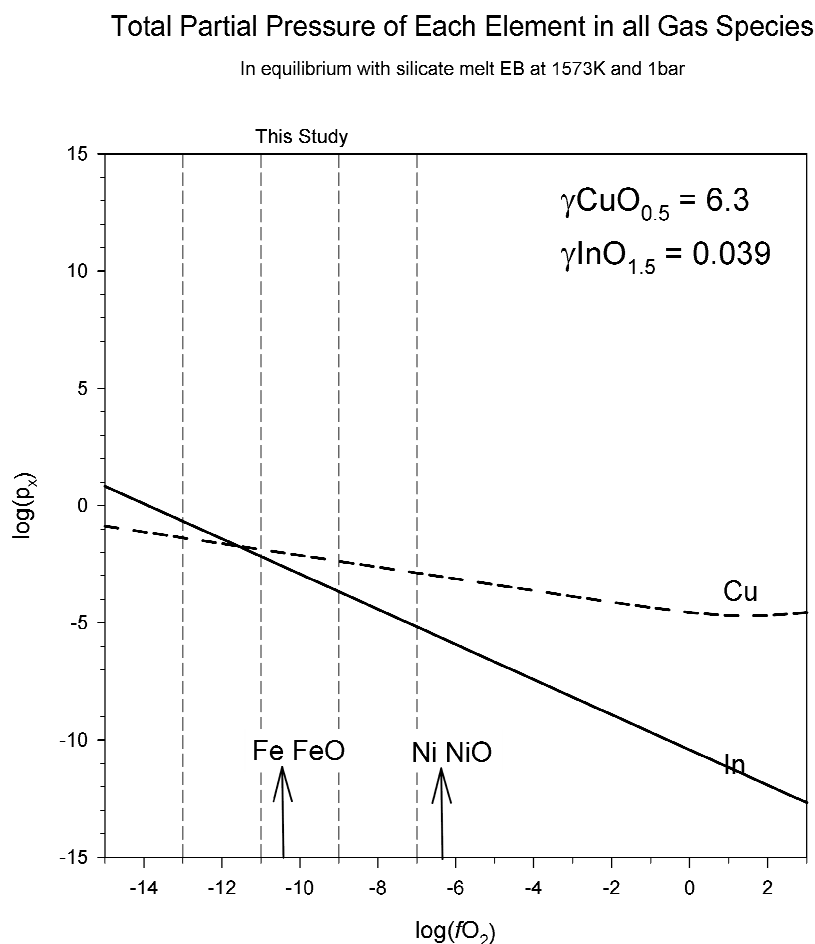


Calculated vapour pressures of In and Cu in equilibrium with ideal silicate melt. The relative pressures suggest that In should be more volatile than Cu below  $\log(f\text{O}_2)$  of  $-7$ . The measured volatilities show that in reality Cu is more volatile than In at these oxygen fugacity values (see Figure 5.17).

Applying the activity coefficient models for copper and indium at the known composition of silicate melt EB, we then compute and plot the vapour pressure for these two elements. As shown in Figure 5.26 below, the activity coefficients are sufficiently different to cause a swap in the relative volatilities of these two elements. The vapour pressures also show that there should be a convergence in the volatility of copper and indium at low oxygen fugacity, between a  $\log(f\text{O}_2)$  value of  $-11$  and  $-13$ . This is indeed what is observed in the measured volatility factor,

with indium and copper exhibiting the same degree of volatile loss in experiments conducted at  $\log(f\text{O}_2) = -13$ .

Figure 5.26—Copper and Indium with Modelled Activity Coefficients



Calculated vapour pressures of In and Cu in equilibrium with non-ideal silicate melt. The activity coefficients come from the metal–silicate partitioning experiments in Chapter 4. The relative pressures show that Cu should be more volatile than In above  $\log(f\text{O}_2)$  of  $-13$ . The measured volatilities agree with these predicted vapour pressures (see Figure 5.17).

## 5.7.2 Non-Ideal Behaviour of Volatile Trace Elements

To assess the impact of non-ideal behaviour in the silicate melt on the computed gas pressures (see Figure 5.19) the ideal gas pressures at each oxygen fugacity value have been plotted against the measured volatility factors (Figures 5.20 to 5.23). A comparison can be made to the same volatility factors plotted against the non-ideal vapour pressures. In each case the correction

afforded by the non-ideal activities shifts most elements towards a more linear relationship in log–log space. It is not believed that a linear relationship is necessarily physical, but it does support the hypothesis that volatile loss is directly related to the total vapour pressure and that material turnover can eliminate diffusivity and kinetic effects at the liquid surface.

However, some of the trace elements are moved away from this trend, such as germanium, tin, and silver, by consideration of their activity in the silicate melt. It is believed that there may be a complication in the vapour pressure calculation of those elements, with some species missing from the calculation. Silver is particularly reactive with chlorine, while tin and germanium can form oxides of multiple valences, for which there are limited thermochemical data. In this study only monatomic elemental gas been considered for germanium, along with stannic (II) oxide for tin.

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## 5.8 Summary

This chapter presented an overview of the design and construction of a stirring one atmosphere gas mixing furnace.

This furnace was used to perform a series of volatile-loss experiments, where the direct measurement of volatile loss was performed at a range of oxygen fugacity values applicable to planetary formation.

The volatility factor has been introduced as an empirical assessment of the volatility of an element. To compare the volatile loss with literature data the total vapour pressure of each element in equilibrium with an ideal melt has been computed. These values were then adjusted to account for the activity coefficients computed in Chapter 4., and the pressure values compared to the measured volatility factors.

Some elements, such as indium and copper, show significant deviation from the ideal behaviour, and that this deviation was sufficient to account for the observed discrepancy between the ideal and the measured degree of volatile loss.

This direct measurement of volatile loss can now be applied to understanding the formation of the Earth.

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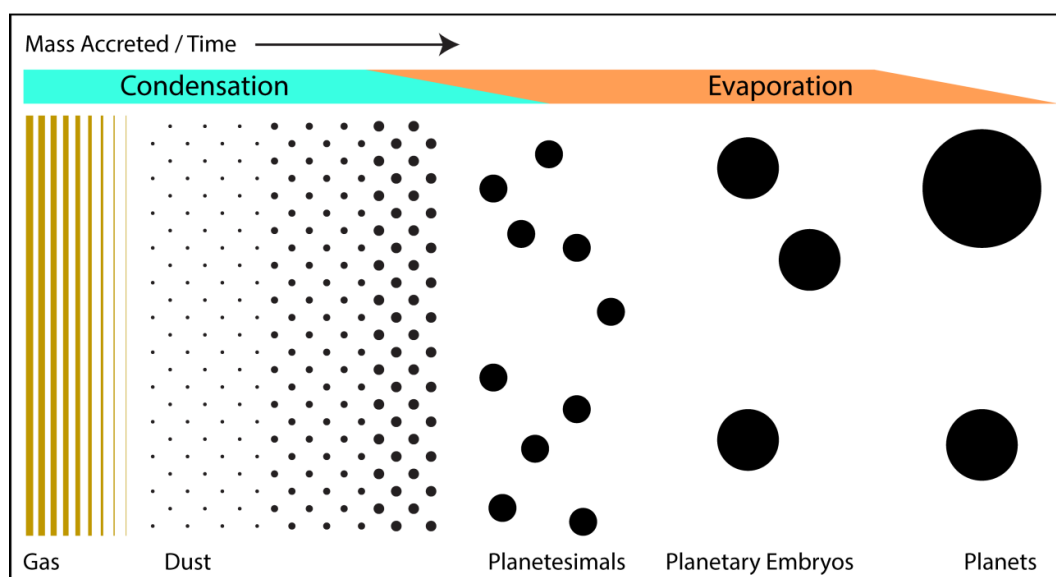
## **6 Earth's volatile Contents Established by Melting and Vaporisation**

### **6.1 Introduction**

As discussed in Chapter 1, the silicate Earth is strongly depleted in moderately volatile elements relative to CI chondrites, the meteorites which compositionally most closely resemble the Sun [Palme and O'Neill 2014]. A cartoon depicting the canonical model of planetary formation processes [Chambers 2001; Chambers 2004] is shown in Figure 6.1. This highlights two distinct time periods during which different processes governed the inventory of volatiles in the growing bodies; condensation from the solar nebula, and subsequent evaporative loss. During the second phase, the volatile inventory of planetary embryos would have changed considerably, undergoing periods of depletion caused by widespread melting from violent impacts, and periods of enrichment due to opportunistic addition of unprocessed material.

Qualitatively the depletion “trend” of the silicate Earth may be explained by accretion of 10-20% of a volatile-rich body to a reduced volatile-free proto-Earth [O'Neill 1991b; Schönbachler *et al.* 2010] followed by partial extraction of some elements to the core. Despite general observations being in support of this model (see Figure 1.1) several issues do remain, notably the overabundance of In in the Silicate Earth which leads to further questions about the sources of Earth's volatiles [Wang *et al.* 2016; Witt-Eickschen *et al.* 2009]. In this chapter an alternative hypothesis of volatile loss from planetesimals due to melting is presented whereby the characteristic signature of volatile depletion in the silicate Earth may be explained. This hypothesis is supported by the direct measurement of trace element volatilities, as outlined in Chapter 5.

Figure 6.1—Evaporation and Condensation during Planetary Accretion



Cartoon representing the major phases of planetary accretion. The earliest stage of accretion to form dust resulted in condensed phases acquiring elemental fractionation relative to solar abundances due to the radial temperature distribution in the solar system. As planetesimals formed there was widespread mixing in the inner solar system and heating from collisions, as the relatively small mass of these bodies, allowed for evaporative loss of volatile elements. As the rocky bodies gained mass direct evaporative loss (i.e. Jeans escape) decreased, but the possibility of hydrodynamic escape from giant impacts increased. The hypothesis presented here is that evaporation from planetesimals and planetary embryos created the characteristic signature of volatile depletion observed in the Silicate Earth.

## 6.2 Experimental Conditions and Summary of Results

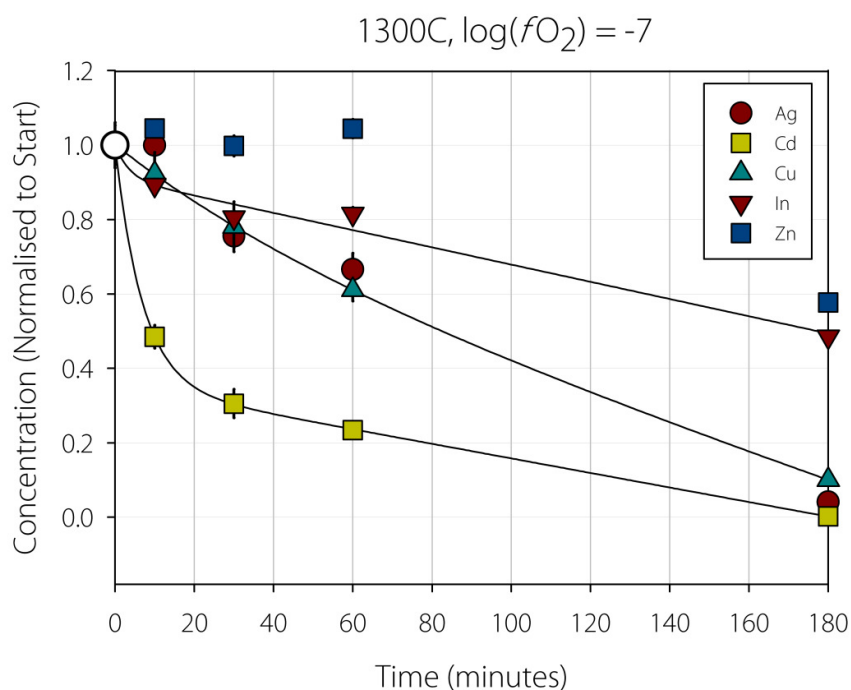
A thorough overview of the volatile loss experiments from this project is presented in Chapter 5, however, to briefly summarise here: Figure 6.2 shows a time series of one-atmosphere stirring-furnace experiments performed at a  $\log(f\text{O}_2)$  of  $-7$  atm. For reference, this is  $0.3 \log(f\text{O}_2)$  units below the Ni–NiO buffer at  $1300^\circ\text{C}$ . As can be seen in the Figure, loss of volatile elements is continuous with time and under these conditions, in contrast to condensation (Figures 1.1 and 6.2) indium is less volatile than Cu or Ag.

To quantify the observed volatility, and in order to compare volatile loss from the silicate melt for each element, the “volatility factor” ( $F_M$ ) has been defined for each trace element  $M$ . The volatility factor is taken to be the final concentration of the trace element divided by the initial

concentration in the starting mixture, which naturally leads to low values corresponding to high volatility.

A particularly important observation (Figure 6.1 and the dataset in Table 5.6) is that the relative order of volatile loss does not change with duration of the experiment, which is evidence that the relative loss rates for all elements are constant, and does not depend on kinetic effects or time. In order to determine the relative element volatilities and their dependence on oxygen fugacity it has been necessary to select a constant experiment duration at which volatility factors were compared. This has to be a time by which the correct volatility order is established and it must not be so long that some of the elements of interest are no longer readily detectable by the analytical method (LA-ICP-MS, see Chapter 3).

Figure 6.2—Volatile Loss Time Series



A modified version of Figure 5.16 showing the concentration of selected elements in the run products, normalised to their starting concentrations, for a time series of experiments performed at 1300°C and an oxygen fugacity of  $10^{-7}$  atm, about 0.3 log units below the Ni-NiO buffer. Note that the order of volatility is  $Cd > Ag > Cu > In > Zn$ , in marked contrast to the anticipated relative volatilities from the condensation temperatures (see Figure 1.1). Error bars are 1 SD.

Given that the correct volatility order is established between 10 and 30 minutes (Figure 6.2) and that some elements are almost completely lost after 3 hours, even under relatively oxidising conditions of  $\log(f\text{O}_2)$  of -7 atm, it was chosen to compare volatility factors after 60 minutes. As such, all volatility factors presented here refer to experiments of 60 minutes duration.

The measured volatility factors of trace elements are plotted against oxygen fugacity in Figure 5.17. As can be seen, there is a clear increase in the volatility of elements with decreasing oxygen fugacity indicating that the gas species are more reduced than the oxide species in the melt.

The oxygen fugacity conditions of these experiments were chosen to reflect the conditions of planetary formation: in the early solar system,  $\text{H}_2$ -rich nebular gas is believed to have dispersed after about 3 Ma [Evans *et al.* 2009] meaning that, afterwards, the conditions of melting induced by radioactive decay and accretion are set by the solid silicate and metal components equilibrated within each planetary or protoplanetary body. In the case of the Earth, Mars and Vesta the oxygen fugacity imposed by core–mantle equilibrium would be in the range 1-3 log units below Fe–FeO equilibrium [Wade and Wood 2005; Righter and Drake 1996]. As such, it would seem that oxygen fugacities of  $10^{-11}$  to  $10^{-13}$  atm at  $1300^\circ\text{C}$  are appropriate for the estimation of volatilities from molten or partially molten silicate bodies undergoing core formation.

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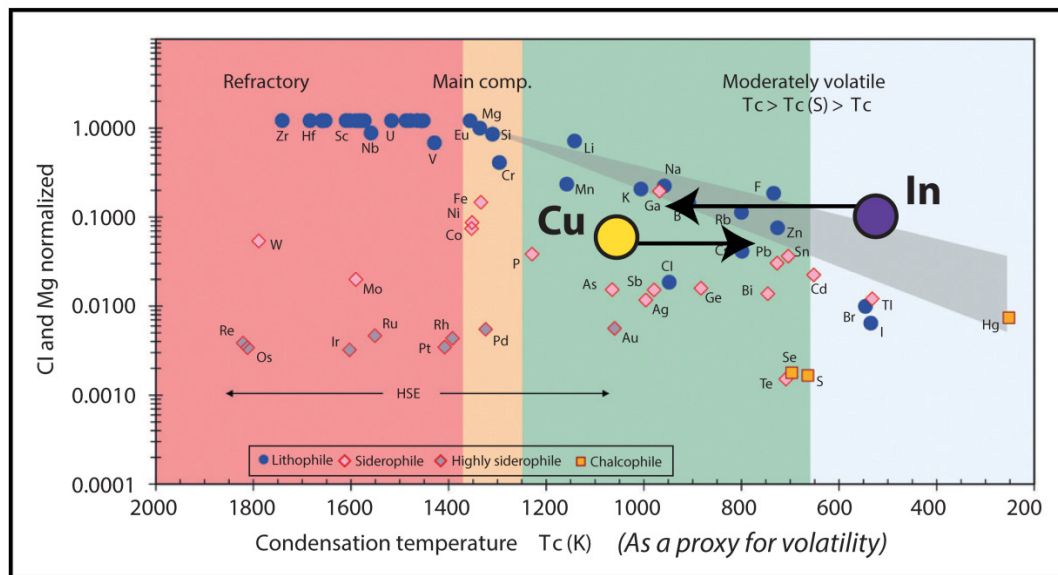
### 6.3 Relative Volatilities of Copper and Indium

Under the experimental conditions, and as shown in Figure 5.17, In is less volatile than Cu, Zn, Pb and Ag; all elements which have higher condensation temperatures (Figure 1.1). The principal reason for this is that solar gases have high concentrations of  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$  and In has stable gaseous S and OH species – InS,  $\text{In}_2\text{S}$ , InOH – which stabilise it in the gas phase, resulting



in calculation of a lower 50% CT. These species are all absent from the experiments, however they do, nevertheless, provide a clue to the origin of the In “anomaly”. This is readily explained if the moderately volatile element contents of the Silicate Earth were established by liquid–gas reaction during melting after the disappearance of the nebular gas. This might reasonably have been established on small precursor bodies for which gravitational escape would have been possible or conceivably during the Moon-forming impact when instabilities in the silicate vapour may have induced significant loss of the Earth-moon atmosphere [Genda and Abe 2003].

Figure 6.2—Modification to Figure from Palme and O’Neill 2014



The canonical plot from Palme and O’Neill 2014 showing the BSE composition normalised by CI Chondrite and magnesium concentration. This figure has been annotated to highlight the elements copper and indium. While the 50%CT values of these elements suggests that indium is more volatile than copper, this study has measured copper to be more volatile than indium at 1300°C and oxygen fugacity values of  $I:W+4$  to  $I:W-2$ .

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## 6.4 Volatile Loss from Planets and Planetesimals

There are a number of well-described mechanisms [Hunten 1993] that describe atmospheric loss from planetary bodies, all of which can be fundamentally described as thermal or kinetic processes.

Thermal mechanisms of atmospheric loss are reviewed in detail by Hunten [1993]. The most direct thermal mechanism is *Jeans Escape*, [Brinkman 1971; Hunten 1982; Volkov *et al.* 2011] which occurs when the velocity of gas molecules exceeds the escape velocity of the body. The formulation is given by:

$$\begin{aligned}\phi_j &= n_c w_j = n_c B U (1 + \lambda_c) \exp(-\lambda_c) / 2\pi^{1/2} \\ \lambda &= \frac{GMm}{kTr} = \frac{r}{H} \\ H &= kT/mg \\ U &= (2kT/m)^{1/2} \\ n_{ct} H_{ct} Q &= 1\end{aligned}$$

Terms are:  $n_c$  is the critical density of the escaping molecule, and the “t” subscript ( $n_{ct}$ ) refers to the total of all constituents;  $w_j$  is the effusion velocity, defined by the second expression shown;  $B$  is a correction factor from 0.5 to 0.8;  $G$  is the Newtonian gravitational constant;  $M$  is the planetary mass;  $m$  is the mass of the molecule;  $k$  is the Boltzmann’s constant;  $T$  is temperature, assuming the exosphere is isothermal;  $r$  is the distance from the centre of the planet;  $H$  is the scale height;  $g$  the gravitational acceleration; and  $Q$  is the collision cross section, typically  $3.3 \times 10^{-15} \text{ cm}^2$ .

Jean's escape occurs at a higher rate for lighter gasses, from bodies at higher temperatures and lower pressures, as the rate of loss is limited by diffusion in the atmosphere. In practice, for trace elements it can only result in minimal loss since their abundance high in the atmosphere,

where the loss occurs, is typically very low. For small precursor bodies at high (several thousand K) temperatures, such as following collisions between planetesimals, or a giant impact (with estimated temperatures of 3000K, Melosh 1990) then many of the gas molecules will have sufficient energy to escape, but under these conditions hydrodynamic escape is expected to dominate. For intermediate temperatures, modelling proves challenging (see Volkov *et al.* 2011) but can provide some insight on loss rates. However, since the loss only occurs high in the atmosphere where the density is lower, the total number of atoms that can be lost is limited, thus time then becomes a crucial, and unconstrained, factor.

A second thermal mechanism is hydrodynamic escape where prolific loss of a light gas molecule (e.g. H<sub>2</sub>, He, or OH) drags heavier gas molecules away in the process. The rate of loss of heavier molecules is mostly determined by their diffusion rate in the lighter gas. While hydrodynamic escape does lead to loss of gravitationally-bound heavy gas molecules, it can only do so if there is a sufficient volume of light molecules available to drive the process. One estimate by Hunten [1993] is that 88 modern terrestrial oceans of water would be needed to blow off all of the Noble gasses from an early Earth.

Kinetic effects refer to physical removal of the atmosphere by rapid propagation of shock waves or pressure waves [Genda and Abe 2003] typically formed during a giant impact. Simulations by Genda and Abe 2003 show that kinetic effects from a giant impact alone are insufficient to strip the atmosphere from a dry planet, and could only remove 25% of the total atmosphere. However, further modelling by Genda and Abe 2005 shows that if a liquid water ocean is present then the entire atmosphere can be removed. They also claim that during the giant impact phase of planetary accretion all planetesimals should have had water oceans of some degree.

Finally, atmospheric loss under more extreme conditions is an active field of ongoing research [Erkaev *et al.* 2015] and depends on many factors (such as atmospheric temperature, solar output, interplanetary gas pressure, and planetary magnetic field strength) that are all relatively unconstrained in the accretion phase of planetary formation.

In light of the many known processes that result in loss of planetary atmospheres during accretion, it seems most likely that a number of processes occurred, with heavy volatile elements lost via Jeans Escape from small hot planetesimals, and by hydrodynamic escape during giant impacts. Consideration should also be given to the possibility of a double impact during Moon formation, where the first impact created a large hot silicate atmosphere [Pahlevan and Stevenson 2007] and then a second impact stripped this atmosphere via kinetic effects. Such a double-impact would not necessarily require two impactors, since ejecta from the primary impact, or a glancing blow, could then impact the Earth on subsequent solar orbits [Asphaug *et al.* 2006].

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## 6.5 Volatile Depletion in the Silicate Earth

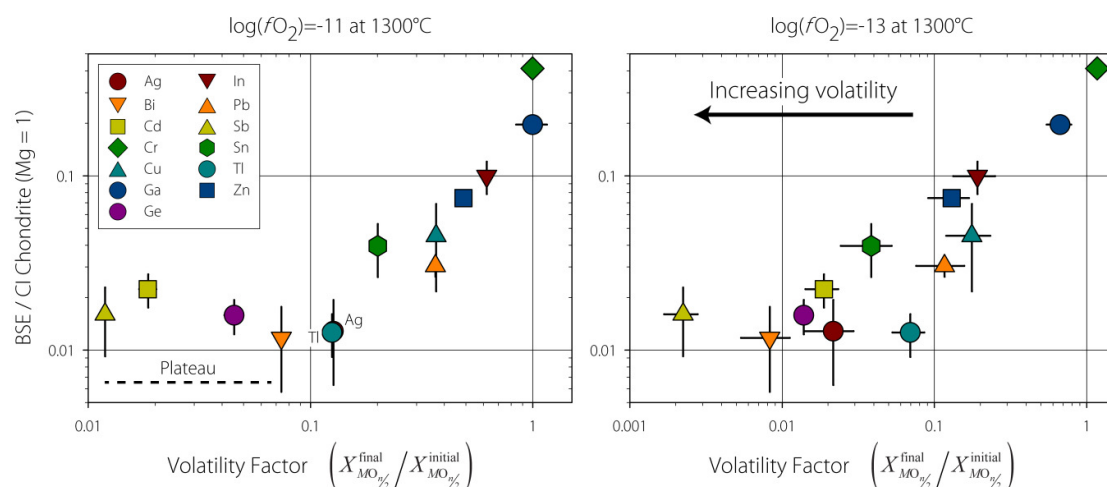
Expanding on the suggestion that volatile loss from planetesimals by evaporation was the primary cause of volatile trace element depletion in the Earth, Figures 6.4a and 6.4b plot volatility factors (measured at 1300°C and  $\log(f\text{O}_2)$  of -13 and -11) against Silicate Earth abundance relative to CI.

As can be seen in the figures, the pattern of depletion agrees closely with the measured volatility factors under these conditions, which are appropriate for core formation on precursor bodies and Earth. The degree of correlation appears to be much more significant than previously shown (Figure 1.1) for 50%CT. In detail, In, Cu and Zn all have similar volatilities, consistent

with their similar relative abundances in silicate Earth while Sn is more volatile and Cd, Ag and Ge are much more volatile than Zn, also consistent with their relative abundances. The refractory elements W and V have been omitted from the plot, since they show a clear signature of segregation into the core, and minimal volatile loss from the experiments.

At first, the plateau in abundances on the left hand side of Figures 6.4a and 6.4b seems to deviate from the general trend of the plot. However, this plateau is consistent with the late addition of a chondritic component after the vast majority of volatile loss occurred. Such addition could have been the addition of  $2 \pm 1\%$  of Earth's C, H and some noble gases [Marty 2012] and/or the “late veneer” which delivered  $\sim 0.5\%$  of Earth's highly siderophile elements after core formation ceased [Wang *et al.* 2013].

Figure 6.4—BSE/CI Chondrite vs Measured Volatility Factors



Concentrations in the Bulk Silicate Earth (BSE) of elements studied here relative to their concentrations in CI chondrite meteorites [Palme and O'Neill 2013] (normalised to a concentration ratio of Mg of 1.0) plotted versus their measured volatility factors at  $\log(fO_2)$  of -11 and -13 atm and 1300°C. Vertical error bars are as in Fig 1, and horizontal error bars are 2 standard errors. The line labelled “plateau” refers to the region where late addition of chondritic material may have raised the concentration of the most volatile elements.

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## 6.6 Summary

This chapter presents the hypothesis that the pattern of volatile element abundances in the Silicate Earth is much more consistent with their measured volatilities from a silicate melt at low  $f\text{O}_2$  than with their modelled volatilities (50% condensation temperatures) in a solar gas. To support this claim, the experimental data strongly suggest that the pattern of volatile element depletion was established by melt-vapour equilibrium (evaporation and re-condensation) in the absence of the reducing nebular gas. It is proposed that this process occurred on small molten precursor bodies where gravitational escape of volatiles was likely, or possibly from the Earth-moon system following the giant impact. After cessation of volatile loss from the Earth, there is evidence for the late addition of some 1% of volatile material, which enriched the most depleted volatile elements.

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## 7 Peripheral Insights and Direction for Future Study

In addition to the primary discussion of Chapter 6, there are other avenues of enquiry left to explore. This chapter outlines these, which include volatile loss from other planetary processes, such as the formation of the moon, volatile degassing of planetesimals, and terrestrial processes such as volcanism. Directions for future research will also be introduced.

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### 7.1 Peripheral Applications

#### 7.1.1 Volatile Loss during the Moon-Forming Giant Impact

There is a growing body of evidence (see Chapters 1 & 6 and references therein) that the Earth's moon was formed when a Mars-sized body (*Theia*) impacted the Earth, caused widespread melting of the mantle [Melosh 1990; Canup 2001; Canup and Asphaug 2001; Pahlevan and Stevenson 2007] and ejected sufficient material into orbit to form the Moon. Following this dramatic event an early Moon would have coalesced from a disk of material in orbit around the Earth, comprising molten silicate and gas ejected from both the Earth's mantle and the impactor [Cameron and Benz 1991; Canup 2001; Canup and Asphaug 2001]. There is some uncertainty as to how much of the impactor's composition would be incorporated into the Moon, with impact modelling suggesting the Moon is expected to be comprised mostly of impactor material, a view contradicted by numerous isotope ratios, such as calcium [Valdes *et al.* 2014], chromium [Lagmair and Shukolyukov 1998], iron [Beard and Johnson 1999], magnesium [Chakrabarti and Jacobsen 2010], oxygen [Hallis *et al.* 2010], potassium [Humayun and Clayton 1995], silicon [Armytage *et al.* 2012], stable isotopes of strontium [Charlier *et al.* 2012], titanium [Zhang *et al.* 2012], tungsten [Touboul *et al.* 2007], and zirconium [Schönbächler *et al.* 2003], that are indistinguishable between the Earth and the Moon. The isotopic similarities between the Earth and Moon are difficult to explain without drawing one of

two broad conclusions: the Earth and the Moon are made from the same mixed reservoir of material, or the Earth and Moon underwent chemical exchange and equilibrium shortly after the giant impact [Pahlevan 2007; Pahlevan 2014].

If the Moon formed during a hot process then some signature of volatile depletion should remain in its composition. It has long been believed [O'Neill 1991a and references therein] that the moon was entirely depleted in highly volatile elements such as water, yet recent measurements of the water contents of lunar basalts [Saal *et al.* 2008; Hauri *et al.* 2015] have pegged the lunar volatile budget at approximately  $0.25 \times \text{BSE}$ . The exact mechanism of volatile depletion of the bulk Moon is currently unconstrained, but if we accept the evidence for moderate to heavy depletion of highly volatile elements relative to BSE, then some signature of depletion of the volatile elements from this study may also be present.

To compare the bulk silicate Moon (BSM) to the BSE requires a viable composition for the BSM. Estimation of the BSM has been attempted by numerous authors [Wanke *et al.* 1975; Ringwood and Kesson 1977; Rasmussen and Warren 1985; O'Neill 1991a; Ringwood 1992; Albarede *et al.* 2014]. Establishing the composition of the BSM requires consideration of the source material and planetary processes, such as core formation. The internal structure of the Moon can be estimated by measuring spatial variation in the Moon's gravitational field. Data from lunar satellites *Kaguya* and *Lunar Prospector* have constrained the Moon's core to be less than 400 km in radius [Shimizu 2013] which comprises no more than 1.2% by volume and 1.8% by mass of the Moon. As mentioned in Chapter 6, the most volatile elements of interest to this study are not strongly siderophile, and for the purpose of this first-order investigation, core and sulphide segregation will be ignored.



Clear evidence for the Moon’s volatile degassing history may be found by investigating the volatile depletion of the lunar basalts collected by the Apollo sample return missions. The main advantage is that our knowledge of their compositions is only influenced by analytical uncertainty and sampling bias. Unfortunately, the volatile elements of interest to this study have not been reported in most published results. To collate a mean composition for the low-Ti Lunar basalt samples, three references [Wolf and Anders 1980; Ringwood and Kesson 1977; Neal 2001] were consulted for concentration data, all of which are presented in Table 7.1 below.

**Table 7.1—Low-Ti Lunar Basalt Composition**

| Trace Element | Low-Ti Lunar Basalt | Std. Dev. | Source            |
|---------------|---------------------|-----------|-------------------|
| Ag            | 0.001               | 0.0002    | W&A80; R&K77      |
| Bi            | 0.00024             | 0.00004   | W&A80; R&K77      |
| Cd            | 0.002               | 0.0004    | W&A80; R&K77      |
| Cr            | 3656                | 1635      | N01; R&K77        |
| Cu            | 14.8                | 5.6       | N01; R&K77        |
| Ga            | 3.85                | 0.68      | N01; R&K77        |
| Ge            | 0.006               | 0.002     | W&A80; R&K77      |
| In            | 0.0008              | 0.0003    | W&A80; R&K77      |
| Mo            | 0.14                | 0.08      | N01               |
| Pb            | 0.65                | 0.84      | N01               |
| Sb            | 0.00006             | 0.00003   | R&K77             |
| Sn            | 0.045               | 0.02      | W&A80             |
| Tl            | 0.00034             | 0.00006   | W&A80             |
| V             | 210                 | 87        | N01               |
| W             | 0.13                | 0.09      | N01; R&K77        |
| Zn            | 8.4                 | 13.2      | N01; W&A80; R&K77 |

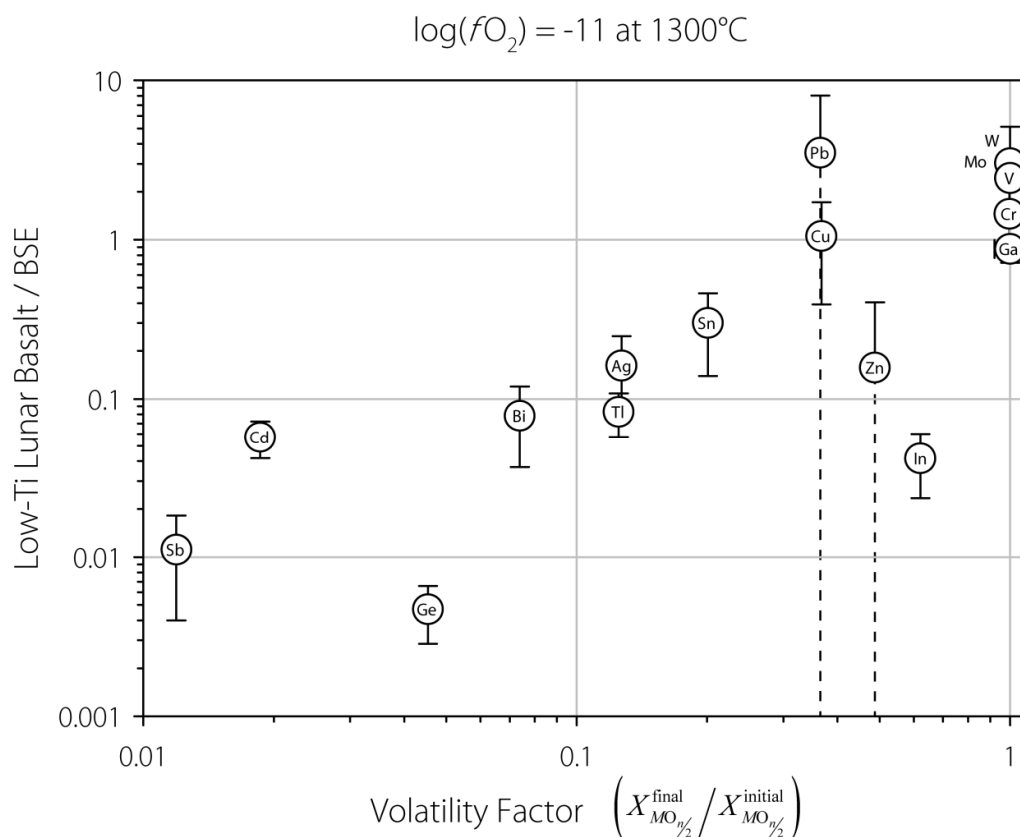
*All compositions in  $\mu\text{g.g}^{-1}$*

Key to source datasets: W&A80: Wolf and Anders 1980; R&K77: Ringwood and Kesson 1977; N01: Neal 2001

The concentration of these volatile elements in lunar basalt have been normalised to the BSE composition [Palme and O’Neill 2014] and plotted in Figure 7.1 against the volatility factor (see Chapter 5) measured at a  $\log(f\text{O}_2)$  of -11 atm and 1300°C. This particular set of volatility factors was chosen to reflect the conditions closest to the Fe–FeO buffer, which should be a reasonable estimate for the Moon due to the presence of some degree of lunar core formation. The figure shows remarkable agreement between the observed depletion and measured volatility factors, strongly suggesting that these materials experienced direct volatile loss under conditions similar to the experiments.

As remarkable as the correlation appears, it must be noted that the low-Ti Lunar basalts samples are likely to have degassed during their eruption, so it is possible that the trend in Figure 7.1 is due solely to a localised process, and is not actually a signature of volatile depletion in the entire BSM.

Figure 7.1—Lunar Basalt Depletion vs Volatility Factor



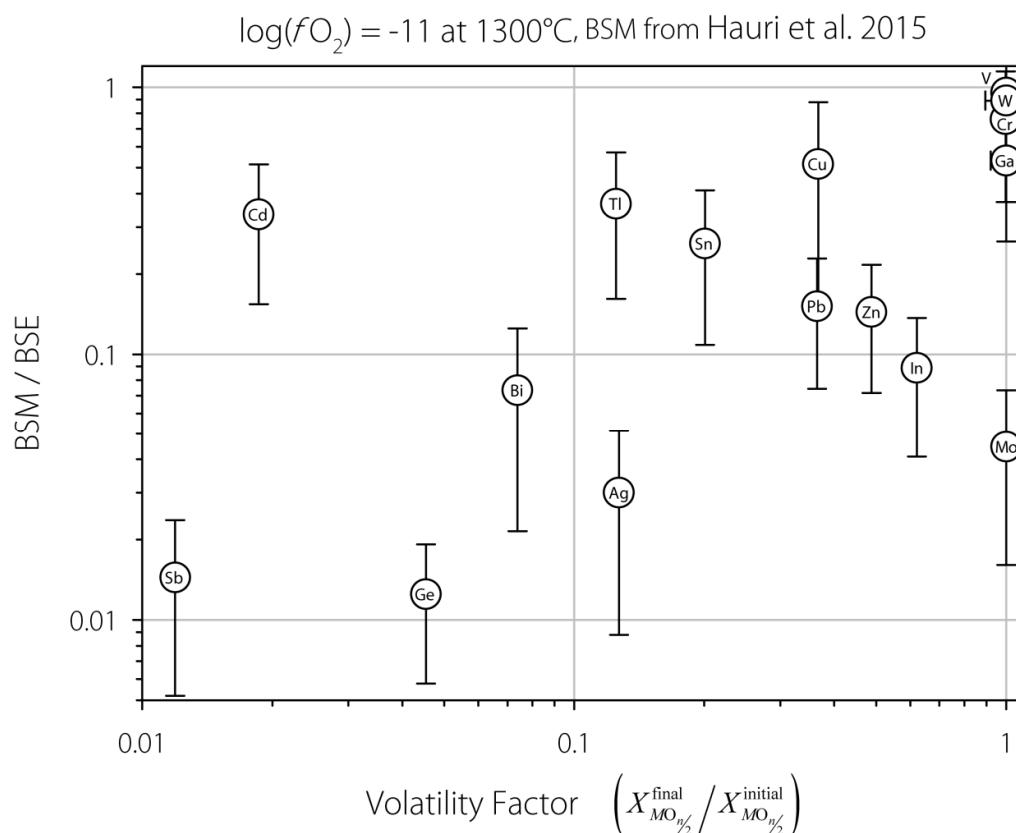
The depletion in the low-Ti lunar basalt shows a clear trend with volatility factor, as measured in this study at  $\log(fO_2) = -11$  and  $1300^\circ\text{C}$ . The error bars are 1SD and include the observed composition range and the estimated uncertainty in the BSE. Elements Pb and Zn show a wide range, exceeding the scale of the chart.

To explore whether the same trend can be seen in the BSM, the reported composition of Hauri *et al.* [2015] has also been plotted against the same volatility factors, and is shown in Figure 7.2.

Here the trend is not so clear, yet one must ask if the significant deviations, for elements such as Cd, are simply due to assumptions made in the BSM model, an additional complication of which is the lack of any uncertainty reported in that study. Further work is needed, but as a

starting point, the experiments from this project have confirmed a clear signature of volatile depletion on the Moon, relative to the BSE.

Figure 7.2—BSM Depletion vs Volatility Factor



The depletion in the BSM composition from Hauri *et al.* 2015 shows a somewhat positive correlation with volatility factor, as measured in this study at  $\log(fO_2) = -11$  and 1300°C. There is no uncertainty estimate for the BSM calculation, so the error bars show an assumed range of 50% combined with the estimated uncertainty in the BSE. The outlier element Cd is thought to be due to treatment in the BSM model.

### 7.1.2 Volatile Degassing from Molten Planetesimals

As outlined in section 6.3, small hot planetesimals should have experienced volatile loss via Jeans escape, or periodic atmospheric stripping following energetic impacts. As previously observed for the bulk silicate Earth (Chapter 6) and lunar basalts (Section 7.1.1) evidence for volatile depletion should be preserved in the trace element compositions of these bodies. While most planetesimals from the primitive solar system have either accreted into planets or been lost to the sun, a record is preserved to some extent in meteorite data. During the earlier stages

of planetary formation (Figure 6.1) the oxygen fugacity within the solar nebula would have been dominated by abundant levels of H<sub>2</sub> gas, which is believed to have cleared the early solar system by 3 Myr [Evans *et al.* 2009]. Afterwards, oxygen fugacity would have been determined by variable degrees of core formation on rapidly-growing planetesimals, suggesting there would be some variation and that it may be possible to use the volatility measurements from this study to fingerprint oxygen fugacity at the time of volatile loss.

The volatile loss experiments from Chapter 5 show representative signatures at each oxygen fugacity measured. In particular antimony depletion shows a dramatic change in volatility over the range of relevant oxygen fugacity values, exhibiting more volatility than cadmium below oxygen fugacity ( $f_{O_2}$ ) values on the iron—iron wustite (I:IW) buffer at 1300°C, and lower volatility above it.

By measuring the correlation between volatility factor and planetesimal trace element depletion relative to CI chondrites the oxygen fugacity at the time of depletion can in principle be constrained. Table 6.2 shows the Pearson correlation index between depletion in the angrite NWA7533 and the volatility factors measured in this study. The trend in the correlation index suggests that volatile loss from the NWA7533 parent body may have occurred at more oxidising conditions, such as greater than I:IW+4 at a temperature of 1300°C.

**Table 6.2—Correlation between Angrite NWA7533/CI Depletion and Volatility Factors by Oxygen Fugacity**

| log( $f_{O_2}$ ) | I:IW at 1300°C | Pearson Correlation |
|------------------|----------------|---------------------|
| -7               | 4              | 0.46                |
| -9               | 2              | 0.48                |
| -11              | 0              | 0.35                |
| -13              | -2             | 0.36                |

Unfortunately it is difficult to perform this analysis using more meteorite compositions as the volatile metals from this study are often omitted from trace element quantification. There would be considerable advantage to performing more stirring furnace experiments at major element compositions closer to those of meteoritic material and a wider range of oxygen fugacity value, or indeed with a hydrogen atmosphere.

### 7.1.3 Glass Reference Materials

A larger crucible can be used for the stirring furnace experiments to manufacture bespoke glass standards for EPMA and LA-ICP-MS. These glasses can be manufactured in arbitrary gas compositions, so chosen as to suppress the volatility of the elements of interest. Indeed, by knowing ahead of time what volatiles losses will occur, the starting mixture composition can be customised to achieve close to the exact target composition at the end of the experiment. Such control ensures that desirable elements are retained while undesirable elements, that may pose analytical inferences, can be excluded or minimised in concentration.

Given the apparatus described in Chapter 5, then at  $pO_2$  of 1 atm a 30 minute experiment at 1300°C should yield homogenous glasses with well-controlled trace element abundances.

### 7.1.4 Gas Speciation during Volatile Loss

Knowing the abundance of a gas species, or the ratios of gas species, in the vapour phase during a volatile loss experiment will allow further refinement of the thermochemical data. Such measurements are fraught with difficulty due to the hostile high temperature environment inside the furnace. Any attempt to remove gas molecules for analysis will ultimately fail, since transporting the gas will affect its temperature. Direct sampling of the gas *in situ* should be possible by inserting a pin-hole aperture directly into the furnace hot zone, with the opening leading to a quadrupole mass spectrometer. Such a device would operate in a similar manner to a

Knudsen cell mass spectrometer, with the furnace interior acting as the Knudsen cell. Such a device may not be practical due to the difficulty of insulating the mass spectrometer from the substantial heat output (3-6kW) of the furnace elements.

A more reasonable suggestion is to perform IR/UV/Visible light spectroscopy directly through the furnace tube. A top-to-bottom sampling path would be straight forward to implement but interpreting the results would be problematic due to the considerable temperature gradient encountered in conjunction with the *hot zone* path length (10cm) only representing 13% of the entire furnace tube path length (73cm). A side-through sampling path would overcome these difficulties, yet the alumina tube is opaque and a quartz tube would soften at the high temperatures of interest. Fitting transparent windows would be difficult to implement due to the considerable complications associated with sealing the windows against the alumina tube.

Much consideration has been given to this problem over the course of this project, and it is the author's opinion that the approach most likely to succeed will involve a side-through sampling path via small (2-5mm diameter) opposing apertures drilled through the furnace tube and not sealed with any windows at all. The oxygen fugacity of the experiment would be controlled in the usual way, but in addition the entire furnace box would be sealed using aluminium and Perspex sheeting. This approach is not without complications, the main one being that MoSi<sub>2</sub> furnace elements are unstable in reducing atmospheres and would require an alternative material, such as wound Pt wire, to be used instead. Minor alterations would include the use of mass flow controllers capable of delivering higher flow to purge the greater volume, and inlets would have to be added to both the top and bottom of the furnace tube. Despite these modifications, this approach should be feasible to implement.

### 7.1.5 Thermochemical Data

Some of the thermochemical data used in this study have been estimated or approximated. While some data may ultimately be unknowable due to the inherent instability of some species, there is considerable scope for improvement in this area leading to refinement of the silicate melt activity models presented in Chapter 4.

#### 7.1.5.1 *Solubility of Cadmium in Liquid Iron*

The solubility of Cd has been measured by Elliot and Chipman [Elliot and Chipman 1950] at 500°C in a range of molten solutions: Cd–Bi, Cd–Sb, Cd–Sn, and Cd–Pb. It would be both interesting and useful to take these experiments to higher temperature and attempt a solubility measurement of Cd in liquid Fe. Recent work [Qin 2014] states “present assessment of the Cd–Fe system focus on the solubility on the Cd-rich side.” The work in this study shows that there is indeed some solubility of cadmium in iron, so there is merit in pursuing these measurements. However, due to the high vapour pressure of Cd above the melting point of Fe (1560°C), the experiment should be performed in the piston-cylinder apparatus.

### 7.1.6 Volcanic Systems

The data collected during this study are particularly applicable to the understanding of volatile loss from volcanic systems. However, such systems are characterised by the presence of additional components such as sulphur, halogens, alkali metals, and water. All of these components are expected to alter the activity coefficients of the trace elements as they are all known to significantly adjust silicate melt structure and the effusion of volatile metals from volcanic systems [Johnson and Canil 2011]. Furthermore, the vapours assessed in this study have been limited to only those gaseous compounds formed by the trace elements and oxygen. A more comprehensive study is required to include alkali, sulphide, halide, hydroxide, and

chloride gas species in the vapour pressure calculation. In some cases the thermochemical data may be absent from the literature and more work will be required to collate the values required.

As a continuation of this study it is the author's opinion that much progress could be made by performing more of the high pressure and volatile-loss experiments over a wider range of silicate melt compositions. In addition, a campaign to measure those much-needed thermochemical data will undoubtedly be of benefit.

For a first-order approximation the volatile loss experiments from Chapter 5 could be used to estimate the effusion of volatile elements from stagnant pools of magma exposed at the Earth's surface. What can be stated, based on the work in this study, is that a nominal basaltic melt<sup>29</sup> exposed to air<sup>30</sup> with an absence of other gas-forming elements, will effuse the following series of elements in order from most to least volatile: Tl, Cd, Pb, Mo, Ag, V, Bi, Cu, Cr, Zn, Sb, W, Sn, Ga, In, and Ge. This series is computed from the partial gas pressures of each element taking into account the activity coefficients calculated in Chapter 4. A natural continuation of this work would be to perform a series of experiments at oxygen fugacity values relevant to those at the Earth's surface.

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## **7.2 Direction of Future Work**

### **7.2.1 Isotopic Analysis**

The stirring furnace experiments from this study would make ideal candidates for isotopic analysis of the trace elements. Sufficient sample is present for an acid dissolution prior to analysis by multi-collector ICP-MS. As introduced in Chapter 1, isotopic fractionation caused by volatile loss is specific to the process, element, and conditions, and as such has to be

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<sup>29</sup> Specifically composition EB from Chapter 5

<sup>30</sup> i.e. much more oxidised than the volatile loss experiments performed in Chapter 5



determined experimentally. Isotopic fractionation should be most readily measured in the lighter more volatile elements, such as Ge, Zn and Cu. Expanding the range of  $fO_2$ , temperature, and melt composition of the volatile loss experiments may reveal fascinating degrees of fractionation, or equally interesting, no dependence at all. Such data would provide valuable input to modelling the geochemical histories of the terrestrial planets.

### 7.2.2 Improved Stirring Furnace Experiments

The stirring furnace experiments can be expanded and improved by repeating them at a wider range of oxygen fugacity values, extending at least as high as air (0.2 atm of  $O_2$ ). This will allow a more direct application of the results to volcanic systems at the Earth's surface, as well as industrial processes and the manufacturing of glass reference materials.

The temperature range of the experiments can be expanded, though this will require replacing the nickel crucible and stirrer components with a high melting temperature noble metal such as platinum. This may present complications by altering the iron concentration of the melt, which can be mitigated through altering the composition of the melt or pre-saturating the platinum with iron beforehand.

The apparatus can be enhanced to permit *in situ* spectroscopic measurement of gas speciation by the addition of a transverse-oriented visible light absorption spectrometer.

The melt composition should be expanded to include a range of additional components, such as alkalis, halogens, and water, as these components are expected to alter volatility by changing the melt structure, as well as stabilising additional species in the gas phase. The gas mixture can also be adjusted to incorporate sulphur into the gas, melt, or both. Use of meteoritic compositions

would allow for greater applicability of the results to understanding volatile loss during accretion processes.

Iron-silicate partitioning experiments at the same compositions can be performed to provide additional controls on the activities in the silicate melt.

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### **7.3 Conclusion**

In this study a series of high pressure metal-silicate partitioning experiments have been undertaken and the partition coefficients of sixteen trace elements used to compute the activity coefficients in the silicate melt. By performing these experiments at a range of silicate melt compositions in the CMAS+Fe composition space, models describing variation with melt composition have been determined by linear regression. The activity coefficients have been used together with available thermochemical data to compute the partial vapour pressures of all gas species for each trace element in equilibrium with a silicate melt of nominal basaltic composition.

A one-atmosphere gas-mixing furnace was constructed that is capable of stirring a 5cm<sup>3</sup> crucible of silicate melt. Natural basalt was doped with trace elements and a series of volatile loss experiments performed at 1300°C covering a range of time spans from 5 to 180 minutes.

By defining the volatility factor for a trace element to be the concentration after one hour divided by the starting concentration, a useful metric of element volatility is obtained. It has been compared to both ideal and non-ideal computations of gas pressures. The volatility factors provide a direct measurement of trace element volatile loss under conditions of planetary accretion, a process distinctly different to condensation from a solar nebular at much lower  $fO_2$ .

The results show this difference most clearly for two elements, In and Cu, with In condensing at a lower temperature than Cu, while experiencing less volatile loss during evaporation.

Comparison between the measured volatility factors and trace element depletions in the BSE shows excellent agreement, providing evidence that the Earth formed from hot molten planetesimals that had previously lost some, or all, of their atmosphere, or that the moon forming impact resulted in volatile depletion of the entire Earth-Moon system. Evidence for enrichment of the most volatile elements supports the late addition of volatiles to the proto-Earth.

Finally, the measured volatility factors from this study have been applied to a wide range of interesting problems, such as evidence for volatile depletion of the Earth's Moon.

Future research will greatly expand the applicability of these data and allow for volatile loss to be understood and applied to a wider range of problems.



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## Appendix: *Metal/Act* Calculation Source Code (PHP)

```
function METALACT_LIB_compute($composition, $temp, $e, $gamma_zeros, $lot =
1,$compute_carbon_content = true) {

    // =====
    // =====

    // Calculate activity coefficients for Fe

    // =====
    // =====

    // Compute the free energy of C dissolved in Fe
    $dg = -36681.0 + ($temp * 41.717) - (0.013968 * $temp * $temp);

    // The gamma_zeros come to us in a crappy form, restructure
    $gamo = array();
    foreach($gamma_zeros as $row) {
        $gamo[$row[0]] = $row[1];
    }

    // =====
    // =====

    // Zeroth: Normalise composition
    $x = METALACT_LIB_normalise_composition($composition);

    // Save the solvent element (we need it later)
    $x_METALACT_SOLVENT_ELEMENT = $x[METALACT_SOLVENT_ELEMENT];

    // Zeroth - Take Two: Strip out reference element (Fe)
    unset($x[METALACT_SOLVENT_ELEMENT]);

    // =====
    // =====
    // The following section is the computation of the "ln gamma 1" term
    // Which is equation [23] from the reference paper

    // First: do single terms
    $gams = 0;
    foreach($x as $el=>$mole_fraction) {

        $gams += $e[$el][$el] * ( $x[$el] + log(1 - $x[$el]) );

    }

    // These are used for the numeric loops below
    $array_keys = array_keys($x);

    $max_index = count($x) - 1;

    // Second: There are 4 more terms, two are {N;N} and two are {N-1;N}

    for($j=0;$j < $max_index;$j++) { // $j ranges from start of elements (not
including Fe) to second to last
        for($k = $j+1;$k <= $max_index; $k++) { // $k ranges from $j + 1 to
last element

            $el_j = $array_keys[$j];
            $el_k = $array_keys[$k];

            // Skip zero compositions (although the math _should_ make such
terms zero)
            if (($x[$el_j] == 0) || ($x[$el_k] == 0)) { continue; }

            // Compute the second order term (first {N-1;N} loop)

            // Regular PHP math
            $gams -= $e[$el_j][$el_k] * $x[$el_j] * $x[$el_k] * ( 1 +
(log(1 - $x[$el_j]) / $x[$el_j]) + (log(1 - $x[$el_k]) / $x[$el_k]) );

            // Compute the fourth order term (second {N-1;N} loop)
            // Regular PHP math
```

```

        $gams += 0.5 * $e[$el_j][$el_k] * $x[$el_j] * $x[$el_j] *
$x[$el_k] * $x[$el_k] * ( (1 / (1 - $x[$el_j])) + (1 / (1 - $x[$el_k])) - 1 );
    }
}

// Third: There are now only two terms left to compute, these loop over {N;N}

for($i=0;$i <= $max_index;$i++) {      // $i ranges from start of elements
(not including Fe) to last element
    for($k = 0;$k <= $max_index;$k++) {  // $k ranges from start of
elements (not including Fe) to last element

        // We don't want $i to equal $k, so skip these ones
        if ($i == $k) { continue; }

        $el_i = $array_keys[$i];
        $el_k = $array_keys[$k];

        // Compute the third order term (first {N;N} loop)
        $gams += $e[$el_i][$el_k] * $x[$el_i] * $x[$el_k] * ( 1 +
(log(1- $x[$el_k]) / $x[$el_k]) - (1 / (1 - $x[$el_i])) );

        // Compute the fifth order term (second {N;N} loop)
        $gams -= $e[$el_i][$el_k] * $x[$el_i] * $x[$el_i] * $x[$el_k] *
$x[$el_k] * ( (1 / (1 - $x[$el_i])) + (1 / (1 - $x[$el_k])) + ($x[$el_i] / (2 * pow(1 -
$x[$el_i],2))) - 1 );

    }
}

// =====
// We now have $gams, the activity cooefficient for the solvent, Fe
// =====
// Now we compute the activity cooefficient for the solute

// =====
// =====
// The following section is the computation of the "ln gamma i" term
// Which is equation [24] from the reference paper
// We do this for *ALL* elements, not just those in the composition

// Build composition array for all supported elements (bar Fe)

$x_all = array();
$el_all = METALACT_LIB_supported_elements();
foreach($el_all as $el) {
    if ($el != METALACT_SOLVENT_ELEMENT) {
        if (isset($x[$el])) {
            $x_all[$el] = $x[$el];
        }
        else {
            $x_all[$el] = 0; // This is actually implied, the
if/else is just for readability and to minimise errors
        }
    }
}

}

solution

$gamsol = array();      // We compute a $gamsol term for each element in the

$array_keys = array_keys($x_all);
$max_index = count($x_all) - 1;

for($i=0;$i <= $max_index;$i++) {      // $i ranges from start of elements
(not including Fe) to last element

    $el_i = $array_keys[$i];

    // First order term
    $gamsol[$el_i] = $gamo[$el_i] + $gams - ($e[$el_i][$el_i] * log(1 -
$x_all[$el_i]));

```

```

        // There are now only two terms left to compute
        for($k=0;$k <= $max_index;$k++) {           // $k ranges from start of
elements (not including Fe) to last element

                // We don't want $i to equal $k, so skip these ones
                if ($i == $k) { continue; }

                $el_k = $array_keys[$k];

                // PHP math
                $gamsol[$el_i] -= $e[$el_i][$el_k] * $x_all[$el_k] * (1
+ (log(1 - $x_all[$el_k])/$x_all[$el_k]) - (1 / (1 - $x_all[$el_i])) );

                // PHP math
                $gamsol[$el_i] += $e[$el_i][$el_k] * $x_all[$el_k] *
$x_all[$el_k] * $x_all[$el_i] * ( (1 / (1 - $x_all[$el_i])) + (1 / (1 - $x_all[$el_k])) +
($x_all[$el_i] / (2 * pow(1 - $x_all[$el_i],2)) ) - 1 );

        }

    }

    // =====
    // =====
    // We now have all the gammas
    // =====
    // =====

    // Check deviation
    if ($compute_carbon_content) {
        /*
        if (round($x[METALACT_ELEMENT_C],5) == 0) {
            $xdev = 0;
        }
        elseif ($x[METALACT_ELEMENT_Si] > 0.1 ) {
            $xdev = 0;
        }
        else {
            */
            // Adjust the composition of carbon
            $xdev = 0;
            $xdev = $x[METALACT_ELEMENT_C] - exp( (0 - ($dg + 8.314 * $temp
* $gamsol[METALACT_ELEMENT_C])) / (8.314 * $temp) );
            $xnew = $x[METALACT_ELEMENT_C] - 0.2 * $xdev;
            $x[METALACT_ELEMENT_C] = $xnew;
            //}
        }

        // Will we iterate again?
        if ( ($compute_carbon_content && ((abs(round($xdev,3)) >
METALACT_COMPUTATION_STDEV_THRESHOLD) AND ($lot < METALACT_COMPUTATION_MAX_ITERATIONS))) {
            // Yes, run the computation again

            // Add back the solvent element to the new composition
            $x[METALACT_SOLVENT_ELEMENT] = $x_METALACT_SOLVENT_ELEMENT;

            $lot++;

            return METALACT_LIB_compute($x, $temp, $e, $gamma_zeros,
$lot,$compute_carbon_content);
        }
        else {

            // Now take take the exponent (undo the ln) for all of the computed
terms

            $gamsol[METALACT_SOLVENT_ELEMENT] = $gams;

            foreach($gamsol as $el=>$ln_gamma) {
                $gamsol[$el] = bcexp($ln_gamma);
            }

            // Flag this as not converging
            if ($lot >= METALACT_COMPUTATION_MAX_ITERATIONS) {

```

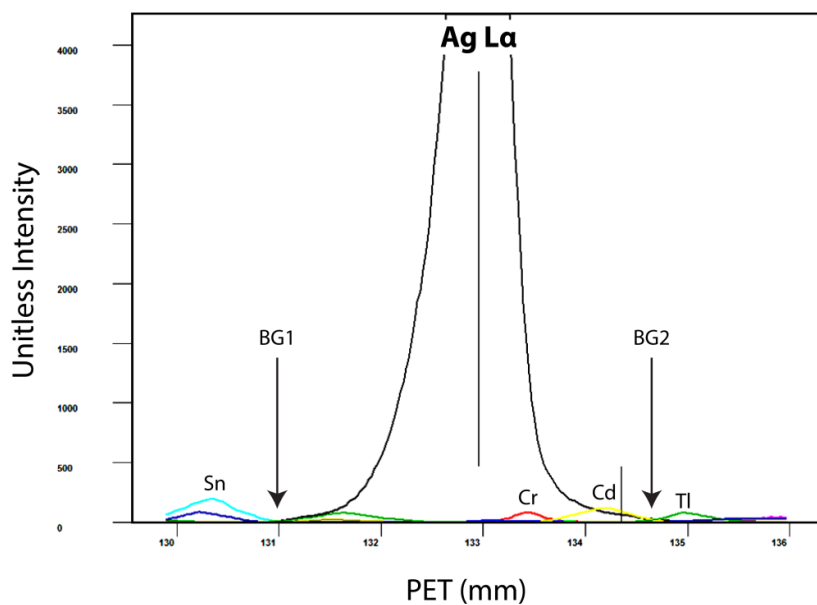
```

class="error">'.$lot.'

```

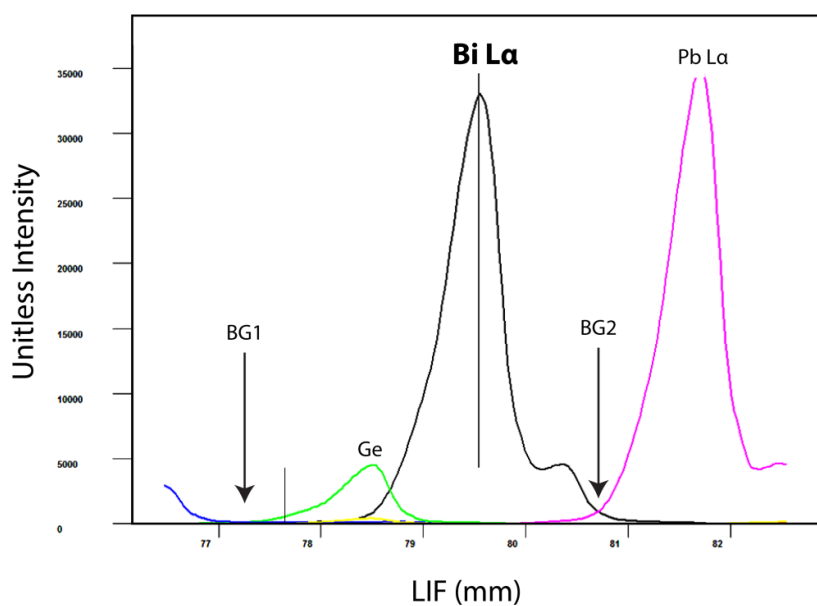
## Appendix—EPMA Trace Elements in Iron—Background Positions

### Silver (Ag)



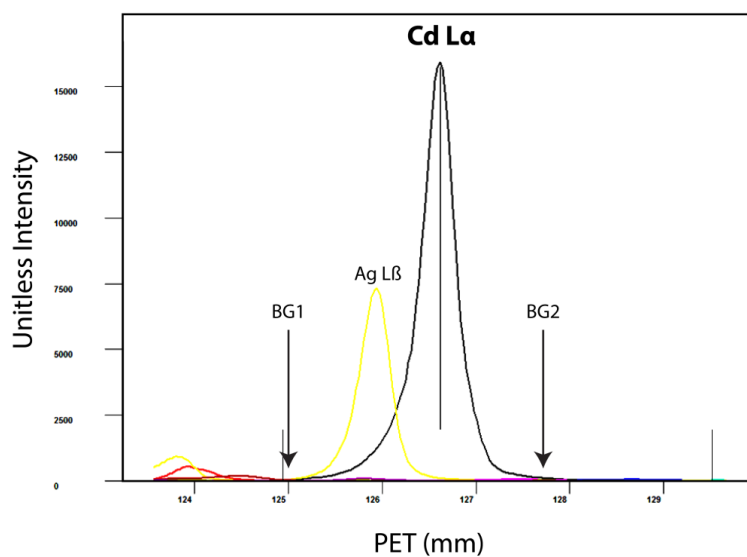
### Bismuth (Bi)

Ge K $\beta$ 1 very close on low side. Pb La1 very close on high side.



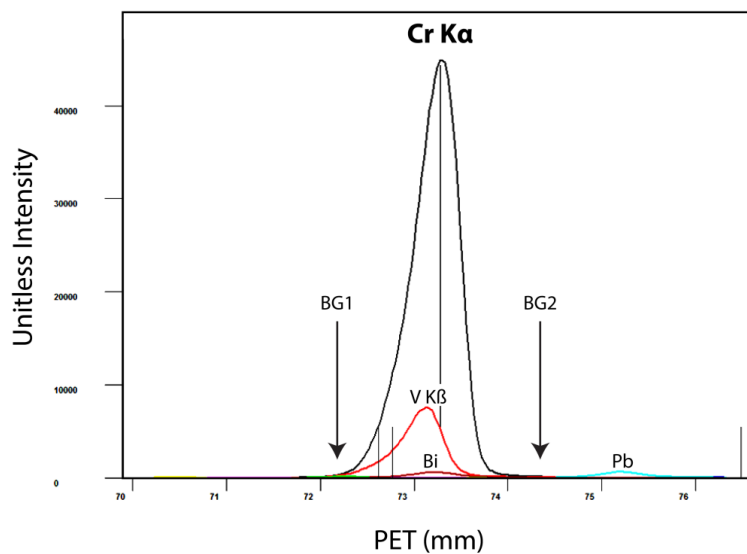
## Cadmium (Cd)

Ag L $\beta$ 1 very close on low side, almost an overlap, but not quite. Fe K $\beta$  2<sup>nd</sup> on low side, background pulled in slightly to avoid.

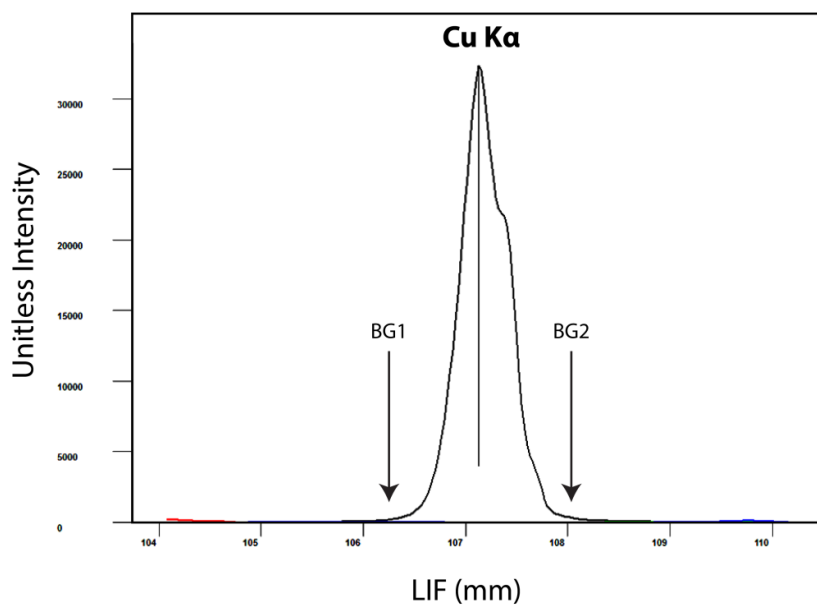


## Chromium (Cr)

Overlap correction for V K $\beta$  required.

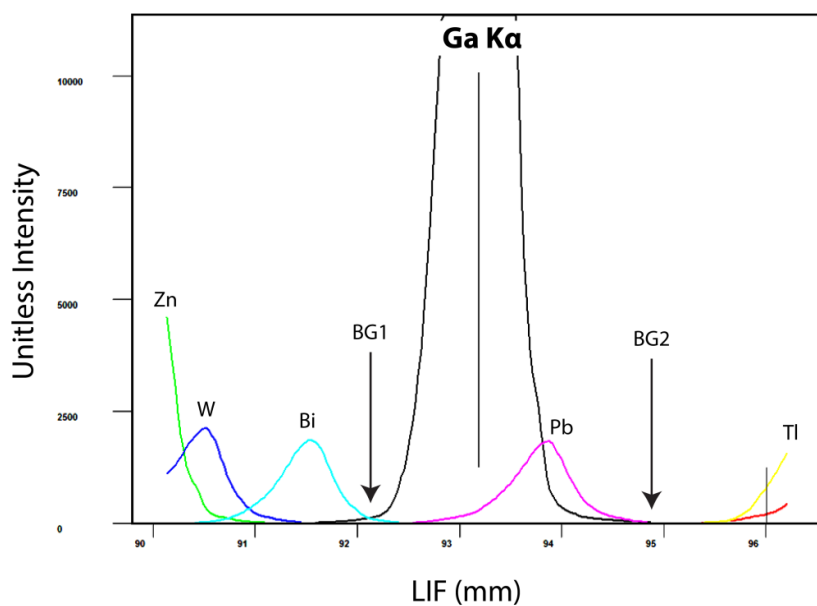


## Copper (Cu)



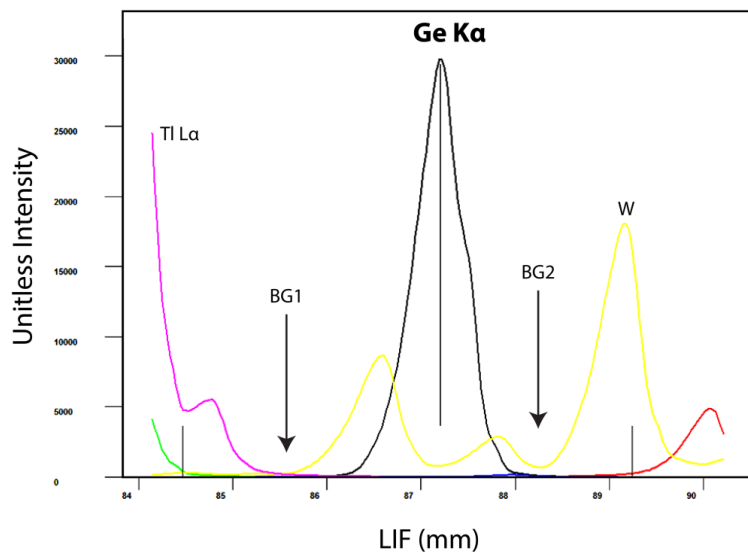
## Gallium (Ga)

Pb Li very close on high side. Minor Bi, W, and Zn lines encroaching on low side.



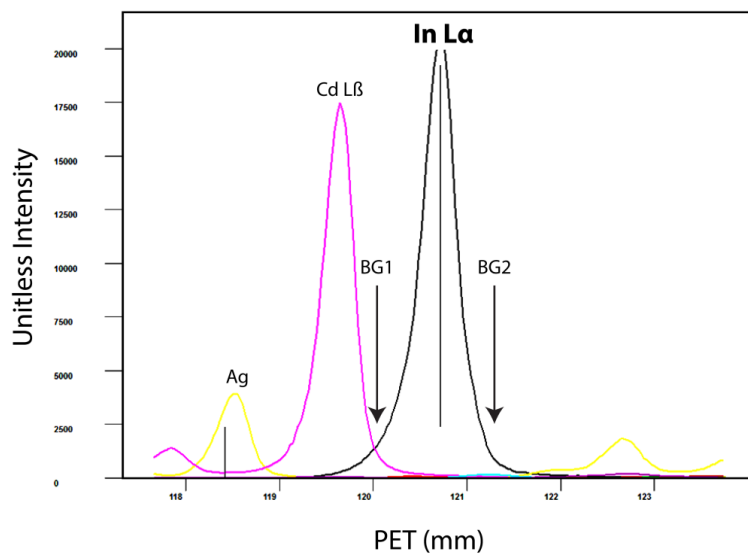
## Geranium (Ge)

W L $\beta$ 2 and L $\beta$ 3 lines overlap. An overlap is required if W present above trace levels.



## Indium (In)

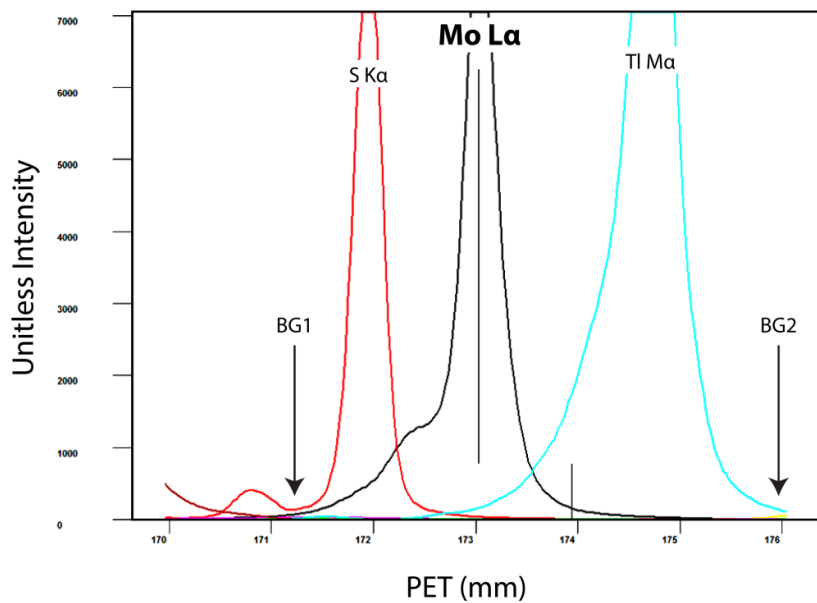
CdL $\beta$ 1 very close on low side. Ag L $\beta$ 2 on low side, and Ag L $\beta$ 3 on high side. Calibrate with -1.200 and +0.840 but pull in backgrounds to positions shown for trace analysis.





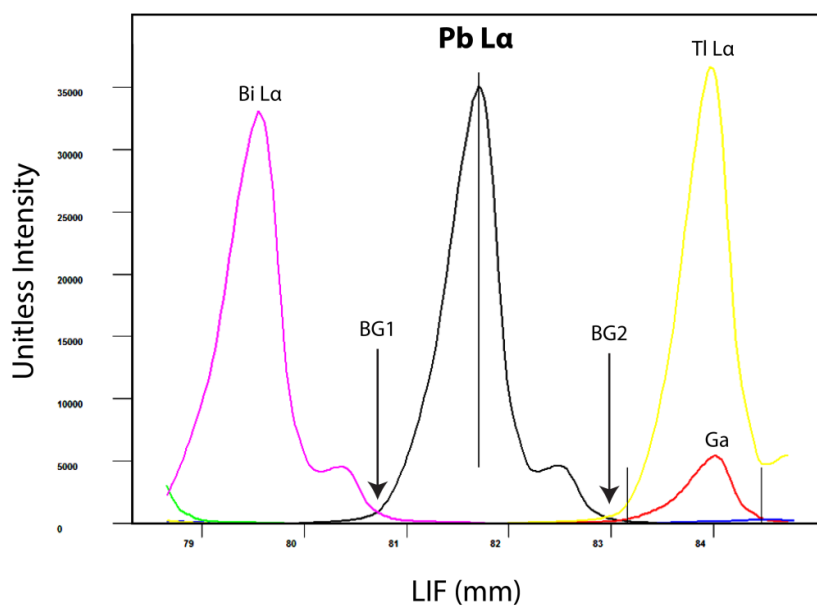
## Molybdenum (Mo)

S K $\alpha$  very close on low side. Tl M $\alpha$  very close on right side.



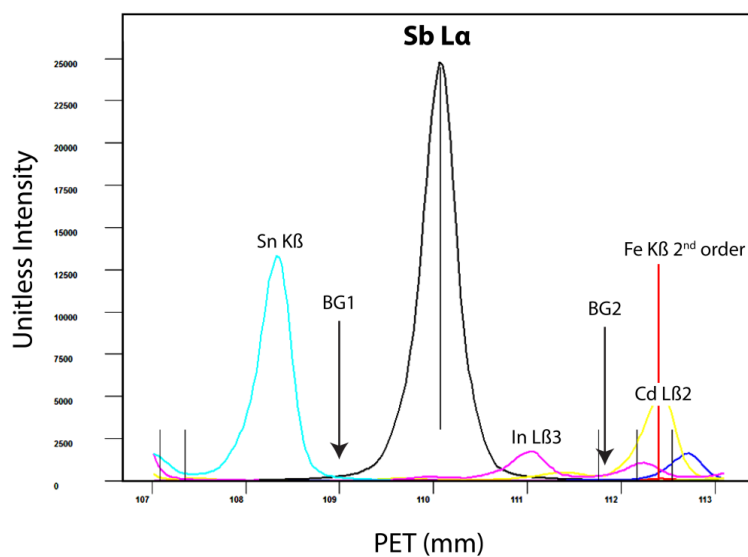
## Lead (Pb)

Bi L $\alpha$  on low side. Tl L $\alpha$  on high side.



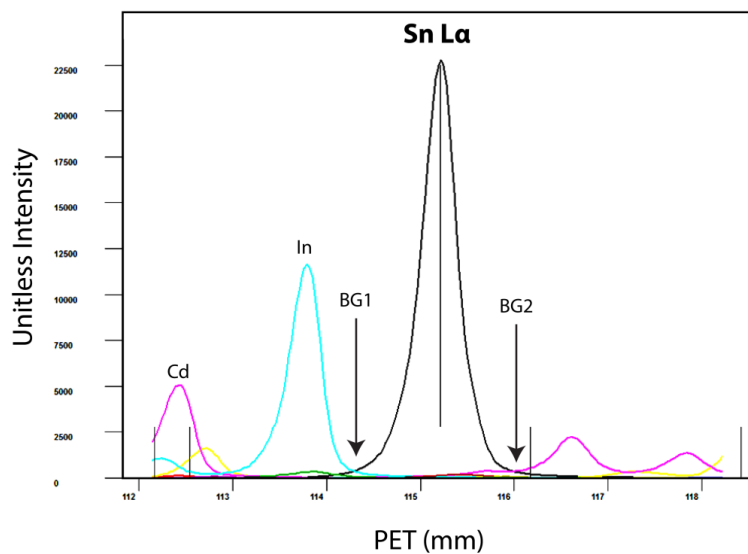
## Antimony (Sb)

Fe K $\beta$  2<sup>nd</sup> order on high side. Sn L $\beta$ 1 close on low side. In L $\beta$ 3 and L $\beta$ 4 on high side. Cd L $\beta$ 2 on high side.



## Tin (Sn)

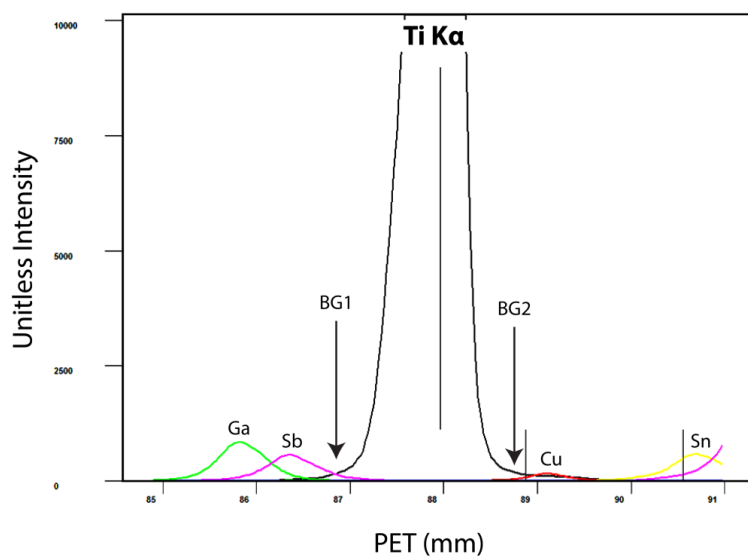
In L $\beta$ 1 very close on low side. Cd L $\beta$ 3 on high side. Calibrate with  $-1.100$  and  $+1.100$ .



## Titanium (Ti)

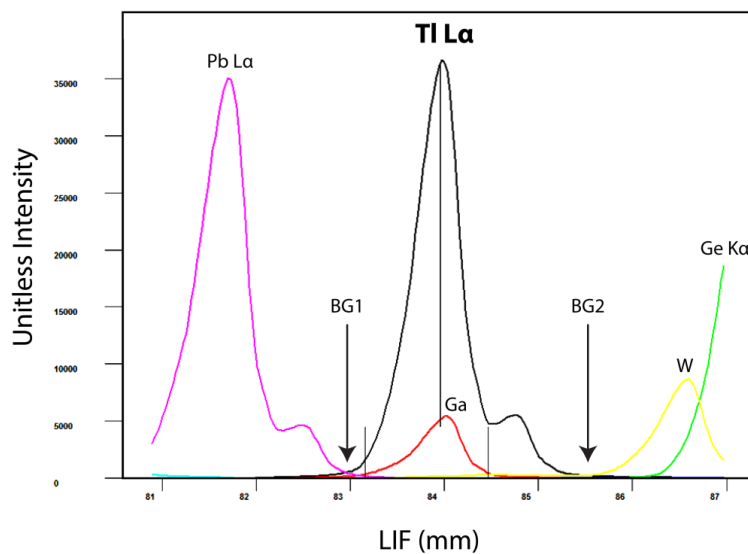
Minor lines of Ge, Sb, Cu, and Sn, on either side of peak. Backgrounds should avoid these.

Calibrate with  $-1.000$  and  $+1.000$ .



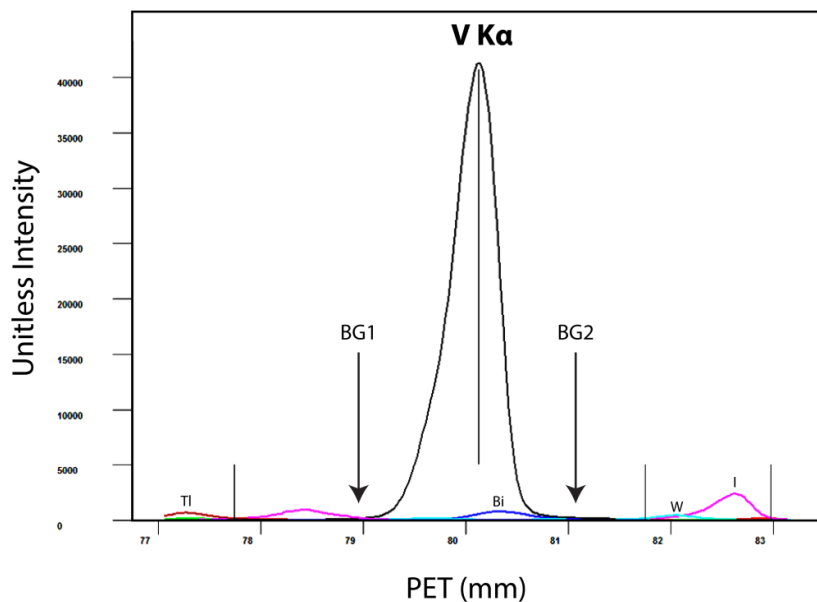
## Thallium (Tl)

Pb  $L\alpha$  on low side. Overlap from Ga  $K\beta$ . Minor W and Ge lines on high side.

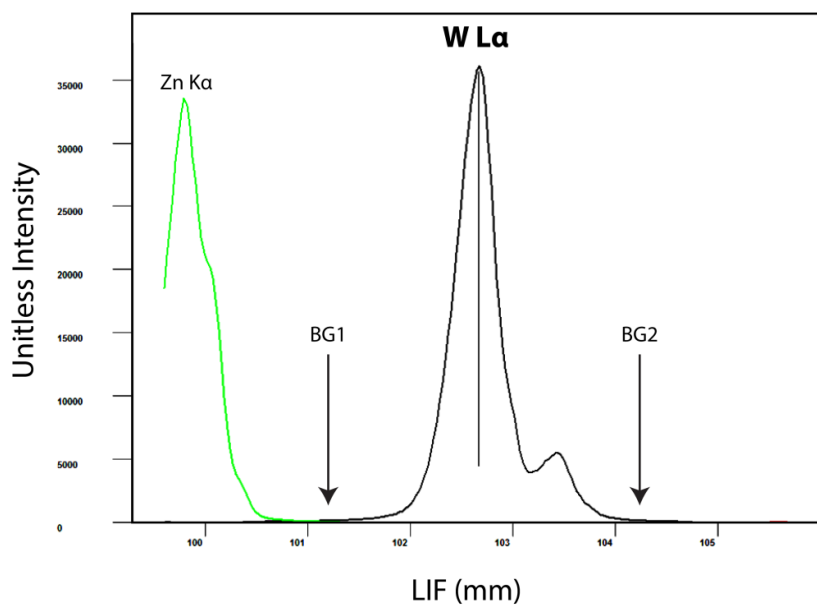


## Vanadium (V)

Overlap correction for Ti K $\beta$  required (line not shown in figure). Minor lines of Tl, Bi, W and I present on either side of peak.

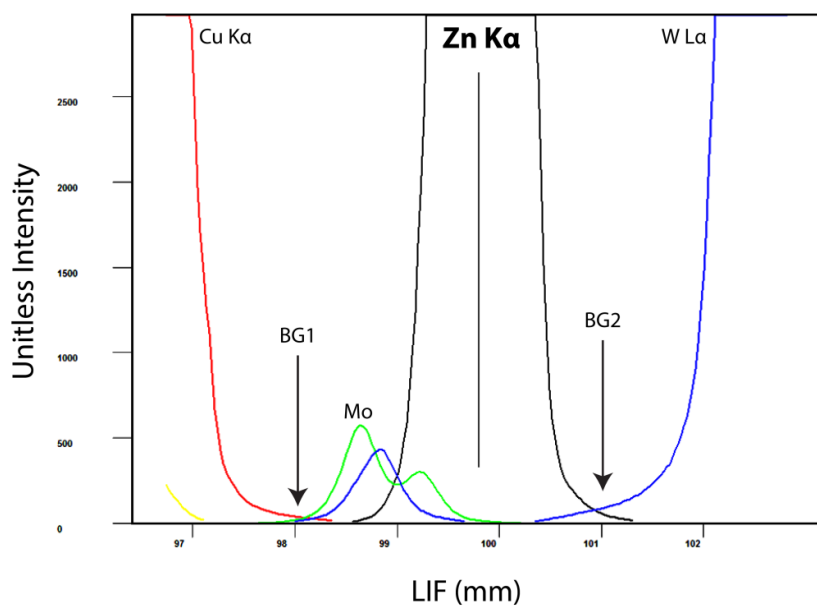


## Tungsten (W)



## Zinc (Zn)

Cu K $\alpha$  on low side and W L $\alpha$  on high side. Minor Mo lines present on low side but can be avoided.



## Appendix—PENEPM Simulation Compositions (10x10 Grid)

| #  | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | FeO   | MgO   | CaO   | Total  |
|----|------------------|--------------------------------|-------|-------|-------|--------|
| 1  | 32.61            | 16.21                          | 14.99 | 15.84 | 21.17 | 100.81 |
| 2  | 32.76            | 17.33                          | 15.50 | 13.20 | 22.42 | 101.22 |
| 3  | 32.37            | 17.39                          | 15.41 | 13.17 | 22.67 | 101.00 |
| 4  | 33.65            | 14.00                          | 14.10 | 21.52 | 17.89 | 101.17 |
| 5  | 32.49            | 17.10                          | 15.14 | 13.10 | 22.54 | 100.38 |
| 6  | 32.66            | 17.53                          | 15.34 | 13.35 | 22.53 | 101.41 |
| 7  | 40.32            | 0.01                           | 10.31 | 49.55 | 0.04  | 100.23 |
| 8  | 32.48            | 16.59                          | 15.44 | 14.62 | 21.95 | 101.07 |
| 9  | 32.64            | 17.26                          | 15.33 | 13.34 | 22.59 | 101.17 |
| 10 | 32.67            | 17.52                          | 15.49 | 13.29 | 22.52 | 101.49 |
| 11 | 32.61            | 17.35                          | 15.64 | 13.30 | 22.62 | 101.51 |
| 12 | 39.44            | 0.65                           | 10.31 | 48.52 | 0.54  | 99.46  |
| 13 | 40.28            | 0.00                           | 10.09 | 49.53 | 0.04  | 99.95  |
| 14 | 32.38            | 17.39                          | 15.67 | 13.39 | 22.42 | 101.24 |
| 15 | 32.87            | 17.66                          | 15.74 | 13.18 | 22.38 | 101.83 |
| 16 | 32.94            | 14.91                          | 15.21 | 19.25 | 19.50 | 101.81 |
| 17 | 32.98            | 17.42                          | 15.00 | 13.32 | 22.34 | 101.04 |
| 18 | 32.59            | 17.37                          | 15.61 | 13.31 | 22.44 | 101.31 |
| 19 | 40.10            | 0.00                           | 10.16 | 49.44 | 0.02  | 99.73  |
| 20 | 40.11            | 0.41                           | 10.09 | 48.77 | 0.37  | 99.76  |
| 21 | 32.63            | 17.26                          | 15.62 | 13.31 | 22.65 | 101.47 |
| 22 | 32.73            | 17.41                          | 15.68 | 13.52 | 22.15 | 101.51 |
| 23 | 32.48            | 16.49                          | 15.32 | 15.22 | 21.96 | 101.46 |
| 24 | 32.35            | 17.36                          | 15.32 | 13.17 | 22.28 | 100.48 |
| 25 | 32.68            | 17.50                          | 15.32 | 13.36 | 22.38 | 101.24 |
| 26 | 32.75            | 17.30                          | 15.21 | 13.25 | 22.64 | 101.15 |
| 27 | 32.52            | 17.42                          | 15.40 | 13.30 | 22.30 | 100.94 |
| 28 | 32.95            | 14.27                          | 14.82 | 19.77 | 19.21 | 101.02 |
| 29 | 32.63            | 17.44                          | 15.29 | 13.11 | 22.56 | 101.04 |
| 30 | 32.58            | 17.47                          | 15.51 | 13.34 | 22.48 | 101.38 |
| 31 | 32.52            | 17.26                          | 15.22 | 13.25 | 22.50 | 100.75 |
| 32 | 32.75            | 17.41                          | 15.62 | 13.39 | 22.50 | 101.67 |
| 33 | 32.77            | 17.34                          | 15.44 | 13.09 | 22.46 | 101.10 |
| 34 | 33.03            | 17.37                          | 15.71 | 13.17 | 22.34 | 101.61 |
| 35 | 32.75            | 17.40                          | 15.89 | 13.39 | 22.45 | 101.88 |
| 36 | 32.63            | 16.53                          | 15.68 | 16.09 | 21.45 | 102.38 |
| 37 | 35.63            | 10.62                          | 13.23 | 29.82 | 12.49 | 101.80 |
| 38 | 32.31            | 17.13                          | 15.44 | 13.92 | 21.93 | 100.73 |
| 39 | 37.71            | 6.60                           | 12.10 | 37.59 | 8.25  | 102.26 |
| 40 | 40.12            | 0.09                           | 10.11 | 49.33 | 0.10  | 99.75  |
| 41 | 32.73            | 17.32                          | 15.48 | 13.44 | 22.47 | 101.45 |
| 42 | 32.61            | 17.36                          | 15.58 | 13.33 | 22.31 | 101.19 |
| 43 | 32.88            | 17.45                          | 15.42 | 13.41 | 22.58 | 101.74 |
| 44 | 32.76            | 17.58                          | 15.42 | 13.24 | 22.62 | 101.63 |
| 45 | 32.97            | 17.13                          | 15.37 | 13.08 | 22.33 | 100.88 |
| 46 | 32.82            | 17.35                          | 15.37 | 13.05 | 22.58 | 101.18 |
| 47 | 38.96            | 4.01                           | 11.24 | 42.47 | 4.60  | 101.28 |
| 48 | 40.17            | 0.01                           | 10.13 | 49.69 | 0.02  | 100.02 |
| 49 | 32.66            | 17.66                          | 15.46 | 13.33 | 22.47 | 101.58 |
| 50 | 32.56            | 17.55                          | 15.39 | 13.26 | 22.26 | 101.02 |

20kV; CalcZAF; Bastin PROZA; FFAST MACs

| #   | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | FeO   | MgO   | CaO   | Total  |
|-----|------------------|--------------------------------|-------|-------|-------|--------|
| 51  | 39.98            | 0.07                           | 10.10 | 49.44 | 0.06  | 99.64  |
| 52  | 37.49            | 7.58                           | 12.28 | 36.21 | 9.09  | 102.65 |
| 53  | 39.97            | 0.00                           | 10.10 | 49.42 | 0.02  | 99.51  |
| 54  | 39.74            | 1.37                           | 10.55 | 47.07 | 1.42  | 100.15 |
| 55  | 32.67            | 17.28                          | 15.97 | 13.34 | 22.38 | 101.64 |
| 56  | 32.76            | 17.63                          | 15.54 | 13.49 | 22.40 | 101.82 |
| 57  | 32.66            | 17.45                          | 15.91 | 13.31 | 22.22 | 101.55 |
| 58  | 32.92            | 17.37                          | 15.50 | 13.23 | 22.49 | 101.50 |
| 59  | 32.33            | 17.32                          | 15.68 | 13.27 | 22.46 | 101.05 |
| 60  | 40.09            | 0.00                           | 10.22 | 49.60 | 0.02  | 99.93  |
| 61  | 32.81            | 17.24                          | 15.58 | 13.15 | 22.25 | 101.03 |
| 62  | 40.41            | 0.06                           | 9.97  | 49.44 | 0.07  | 99.96  |
| 63  | 32.66            | 17.53                          | 15.93 | 13.14 | 22.27 | 101.54 |
| 64  | 32.59            | 17.39                          | 15.20 | 13.27 | 22.31 | 100.75 |
| 65  | 40.34            | 0.04                           | 10.19 | 49.43 | 0.05  | 100.05 |
| 66  | 33.00            | 15.45                          | 15.57 | 18.30 | 20.15 | 102.47 |
| 67  | 39.95            | 0.00                           | 10.35 | 49.57 | 0.01  | 99.89  |
| 68  | 32.69            | 17.48                          | 16.01 | 13.19 | 22.40 | 101.75 |
| 69  | 40.00            | 0.00                           | 10.59 | 50.93 | 0.02  | 101.54 |
| 70  | 40.25            | 0.00                           | 10.26 | 49.86 | 0.03  | 100.41 |
| 71  | 32.57            | 17.28                          | 15.50 | 13.27 | 22.56 | 101.19 |
| 72  | 32.86            | 15.18                          | 15.40 | 18.68 | 19.91 | 102.03 |
| 73  | 40.05            | 0.00                           | 10.18 | 49.48 | 0.02  | 99.73  |
| 74  | 32.69            | 17.33                          | 15.67 | 13.06 | 22.49 | 101.23 |
| 75  | 32.48            | 17.34                          | 15.68 | 13.32 | 22.62 | 101.45 |
| 76  | 33.35            | 17.72                          | 15.48 | 13.35 | 22.43 | 102.33 |
| 77  | 32.93            | 17.58                          | 15.23 | 13.41 | 22.75 | 101.90 |
| 78  | 39.82            | 0.00                           | 9.95  | 49.46 | 0.03  | 99.26  |
| 79  | 32.28            | 16.12                          | 15.29 | 16.81 | 21.06 | 101.56 |
| 80  | 32.12            | 17.17                          | 15.32 | 13.18 | 22.57 | 100.36 |
| 81  | 32.33            | 17.43                          | 15.58 | 13.43 | 22.46 | 101.22 |
| 82  | 40.14            | 0.00                           | 10.10 | 49.19 | 0.03  | 99.46  |
| 83  | 32.72            | 17.35                          | 15.57 | 13.44 | 22.85 | 101.93 |
| 84  | 32.32            | 17.59                          | 15.49 | 13.14 | 22.62 | 101.17 |
| 85  | 32.62            | 17.10                          | 15.91 | 13.39 | 22.78 | 101.80 |
| 86  | 32.09            | 17.32                          | 15.63 | 13.44 | 23.00 | 101.47 |
| 87  | 40.09            | 0.01                           | 10.20 | 49.70 | 0.04  | 100.05 |
| 88  | 32.42            | 17.30                          | 15.24 | 13.22 | 22.52 | 100.70 |
| 89  | 34.39            | 12.24                          | 14.16 | 25.84 | 14.82 | 101.44 |
| 90  | 32.25            | 17.36                          | 15.83 | 12.97 | 22.40 | 100.81 |
| 91  | 32.38            | 17.25                          | 15.40 | 13.46 | 22.56 | 101.04 |
| 92  | 33.01            | 14.81                          | 14.99 | 19.34 | 19.28 | 101.43 |
| 93  | 32.56            | 17.45                          | 15.40 | 13.43 | 22.38 | 101.22 |
| 94  | 32.59            | 16.93                          | 15.64 | 13.40 | 22.46 | 101.03 |
| 95  | 32.75            | 17.28                          | 15.54 | 12.96 | 22.59 | 101.12 |
| 96  | 40.26            | 0.01                           | 10.28 | 49.61 | 0.03  | 100.19 |
| 97  | 33.18            | 17.36                          | 15.53 | 13.54 | 22.61 | 102.23 |
| 98  | 33.24            | 17.21                          | 15.31 | 13.05 | 22.68 | 101.49 |
| 99  | 32.70            | 17.21                          | 15.52 | 13.18 | 22.52 | 101.13 |
| 100 | 40.14            | 0.00                           | 10.10 | 49.68 | 0.02  | 99.94  |

20kV; CalcZAF; Bastin PROZA; FFAST MACs

## Appendix—Models Used to Revise Epsilon-Carbon

In the table shown here the terms are:

$$[\text{AlO}_{1.5}] = X_{\text{AlO}_{1.5}}$$

$$[\text{AlO}_{1.5}][\text{SiO}_2] = X_{\text{AlO}_{1.5}} X_{\text{SiO}_2}$$

$$[\text{AlO}_{1.5}]^2 = X_{\text{AlO}_{1.5}}^2$$

For example, the terms in the table would produce the following model for Ag:

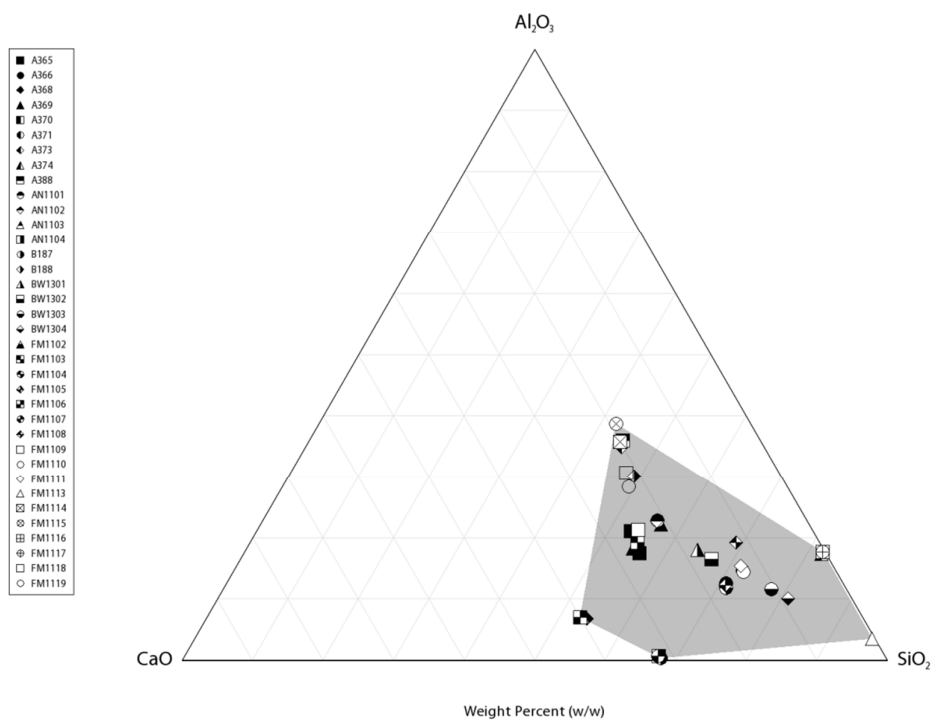
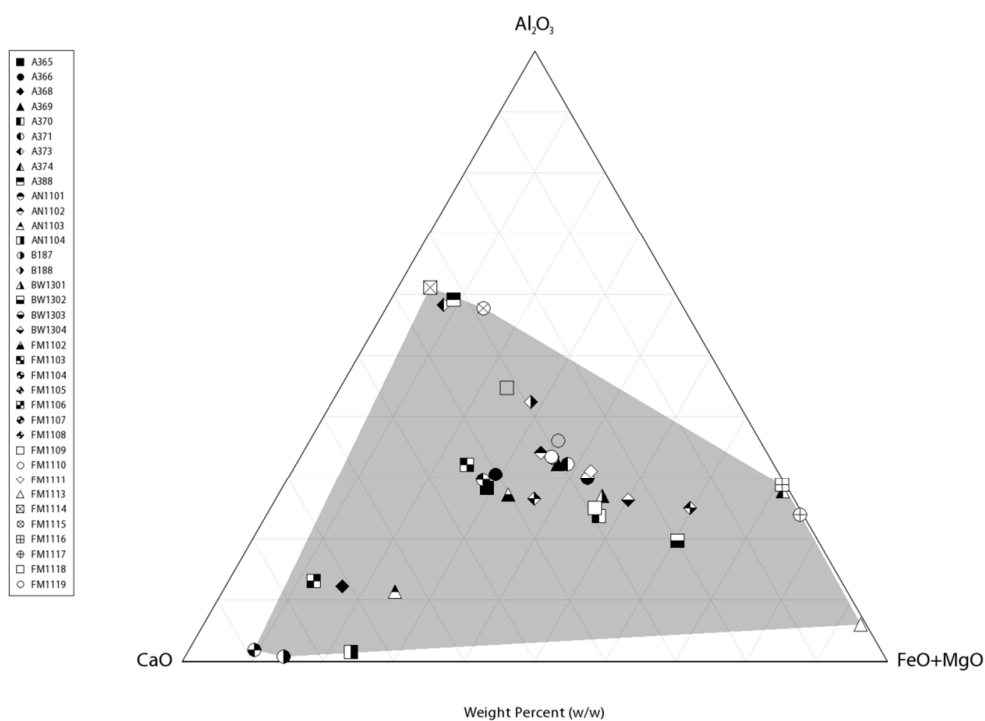
$$RT \ln \gamma_{\text{Ag}} = -42711 + 532991X_{\text{FeO}} + 247848X_{\text{AlO}_{1.5}}X_{\text{MgO}} + 290489X_{\text{CaO}}X_{\text{MgO}} + 109722X_{\text{CaO}}^2$$

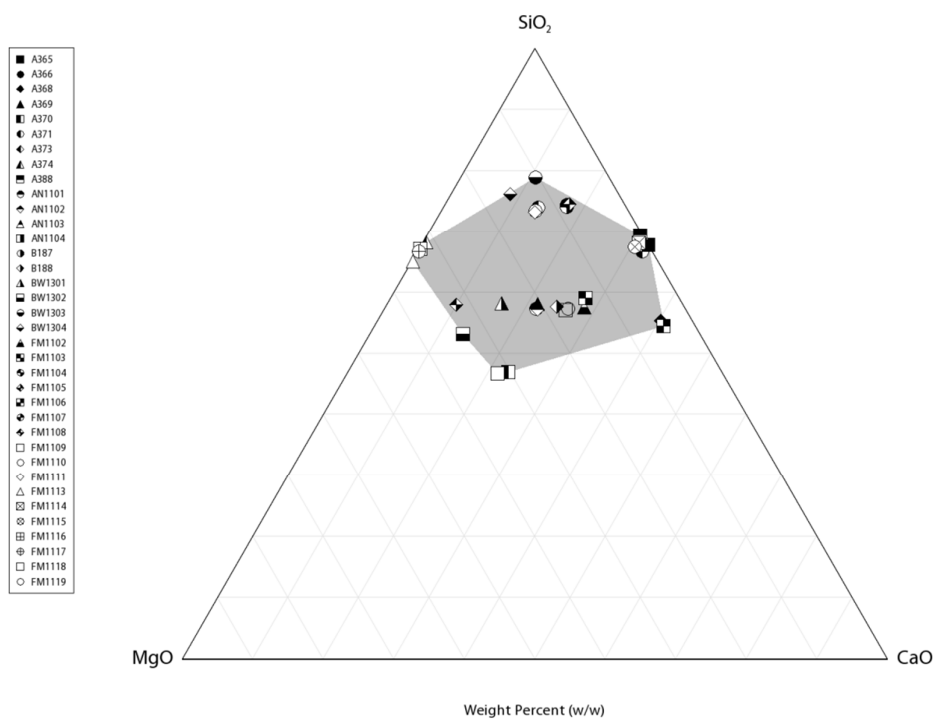
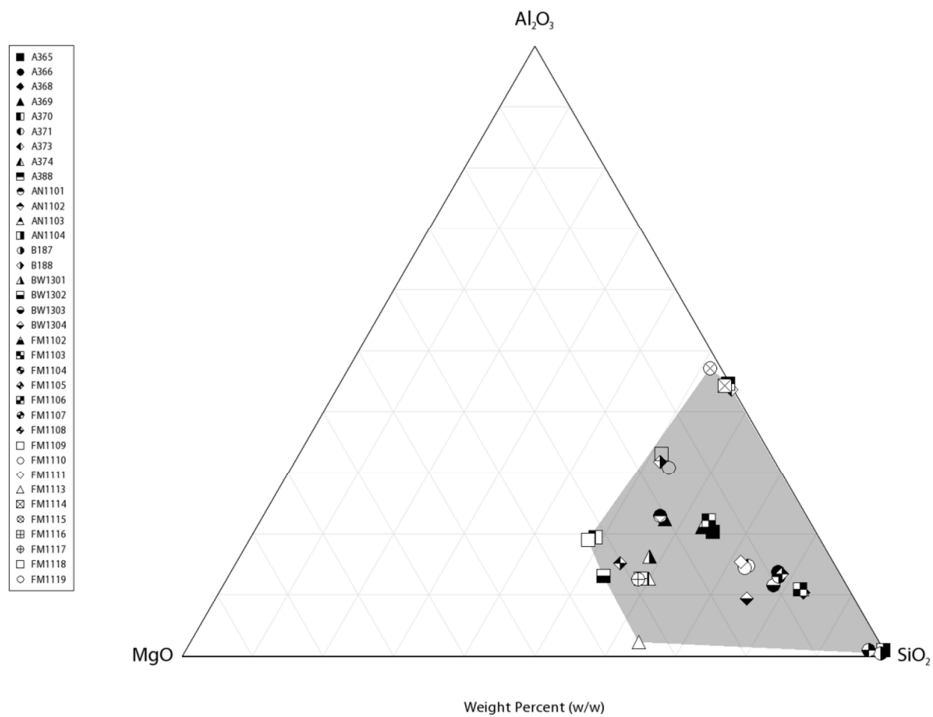


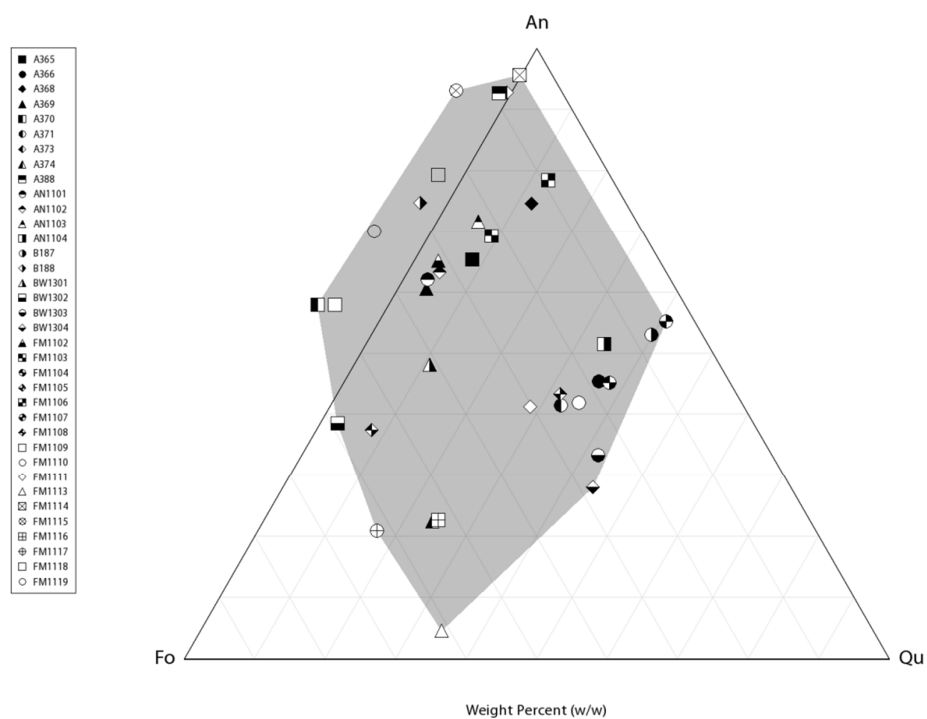
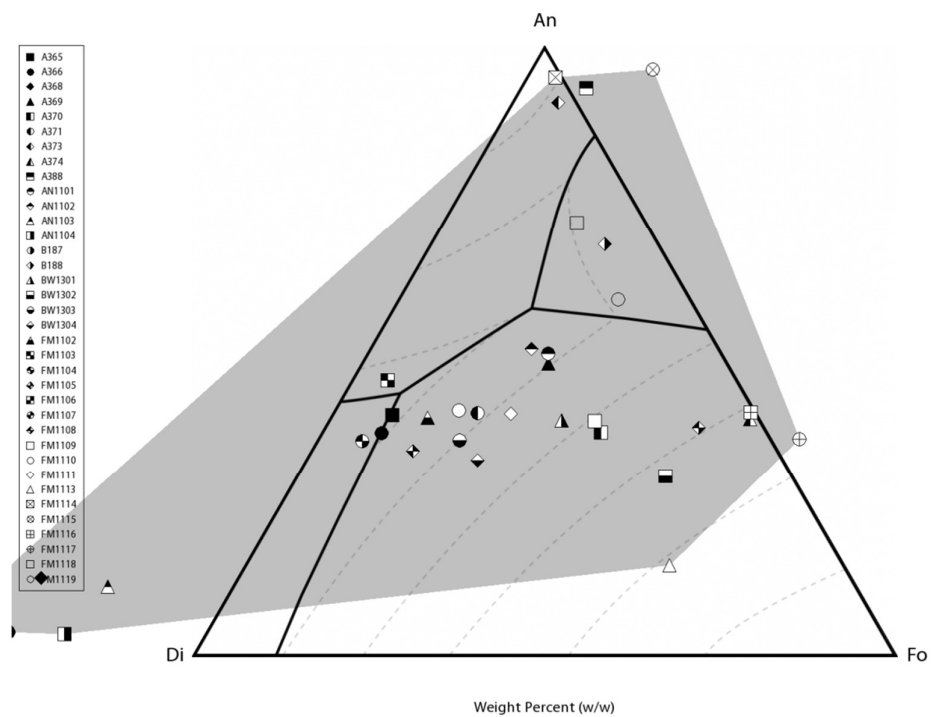
| # Terms                                  | Ag     | Bi     | Cd       | Cr      | Cu    | Ga       | Ge     | In      | Mo       | Pb      | Sb        | Sn      | Tl      | V       | W        | Zn       |
|------------------------------------------|--------|--------|----------|---------|-------|----------|--------|---------|----------|---------|-----------|---------|---------|---------|----------|----------|
|                                          | 5      | 3      | 5        | 5       | 4     | 5        | 3      | 6       | 6        | 5       | 7         | 5       | 4       | 4       | 8        | 5        |
| Constant                                 | -42711 | -50280 | -169397  | -38572  | 25340 | -122573  | -27703 | -79054  | 54550    | 20953   | -1657006  | -67218  | -5973   | -75443  | 265047   | -22110   |
| [AlO <sub>1.5</sub> ]                    |        |        |          |         |       |          |        |         | -163635  |         |           |         |         |         |          |          |
| [CaO]                                    |        |        |          |         |       |          |        |         |          |         |           |         |         |         |          |          |
| [FeO]                                    | 532997 | 624430 | 3427312  | -574950 |       |          |        |         |          |         | 48873971  | 51242   |         |         |          | -207005  |
| [MgO]                                    |        |        |          |         | 12656 |          |        |         |          |         |           |         |         |         | -976282  |          |
| [SiO <sub>2</sub> ]                      |        |        |          |         |       |          |        |         |          |         |           |         |         |         |          |          |
| [AlO <sub>1.5</sub> ][CaO]               |        |        |          |         |       |          |        |         |          | -238915 | 933368    |         | -141144 |         |          |          |
| [AlO <sub>1.5</sub> ][FeO]               |        |        |          |         |       |          |        |         | 1693332  |         |           |         |         |         | -4621424 |          |
| [AlO <sub>1.5</sub> ][MgO]               | 247848 |        |          |         |       | -2784784 |        | 239688  | -1483460 |         |           |         |         |         |          |          |
| [AlO <sub>1.5</sub> ][SiO <sub>2</sub> ] |        |        |          |         |       |          |        |         |          |         |           |         |         |         |          |          |
| [CaO][FeO]                               |        |        |          |         |       | 1095354  | 236743 | 1167593 |          | -189178 |           |         | -242942 |         | -6090592 |          |
| [CaO][MgO]                               | 290489 | 628833 |          |         | 90003 |          |        |         |          | 193240  |           |         | 269398  | -219511 |          |          |
| [CaO][SiO <sub>2</sub> ]                 |        |        |          |         |       |          |        |         |          |         | 152694    |         |         |         |          |          |
| [FeO][MgO]                               |        |        | 1993344  |         | 60137 |          | 825264 | -452815 | 2926526  |         | -15338566 | 716877  |         |         | 3238620  | -2683000 |
| [FeO][SiO <sub>2</sub> ]                 |        |        | -224960  |         |       |          |        |         |          |         |           |         |         |         | -1390677 |          |
| [MgO][SiO <sub>2</sub> ]                 |        |        |          |         |       |          |        |         |          |         |           |         |         |         |          |          |
| [AlO <sub>1.5</sub> ] <sup>2</sup>       |        |        |          | 36881   |       |          |        |         |          |         |           |         |         |         |          |          |
| [CaO] <sup>2</sup>                       | 109722 |        |          | -71887  |       |          |        |         |          |         | -149854   | -113277 |         | -135312 |          |          |
| [FeO] <sup>2</sup>                       |        |        | -2802280 |         |       | 3701610  |        | 4075430 | -2186480 |         | -34345183 |         |         |         | 6961061  |          |
| [MgO] <sup>2</sup>                       |        |        |          |         |       |          |        | 55764   |          |         |           | 52295   |         |         |          | 66453    |
| [SiO <sub>2</sub> ] <sup>2</sup>         |        |        |          | 45721   |       | 67839    |        |         |          | 169866  |           |         |         | 40394   | -132931  |          |

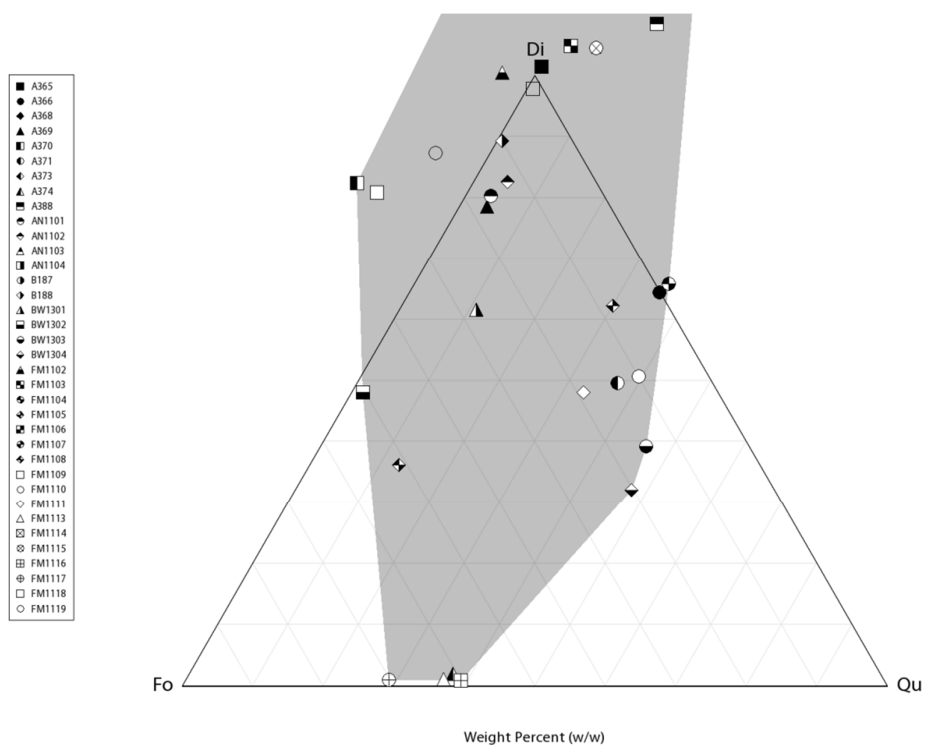
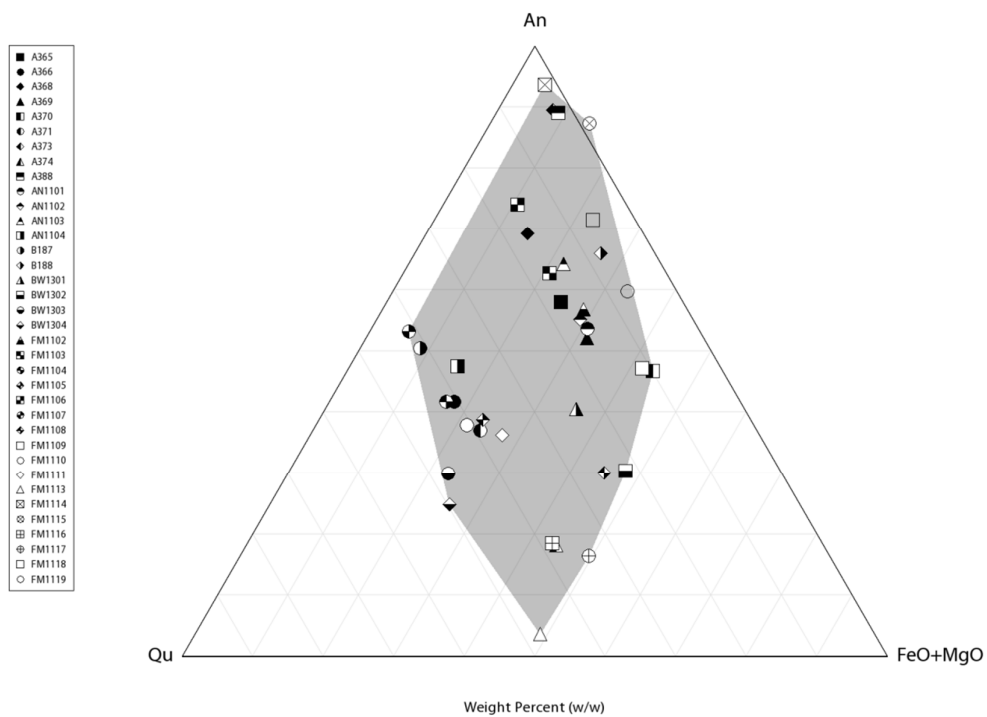
Model Terms

## Appendix—Silicate Melt Composition Ternary Diagrams









## Appendix –High Pressure Experiments

| Year | Date       | Run  | Alias          | Sample    | Trace  | Status | Notes                                                                       |
|------|------------|------|----------------|-----------|--------|--------|-----------------------------------------------------------------------------|
| 2012 |            |      | AN1102         | #5 (ADF)  | A      |        | Iron-Silicate Partitioning Experiment                                       |
| 2012 |            |      | FM1103         | #1 (AD)   | A      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1104         | #2        | A      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1106         | #3        | A      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1107         | #4        | A      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1109         | #6        | A      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1110         | #7        | A      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1113         | #8        | A      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1114         | #9 (AA)   | A      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1116         | #10 (SAF) | A      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1118         | #11       | A      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | AN1101         | #5 (ADF)  | F      |        | Iron-Silicate Partitioning Experiment                                       |
| 2012 |            |      | AN1103         | #3        | F      |        | Iron-Silicate Partitioning Experiment                                       |
| 2012 |            |      | AN1104         | #4        | F      |        | Iron-Silicate Partitioning Experiment                                       |
| 2013 |            |      | FM1112         | #8        | F      | FAILED | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | AN1204         | #8        | F      | FAILED | Iron-Silicate Partitioning Experiment                                       |
| 2012 |            |      | FM1102         | #1 (AD)   | F      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1105         | #2        | F      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1108         | #6        | F      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1111         | #7        | F      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1115         | #9 (AA)   | F      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1117         | #10 (SAF) | F      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2012 |            |      | FM1119         | #11       | F      |        | Iron-Silicate Partitioning Experiment (Run by FM)                           |
| 2013 | 15/04/2013 | B143 | BW1301         | #         | A      |        | Carbon-Free Iron-Silicate Partitioning Experiment (Run by BJW)              |
| 2013 | 16/04/2013 | B144 | BW1302         | #         | F      |        | Carbon-Free Iron-Silicate Partitioning Experiment (Run by BJW)              |
| 2013 | 16/04/2013 | B145 | BW1303         | #         | F      |        | Carbon-Free Iron-Silicate Partitioning Experiment (Run by BJW)              |
| 2013 | 16/04/2013 | B146 | BW1304         | #         | A      |        | Carbon-Free Iron-Silicate Partitioning Experiment (Run by BJW)              |
| 2014 | 13/06/2013 | B162 | BW162A         | #         | Custom |        | Iron Standard (Run by BJW)                                                  |
| 2014 | 14/06/2013 | B163 | BW163F         | #         | Custom |        | Iron Standard (Run by BJW)                                                  |
| 2014 | 04/11/2013 | A348 | BW1326N        | #         | Custom |        | Iron Standard (Run by BJW)                                                  |
| 2013 | 02/12/2013 | A360 | TraceTest Mix1 | #TT1      | Custom |        | Iron-Silicate Partitioning Experiment (Finding Best Reduced Comp Trace Mix) |
| 2013 | 02/12/2013 | A361 | TraceTest Mix2 | #TT2      | Custom |        | Iron-Silicate Partitioning Experiment (Finding Best Reduced Comp Trace Mix) |
| 2013 | 02/12/2013 | A362 | TraceTest Mix3 | #TT3      | Custom |        | Iron-Silicate Partitioning Experiment (Finding Best Reduced Comp Trace Mix) |
| 2013 | 18/12/2013 | A365 | A365           | #1 (AD)   | B      |        | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2013 | 19/12/2013 | A366 | A366           | #2        | B      |        | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2013 | 20/12/2013 | A368 | A368           | #3        | B      |        | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2013 | 20/12/2013 | B187 | B187           | #4        | B      |        | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2014 | 02/01/2014 | A369 | A369           | #5 (ADF)  | B      |        | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2014 | 03/01/2014 | A370 | A370           | #6        | B      |        | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2014 | 03/01/2014 | A371 | A371           | #7        | B      |        | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2014 | 08/01/2014 | A372 | A372           | #8        | B      | FAILED | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2014 | 09/01/2014 | A373 | A373           | #9 (AA)   | B      |        | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2014 | 10/01/2014 | A374 | A374           | #10 (SAF) | B      |        | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2014 | 10/01/2014 | B188 | B188           | #11       | B      |        | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2014 | 31/01/2014 | A388 | A388           | #9 (AA)   | B      |        | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2014 | 31/01/2014 | A386 | A386           | #8        | B      | FAILED | Iron-Silicate Partitioning Experiment (Reduced Comp Trace Mix)              |
| 2014 | 13/08/2014 | A463 | A463           | Mix1      | Custom |        | Iron Standard                                                               |
| 2014 | 19/08/2014 | A565 | A565           | Mix2      | Custom |        | Iron Standard                                                               |
| 2014 | 20/08/2014 | A566 | A566           | Mix3      | Custom |        | Iron Standard                                                               |
| 2014 | 10/09/2014 | A572 | A572           | Mix4      | Custom |        | Iron Standard                                                               |
| 2014 | 10/09/2014 | A573 | A573           | Mix5      | Custom |        | Iron Standard                                                               |
| 2014 | 11/09/2014 | A575 | A575           | Mix6      | Custom |        | Iron Standard                                                               |
| 2015 | 15/04/2015 | A669 | G3A1           | G3A       | Custom |        | Iron Standard                                                               |
| 2015 | 16/04/2015 | A670 | G3A2           | G3A       | Custom |        | Iron Standard                                                               |
| 2015 | 20/04/2015 | A672 | G3Ag1          | G3Ag      | Custom |        | Iron Standard                                                               |
| 2015 | 10/06/2015 | A693 | G3Ti1          | G3Ti      | Custom |        | Iron Standard                                                               |
| 2015 | 11/06/2015 | A694 | G3Pb1          | G3Pb      | Custom |        | Iron Standard                                                               |
| 2015 | 17/06/2015 | A695 | G3Cd1          | G3Cd      | Custom |        | Iron Standard                                                               |
| 2015 | 19/06/2015 | A698 | G3Bi1          | G3Bi      | Custom |        | Iron Standard                                                               |

## Appendix—Stirring Furnace Experiments

| Experiment | Date       | Mix         | Temp (°C) | RunTime (min) | log(fO <sub>2</sub> ) | Run Quality | Notes                                                                                       |
|------------|------------|-------------|-----------|---------------|-----------------------|-------------|---------------------------------------------------------------------------------------------|
| F001       | 22/03/2015 | Albite + Na | 1400      | 10            | Air                   |             | Testing run                                                                                 |
| F002       | 27/03/2015 | Albite      | 1400      | 30            | Air                   |             | Testing run                                                                                 |
| F003       | 30/03/2015 | Albite      | 1400      | 40            | Air                   |             | Failed, dimensions incorrect.                                                               |
| F004       | 31/03/2015 | Albite      | 1400      |               | Air                   |             | Failed, dimensions incorrect.                                                               |
| F005       | 01/04/2015 | Albite      | 1400      | 150           | Air                   |             | Perfect test run.                                                                           |
| F006       | 10/11/2015 | EBT1        | 1300      | 10            | -7                    | GOOD        |                                                                                             |
| F007       | 11/11/2015 | EBT1        | 1300      | 30            | -7                    | GOOD        |                                                                                             |
| F008       | 13/11/2015 | EBT1        | 1300      | 60            | -7                    | GOOD        |                                                                                             |
| F009       | 23/11/2015 | EBT1        | 1300      | 180           | -7                    |             | Crucible jammed on quench, so run time unreliable as it cooled in the guide tube overnight. |
| F010       | 24/01/2015 | EBT1        | 1300      | 180           | -7                    | GOOD        |                                                                                             |
| F011       | 25/11/2015 | EBT1        | 1300      | 180           | -7                    |             | Test run without stirrer turned on.                                                         |
| F012       | 26/11/2015 | EBT1        | 1300      | 5             | -9                    | GOOD        |                                                                                             |
| F013       | 26/11/2015 | EBT1        | 1300      | 30            | -9                    | GOOD        | Guide tube cracked, but sample quenched successfully.                                       |
| F014       | 27/11/2015 | EBT1        | 1300      | 60            | -9                    | GOOD        |                                                                                             |
| F015       | 11/12/2015 | EBT1        | 1300      | 30            | -11                   | GOOD        |                                                                                             |
| F016       | 17/12/2015 | EBT1        | 1300      | 60            | -11                   |             | Sample foamed extensively and jammed, no mount made.                                        |
| F017       | 21/12/2015 | EBT1        | 1300      | 60            | -11                   |             | Sample jammed on quench, fell out 60 mins later. Quench quality and run time unreliable.    |
| F018       | 23/12/2015 | EBT1        | 1300      | 60            | -11                   | GOOD        |                                                                                             |
| F019       | 04/02/2015 | EBT1        | 1300      | 60            | -13                   | GOOD        |                                                                                             |

## Appendix—Starting Composition CMAS Projections

