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## Evaporation of moderately volatile elements from silicate melts: experiments and theory

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### Abstract

Moderately volatile elements (MVEs) are sensitive tracers of vaporisation in geological and cosmochemical processes owing to their balanced partitioning between vapour and condensed phases. Differences in their volatilities allows the thermodynamic conditions, particularly temperature and oxygen fugacity ( $fO_2$ ), at which vaporisation occurred to be quantified. However, this exercise is hindered by a lack of experimental data relevant to the evaporation of MVEs from silicate melts. We report a series of experiments in which silicate liquids are evaporated in one-atmosphere (1-atm) gas-mixing furnaces under controlled  $fO_2$ s, from the Fe-“FeO” buffer (iron-wüstite, IW) to air ( $10^{-0.68}$  bars), bracketing the range of most magmatic rocks. Time- ( $t$ ) and temperature ( $T$ ) series were conducted from 15 to 930 minutes and 1300-1550°C, at or above the liquidus for a synthetic ferrobalt, to which 20 elements, each at 1000 ppm, were added. Refractory elements (*e.g.*, Ca, Sc, V, Zr, REE) are quantitatively retained in the melt under all conditions. The MVEs show highly redox-dependent volatilities, where the extent of element loss as a function of  $fO_2$  depends on the stoichiometry of the evaporation reaction(s), each of which has the general form  $M^{x+n}O_{(x+n)/2} = M^xO_{x/2} + n/4O_2$ . Where  $n$  is positive (as in most cases), the oxidation state of the element in the gas is more reduced than in the liquid, meaning lower oxygen fugacity promotes evaporation. We develop a general framework, by integrating element vaporisation stoichiometries with Hertz-Knudsen-Langmuir (HKL) theory, to quantify evaporative loss as a function of  $t$ ,  $T$  and  $fO_2$ . Element volatilities from silicate melts differ from those during solar nebular condensation, and can thus constrain the conditions of volatile loss in post-nebular processes. Evaporation in a single event strongly discriminates between MVEs, producing a step-like abundance pattern in the residuum, similar to that observed in the Moon or Vesta. Contrastingly, the gradual depletion of MVEs according to their volatility in the Earth is inconsistent with their loss in a single evaporation event, and instead likely reflects accretion from many smaller bodies that had each experienced different degrees of volatilisation.

Keywords: Moderately Volatile Element, Evaporation, Volatile Depletion, Experiment, Silicate Melts

## 1.0. Introduction

Phase transformation from condensed (liquid, l, or solid, s) to gaseous (g) form, termed evaporation, is a ubiquitous geological process occurring during outgassing of ascending magmas (Symonds and Reed, 1993; Mather et al., 2012), upon heating attending meteorite impacts in the crust (Humayun and Koeberl, 2004; Moynier et al., 2009) and, on a larger scale, in planetary accretion processes (O'Neill, 1991; Alexander, 2001; Visscher and Fegley, 2013). The *volatility* of an element refers to its tendency to partition into the gas phase relative to condensed phases, and at equilibrium, depends on the thermodynamic conditions, especially the temperature and  $fO_2$  at which these processes occur.

Under solar nebula conditions, the volatility of an element is quantified by its '50% condensation temperature',  $T_c^{50}$ , the temperature at which half its mass is calculated to condense from a gas of solar composition at equilibrium (Larimer, 1967). As  $T_c^{50}$  of the elements vary among one another, their abundances in chondrites may be used to constrain temperatures at which they accreted (*e.g.*, Keays et al. 1971; Laul et al. 1973), a concept known as 'cosmothermometry' (Urey, 1954). Although elemental abundances in chondrites correlate positively with  $T_c^{50}$ , these temperatures refer to specific conditions; that of a rarified (tenuous) nebular gas, with assumed pressures,  $P_{total}$  of  $10^{-3}$ - $10^{-5}$  bar (Larimer, 1967; Grossman, 1972; Grossman and Larimer, 1974; Lodders, 2003), in which  $H_2$  is the most abundant species, such that  $pH_2 \sim P_{total}$ . The correspondingly low  $H_2O/H_2$  ( $5 \times 10^{-4}$ ; Rubin et al. 1988) of the solar nebula promotes very reducing conditions,  $\sim 7$  log units below the iron-wüstite (IW) oxygen buffer at 1400 K. Low total pressures result in condensation temperatures that are below the silicate, metal and sulfide solidi, such that condensation occurs into solid phases (Ebel, 2004).

In the absence of any other scale,  $T_c^{50}$  has been widely used to quantify element volatility in various other contexts, such as degassing from planetary bodies. Although refractory elements and the main components (Fe, Mg, Si) in the Earth and other planetary bodies (the Moon, Mars, Vesta) have abundances similar to those in chondritic meteorites, the moderately volatile elements (MVEs), with  $650 < T_c^{50}$  (K)  $< 1300$  at  $10^{-4}$  bar (Palme et al., 1988), are variably depleted (Urey, 1954; Ringwood, 1966; Wanke and Dreibus, 1988; O'Neill and Palme, 1998; Albarède et al., 2015). The sub-equal distribution of MVEs between the gas and condensed phases holds promise for quantifying the conditions of volatile loss processes, which neither refractory elements (hardly lost) nor highly volatile elements (almost entirely lost) address.

Chondrite-normalised abundances of lithophile MVEs in the mantles of differentiated rocky bodies plotted against  $T_c^{50}$  define 'volatility trends'. Depletions of siderophile MVEs relative to these trends point to their additional loss to planetary cores (*e.g.*, Wood et al. 2006; Siebert and Shahar 2015). However, the proportions of siderophile MVEs (*e.g.*, Ga, Pb, In) inferred to reside in Earth's core using this approach are irreconcilable with their experimentally-determined metal-silicate partition coefficients

36 (Wang et al. 2016; Blanchard et al. 2017; Ballhaus et al. 2017; Norris and Wood, 2017), suggesting  $T_c^{50}$   
37 may not be an apt descriptor of volatility at the conditions relevant to the formation of Earth.

38 The assumption implicit in the use of  $T_c^{50}$  states that volatile loss occurred under the same solar nebular  
39 conditions experienced by chondritic meteorites, and therefore neglects variations in nebular chemistry  
40 (*cf.* Ebel and Grossman 2000; Schaefer and Fegley 2010), in addition to the likelihood that planetary  
41 bodies continued to accrete following dissipation of the nebular gas. Indeed, numerical simulations of  
42 planetary formation highlight the potential for chemical fractionation to occur throughout their growth  
43 (*e.g.*, Morbidelli et al. 2012; Carter et al. 2015). These *post-nebular* processes include collisional erosion  
44 of differentiated material (O'Neill and Palme, 2008; Bonsor et al., 2015) and melting and evaporation of  
45 planetesimals or planets *via*  $^{26}\text{Al}$  and  $^{60}\text{Fe}$  decay (Sahijpal et al., 2007) or impact heating (Pahlevan et al.,  
46 2011). Models for the Moon-forming impact invoke temperatures  $\geq 4000$  K (*e.g.*, Melosh 1990;  
47 Nakajima and Stevenson 2014) and pressures between  $10^3$  and 100 bar (Canup et al., 2015). The  $f\text{O}_2$  of  
48 the gas evolved by evaporation of silicates is close to the Fayalite-Magnetite-Quartz (FMQ) buffer  
49 (De Maria et al., 1971; Visscher and Fegley, 2013; Costa et al., 2017), orders of magnitude higher  
50 than in the solar nebula. Moreover, elemental depletions in planetary environments reflect not only  
51 volatility, but also the ability for the gas species to be carried away from the locus of vaporisation,  
52 which varies with physical factors such as planetary size, molar mass and atmospheric structure  
53 (Chamberlain and Hunten, 1989). As such, equilibrium is not mandated during evaporation (Young et  
54 al. 2019) and the physical mechanism cannot, *a priori*, be treated as the inverse of equilibrium  
55 condensation. Indeed, MVE depletion patterns in many planetary bodies are quite unlike those in  
56 chondritic meteorites (*e.g.*, O'Neill and Palme, 2008), attesting to their accretion under conditions and/or  
57 *via* mechanisms distinct from those of the solar nebula. Volatility trends established under these post-  
58 nebular conditions should thus diverge from expectations based on  $T_c^{50}$ . Together, these  
59 considerations call for more quantitative descriptions of element volatility relevant to the evaporation  
60 of silicate melts.

61 Existing experimental constraints (Chapman and Scheiber, 1969; Notsu et al., 1978; Bart et al., 1980;  
62 Tsuchiyama et al., 1981; Kreuzberger et al., 1986; Shimaoka et al., 1994; Wulf et al., 1995; Norris and  
63 Wood, 2017; Braukmüller et al., 2018) highlight a dependence of element volatility on  $f\text{O}_2$ ; some  
64 elements (*e.g.*, Zn, Cd, Na) become more volatile at low  $f\text{O}_2$ , whereas others (*e.g.*, Ir, Au, As) become  
65 less so. Differences were found between volatilities inferred from evaporation of silicate melts and  
66 those calculated for solar nebula condensation. While abundances of elements that are refractory in the  
67 solar nebula (*e.g.*, Al, Ti, Sc, REEs) increased in evaporation residues (Chapman and Scheiber, 1969;  
68 Notsu et al., 1978), K ( $T_c^{50} = 1006$  K) was observed to vaporise more readily than Na ( $T_c^{50} = 958$  K)  
69 (Kreuzberger et al., 1986) while In ( $T_c^{50} = 536$  K) was found to be less volatile than Zn ( $T_c^{50} = 726$  K)  
70 (Norris and Wood, 2017). Norris and Wood (2017) argued that, because this order of volatility better  
71 matched the MVE depletions observed in Earth's mantle, they were lost *via* evaporation from silicate

72 melts rather than during nebular condensation. Nevertheless, a theoretical understanding of the process  
73 studied in these experiments has hitherto not been addressed.

74 Here, we present experimental results of trace element loss during Langmuir (free) evaporation of a  
75 ferrobaltic melt composition as a function of run time, temperature and  $fO_2$ . We develop a theoretical  
76 approach based on Hertz-Knudsen-Langmuir (HKL) theory (*e.g.* Knudsen 1909) that quantifies the  
77 effect of  $t$ ,  $T$  and  $fO_2$  on element loss and determines stoichiometries of element vaporisation reactions.  
78 This model enables extrapolation and prediction of evaporative element loss from silicate melts and is  
79 used to better understand the conditions and mechanisms that lead to volatile depletion among rocky  
80 planetary bodies.

## 81 2.0. Methods

### 82 2.1. Experimental Methods

83 Reagent-grade, major-element oxide powders ( $Fe_2O_3$ - $MgO$ - $Al_2O_3$ - $SiO_2$ ) were weighed out and ground  
84 in an agate mortar. Calcium was added as carbonate ( $CaCO_3$ ). The major element composition (Table  
85 1) represents a compromise between achieving a low liquidus temperature whilst still resembling a  
86 realistic planetary mantle composition. To this end, an Anorthite-Diopside eutectic composition was  
87 used, to which roughly 15 wt. % each of forsterite and  $Fe_2O_3$  were added. Trace elements were added  
88 to a separate mixture; the alkalis (Li, Na, K, Rb) were added as carbonates. The remaining elements  
89 were added as oxides, so as to mimic their speciation in silicate melts (addition of elements as  
90 solutions, *e.g.*, nitrates was avoided as this may cause elements to behave abnormally during heating).  
91 Oxides added were:  $Cu_2O$ ,  $Ga_2O_3$ ,  $GeO_2$ ,  $PbO$ ,  $MnO$ ,  $MoO_2$ ,  $V_2O_5$ ,  $ZrO_2$ ,  $Sc_2O_3$ ,  $ZnO$ ,  $TiO_2$ ,  $La_2O_3$ ,  
92  $Gd_2O_3$ ,  $Yb_2O_3$ ,  $Ag_2O$  and  $CdO$ , totalling 20 elements, six of which (Zr, Sc, Ti, and the REEs) are  
93 nominally refractory. All oxides were added in proportions equivalent to one-another, to give  $\approx$   
94 28,000 ppm of the element in the final trace element mix, of which 3.6 wt. % was added to the  
95 FCMAS composition to give  $\approx$  1000 ppm of each element in the final mixture (Table 1). The  
96 ensemble was then decarbonated at 1000 °C for 24 h in air and re-ground. Experiments were also  
97 performed with the FCMAS mix prior to the addition of the trace element mixture to assess the degree  
98 of contamination during the experiments.

99 For each experiment, around 25 mg of powder was mixed into a viscous slurry with 100,000  
100 molecular weight polyethylene oxide and loaded onto a metal wire loop. In order to minimise Fe, and  
101 other metal loss to the loop, Re was used where possible at reducing conditions (below FMQ),  
102 whereas Pt loops (and one Ir loop) were used above FMQ. Oxygen fugacity was externally buffered  
103 by CO-CO<sub>2</sub> gas mixtures metered from Tylan mass flow controllers (range 0–200 and 0–20 standard  
104 cubic centimetres per minute, sccm), whose performance was checked *in-situ* using a yttria-stabilised  
105 zirconia SIRO<sub>2</sub> oxygen sensor at 1000 °C (see O'Neill and Eggins, 2002). The sensor was not used in

106 the actual experiments because of the high temperatures. Oxygen fugacities varied between  $10^{-10}$  bar  
107 ( $\approx IW$ ) to  $10^{-0.68}$  bar (air) at a given temperature, at an estimated accuracy of  $\pm 0.05$  log units. Excepting  
108 experiments in air and at ANU, the total gas flow rate was kept constant at each oxygen fugacity,  $\approx$   
109 200 sccm. Gas flow rates are listed in Table 2, along with run duration and temperature. Experiments  
110 performed at Westfälische Wilhelms-Universität, Münster, are denoted by the code ‘M’, those at the  
111 Research School of Earth Sciences, ANU, by ‘C’ and at the Institut de Physique du Globe de Paris, by  
112 ‘P’.

113 Samples were introduced into the 3-cm-long hotspot of a 42-mm internal-diameter, 70-cm-long  
114 GERO vertical alumina tube furnace directly at the set-temperature, between  $1300 < T$  ( $^{\circ}\text{C}$ )  $< 1550$ ,  
115 with run times between 15 min and 930 min. Gases were allowed to run and equilibrate in the sealed  
116 furnace tube for  $\approx 10$  min prior to sample introduction. The gas continually flowed through the tube,  
117 and was evacuated by a line at the top of the furnace. The volume of the furnace tube relative to that  
118 of the sample is sufficiently large that vapour produced upon sample evaporation was efficiently  
119 removed from the hotspot and condensed in the cold zones of the tube, thereby approximating an open  
120 system. Temperature was controlled with a thermocouple external to the alumina muffle tube by a  
121 Eurotherm® controller, limiting fluctuations to within  $\pm 1$   $^{\circ}\text{C}$ . Temperatures were independently  
122 measured, and adjusted as necessary, with a Type B thermocouple bead (Klemme and O’Neill, 2000)  
123 located  $< 5$  mm above the sample. Run duration is reported from the time of sample insertion and  
124 therefore includes a thermal equilibration time. This time (defined as the time needed to reach 99% of  
125 the set temperature) was determined to be between 4 – 7 minutes, conforming to the relationship  $dT/dt$   
126  $= k(T_{\text{final}} - T)$ , where  $k$  is the response time constant. When integrated with respect to time and  
127 temperature, this gives  $t = (-\ln(T_{\text{final}} - T) + \ln(T_{\text{initial}} - T))/k$ . The value of  $k$  was experimentally determined to  
128 be 0.018 at  $1350^{\circ}\text{C}$  from the observed increase in temperature for a Type B thermocouple bead of  $10^{-4}$   
129 m radius. The response time constant is related to specific heat capacity ( $C_p$ ), mass ( $m$ ) and area ( $A$ ) of  
130 the material by the expression  $k = hA/mC_p$ , where  $h$  is the external heat transfer coefficient and  
131 depends on the properties of the gas phase. Since silicate melt spheres in our experiments have higher  
132 heat capacities ( $\approx 1500$  J/kgK) and surface areas ( $\approx 2 \times 10^{-5}$  m<sup>2</sup>) than the thermocouple bead,  
133 equilibration times are expected to be similar. Charges were quenched by dropping them into a  
134 beaker of distilled water.

## 135 *2.2. Analytical Methods*

136 Trace element abundances in the quenched glasses were measured by Laser-Ablation Inductively-  
137 Coupled Plasma Mass Spectrometry (LA-ICP-MS) at the Institut für Mineralogie, Westfälische  
138 Wilhelms-Universität Münster. Glasses were mounted in epoxy and polished before being placed in a  
139 dual-volume Helix cell filled with He gas ( $\approx 1$  L/min; large cell and 0.33 L/min, small cell). Ablation  
140 was performed by a Photon Machines Analyte G2 193 nm ArF excimer laser with a repetition rate of

141 10 Hz, a total fluence of 4 J/cm<sup>2</sup> and a spot size of 130 μm (25 μm for zoning profiles). The ablation  
142 sequence consisted of 20 s background and 40 s of counting time, in which the ablated material was  
143 carried to the *ThermoFisher* Element II running in low resolution mode. Each mass peak is measured  
144 four times (100 samples per peak with a mass window of 4%) for a total of 0.02 s each. The isotopes  
145 measured for this purpose were: <sup>7</sup>Li, <sup>23</sup>Na, <sup>29</sup>Si, <sup>39</sup>K, <sup>43</sup>Ca, <sup>45</sup>Sc, <sup>47</sup>Ti, <sup>49</sup>Ti, <sup>51</sup>V, <sup>53</sup>Cr, <sup>55</sup>Mn, <sup>60</sup>Ni, <sup>63</sup>Cu,  
146 <sup>66</sup>Zn, <sup>69</sup>Ga, <sup>72</sup>Ge, <sup>73</sup>Ge, <sup>85</sup>Rb, <sup>90</sup>Zr, <sup>93</sup>Nb, <sup>95</sup>Mo, <sup>107</sup>Ag, <sup>111</sup>Cd, <sup>115</sup>In, <sup>133</sup>Cs, <sup>139</sup>La, <sup>157</sup>Gd, <sup>172</sup>Yb, <sup>182</sup>W,  
147 <sup>185</sup>Re, <sup>193</sup>Ir, <sup>195</sup>Pt, <sup>208</sup>Pb, totalling an analytical pass time of roughly 0.6 s. Oxide production rates, as  
148 monitored by the <sup>232</sup>Th<sup>16</sup>O/<sup>232</sup>Th ratio, were < 0.1 %.

149 Samples were ablated between 6 – 12 times, with care taken to analyse both the core and rim of the  
150 glass bead, permitting detection of any zoning. Standards bracketed sample ablation every 12 – 24  
151 points (*i.e.*, every two samples), and consisted of a set of three NIST-612 and two basaltic standards  
152 (either BCR-2G, GSD-1G, GSE-1G or BIR-1G, depending on the session). Standardisation was  
153 performed in two stages. Firstly, the NIST-612 standard glass, in which trace elements are present at ≈  
154 40 ppm levels, was used to produce calibration curves relating counts per second to concentration for  
155 a given isotope. Following this initial normalisation, <sup>29</sup>Si was used as an internal standard (41 wt. %  
156 SiO<sub>2</sub> in samples) to correct for matrix effects between the samples and NIST-612 by comparison with  
157 BCR-2G, GSD-1G, GSE-1G or BIR-1G, whose matrix is a good analogue for the experimental  
158 glasses.

159 Relative standard deviation (RSD) across all elements in a given sample was 5.1±0.4% (SD),  
160 excluding cases where the element concentration was near the detection limit (frequently Cd and Ag,  
161 but also in some experiments where elements have been quantitatively lost). In these instances, the  
162 RSD increases to 15 – 20%, while Li also has a high RSD (≈10%), presumably owing to the analyses  
163 of Li tetra- and metaborate-fluxed fused discs on the LA-ICP-MS system. For major elements and  
164 those with interference-free masses (*e.g.*, Na, Sc, V, Cr, Mn, Rb and the REE), RSD is typically 2-3  
165 %. Analytical accuracy was assessed by analyses of basaltic reference materials; concentrations of all  
166 elements were found to be within 10% (and often 5%) of the most recent published analyses using  
167 femtosecond LA-ICP-MS (Jochum et al. 2014; Li et al. 2015; Electronic Annex A). The sole  
168 exception is Ge; its measured abundance is systematically higher in BCR-2G (<sup>72</sup>Ge, 2.16±0.10 and  
169 <sup>73</sup>Ge, 2.23±0.16 ppm) and BIR-1G (<sup>72</sup>Ge, 4.25±0.60 and <sup>73</sup>Ge, 2.18±0.44 ppm) compared to published  
170 values (1.51±0.10 and 1.2±0.1 ppm, respectively). This discrepancy disappears for synthetic basaltic  
171 glasses with higher Ge contents; GSD-1G (39.07±0.99 vs. 40±1 ppm) and GSE-1G (391.6±13.6 vs.  
172 402±16 ppm), pointing to the production of <sup>56</sup>Fe<sup>16</sup>O<sup>+</sup> and lesser amounts of <sup>57</sup>Fe<sup>16</sup>O<sup>+</sup> and <sup>56</sup>Fe<sup>16</sup>O<sup>1</sup>H<sup>+</sup>  
173 on <sup>72</sup>Ge and <sup>73</sup>Ge, respectively. While these interferences degrade the accuracy of Ge measurements at  
174 low abundances (≈ 1 ppm), they are negligible at the concentrations relevant to the experiments (10 –  
175 1000 ppm).

176 3.0. Theoretical Framework

177 The kinetic theory of gases states that particles in an isothermal ideal gas have a Maxwell-Boltzmann  
 178 distribution of kinetic energies (Maxwell, 1860; Boltzmann, 1872). Such molecular chaos  
 179 (*stosszahlansatz*) occurs when the mean free path, the average distance travelled by a gaseous  
 180 molecule prior to collision, is greater than the diameter of the particles. At 1673 K and 1 bar, the mean  
 181 free path is  $\approx 5 \times 10^{-6}$  metres,  $10^4$  times larger than typical molecular diameters (Chapman and Cowling,  
 182 1970). In this framework, the number of particles striking a surface over a given time interval is given  
 183 by the Hertz-Knudsen-Langmuir (HKL) equation (Hertz, 1882; Knudsen, 1909; Langmuir, 1916;  
 184 Hirth and Pound, 1963; Richter et al., 2002):

$$\frac{dn_i}{dt} = -A \frac{\alpha_e p_{i,sat} - \alpha_c p_i}{\sqrt{2\pi RMT}}, \quad (1)$$

185 Here,  $\frac{dn_i}{dt}$  is the flux (mol/s),  $A$  the surface area ( $m^2$ ),  $p_{i,sat}$  is the equilibrium partial pressure of the  
 186 gas species of element  $i$  (Pa) and  $M$  its molar mass (kg/mol),  $p_i$  its partial pressure at the surface,  $\alpha_e$   
 187 and  $\alpha_c$  the dimensionless Langmuir coefficients for evaporation and condensation respectively,  $R$  the  
 188 gas constant (J/mol.K) and  $T$  absolute temperature.

189 Langmuir evaporation ( $p_{i,sat} \gg p_i$ ) involves liquid-gas equilibrium only at infinitesimally small  
 190 intervals, after which each parcel of gas is removed from the system, rendering it thermodynamically  
 191 irreversible. Theoretically, the HKL equation implicitly assumes thermal equilibrium between liquid  
 192 and gas. The high thermal mass of the surrounding gas with respect to sample in the furnace hotspot  
 193 satisfies this condition, under which the HKL equation accurately describes the Langmuir evaporation  
 194 flux (Littlewood and Rideal, 1956; Persad and Ward, 2016).

195 The evaporation rate is maximal when  $p_i = 0$  (eq. 1). Though not measurable in these experiments,  $p_i$   
 196 relates to the accumulation of molecules of  $i$  at the evaporating surface and hence depends on the  
 197 evaporation rate relative to the transport rate of  $i$  away from the surface. At our experimental  
 198 conditions, element evaporation rates are relatively slow ( $\approx 10^{-4}$  cm<sup>2</sup>/s) relative to transport rates,  
 199 which are due to both diffusion and advection, and are of the order of several cm<sup>2</sup>/s (Electronic Annex  
 200 B). In this limit the gas is instantaneously removed from the locus of evaporation, maintaining  $p_i \approx 0$   
 201 and, for a sphere, eq. 1 reduces to:

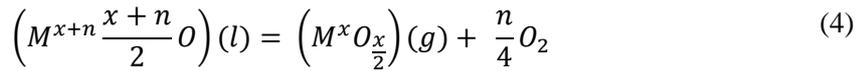
$$dn_i = -4\pi r^2 \frac{\alpha_e p_{i,sat}}{\sqrt{2\pi RMT}} dt. \quad (2)$$

202 Dividing eq. 2 by the total number of moles  $n_T^0$ , since  $\left(\frac{n_i}{n_T^0}\right) = X_i$  and  $n_T^0 = \frac{4\pi r^3 \rho}{3M}$ , gives:

$$dX_i = -\alpha_e p_{i,sat} \frac{3}{r\rho} \sqrt{\frac{M}{2\pi RT}} dt. \quad (3)$$

203 Element loss rate is also affected by the radius ( $r$ ) and density ( $\rho$ ) of the sample (eq. 3). A factor of 2  
 204 variation in  $r$  results in differences in concentration of  $\leq 7\%$ , and, because the major elements (Si,  
 205 Mg, Fe, Al and Ca) are non-volatile in the experiments,  $\rho$  is near-constant (Electronic Annex B).  
 206 Thus,  $r = 0.001$  m was used for all experiments and  $\rho$  was calculated for each run using the model of  
 207 Bottinga and Weill (1970) and varied between 2761 and 2905 kg/m<sup>3</sup>.

208 Though the equilibrium partial vapour pressure,  $p_{i,sat}$ , is not directly measurable in these kinetic  
 209 experiments, it may be calculated from equilibrium thermodynamics if the chemical reaction(s)  
 210 describing the vaporisation are known. In the general case of the evaporation of a metal oxide species  
 211 dissolved in the melt,  $(M^{x+n} \frac{x+n}{2} O)(l)$ , to a gaseous species that may have a different valence  
 212 state,  $(M^x O_{\frac{x}{2}})(g)$ , the reaction is:



213 Here,  $M$  is the metal,  $x$  its formal charge (an integer value) and  $n$  the number of electrons in the  
 214 reaction. Because the evaporating gas is tenuous, we assume ideal gas behaviour, such that  $f = p$ .  
 215 The equilibrium constant of eq. 4,  $K_{(4)}$ , re-arranged to solve for  $p$ , the partial pressure of  $M^x O_{\frac{x}{2}}$  in the  
 216 gas, is:

$$p(M^x O_{\frac{x}{2}}) = \frac{K_{(4)} X(M^{x+n} O_{\frac{x+n}{2}}) \gamma(M^{x+n} O_{\frac{x+n}{2}})}{f(O_2)^{n/4}}. \quad (5)$$

217 In eq. 5,  $X$  and  $\gamma$  refer to the mole fraction and activity coefficient, respectively, of  $M^{x+n} O_{\frac{x+n}{2}}$  in the  
 218 liquid. For clarity, we make the substitution  $i = M^{x+n} O_{\frac{x+n}{2}}$ . We take the standard state as that of the  
 219 pure liquid oxide at the temperature and pressure of interest. We assume that the concentration of an  
 220 evaporating element is in the Henry's law region, such that its activity coefficient,  $\gamma_i$ , is equivalent to  
 221 that at infinite dilution,  $\gamma_i^\infty$ . Where  $\gamma_i^\infty = 1$ , the solution of component  $i$  in the liquid is ideal.  
 222 Likewise, when the Langmuir evaporation coefficient  $\alpha_e$  is unity, Langmuir evaporation is considered  
 223 ideal. As the values of  $\alpha_e$  and  $\gamma_i^\infty$  are not known *a priori*, it is convenient to define a modified  
 224 equilibrium constant,  $K^*$ :

$$K^* = \alpha_e \gamma_i^\infty K. \quad (6)$$

225 It is the composite parameter  $K^*$  that will be determined from the experiments. For some elements,  $K$   
 226 and  $\gamma_i^\infty$  are known from independent equilibrium thermochemical measurements, allowing  $\alpha_e$  to be  
 227 calculated using eq. 6. Alternatively, if  $\alpha_e$  is defined then  $\gamma_i^\infty$  may be computed by the quotient  $K^*/K$ .  
 228 With this simplification, eqs. 5 and 6 may be substituted into eq. 3, giving:

$$dX_i = -\frac{K_{(4)}^*}{f(O_2)^{n/4}} \frac{3}{r\rho} \sqrt{\frac{M}{2\pi RT}} dt \quad (7)$$

229 Integrating eq. 7 with respect to  $dX_i$  and  $dt$  yields:

$$\frac{X_i^t}{X_i^0} = \exp\left(-\frac{K_{(4)}^*}{f(O_2)^{n/4}} \frac{3}{r\rho} \sqrt{\frac{M}{2\pi RT}} (t - t_0)\right) \quad (8)$$

230 Equation 8 returns the mole fraction of element  $i$  remaining in the melt after a given time,  $t$ , ( $X_i^t$ )  
 231 relative to its initial mole fraction  $X_i^0$ , a ratio that is experimentally-measured. It has three refinable  
 232 parameters: the physically significant quantities  $K^*$  and  $n$ , and  $t_0$ , a lag time that depends on the  
 233 experimental arrangement (*e.g.*, heating time). They are found by minimising the misfit of  $\frac{X_i^t}{X_i^0}$   
 234 calculated by eq. 8 to the measured value, summed over a set of  $N$  experiments at a single temperature  
 235 and run time but variable  $fO_2$  by non-linear least squares:

$$\chi^2(K^*, n, t_0) = \sum_N \left( \frac{\left( \frac{X_i^t}{X_i^0} \right)_{meas} - \left( \frac{X_i^t}{X_i^0} \right)_{calc}}{s \left( \frac{X_i^t}{X_i^0} \right)_{meas}} \right)^2, \quad (9)$$

236 where  $s$  denotes the standard deviation. The values of  $K^*$  and  $n$  are derived solely from fits to the  
 237 experimental data using eq. 9 and do not depend on any *a priori* knowledge of thermodynamic  
 238 quantities. By default,  $t_0$  is set to 0 but is refinable within the limits  $0 \leq t_0 \leq t$ .

239 Plotted against  $\log fO_2$ ,  $\frac{X_i^t}{X_i^0}$  varies as a sigmoid, where  $n$  determines the slope. If the oxidation state of  
 240 an element in the melt is known, then that in the gas may be inferred from the slope of the curve  
 241 defined by the experimental data. If  $n > 0$ , the oxidation state of the element in the gas is lower than  
 242 that in the liquid, and vice-versa. The change in element volatility with  $fO_2$  becomes sharper (steeper  
 243 slopes) as  $n$  diverges from 0. The  $K^*$  controls the displacement of the curve along the  $\log fO_2$  axis,  
 244 where higher values of  $K^*$  result in lower  $\frac{X_i^t}{X_i^0}$  (*i.e.*, more evaporative loss), all else being equal. At  
 245 constant temperature, a systematic increase of  $K^*$  with run time signals a non-zero  $t_0$  (evaporation  
 246 begins only after some time,  $t_0$ ).

247 Values of  $p_{i,sat}$  reflect the sum of each of the possible vaporisation reactions that may be written  
 248 between all relevant components containing  $i$  in the melt, and all gas species containing  $i$  in the  
 249 vapour. If the element of interest has a given number,  $N_{liq}$  of valence states in the melt and  $N_{gas}$   
 250 species in the gas, there will be  $(N_{liq}+N_{gas}-1)$  independent reactions (*e.g.*, one reaction if  $N_{liq}=1$  and  
 251  $N_{gas}=1$ ). We identify five possible scenarios in order of increasing complexity:

- 252 1) Congruent associative evaporation with one species in both liquid and gas, the species  
 253 having the same oxidation states ( $n=0$ ).

254 
$$\frac{x_i^t}{x_i^0} = \exp\left(-K^* \frac{3}{r\rho} \sqrt{\frac{M}{2\pi RT}} (t - t_0)\right) \quad (10)$$

- 255 2) Congruent dissociative evaporation with one metal-bearing species in both liquid and gas,  
 256 the species having different oxidation states ( $n \neq 0$ ). Elemental loss is given by eq. 8.  
 257 3) Congruent dissociative evaporation with a single oxidation state in the liquid and multiple  
 258 in the gas.

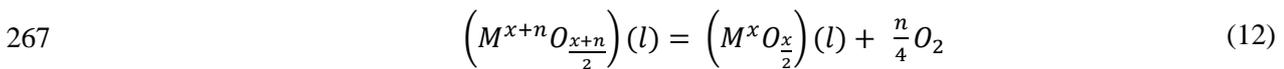
259 This equation is a sum of the partial pressures of the gas species involved in the  
 260 vaporisation of a given element:

261 
$$\frac{x_i^t}{x_i^0} = \exp\left(-\left(\frac{K_{(4a)}^*}{f(O_2)^{na/4}} + \frac{K_{(4b)}^*}{f(O_2)^{nb/4}}\right) \frac{3}{r\rho} \sqrt{\frac{M}{2\pi RT}} (t - t_0)\right) \quad (11)$$

262 Where  $a$  and  $b$  refer to the different stoichiometries of eq. 4.

- 263 4) Congruent dissociative evaporation with multiple oxidation states in the liquid and a  
 264 single gas species.

265 The homogeneous equilibrium between two melt oxide components with different  
 266 oxidation states may be written:



268 The  $\log K_{(12)}^*$  is related to the equilibrium constant in the pure M-O system by the  
 269 equation:

270 
$$\log K_{(12)}^* = \log K_{(12)} - \log\left(\frac{\gamma\left(M^{x+n}O_{\frac{x+n}{2}}\right)}{\gamma\left(M^xO_{\frac{x}{2}}\right)}\right). \quad (13)$$

271 The melt oxide components  $\left(M^{x+n}O_{\frac{x+n}{2}}\right)$  and  $\left(M^xO_{\frac{x}{2}}\right)$  are denoted  $i$  and  $j$  respectively.

272 Expressions for the partial pressure of a given gas species can be substituted into eq. 3  
 273 (see Appendix A for derivation) and integrated in a manner identical to that for eq. 8 to  
 274 give:

275 
$$\frac{x_i^t}{x_i^0} = \exp\left(-\frac{\alpha_e \gamma_j K_{(4)} f(O_2)^{-n_{(4)}/4}}{\left(K_{(12)} f(O_2)^{n_{(12)}/4} \frac{\gamma_j}{\gamma_i} + 1\right)} \frac{3}{r\rho} \sqrt{\frac{M}{2\pi RT}} (t - t_0)\right) \quad (14)$$

276 Although  $K_{(12)}$  is given by thermodynamic data in the pure metal oxide system, eq. 14 has an  
 277 additional degree of freedom, the ratio of the melt oxide activity coefficients,  $\frac{\gamma_j}{\gamma_i}$ . Therefore eq. 14  
 278 requires independent knowledge of  $\frac{\gamma_j}{\gamma_i}$  to be able to solve uniquely for  $K^*$ .

279 5) Congruent dissociative evaporation with multiple oxidation states in the liquid and in the  
 280 gas.

281 This equation is the sum of the partial pressures of two gas species as derived in eq. 14

282 
$$\frac{x_i^t}{x_i^0} = \exp\left(-\left(\left(\frac{\alpha_e \gamma_j K_{(4a)} f(O_2)^{-n_{(4a)}/4}}{\left(K_{(12)} f(O_2)^{n_{(12)}/4} \frac{\gamma_j}{\gamma_i} + 1\right)}\right) + \left(\frac{\alpha_e \gamma_j K_{(4b)} f(O_2)^{-n_{(4b)}/4}}{\left(K_{(12)} f(O_2)^{n_{(12)}/4} \frac{\gamma_j}{\gamma_i} + 1\right)}\right)\right) \frac{3}{r\rho} \sqrt{\frac{M}{2\pi RT}} (t - t_0)\right) \quad (15)$$

283 These equations may be applied to any element. New evaporation experiments in the future would  
 284 provide additional tests on the theory developed herein.

## 285 4.0. Results

286 A total of 48 experiments were performed at temperatures of 1300, 1400, 1500 and 1550 °C with run  
 287 durations of 15, 60, 120, 720 and 930 minutes and  $\log fO_2$ s between air (-0.68) and -10 (Table 2). All  
 288 experiments quenched to homogeneous glasses (Fig. 1), with the exception of some of the 1300 °C  
 289 experiments at low  $fO_2$ , which contain  $\approx 5\%$  microphenocrysts of olivine and spinel (Electronic Annex  
 290 C), suggesting the liquidus temperature is close to 1300 °C. Samples run on Pt loops at low  $fO_2$   
 291 experienced minor ( $\approx 5\%$ ) Fe loss to the wire (Electronic Annex C).

### 292 4.1. Contamination and blank runs

293 Four experiments performed at  $\log fO_2 = -8$  ( $N = 3$ ) and  $-0.68$  ( $N = 1$ ) at 1400°C and 1500°C on the  
 294 FCMAS mixture without trace elements ('blank' runs) were analysed to quantify any contamination  
 295 within the furnace. At  $\log fO_2 = -8$ , the concentrations of all 20 trace elements were  $< 1\%$  of 1000  
 296 ppm, with an average of 1.8 ppm (Table 2). These values indicate negligible vapour pressures of  
 297 volatile elements in the furnace hotspot, ruling out re-condensation and verifying the condition  $p_i \approx$   
 298 0. In the air experiment (P28/05/18), all elements are present below 3 ppm, excepting Na and K at  
 299 92.1 ppm and 77.7 ppm. That Na and K should not have appreciably evaporated after 15 minutes at  
 300 1400°C in air suggests they occur as impurities in the major oxides.

301 In the trace element-bearing experiments, abundances of K and particularly Na, increased through  
 302 contamination up to 2075 and 20028 ppm from their initial concentrations of  $944 \pm 128$  ppm and  
 303  $3252 \pm 281$  ppm in the starting mixture, respectively. Contamination affected only the samples run at

304 WWU Münster, likely reflecting the experimental history of the furnace and/or its alumina muffle  
305 tube. As such, only the experiments performed at RSES ANU (C-17,18/12/15) and IPGP, Paris (P-  
306 xx/xx/17,18), which have low background Na contents (Table 2; Tuff and O'Neill 2010) are  
307 considered for Li, Na and K.

#### 308 *4.2. Experimental reproducibility*

309 We duplicated four experiments at 1400°C (Table 2). Experiments for pair P09-06-18b and P09-06-  
310 18a, were run on Pt- and Re loops, respectively. The concentrations of volatile elements (K, Cr, Cu,  
311 Zn, Ga, Ge, Rb, Mo, Ag, Cd, Pb; N = 38) are compared in Fig. 2 and adhere closely to the 1:1 line.  
312 The median misfit between the four pairs for elements with non-zero (> 5 ppm) concentrations is 6.0  
313 % relative. This is two- to three-times larger than the analytical RSD (see section 2.2.), reflecting the  
314 experimental error. These random errors include the mass and shape of the experimental charge  
315 (section 3.0.; Electronic Annex B) as well as measurement of the temperature, run duration and  $fO_2$   
316 (section 2.2.).

#### 317 *4.3. Metal Loops*

318 Because the solubility of an element into metal increases as  $fO_2$  decreases, depletion of some elements  
319 in the glasses at low  $fO_2$  may be partially attributable to alloying with noble metal wires. In order to  
320 test this hypothesis, the trace element content of wires in 10 experiments (Table 2) were analysed  
321 (Electronic Annex C).

322 No elements other than the metal were detected in the Ir loop experiment (C18/12/15) and three Re  
323 loop experiments measured (1M-1/3/16, 1M-1/3/16b and C17/12/15c). For Pt loop experiments, Ga  
324 and Cu dissolved into Pt metal, along with very minor Ag ( $Ag/Pt < 2 \times 10^{-4}$ ) and Pb ( $Pb/Pt < 7 \times 10^{-4}$ ) in  
325 experiments 1M-PS4, 1M-PS5 and 2M-15-07-16f. This latter pair is so volatile that their abundances  
326 were already negligible in silicate liquid.

327  
328 Although Ga/Pt ratios are typically  $< 7 \times 10^{-4}$ , in one sample, 2M-17-07-16c ( $\log fO_2 = -8$ ,  $T = 1500^\circ C$ ,  $t$   
329 = 60 mins), Ga/Pt reaches  $2.4(\pm 0.1) \times 10^{-3}$ . The melt is also strongly depleted in Ga (67.4 ppm) with  
330 respect to the run at  $\log fO_2 = -5.5$  (775.1 ppm). Gallium abundances in Pt loops (P09-06-18b) and Re  
331 loops (P09-06-18a) at 1400°C and  $\log fO_2 -9.23$  are similar (439.9 ppm and 409.4 ppm), suggesting  
332 that partitioning of Ga into Pt wire has no resolvable influence on the quantity measured in the melt.

333  
334 The Cu/Pt ratios of the Pt wire reach  $4.7 \pm 2.9 \times 10^{-3}$ , but are highly heterogeneous, reflecting the low  
335 diffusion coefficient of Cu in Pt,  $10^{-13} \text{ m}^2/\text{s}$  at 1673 K (Liu et al., 2009). For a 15-minute experiment,  
336 Cu would have diffused only 9  $\mu\text{m}$  into the 0.1 mm diameter Pt wire. For a 0.5 cm length with mass  
337 of 0.84 mg ( $\approx 7\%$  of sample mass), the Cu budget in the wire, assuming 4000 ppm in the affected  
338 zone, is 9%. Experiments P09-06-18b (Pt) and P09-06-18a (Re) have similar Cu contents of 40.5 and

339 11.2 ppm, respectively. It is concluded that the partitioning of any given element into the metal wire  
340 has no resolvable effect within experimental error ( $\pm 6\%$  relative) on its observed depletion in the  
341 silicate melt.

342

#### 343 4.4. Elemental Zoning

344 Implicit in the theoretical framework in *section 3.0.* is the homogeneous distribution of evaporating  
345 elements in the liquid. To test homogeneity, element concentrations were measured in each sample  
346 with at least three 130  $\mu\text{m}$  laser spots in both the core and rim, often with a few points in between ( $N$   
347 = 6-12; Fig. 1). In addition, a representative subset of seven samples (two each at 1300°C, 1400°C,  
348 1500°C and one at 1550°C; Table 2; Electronic Annex C) were analysed in detail by taking linear  
349 profiles from rim to core, consisting of ten to fifteen 25  $\mu\text{m}$  spots spaced at 50  $\mu\text{m}$  intervals (Fig. 3a).

350 Excepting one sample, 2M-15-07-16f, which represents the extremes of lowest temperature (1300  
351 °C),  $f\text{O}_2$  ( $10^{-10}$  bar) and shortest run time (15 mins) of the experiments, all elements in all other  
352 samples measured show no analytically-resolvable compositional zoning from core to rim (Fig. 3b  
353 and Electronic Annex C). Homogeneous zoning profiles indicate that the characteristic timescale of  
354 evaporation,  $t_{HKL}$ , found by solving for  $t$  in eq. (8), is greater than the diffusive timescale,  
355 approximated by  $t_D = r^2/2D$ , where  $D$  is the diffusion coefficient (see Electronic Annex D). The lack  
356 of zoning can therefore set lower limits on the value of  $D$ . In sample 2M-15-07-16f, the extent of  
357 element zoning is inversely proportional to the fraction remaining after volatile loss. This suggests  
358 zoning is more pronounced for elements with higher evaporation rates relative to their diffusion rates.  
359 This ratio increases (and hence zoning is more likely) for most elements to lower  $f\text{O}_2$ , because  
360 vaporisation rates increase whereas diffusion rates are constant as long as the melt oxide species is  
361 unchanged. Accordingly, only sample 2M-15-07-16f was rejected from the dataset. For the remaining  
362 experiments, diffusion in the liquid was not the rate-limiting step controlling measured element  
363 abundances, thereby leaving evaporation from the surface.

#### 364 4.5. Data fitting

365 Three groups of elements can be classified *i)* ‘non-volatile’ elements (Mn, Sc, Ti, V, Zr and the REEs)  
366 for which no statistically discernible change from their initial concentrations is observed, *ii)* volatile  
367 elements that become relatively more volatile with decreasing  $f\text{O}_2$  ( $n > 0$ ; Na, K, Cu, Zn, Ga, Ge, Rb,  
368 Pb, Ag, Cd) and *iii)* volatile elements that become relatively more volatile with increasing  $f\text{O}_2$  ( $n < 0$ ;  
369 Cr, Mo). Lithium is similarly volatile over the range of  $f\text{O}_2$  investigated. At a given  $f\text{O}_2$ , loss of  
370 elements belonging to groups *ii)* and *iii)* also increases with a) temperature and b) run time. Values of  
371  $t_0$ ,  $n$  and  $\log K^*$  fitted to the data for all volatile elements are shown in Table 3.

372 4.5.1. Congruent Dissociative Evaporation with one metal-bearing species in both  
373 liquid and gas, the species having different oxidation states

374 *One electron (n = 1) reactions (Na, K, Rb, Cu, Ag)*

375 The order of alkali volatility observed in the experiments increases down the group;  $\text{Li} < \text{Na} < \text{K} < \text{Rb}$   
376 (Fig. 4a-c), in line with the equilibrium vapour pressures above their pure oxides (Lamoreaux and  
377 Hildenbrand, 1984). All alkali metals exist in silicate melts as  $\text{M}^+\text{O}_{0.5}$  species (*e.g.*, Charles 1967).  
378 Lithium is dealt with separately owing to its distinct vaporisation behaviour.

379 At 1400 °C, sodium and potassium become increasingly volatile at low  $f\text{O}_2$  (Fig. 4a, b). This  
380 behaviour results from a lower mean valence state of these elements in the gas compared to the liquid.  
381 Using eq. 8 to fit the data, both Na and K conform to an  $n = 1$  reaction (Fig. 4a, b), implying the  
382 reaction  $\text{M}^+\text{O}_{0.5}(\text{l}) = \text{M}^0(\text{g}) + \frac{1}{4}\text{O}_2$  (Fig. 4a, b). This stoichiometry is supported by thermodynamic data  
383 that show the overwhelming stability of the monatomic gas above  $\text{Na}_2\text{O}(\text{s})$  and  $\text{K}_2\text{O}(\text{s})$  (Lamoreaux  
384 and Hildenbrand, 1984), and above natural silicate melts from Naughton et al. (1971), De Maria et al.  
385 (1971) *via* Knudsen Effusion Mass Spectrometry (KEMS) and Tsuchiyama et al. (1981) *via* Langmuir  
386 evaporation. The higher  $\log K^*$  of the evaporation reaction for K ( $-3.95 \pm 0.06$ ) relative to Na ( $-$   
387  $4.25 \pm 0.10$ ) at 1400°C attests to its higher volatility (Fig. 4a, b, Table 3).

388 Rubidium is more volatile than either Na or K (Fig. 4c). Like Na and K, its dependence on  $f\text{O}_2$  is  
389 consistent with an  $n = 1$  reaction, meaning  $\text{Rb}^0$  is the stable gas species (Lamoreaux and Hildenbrand  
390 1984). In fitting the equilibrium constant of the Rb vaporisation reaction, a positive dependence of  
391  $\log K^*$  with the time series (15, 60, 120 minutes) was observed. In order to account for this, an  
392 experimental ‘lag time’ is introduced, which describes the time at which Rb starts evaporating after  
393 sample insertion. A best fit is found at  $t_0 = 14.4$  min (863 s), a constant for all time- and temperature  
394 series.

395 Copper is observed to become more volatile at lower  $f\text{O}_2$  (Fig. 4d), signalling a lower oxidation state  
396 of Cu in the gas relative to the melt. Although copper is expected to be dominantly cuprous ( $\text{Cu}^+$ ) in  
397 silicate melts at very high  $f\text{O}_2$  (*e.g.*, in air), it may also be present as  $\text{Cu}^{2+}\text{O}(\text{l})$  (*e.g.* Schreiber 1987).  
398 Only  $\text{Cu}^+$  is detected in alkali-free, CMAS and CMAS+Fe liquids at 1300°C up to  $\Delta\text{FMQ}-1.5$ ,  
399 (Holzheid and Lodders 2001, and references therein). Nevertheless, to check for the presence of  $\text{Cu}^{2+}$ ,  
400 fits to the experimental data were performed for  $n$  in eq. 8. At 1300°C, a formal valence of 1.14 is  
401 calculated, at 1400°C it is 1.17, 0.84 at 1500°C, and 0.98 at 1550°C, yielding a weighted average of  
402  $1.06 \pm 0.15$ . Therefore,  $\text{CuO}_{0.5}$  is the only stable liquid oxide species considered, meaning  $n$  is set equal  
403 to 1, implying the stability of  $\text{Cu}^0(\text{g})$ .

404 Silver is in its 1+ oxidation state in silicate melts, occurring as  $\text{AgO}_{0.5}(\text{l})$ , however, due to its high  
405 volatility, its vaporisation stoichiometry is not well constrained by the present set of experiments. The  
406 few data points at 1300°C allow the expected one-electron ( $n = 1$ ) reaction to be fit (Table 3).

407 *Two electron (n = 2) reactions (Zn, Ge, Cd)*

408 The volatility of zinc is very sensitive to  $fO_2$ . Although it is less volatile than Cu or K in air, under  
409 reducing conditions ( $\leq \log fO_2 = -8$ ), its abundance in the melt is negligible at all temperatures (Fig  
410 5a). The experimental data are best fit with an  $n = 2$  reaction, reflecting the evaporation of ZnO(l), its  
411 only stable melt component, to Zn<sup>0</sup>(g). Thermodynamic data for gases above ZnO(s) also show that  
412 Zn exists as Zn<sup>0</sup>(g), be it below the IW buffer or in air, though ZnO(g) becomes important <1000 K in  
413 air (Lamoreaux et al., 1987). As for Rb, if  $t_0 = 0$  in eq. 8, then a positive dependence of  $\log K^*$  with  
414 time is observed. For Zn, this time dependence is removed for a time lag of 9 minutes ( $t_0 = 540$  s),  
415 applied to all run durations and temperatures.  $\log K^*$ s increase systematically with temperature (Fig.  
416 5a; Table 3).

417 The vaporisation behaviour of Ge closely mirrors that of Zn (Fig. 5b). Although in silicate liquids Ge  
418 transitions to 2+ at low  $fO_2$ , where  $Ge^{2+}/\sum Ge = 0.5$  at IW and 1 atm for a CMAS composition (Mare  
419 et al., 2016), it exists exclusively as Ge<sup>4+</sup> over the  $fO_2$  range covered in our experiments. The data are  
420 best fit with an  $n = 2$  reaction, implying GeO(g) is stable. This is also corroborated by thermodynamic  
421 data for vaporisation of GeO<sub>2</sub>(s) (Lamoreaux et al., 1987). Like Zn, a constant ‘time lag’ of  $t_0 = 624$  s  
422 (10.4 min) accounts for the observed dependence of  $\log K^*$  on time. The proportion of Ge lost from  
423 the melt is indistinguishable from that of Zn at 1300°C, attested to by their overlapping  $\log K^*$ s (Table  
424 3), but at higher temperatures Ge becomes relatively more volatile than Zn (Fig. 5).

425 Cadmium, like silver, was too volatile to permit assessment of its evaporation stoichiometry; only two  
426 experiments contain measurable quantities of Cd, 2M-15-07-16c and 2M-15-07-15d,  $\log fO_2 = -0.67$   
427 and  $-3.44$ , for 15 min at 1300°C, respectively. Cadmium, which occurs as Cd<sup>2+</sup> in silicate melts,  
428 evaporates as Cd<sup>0</sup>(g) over all  $fO_2$  above CdO(s) (Lamoreaux et al., 1987) suggesting  $n = 2$ , the value  
429 adopted for the fitting.

#### 430 4.5.2. Congruent dissociative evaporation with a single oxidation state in the liquid 431 and multiple in the gas (Li, Ga, Pb)

432 For an element with a single melt oxidation state, and more than a single species in the gas, the total  
433 partial pressure of the element in the gas phase is the sum of two or more partial pressures (eq. 11).  
434 This applies to the vaporisation of Li, Ga and Pb over the T- $fO_2$  conditions investigated.

435 The vaporisation behaviour of Li is distinct from that of other alkali metals; it is equally volatile at  
436 high  $fO_2$  as it is at low  $fO_2$  (Fig. 6a). The high-temperature gas species of Li above Li<sub>2</sub>O(s) are Li(g),  
437 Li<sub>2</sub>O(g), and LiO(g) (e.g., Kimura et al. 1980), of which Li<sub>2</sub>O(g) is the most stable (Lamoreaux and  
438 Hildenbrand, 1984). However, since  $p(Li_2O)$  is proportional to  $a(LiO_{0.5})^2$ , for  $a(LiO_{0.5}) \approx 10^{-3}$  as in our  
439 experiments, Li<sub>2</sub>O is no longer the predominant gas species, leaving Li(g) and LiO(g) (see Electronic  
440 Annex E). Lithium depletion is generally observed in long ( $\geq 120$  minute) duration experiments at  
441 1400°C, and only these runs are fit. The time series in air gives a  $\log K^*$  for the reaction  $LiO_{0.5}(l) +$

442  $\frac{1}{4}\text{O}_2 = \text{LiO(g)}$  of -3.39, whereas at  $\log f\text{O}_2 = -8$  the  $\log K^*$  for  $\text{LiO}_{0.5}(\text{l}) = \text{Li(g)} + \frac{1}{4}\text{O}_2$  is -5.36 (Table  
443 3, Fig. 6a).

444 No Ga evaporation is observed at 1300°C, but at higher temperatures Ga becomes more volatile at  
445 lower  $f\text{O}_2$  with close to an  $n = 2$  stoichiometry (Fig. 6b). Since Ga occurs as  $\text{GaO}_{1.5}$  in silicate melts,  
446 there is no suitable Ga-bearing gas species that would result in an  $n = 2$  reaction. Above  $\text{Ga}_2\text{O}_3(\text{s})$ , the  
447 stable gas species is  $\text{Ga}_2\text{O(g)}$  (Burns, 1966; Lamoreaux et al., 1987), whose partial pressure is  
448 proportional to  $f\text{O}_2$  (an  $n = 4$  reaction). However, as for Li,  $p(\text{Ga}_2\text{O})$  is proportional to  $a(\text{GaO}_{1.5})^2$ ,  
449 meaning its stability decreases sharply as the activity of  $\text{GaO}_{1.5}$  in the melt falls (Electronic Annex E),  
450 such that it is stable only below IW-1 at 1700 K for  $a(\text{GaO}_{1.5}) = 10^{-3}$  (1000 ppm). Instead, the data is  
451 fit by a combination of the  $n = 1$  reaction involving  $\text{GaO(g)}$  and the  $n = 3$  reaction with  $\text{Ga(g)}$  (Table  
452 3).

453 Lead is lost rapidly from the melt, and measurable amounts remain only in runs performed at 1300°C  
454 and at high  $f\text{O}_2$  at 1400°C. In all cases, Pb becomes more volatile with decreasing  $f\text{O}_2$  with an  
455 observed value of  $n$  that is close to 1 (Fig. 6c). In silicate melts, Pb is present as  $\text{Pb}^{2+}\text{O}$ , be it at  
456 oxidised ( $\approx\text{NNO}$ ) or reduced ( $\approx\text{IW}$ ) conditions (Watson et al., 1997; Wood and Halliday, 2010).  
457 Evaporation of pure  $\text{PbO(s, l)}$  shows that  $\text{Pb(g)}$  is dominant below IW, both  $\text{Pb(g)}$  and  $\text{PbO(g)}$  are  
458 found between IW and air, above which the oxidised species predominates (Lamoreaux et al., 1987;  
459 Kobertz et al., 2014; Kobertz, 2019a). As such, both the  $n = 0$  and  $n = 2$  reactions are fit to the  
460 experimental data. The partial pressures of  $\text{Pb(g)}$  and  $\text{PbO(g)}$  are found to be similar (Table 3) to  
461 reproduce the  $n \approx 1$  slope of the data.

462 4.5.3. Congruent dissociative evaporation with multiple oxidation states in the  
463 liquid and a single gas species (Mo)

464 Oxygen fugacity may also influence the oxidation state of a metal oxide dissolved in a silicate melt.  
465 This is the case for molybdenum, whose two silicate melt components,  $\text{Mo}^{4+}\text{O}_2(\text{l})$  and  $\text{Mo}^{6+}\text{O}_3(\text{l})$   
466 (Holzheid et al., 1994; O'Neill and Eggins, 2002) are related by  $(f\text{O}_2)^{1/2}$  (see Appendix A).

467 Unlike the aforementioned elements, Mo becomes increasingly volatile at increasing  $f\text{O}_2$  (Fig. 7a),  
468 reflecting the higher mean oxidation state of Mo in the gas phase compared to the silicate melt.  
469 Because the melt has  $\text{Mo}^{4+}/\sum\text{Mo} < 1$ , this behaviour implies the presence of  $\text{Mo}^{6+}\text{O}_3(\text{g})$ . Indeed,  
470 calculation of Mo gas species from thermodynamic data (Chase, 1998) shows the clear predominance  
471 of  $\text{MoO}_3(\text{g})$  at all  $f\text{O}_2 > \text{IW}-2.5$  (Electronic Annex E), and hence only this species is considered in  
472 fitting the experimental data.

473 Because  $\text{Mo}^{4+}/\text{Mo}^{6+}$  of the melt decreases with  $(f\text{O}_2)^{1/2}$ , the effective value of  $n$  must also decrease as  
474  $f\text{O}_2$  increases. This behaviour necessitates the use of eq. (14) to fit the data. Unique solutions for  
475  $p(\text{MoO}_3)$  require that  $\gamma(\text{MoO}_3)$  and  $\gamma(\text{MoO}_2)$  are known. Here, a value of  $\gamma(\text{MoO}_3) = 0.3$  is chosen

476 from CMAS liquids (O'Neill and Eggins, 2002). The slope of the data ( $n$ ) with  $fO_2$  depends on  
477  $\gamma(MoO_3)/\gamma(MoO_2)$ , with a best fit across the experimental range found at a ratio of 20.7. These  
478 assumptions render the values for the  $\log K^*$ s listed in Table 3 approximate.

479 4.5.4. Congruent dissociative evaporation with multiple oxidation states in the  
480 liquid and in the gas (Cr)

481 Chromium, like Mo, becomes more volatile from silicate melts at increasing  $fO_2$  (Fig. 7b) because Cr  
482 in the gas has a higher mean valence than in the liquid. In the liquid, both  $Cr^{2+}$  and  $Cr^{3+}$  occur (*cf.*  
483 Berry and O'Neill 2004), while four Cr-bearing gas species are stable at high temperatures;  $Cr(g)$ ,  
484  $CrO(g)$ ,  $CrO_2(g)$  and  $CrO_3(g)$ . However, only  $CrO_2(g)$  is important for  $IW < fO_2 < FMQ+3$ , with  
485  $CrO_3(g)$  only becoming dominant in air, though its stability increases to lower temperatures (see  
486 Electronic Annex E). Tungsten also has oxidised gas species;  $WO_2$  and  $WO_3$  (see also Fegley and  
487 Palme 1985; O'Neill 1991), indicating that this is a general feature of Group VI metals.

488 Two conditions are imposed in the fitting *i*)  $\gamma(CrO) = 3$  (Pretorius and Muan, 1992) and *ii*) the  
489  $\gamma(CrO_{1.5})/\gamma(CrO)$  ratio at 1400 °C is fixed at 6.13 to give a  $\log K^*$  of 2.26 for the equilibrium  $CrO(l)$   
490  $+ \frac{1}{4}O_2 = CrO_{1.5}(l)$  (at an optical basicity of 0.645 for the ferrobalt; Berry et al. 2006) and is taken to  
491 remain constant at all temperatures. Fitting with  $CrO_3(g)$  did not improve the misfit and was therefore  
492 neglected, hence the data was fit using eq. (14) with  $CrO_2(g)$  as the stable species. The 1300°C  
493 experiments are anomalously more depleted than at higher temperatures and were not fit. For these  
494 reasons, the  $\log K^*$ s derived from fitting Cr data shown in Table 3 are semi-empirical.

495

496 4.6. Evaporation coefficients and activity coefficients of metal oxide species in silicate melts

497 In these experiments, gas speciation and thus reaction stoichiometries were not measured, but inferred  
498 from fits to concentration- $T$ - $fO_2$  relations (Figs. 4 – 7), the potential complexity of which limits the  
499 extraction of reliable thermodynamic quantities ( $K^*$ ,  $n$ ) to elements with simple vaporisation  
500 stoichiometries (eq. 8, 10). The sum of the experimental uncertainties that may affect precise  
501 determination of  $K^*$  and  $n$ , including sample properties (size, shape, density) and other kinetic factors  
502 that may influence vaporisation rate (diffusion-limited evaporation, gas flow rate), is relatively small  
503 ( $\pm 6\%$ ; section 4.2.). As the determination of  $n$  relies on how  $\left(\frac{x_i^t}{x_i^0}\right)$  changes relative to other  
504 experiments in a given  $fO_2$  series, it depends only on these random experimental variables and is  
505 derived with good precision and accuracy.

506 An additional experimental uncertainty arises for Rb, Zn and Ge because of the time lag from sample  
507 insertion to vaporisation ( $t_0 = 9 - 14$  minutes; Table 3), which almost coincides with measured heating  
508 times (4 – 7 minutes, section 2.1.). In equilibrium techniques such as KEMS, it is routine to run a

509 standard material with known partial pressures under identical conditions (Margrave, 1967; Drowart  
510 et al. 2005) to identify any systematic errors (*e.g.*, choice of  $r$ , effect of  $t_0$ , deviations from Langmuir  
511 conditions), thereby calibrating  $K^*$  values. This was not done for these experiments. Therefore,  
512 although  $K^*$  values are relatively precise ( $\approx \pm 5\%$  to  $\pm 30\%$ ; Table 3), their accuracy is harder to  
513 quantify.

514 Here, accuracy is assessed by comparing the experimentally-determined equilibrium constant of the  
515 vaporisation reaction of the oxide component from silicate melts ( $K^*$ ), with the known equilibrium  
516 constant for the equivalent vaporisation reaction of the pure oxide ( $K$ ) calculated from thermodynamic  
517 data (*e.g.*, Lamoreaux et al. 1987; Chase 1998; Glushko et al. 1999). The values  $K^*$  and  $K$  are related  
518 by eq. 6, and are not equivalent if  $\gamma_i^\infty$  or  $\alpha_e$  deviate from unity. For  $\frac{K^*}{K} > 1$  the vapour species is  
519 favoured over the liquid component of the silicate melt relative to the same reaction between the pure  
520 liquid oxide and gas, and vice-versa.

521 Activity coefficients of metal oxide species in silicate melts vary by orders of magnitude with  
522 composition (*e.g.*, Rammensee and Fraser 1982; Wood and Wade 2013), temperature (*e.g.*, Reyes and  
523 Gaskell 1983) and metal oxidation state (O'Neill and Eggins, 2002), with theoretical limits between  
524  $1/\infty < \gamma_i < \infty$ . However, for many trace elements, activity coefficients remain poorly known.  
525 Constraints on Langmuir evaporation coefficients are similarly sparse. Because the HKL equation  
526 describes only the flux of particles striking a surface,  $\alpha_e$  was introduced *a posteriori* as an *ad-hoc*  
527 adjustment to account for the energy required in the transformation of element  $i$  from the condensed  
528 to gaseous state (see Ackermann et al. 1962) and thus has theoretical limits  $1/\infty < \alpha_e \leq 1$ . Unlike  $\gamma_i$ ,  
529  $\alpha_e$  may depend not only on liquid composition, temperature and redox state, but also on the activation  
530 energy of evaporation, surface properties, vaporisation rate and nature of the gas phase (*e.g.*, Knacke  
531 and Stranski 1956; Persad and Ward 2016) and hence cannot be determined *ab-initio*. Although  
532 evaporation coefficients from simple solid metal or binary metal oxides are  $< 1$ , the equivalent liquids  
533 have  $\alpha_e$  of unity (Burns, 1966; Safarian and Engh, 2013; Shornikov, 2015). For vaporisation of major  
534 components from silicate melts Alexander (2002) and Fedkin et al. (2006) employed MELTS to  
535 calculate  $\gamma_i$  and found  $0.01 < \alpha_e < 0.5$  from fits to experimental data. Given the potential variation of  
536  $\alpha_e$  and  $\gamma_i^\infty$  in our system, values of  $\alpha_e$  are calculated using independent estimates of  $\gamma_i$ , providing a  
537 test of the accuracy of our theoretical framework (section 3.0.).

538 Evaporation coefficients calculated from eq. 6 are shown in Table 4. The activity coefficients of Na  
539 and K are well-characterised (O'Neill, 2005; Grant and Wood, 2008; Borisov, 2009; Mathieu et al.,  
540 2011) due to their importance in the vaporisation of chondrules (*e.g.*, Tsuchiyama et al. 1981;  
541 Shimaoka and Nakamura 1991; Georges et al. 2000) and lunar basalts (De Maria et al., 1971; Gibson  
542 and Hubbard, 1972; Gooding and Muenow, 1976; Donaldson, 1979). From the Na vapour pressures  
543 measured over natural basalts by DeMaria et al. (1971) and Gooding and Muenow (1976), activity

544 coefficients  $\approx 10^{-3}$  were calculated. Mathieu et al. (2008) also report  $\gamma_{NaO_{0.5}} = 10^{-3}$  in the CMAS  
 545 system and  $8.4 \times 10^{-4} - 2.2 \times 10^{-3}$  in the simpler CMS system (Mathieu et al., 2011). This gives  $\alpha_{e,NaO_{0.5}}$   
 546 between 0.3 – 1.7 for our experiments at 1400 °C. Values of  $\gamma_{KO_{0.5}} \approx 5 \times 10^{-5}$  to  $7 \times 10^{-4}$  were calculated  
 547 from De Maria et al. (1971), Gooding and Muenow (1976) in natural basalts and Hastie and Bonnell  
 548 (1985) for the KFCAS system, resulting in  $\alpha_{e,KO_{0.5}}$  from 0.3 to 3.4 at 1400 °C.

549 Reyes and Gaskell (1983) found  $\gamma_{ZnO} = 0.25, 0.43,$  and  $0.58$  at 1400, 1500 and 1550 °C, respectively  
 550 in CAS melts by transpiration, yielding  $\alpha_{e,ZnO} \approx 2$ . Holzheid and Lodders (2001) determined  $\gamma_{CuO_{0.5}}$   
 551  $= 10 \pm 1$  at 1300°C for Fe-poor basaltic compositions, returning  $\alpha_{e,CuO_{0.5}} = 2.4 \pm 0.8$ . If the trends of  $K^*$   
 552 are extrapolated with temperature to 1650°C, then the  $\gamma_{CuO_{0.5}} = 3.5$  determined by Wood and Wade  
 553 (2013) at this temperature gives  $\alpha_{e,CuO_{0.5}} = 1.2$ . The two stable gases species evaporating over PbO(l)  
 554 allows  $\alpha_{e,PbO}$  to be calculated from both reactions (Table 4). Although the two points for Pb  
 555 evaporation do not permit extrapolation to higher temperatures,  $\alpha_{e,PbO}$  ranges between 0.3 and 1.7  
 556 when calculated from  $\gamma_{PbO}$  of Wood and Wade (2013), 0.22, at 1650°C for an SiO<sub>2</sub>-rich melt.

557 Therefore, evaporation coefficients are close to unity (within a factor of 2 - 3) for all elements for  
 558 which *i*) the experimentally determined  $K^*$  is robust, *ii*) melt compositions and temperatures are  
 559 similar to literature data, and *iii*) the activity coefficient is well-determined (particularly Na, Cu and  
 560 Zn). Based on these observations  $\alpha_e$  is set to 1 and  $\gamma_i^\infty$  is calculated from  $K^*/K$  (eq. 6; Table 4, Fig.  
 561 8). The uncertainties on the reported activity coefficients represent only the precision on the fit, and  
 562 do not include the uncertainties in  $\alpha_e$  just discussed.

563 Aside from Li, alkali dissolution in silicate melts is strongly non-ideal ( $\gamma_i^\infty \ll 1$ ), meaning their  
 564 volatilities are much reduced from those of pure alkali oxides. Furthermore, alkali metal oxide activity  
 565 coefficients decrease in the order  $Li \gg Na > K > Rb > (Cs)$  (*cf.* Charles, 1967; Borisov, 2009), a hierarchy  
 566 that is inversely proportional to their volatilities.

567 Zinc oxide activity coefficients, like other divalent, first-row transition metals (O'Neill and Eggins,  
 568 2002), are close to unity but show a weak positive dependence on temperature. This behaviour is  
 569 mimicked by  $\gamma_{GeO_2}^\infty$ , albeit at lower absolute values. By contrast,  $\gamma_{CuO_{0.5}}^\infty$  is  $>1$ , (see also Holzheid et  
 570 al., 2001; Wood and Wade, 2013), and decreases to higher temperatures. In these three cases,  $\gamma_i^\infty$   
 571 tends towards unity at high temperatures, a phenomenon described by the van't Hoff equation:

$$\frac{d \ln \gamma_i^\infty}{d(1/T)} = - \frac{\Delta H}{R}, \quad (16)$$

572 where  $\Delta H$  refers to the partial molar enthalpy of solution of *i* in the silicate melt. For CuO<sub>0.5</sub>, this is  
 573 calculated at  $121 \pm 12$  kJ/mol,  $-143 \pm 15$  kJ/mol for ZnO (compared with  $-135$  kJ/mol from Reyes and  
 574 Gaskell, 1983) and  $-147 \pm 25$  kJ/mol for GeO<sub>2</sub> over the temperature range 1573 to 1823 K.

575

576 4.7. Gibbs Free Energy of vaporisation using the ‘2<sup>nd</sup> law method’

577 The modified equilibrium constants of vaporisation reactions ( $K^*$ ) may be converted into Gibbs Free  
578 Energies ( $\Delta G^*$ ):

$$\Delta G^* = -RT \ln K^*. \quad (17)$$

579 The asterisk denotes that the Gibbs Free Energy of reaction includes *i*) the non-ideality of trace  
580 element dissolution in silicate melts and *ii*) any deviation of the evaporation coefficient from unity  
581 and/or variation with temperature. Hence,  $\Delta G^*$ s calculated are relevant only to the investigated melt  
582 composition at 1 bar pressure and temperatures between 1573 and 1823 K.

583 Variation of  $\Delta G^*$  of a volatilisation reaction against the absolute temperature,  $T$ , in an Ellingham  
584 diagram, results in a straight line (Fig. 9), independent of run time. This confirms that a reproducible,  
585 thermally-activated process is controlling elemental loss, namely, the equilibrium partial pressure.

586 At constant total pressure, the Gibbs-Helmoltz equation is:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (18)$$

587 Hence, the slope of the line is equivalent to  $-\Delta S^*$  (entropy) and its intercept  $\Delta H^*$  (enthalpy), which  
588 are average values determined for the mid-point temperature over the temperature range. This is a 2<sup>nd</sup>  
589 law treatment of the vaporisation data, requiring two or more measurements of the equilibrium  
590 constant, and is analogous to the integration of the Clausius–Clapeyron equation generally used for  
591 interpretation of vapour pressure data (Drowart and Goldfinger, 1967; Drowart et al., 2005; L’vov,  
592 2007). It implicitly assumes that  $\Delta H^*$  is much greater than the product of  $\Delta C_p^0$  (molar heat capacity at  
593 constant pressure) and temperature over the interval of interest, such that slopes can be approximated  
594 as linear within experimental uncertainty.

595 Values for the entropy and enthalpy of reaction, along with those for the pure system, are listed in  
596 Table 5. Typical relative standard deviations for  $\Delta H^*$  and  $\Delta S^*$  range from 5 – 15 %, as compared with  
597 1 – 2 % for KEMS measurements for vaporisation of multicomponent systems (silicate melt, Markova  
598 et al., 1986, Fraser and Rammensee, 1987; olivine, Costa et al. 2017) or pure metal oxides (Kobertz  
599 2019a, b). It is observed that  $\Delta H^*$  and  $\Delta S^*$  are positively correlated (Fig. 10a), indicative of enthalpy-  
600 entropy compensation, where  $\Delta G$  tends to a common value at infinite temperature (see Exner 1973;  
601 Kemeny and Rosenberg 1973). The same is true of thermodynamic data in the pure M-O system,  
602 though less marked (compare Fig. 10a and b). The gross effect of  $\gamma_i^\infty$  is to smooth out variability in  
603  $\Delta H^*$  vs.  $\Delta S^*$  compared with  $\Delta H^0$  and  $\Delta S^0$ . Activity coefficients of divalent first-row transition metal  
604 cations are  $\approx 1$  in geologically-relevant silicate melts (Pretorius and Muan, 1992; Ohta and Suito,  
605 1995; Holzheid et al., 1997; O’Neill and Eggins, 2002) and furthermore depend on melt composition

606 in a similar manner (O'Neill and Eggins, 2002). With these caveats in mind, their  $\Delta H^o$  and  $\Delta S^o$  from  
 607 pure system thermodynamic data (Chase, 1998) are also shown in Table 5.

#### 608 4.8. Comparison with previous work

609 Tsuchiyama et al. (1981) studied Na evaporation from chondrule-like melts at varying  $\log fO_2$  (-5 to -  
 610 10) between 1450 and 1600 °C (Fig. 11a). Their data are well-modelled by eq. (8), conforming to an  $n$   
 611 = 1 reaction with  $\log K^*$ s that define  $\Delta G^* = 444.4(\pm 0.2) - 0.166(\pm 0.003)T$  (kJ/mol) for their  
 612 'composition 1'. Na evaporation from 'composition 2', with  $SiO_2$  (43.55 wt. %) and  $FeO^T$  (18.52 wt.  
 613 %) contents similar to the ferrobalt, has  $\log K^*$  0.5 log units higher ( $\log K^* = -3.30$  at 1586 °C),  
 614 suggesting a compositional control on  $\gamma_{NaO_{0.5}}$  (cf. O'Neill 2005; Borisov 2009; Mathieu et al. 2011).

615  
 616 The experiments of Kreutzberger et al. (1986) were performed on a  $Di_{75}An_{25}$  melt. The volatility  
 617 behaviour of Na, K and Rb is fit as a function of time (Fig. 11b) using an  $n = 1$  reaction. A uniform  
 618 sample radius of 0.0015 m and density of 2750 kg/m<sup>3</sup> was assumed. The order of volatility observed  
 619 (Na < K < Rb) is in good agreement with this work, and the fitted  $\log K^*$ s for Na (-4.15) and Rb (-  
 620 3.04) overlap with our determination (-4.25±0.10 and -3.12±0.10, respectively, Table 3), while that of  
 621 K is much higher (-3.26 compared to -3.95±0.06, Table 3).

622  
 623 Norris and Wood (2017) performed vaporisation experiments on a trace element-doped MORB melt,  
 624 stirred in an Ni crucible. The agreement in the order of volatility for elements common in both studies  
 625 is reasonable. At  $\log fO_2 = -10$  and 1300 °C, Norris and Wood (2017) show  $Cr < Ga < Zn < Pb \approx Cu <$   
 626  $Ag < Ge < Cd$  (Fig. 11c), compared with  $Cr < Ga < Cu < Zn \approx Ge < Pb < Ag \approx Cd$  in this work.  
 627 Given that not all variables (e.g., stirring rate, eccentricity) were kept constant between their  
 628 experiments, element depletion factors in Norris and Wood (2017) were normalised to a second  
 629 element,  $j$ , such that physical factors affecting element loss cancel, leaving:

$$\frac{\ln\left(\frac{X_i^t}{X_i^0}\right)}{\ln\left(\frac{X_j^t}{X_j^0}\right)} = \frac{K_i^*}{K_j^*} (fO_2)^{\frac{\Delta n_{j-i}}{4}} \sqrt{\frac{M_i}{M_j}} \quad (19)$$

630 Here,  $j = Zn$ , and hence depletion of an element  $\left(\frac{X_i^t}{X_i^0}\right)$  by a single vaporisation reaction will be  
 631 proportional to a constant multiplied by  $(fO_2)^{\frac{\Delta n_{j-i}}{4}}$  (eq. 19). Relative to the Zn vaporisation reaction  
 632 ( $n=2$ ),  $\Delta n_{Zn-Cu} = 1$  and best fits are found with  $\frac{K_{Cu}^*}{K_{Zn}^*} = 10^3$ ; this compares with  $10^1$  from our work  
 633 (Table 3). For Pb, due to the reducing conditions only  $Pb(g)$  is considered, hence  $\Delta n_{Zn-Pb} = 0$  and  $\frac{K_{Pb}^*}{K_{Zn}^*}$   
 634  $\approx 1.2$ , in reasonable agreement with  $\frac{K_{Pb}^*}{K_{Zn}^*} = 4$  determined herein (Table 3). Similarly, only  $Ga(g)$   
 635 should be stable below < FMQ (Electronic Annex E), thus  $\Delta n_{Zn-Ga} = -1$ . Satisfactory agreement is

636 found when  $\frac{K_{Ga}^*}{K_{Zn}^*} = 10^{-3}$ . For  $\Delta n_{Zn-Ge} = 0$  as determined in this work, no constant value fits the gradual  
 637 decline in  $\frac{X_{Ge}^t}{X_{Ge}^0}$  with  $\log fO_2$  observed, suggesting that  $\Delta n_{Zn-Ge}$  increases with decreasing  $fO_2$ .  
 638 Phenomenologically, this is consistent with increasing proportions of  $Ge^{2+}$  in the melt <IW,  
 639 potentially explaining its more volatile behaviour in Norris and Wood (2017) than reported here.

640

## 641 5.0. Discussion

642

643 Our approach is to provide experimental constraints on element vaporisation from silicate melts under  
 644 a set of known and controlled experimental conditions rather than to replicate any specific natural  
 645 process. As such, use of the results to quantify vaporisation in natural samples is associated with  
 646 numerous caveats. We assume the synthetic ferrobasalt is a good approximation of natural melts,  
 647 however, activity coefficients can vary with composition (O'Neill and Eggins, 2002; Borisov, 2009;  
 648 section 4.6.) meaning our results are only indicative for other basaltic melts. Moreover, the absence of  
 649 major volatiles (H, C, N, S and the halogens) in our experiments prevents their complexation of  
 650 metal-bearing gas species, which could otherwise modify element volatility (Schaefer et al., 2012;  
 651 Fegley et al., 2016; Renggli et al., 2017). Nevertheless, even in volatile-laden volcanic gases, higher  
 652 temperatures and lower pressures favour simple species (monatomic gases, oxides) with respect to  
 653 associated molecules (*e.g.*, Churakov et al., 2000). At low pressures ( $\leq 1$  bar), the major volatiles are  
 654 either sparingly soluble in silicate melts (*e.g.*, Carroll and Webster 1995) and/or highly volatile,  
 655 leaving  $O_2$  as the major volatile species. Such conditions may be relevant to degassed planetesimals,  
 656 with escape velocities too low to retain an atmosphere of light elements (*cf.* Hin et al. 2017), as well  
 657 as volatile-poor chondrules (Fedkin and Grossman, 2013; Oulton et al., 2016), tektites (Chapman and  
 658 Scheiber, 1969; Koeberl, 1986) and other 1 atm furnace experiments (Ertel et al., 1997). Experimental  
 659 and thermodynamic studies show that, in a vacuum, silicate vaporisation sets the  $fO_2$  of the vapour  
 660 phase close to the FMQ buffer (De Maria et al., 1971; Visscher and Fegley, 2013; Costa et al., 2017),  
 661 precisely the conditions covered by our experiments. We hereafter discuss our results in the context of  
 662 evaporation of planetary bodies.

663

### 664 5.1. Equilibrium evaporation and evaporation temperatures

665 Experimentally-derived thermodynamic data (Table 5), permit calculation of evaporation  
 666 temperatures. The partial pressure of an element  $i$  in the gas phase is related to its mole fraction  
 667 ( $X_i^{vap}$ ) and total pressure,  $P_T$ :

$$p_i = X_i^{vap} P_T. \quad (20)$$

668 Because the fraction of  $i$  in the gas ( $f_i^{vap}$ ) and in the liquid,  $f_i^{liq}$  must sum to 1, and  $f_i^{liq} = X_i^{liq}/X_0^{liq}$   
 669 where  $X_0^{liq}$  is the original mole fraction of element  $i$ , it follows that:

$$p_i = (X_0^{liq} - X_i^{liq})P_T. \quad (21)$$

670 Substituting eq. (21) into eq. (5), combining it with eq. (17) and solving for the temperature ( $T_e$ ) at  
 671 which a fraction,  $f$ , of an element,  $i$ , has evaporated, gives, for congruent dissociative evaporation  
 672 reactions (eq. 4):

$$T_{e,i}^f = \frac{-\Delta H_i^*}{\left( R \left( \frac{n}{4} \ln fO_2 + \ln P_T + \ln \frac{f_i^{vap}}{(1 - f_i^{vap})} \right) - \Delta S_i^* \right)}. \quad (22)$$

673 For more complicated evaporation stoichiometries  $T_{e,i}^f$  is computed analytically. Although 50%  
 674 condensation temperatures are calculated by convention, any fraction evaporated could be chosen.  
 675 Here, because the temperatures of the experiments range between 1573 K and 1823 K, it is favourable  
 676 to keep the eventual calculated  $T_e^f$  within this range to minimise extrapolation and therefore  
 677 uncertainties. As such, 1% evaporation temperatures,  $T_e^1$ , are calculated, at  $\log fO_2$ s; -10 ( $T_e^{1,-10}$ ), -5  
 678 ( $T_e^{1,-5}$ ) and in air,  $T_e^{1,air}$  (Table 6).

679 Relative to nebular  $T_c^{50}$  (Lodders, 2003, Fig. 12a; Wood et al. 2019, Fig. 12b), the higher total  
 680 pressures (1 bar) and oxygen fugacities at which  $T_e^{1,-10}$  are calculated offsets them to higher  
 681 temperatures (eq. 22; Fig. 12). These effects notwithstanding, the correlation between  $T_e^{1,-10}$  and  $T_c^{50}$   
 682 for lithophile elements, (Cr), Mg, Li, Mn, (Ga), Na, K, Rb and Zn, is excellent ( $r^2 = 0.93$  for Lodders,  
 683 2003;  $r^2 = 0.90$  for Wood et al. 2019). Siderophile and chalcophile elements tend to have relatively  
 684 lower  $T_e^{1,-10}$  than their lithophile counterparts at a given  $T_c^{50}$  (Fig. 12). This likely reflects their early  
 685 condensation, under nebular conditions, into an Fe-alloy or sulfide phase. An exception is Pb, for  
 686 which Lodders (2003) calculated  $T_c^{50}$  as 727 K by assuming ideal condensation into Fe metal  
 687 whereas Wood et al. (2019), considering its low solubility in Fe as  $Pb^0$  and in FeS as PbS, calculated  
 688 495 K. As such, Pb sits below and above, respectively, the lithophile element trends in Fig. 12. This  
 689 highlights not only the need for solubility data for trace elements in major nebula condensate phases  
 690 to better constrain  $T_c^{50}$ , but also that element volatility is sensitive to the phases present (silicate melt  
 691 in our experiments; solid FeS, silicates and metal in the solar nebula).

692 A volatility scale of elements evaporating from a ferrobasaltic liquid at 1 bar (Table 6) as a function  
 693 of  $fO_2$  is shown in Fig. 13. Lead has  $T_e^1$  within liquidus temperatures of basaltic rocks ( $\approx 1573$  K),  
 694 even at oxidising conditions, suggesting Pb (and more volatile elements such as Tl and Cd) might be  
 695 slightly volatile in subaerial eruptions (see also Norman et al. 2004; Johnson and Canil 2011;  
 696 Vlastélic et al. 2013; Edmonds et al. 2018). Zinc and Ge show similar volatility over all  $fO_2$  due to

697 their equivalent  $n = 2$  vaporisation reactions, where deviations in Zn/Ge should signal metal  
698 segregation, as Ge is more siderophile than Zn (*e.g.*, Siebert et al. 2011; Wood et al. 2014). Alkali  
699 metal volatilities increase monotonically down Group I, with Na, K and Rb showing identical  
700 vaporisation stoichiometries. Lithium is the least volatile of the alkalis, except under oxidising  
701 conditions, and becomes more refractory than either Ni (<FMQ-2) or Co (<IW+1). Manganese also  
702 becomes more volatile than Li at  $\approx$ IW-6, a prediction verified by the observation of slightly  
703 decreasing Mn/Li with increasing volatile depletion in carbonaceous chondrites (Siebert et al., 2018)  
704 and lower  $T_c$  calculated by Wood et al. (2019). Thus, Mn (and Fe and Mg) vaporises sparingly in  
705 oxidising, post-nebular settings. The depletion of these elements by volatility is therefore a hallmark  
706 of nebular depletion where  $fO_2$  is sufficiently low to render them volatile (O'Neill and Palme, 2008).  
707 Although Cr is relatively refractory at low  $fO_2$ , it becomes more volatile with  $fO_2$ , such that  $T_{e,Cr}^1 =$   
708 1785 K in air is lower than all elements studied except Pb. The same progression is observed for Mo  
709 (and W), and hence ratios of the abundances of these Group VI elements to volatile metals with  
710 opposite behaviour ( $n > 0$ ) are able to constrain  $fO_2$  during evaporation (see also Fegley and Palme  
711 1985).

## 712 5.2. Origin of moderately volatile elements in the terrestrial planets

713 Element depletion factors relevant to planet-building processes after dispersal of the solar nebula are  
714 conveniently expressed by normalising to the main lithophile element in rocky planets, Mg. These  
715 depletion factors, defined as  $\frac{X_i^t}{X_i^0} / \frac{X_{Mg}^t}{X_{Mg}^0}$ , were calculated as a function of temperature (1373 K to 1973  
716 K) and  $fO_2$  (FMQ-4 to FMQ+4) at 1 bar, and plotted in Fig. 14.

717 Differences in molar mass play only a secondary role in controlling  $\frac{X_i^t}{X_i^0}$  (eq. 19) because equilibrium  
718 partial pressures of stable gas species of moderately volatile elements vary by orders of magnitude  
719 among one another. This is manifest in the pronounced discrimination of MVE abundances in  
720 evaporation residues at a given  $fO_2$  and  $T$ . That is, the most volatile MVEs (*e.g.*, Pb and Ge), will be  
721 quantitatively vaporised before evaporation of more refractory elements, including Fe and Mg, has  
722 begun (Fig. 14). Evaporation therefore results in a near-binary distribution of elements in the residue;  
723 those that are preserved and those that are vaporised, with the transition between them defining a  
724 sharp 'cut-off' temperature. While this cut-off temperature will vary with total pressure and  $fO_2$  (eq.  
725 22), the general step-function form of the MVE pattern in the residuum is insensitive to these  
726 variables, or indeed to the accuracy of the  $K^*$  values. The binary element distribution results from  
727 *relative* differences in partial pressures among MVEs, making it a diagnostic feature of single-stage  
728 evaporation.

729 Urey (1952, 1954) first proposed that volatile element abundances could be used as  
730 ‘cosmothermometers’ to track accretion temperatures of planetary materials, an approach rendered  
731 quantitative by the calculation of condensation temperatures (Larimer, 1967). The fact that MVEs are  
732 easily decoupled during evaporation was recognised, and employed as an argument by Anders (1964)  
733 and further developed by Keays et al. (1971), Laul et al. (1973), Larimer (1973) and Grossman and  
734 Larimer (1974) to exclude vaporisation as a major contributor to the gradual depletion of MVE with  
735 volatility observed in chondrites as there is “*no one temperature at which they will all be condensed*  
736 *to the same fractional degree*”. As in chondrites, the abundances of lithophile MVEs in the BSE  
737 decline smoothly as a function of volatility (Fig. 14).

738 Volatile depletion in the Earth must reflect both *i*) the fraction of the element in the atmosphere (Fig.  
739 14) and, unlike chondrites, *ii*) its proclivity to escape. Atmospheric escape from Earth is, however,  
740 ineffective in fractionating MVEs abundances. Thermally-based Jeans escape requires prohibitively  
741 high temperatures (>10000 K) due to the Earth’s high escape velocity (11.2 km/s) and would produce  
742 a correlation with  $M^{-0.5}$ , which is not observed (Sossi and Fegley, 2018). Both hydrodynamic escape  
743 (Hunten et al., 1987; Genda and Abe, 2003; Young et al. 2019) and outflow of ionised particles  
744 (Yamauchi and Wahlund, 2007) are nearly mass-independent processes, meaning MVE losses should  
745 reflect their equilibrium partial pressures (*cf.* Fig. 14).

746 Many MVE ratios in the Earth are chondritic (*e.g.*, O’Neill and Palme, 2008; Mann et al., 2009;  
747 Siebert et al., 2018) suggesting minimal post-nebular perturbation by evaporative processes. Unlike  
748 elemental ratios, isotope ratios are readily mass-fractionated during Langmuir evaporation (Humayun  
749 and Clayton, 1995; Yu et al., 2003; Wombacher et al., 2004; Richter et al., 2007). Hence, the  
750 agreement in MVE stable isotope compositions between Earth and carbonaceous chondrites (*e.g.*  
751 Wombacher et al. 2008; Pringle et al., 2017; Sossi et al., 2018) also suggests terrestrial volatile  
752 depletion occurred in a similar manner to that in chondrites. Contrastingly, the higher abundance of In  
753 ( $T_c^{50} \approx 530$  K) relative to Cd ( $T_c^{50} \approx 500 - 650$  K) and Zn ( $T_c^{50} \approx 700$  K) in the BSE despite its higher  
754 siderophilicity and volatility permits deviation from canonical nebular conditions during volatile loss  
755 (Wang et al., 2016; Norris and Wood, 2017), though other explanations, including collisional erosion,  
756 are feasible (Witt-Eickschen et al. 2009). Indeed, the condensation/vaporisation behaviour of these  
757 highly volatile elements ( $T_c^{50} < 750$  K), whose abundances flatten out with  $T_c^{50}$  in carbonaceous  
758 chondrites (Wolf et al., 1980; Humayun and Cassen, 2000; Braukmüller et al., 2018), is poorly  
759 understood. Whether these elements also define a constant-abundance plateau in the BSE requires  
760 additional work to distinguish between the relative effects of core formation and volatility (*cf.* Wang  
761 et al., 2016; Ballhaus et al., 2017). For the MVEs, their gradual depletion with volatility in Earth’s  
762 mantle, coupled with their chondritic elemental and isotope ratios, appear at-odds with partial  
763 evaporation and loss at a single temperature and  $fO_2$  such as may be expected during a giant impact  
764 (Fig. 14).

765 A potential mechanism that could satisfy both isotopic and elemental constraints is the accretion of  
766 the Earth from a distribution of partially vaporised bodies. In each body, the elements below a given  
767 cut-off temperature are lost entirely while those above it are not lost at all (normalised abundances are  
768 '1' above and '0' below), where the cut-off point varies stochastically from body to body. Integration  
769 of material from many such bodies, each with its own binary pattern, would sum to a smooth pattern  
770 in which MVE depletion correlates with volatility, but whose MVE isotopic composition is dominated  
771 by the contributions from material that has seen negligible volatilisation.

772 By contrast, smaller bodies such as Vesta, the Ureilite and Angrite parent bodies and the Moon record  
773 significant depletions,  $<10^{-3} \times \text{CI}$ , in highly volatile elements (Cd, Ag, Pb, Ge, Zn) coupled with  
774 modest losses ( $\approx 10^{-1}$  to  $10^{-2} \times \text{CI}$ ) of the moderately volatile elements, such as Na, K and Ga (Janssens  
775 et al., 1987; O'Neill, 1991; Ruzicka et al., 2001) and a lack of depletion in elements more refractory  
776 than Li (see also Magna et al. 2006). Volatile element abundances in the Moon exemplify a highly  
777 fractionated, binary pattern consistent with single-stage evaporation, where Mg-normalised  
778 abundances of Ge, Zn, and the alkalis are very low (Wolf and Anders, 1980), whereas Li and Mn are  
779 undepleted relative to Earth's mantle (Fig. 14). Furthermore, these bodies do exhibit fractionated  
780 stable isotope signatures in elements such as Zn (*e.g.* Paniello et al. 2012), K (Wang and Jacobsen,  
781 2016), Ga (Kato and Moynier, 2017) and Cl (Boyce et al., 2018); but not Li (Magna et al. 2006),  
782 consistent with its retention during volatility-related processes. These lines of evidence are more  
783 compatible with a partial evaporation origin, the conditions and mechanisms of which will require  
784 quantitative assessment of temperatures, gas compositions, accretion scenarios and vapour loss  
785 processes.

## 786 **Conclusion**

787 In order to determine the behaviour of moderately volatile elements during evaporation of silicate  
788 melts, experiments were conducted in 1-atm vertical tube gas-mixing furnaces in which samples of  
789 synthetic ferrobalt in the FCMAS system, doped with 1000 ppm each of Li, Na, K, Cu, Rb, Ga, Ge,  
790 Pb, Mn, Mo, Zn, V, Zr, Sc, Ti, La, Gd, Yb, Ag and Cd, were suspended on noble metal wire loops and  
791 heated to 1300 °C, 1400 °C, 1500 °C and 1550 °C for between 15 and 930 minutes at  $\log f_{\text{O}_2}$ s between  
792 air (-0.68) and -10. Element loss from the melt, as determined from LA-ICP-MS measurements of the  
793 quenched glasses, varied strongly with  $f_{\text{O}_2}$ . Alloying with the metal wire and incomplete diffusion of  
794 the element to the surface were unimportant, leaving vaporisation as the sole cause of the observed  
795 depletion relative to the starting composition.

796 The degree of elemental loss depends on the stoichiometries of the vaporisation reaction(s), which  
797 have the general form  $\text{M}^{x+n}\text{O}_{(x+n)/2}(\text{l}) = \text{M}^x\text{O}_{x/2}(\text{g}) + n/4\text{O}_2$ . These reactions are solved for the  
798 equilibrium partial pressure of the gas species and incorporated into the Hertz-Knudsen-Langmuir  
799 equation, enabling element evaporation from a sphere to be quantitatively modelled. Stoichiometries

800 of the reaction(s),  $n$ , and equilibrium constant(s),  $K^*$  are calculated from fits to the experimental data.  
801 Most MVEs evaporate with  $n > 0$ , where stoichiometries of 1 (Cu, Na, K, Rb, Ag) and 2 (Zn, Ge, Cd)  
802 are common. The Group VI metals, Cr and Mo, show the inverse behaviour ( $n < 0$ ) by virtue of their  
803 stable oxide-bearing gas species with oxidation states higher than those in the silicate liquid. The  $K^*$   
804 value is the product of the activity coefficient,  $\gamma_i$ , the evaporation coefficient,  $\alpha_e$  and the equilibrium  
805 constant of reaction ( $K$ ), the first two of which are not known *a priori*. Evaporation coefficients  
806 calculated using literature values for activity coefficients return values near unity, verifying the  
807 accuracy of the approach and suggesting evaporation is near-ideal. Given  $\alpha_e$  of 1,  $\gamma_i$  of melt oxide  
808 components vary by  $\sim 10^5$ , shifting their volatilities compared with evaporation from pure oxides. For  
809 all volatile elements,  $\log K^*$  increases with temperature, which, when converted to  $\Delta G^*$ , allows a  
810 straight line to be fit to the data, where the slope is equal to  $-\Delta S^*$  and the intercept  $\Delta H^*$ .

811 These fundamental data are useful for understanding vapour loss during chondrule melting, degassing  
812 of anhydrous magmas, tektite formation and other 1 atm furnace experiments. Although lithophile  
813 elements show good agreement with nebular condensation temperatures at low  $fO_2$ , chalcophile and  
814 siderophile elements are generally more volatile during evaporation of silicate melts relative to solar  
815 nebular environments. Evaporation of a silicate melt at a single temperature and  $fO_2$  results in a near-  
816 binary element distribution in the residuum, strongly discriminating the volatile elements from the  
817 non-volatile. This type of fractionation among MVEs is observed in small telluric bodies (Moon,  
818 Vesta) but not on Earth, where element depletion is a gradual function of volatility. This observation  
819 argues against volatile loss from Earth during a giant impact, suggesting that it accreted from already  
820 volatile-depleted components.

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## 1228 Figure captions

1229 *Fig. 1.* Back-scattered electron images of four experimental glasses at the same magnification (1000  $\mu\text{m}$  scale bar shown), a)  
 1230 3M-29/02/16, 1400  $^{\circ}\text{C}$ ,  $\log f\text{O}_2 = -0.68$ , 60 minutes; b) 1M-1/3/16, 1400  $^{\circ}\text{C}$ ,  $\log f\text{O}_2 = -10.01$ , 60 minutes; c) 2M-16/07/16h,  
 1231 1550  $^{\circ}\text{C}$ ,  $\log f\text{O}_2 = -6.01$ , 15 minutes; d) P-11/06/18b, 1550  $^{\circ}\text{C}$ ,  $\log f\text{O}_2 = -5.48$ , 15 minutes.

1232 *Fig. 2.* Concentrations of volatile elements (K, Cr, Cu, Zn, Ga, Ge, Rb, Mo, Ag, Cd, Pb; N = 38) in an experimental glass  
 1233 (pair 1) plotted relative to their concentrations in another experimental glass run under the same conditions (pair 2) for four  
 1234 experimental pairs. The different shades correspond to the following experimental pairs (pair 1, pair 2): black (P-09/06/18b,  
 1235 P-09/06/18a), 1400  $^{\circ}\text{C}$ ,  $\log f\text{O}_2 = -9.23$ , 15 minutes; dark grey (P-08/02/17b, 3M-29/2/16), 1400  $^{\circ}\text{C}$ ,  $\log f\text{O}_2 = -0.68$ , 60  
 1236 minutes; light grey (P-09/06/18c, 1M-PS1), 1400  $^{\circ}\text{C}$ ,  $\log f\text{O}_2 = -5.50$ , 60 minutes; white (1M-2/3/16, C18/12/15), 1400  $^{\circ}\text{C}$ ,  
 1237  $\log f\text{O}_2 = -3.07$ , 60 minutes.

1238 *Fig. 3.* Measurement of elemental zoning profiles in sample 3M-29/02/16 (1400  $^{\circ}\text{C}$ , 60 mins, air). Panel a) shows a reflected  
 1239 light image of the glass and laser spot profiles. Panel b) displays the fraction of a volatile element  $i$  remaining in the glass  
 1240 (Ga, green; Zn, red; Cu, blue; Ge, purple; Rb, blue; Mo, orange) as a function of distance from rim to rim, corresponding to  
 1241 the uppermost profile in panel a), with 25  $\mu\text{m}$  spots at 100  $\mu\text{m}$  spacing.

1242 *Fig. 4.* Vaporisation of a) Na, b) K, c) Rb, and d) Cu – elements with one oxidation state in the liquid and one species in the  
 1243 gas, corresponding to vaporisation reactions with  $n = 1$  stoichiometry (eq. 4). The fraction of the element remaining in the  
 1244 glass after a run duration of 60 minutes (Na and K) or 15 minutes (Rb and Cu), relative to its initial concentration in the glass  
 1245  $\left(\frac{x_i^f}{x_i^0}\right)$  are plotted as a function of  $\log f\text{O}_2$ . Lines at the top denote the location of the FMQ buffer as a function of temperature.  
 1246 Curves are non-linear least-squares fits (see eq. 9) to the experimental data using eq. (8), shown along with the  $\log K^*$  values  
 1247 to which they correspond. Colours of lines, curves and symbols denote the temperature of the experiment; blue = 1300  $^{\circ}\text{C}$ ,  
 1248 green = 1400  $^{\circ}\text{C}$ , yellow = 1500  $^{\circ}\text{C}$ , red = 1550  $^{\circ}\text{C}$ .

1249 *Fig. 5.* Vaporisation of a) Zn and b) Ge – elements with one oxidation state in the liquid and one gas species, corresponding  
 1250 to vaporisation reactions with  $n = 2$  stoichiometry (eq. 4). The fraction of the element remaining in the glass after a run  
 1251 duration of 15 minutes, relative to its initial concentration in the glass  $\left(\frac{x_i^f}{x_i^0}\right)$  is plotted as a function of  $\log f\text{O}_2$ . Lines at the top  
 1252 denote the location of the FMQ buffer. Colours and nomenclature are as per Fig. 4.

1253 *Fig. 6.* Vaporisation of a) Li, b) Ga and c) Pb – elements with one oxidation state in the liquid and multiple species in the  
 1254 gas. The fraction of the element remaining in the glass after an experimental run, relative to its initial concentration in the  
 1255 glass  $\left(\frac{x_i^f}{x_i^0}\right)$  is plotted as a function of a) time for Li. Shown are experiments performed at a single temperature, 1400  $^{\circ}\text{C}$ , at  
 1256 two  $\log f\text{O}_2$ s, -0.68 (white circles) and -8.00 (black circles). Both series are fit by non-linear least squares using eq. 8  
 1257 corresponding to the reactions  $\text{LiO}_{0.5}(\text{l}) + \frac{1}{4}\text{O}_2 = \text{LiO}(\text{g})$  for a  $\log K^*$  of -3.39 (white circles) and  $\text{LiO}_{0.5}(\text{l}) = \text{Li}(\text{g}) + \frac{1}{4}\text{O}_2$   
 1258 with  $\log K^*$  of -5.36 (black circles). Parts b) and c) plot  $\left(\frac{x_i^f}{x_i^0}\right)$  against  $\log f\text{O}_2$  for Ga and Pb, respectively. Lines at the top  
 1259 denote the location of the FMQ buffer. Symbols and nomenclature as per Fig. 4. All experiments shown were run for 15

1260 minutes. The two  $\log K^*$ s for Ga correspond to the reactions  $\text{GaO}_{1.5}(\text{l}) = \text{GaO}(\text{g}) + \frac{1}{4}\text{O}_2$  (normal script) and  $\text{GaO}_{1.5}(\text{l}) = \text{Ga}(\text{g})$   
1261  $+ \frac{3}{4}\text{O}_2$  (italic); and for Pb,  $\text{PbO}(\text{l}) = \text{PbO}(\text{g})$  (normal script) and  $\text{PbO}(\text{l}) = \text{Pb}(\text{g}) + \frac{1}{2}\text{O}_2$  (italic).

1262 *Fig. 7.* Vaporisation of the Group VI elements – a) Mo and b) Cr – that have multiple species in the liquid and at least one  
1263 species in the gas, whose net vaporisation reactions have  $n < 0$  stoichiometry (see eq. 4). The fraction of the element  
1264 remaining in the glass after a run duration of 15 minutes, relative to its initial concentration in the glass  $\left(\frac{X_i^t}{X_i^0}\right)$  is plotted as a  
1265 function of  $\log f\text{O}_2$ . Lines at the top denote the location of the FMQ buffer. Colours and nomenclature are as per Fig. 4. For  
1266 Mo, the  $\log K^*$  values shown correspond to the reaction:  $\text{MoO}_3(\text{l}) = \text{MoO}_3(\text{g})$ , and for Cr the  $\log K^*$  values shown correspond  
1267 to the reaction:  $\text{CrO}(\text{l}) + \frac{1}{2}\text{O}_2 = \text{CrO}_2(\text{g})$ .

1268 *Fig. 8.* Activity coefficients ( $\gamma$ ) of melt oxide species (i) at infinite dilution ( $\infty$ ) in a ferrobaltic FCMAS liquid calculated  
1269 by eq. 6, as a function of temperature. Melt oxide species are:  $\text{CuO}_{0.5}$  = teal,  $\text{LiO}_{0.5}$  = yellow,  $\text{AgO}_{0.5}$  = grey,  $\text{ZnO}$  = blue,  
1270  $\text{PbO}$  = light orange,  $\text{CdO}$  = red,  $\text{GeO}_2$  = purple,  $\text{NaO}_{0.5}$  = sky blue,  $\text{KO}_{0.5}$  = dark orange,  $\text{RbO}_{0.5}$  = black. The two light  
1271 orange ‘PbO’ series denote  $\gamma_{\text{PbO}}^\infty$  calculated by two reactions,  $\text{PbO}(\text{l}) = \text{PbO}(\text{g})$  (lower series) and  $\text{PbO}(\text{l}) = \text{Pb}(\text{g}) + \frac{1}{2}\text{O}_2$   
1272 (upper series). The two data points shown for  $\text{LiO}_{0.5}$  denote  $\gamma_{\text{LiO}_{0.5}}^\infty$  calculated at  $\log f\text{O}_2$  -8.00 by the reaction  $\text{LiO}_{0.5}(\text{l}) = \text{Li}(\text{g})$   
1273  $+ \frac{1}{4}\text{O}_2$  and at  $\log f\text{O}_2 = -0.68$  by the reaction  $\text{LiO}_{0.5}(\text{l}) + \frac{1}{4}\text{O}_2 = \text{LiO}(\text{g})$ .

1274 *Fig. 9.* The Gibbs Free Energy,  $\Delta G^*$ , in kJ/mol against temperature (K) for element vaporisation reactions from a  
1275 ferrobaltic liquid in the FCMAS system at 1 bar of a) Rb,  $\text{RbO}_{0.5}(\text{l}) = \text{Rb}(\text{g}) + \frac{1}{4}\text{O}_2$  b) Cu,  $\text{CuO}_{0.5}(\text{l}) = \text{Cu}(\text{g}) + \frac{1}{4}\text{O}_2$  c) Zn,  
1276  $\text{ZnO}(\text{l}) = \text{Zn}(\text{g}) + \frac{1}{2}\text{O}_2$  d) Ge,  $\text{GeO}_2(\text{l}) = \text{GeO}(\text{g}) + \frac{1}{2}\text{O}_2$ . Greyscale denotes  $f\text{O}_2$  series run at constant temperature with  
1277 different times, White = 15 minutes, Black = 60 minutes, Grey = 120 minute. Best fits to all data points *via* the 2<sup>nd</sup>-law  
1278 method yield the  $\Delta G^*$  as a function of temperature (shown in panel).

1279 *Fig. 10.* Enthalpy ( $\Delta H$ )-Entropy ( $\Delta S$ ) correlations for vaporisation reactions that are a) experimentally-derived (see section  
1280 4.7. and Table 5) and b) in the pure system (see Table 5). Labels refer to the stable gas species. Colours as per Fig. 8 with the  
1281 addition of Ga and GaO (fuchsia),  $\text{CrO}_2$  (green) for the reaction  $\text{CrO}(\text{l}) + \frac{1}{2}\text{O}_2 = \text{CrO}_2(\text{g})$  and  $\text{MoO}_3$  (magenta) for the  
1282 reaction  $\text{MoO}_2(\text{l}) + \frac{1}{2}\text{O}_2 = \text{MoO}_3(\text{g})$ .

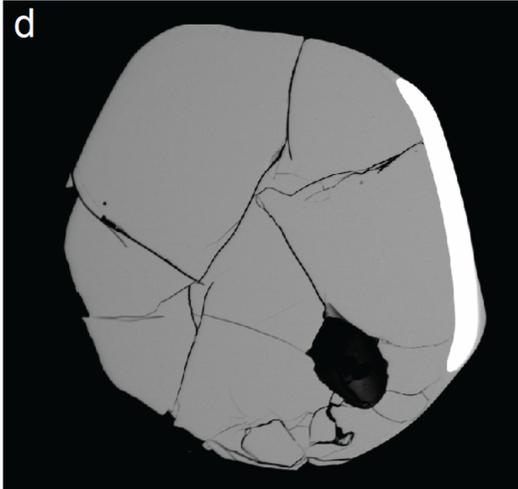
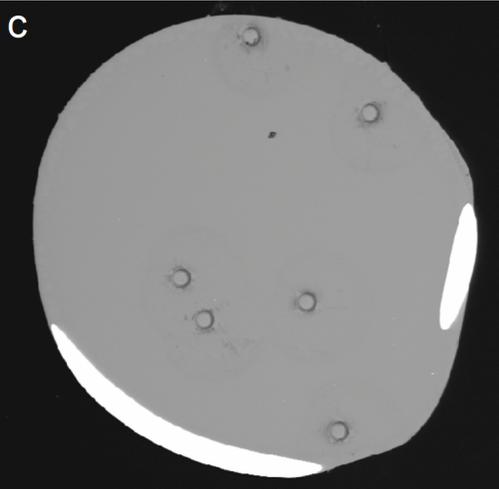
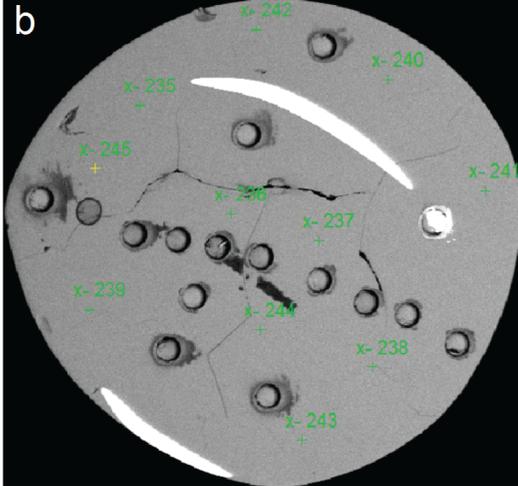
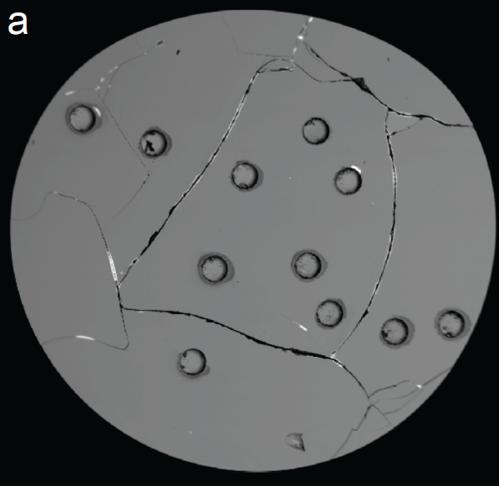
1283 *Fig. 11.* Experimental data from the literature. a) Fraction of Na remaining in chondrule-like glass as a function of time at  
1284 different temperatures (Tsuchiyama et al., 1981). Circles refer to ‘composition 1’; blue = 1450 °C, green = 1500 °C, yellow  
1285 = 1550 °C, red = 1600 °C; the square symbols refer to ‘composition 2’ at 1586 °C. Curves are fits with eq. 8 assuming an  $n =$   
1286 1 evaporation stoichiometry, and numbers correspond to  $\log K^*$  values. b) Data of Kreuzberger et al. (1986) showing the  
1287 fraction of Na (blue), K (orange) and Rb (black) remaining in a  $\text{Di}_{75}\text{An}_{25}$  glass composition at 1400 °C in air as a function of  
1288 time. Curves are fits with eq. 8 assuming an  $n = 1$  evaporation stoichiometry, and numbers correspond to  $\log K^*$  values. c)  
1289 Data of Norris and Wood (2017) showing the fraction of Cu (teal), Zn (blue), Ga (crimson), Ge (purple) and Pb (orange)  
1290 remaining in MORB glass after 60 minutes at 1300 °C, as a function of  $\log f\text{O}_2$ . The fits to the data are made relative to Zn,  
1291 with eq. (19).

1292 *Fig. 12.* Nebular half condensation temperatures ( $T_c^{50}$ ) of a) Lodders (2003) and b) Wood et al. (2019) compared to 1%  
1293 evaporation temperatures for metal oxides from a ferrobaltic silicate melt at 1 bar and  $\log f\text{O}_2 = -10$ , calculated from the  
1294 experiments, except for Mn, Mg, Fe, Co, Ni and Cr, which are taken from thermodynamic data in the pure system (Table 5).  
1295 Chalcophile = orange, Siderophile = grey, Lithophile = green. Line of best fit (black) to lithophile elements only.

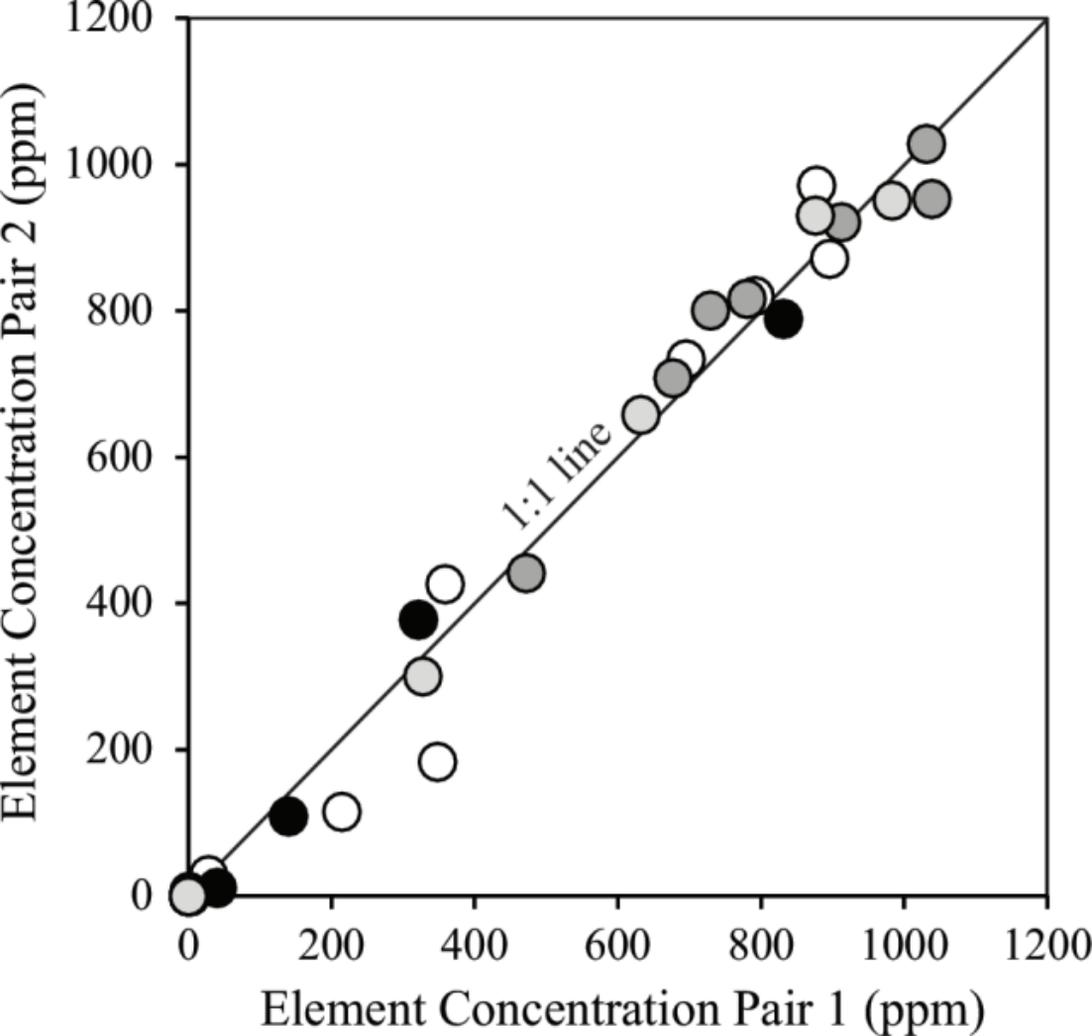
1296 *Fig. 13.* 1% evaporation temperatures for metal oxides from a ferrobaltic in the FCMAS system at 1 bar as a function of  $\log$   
1297  $f\text{O}_2$ , calculated from thermodynamic data from the experiments, except for Mn, Mg, Fe, Co, Ni and Cr (below IW-1), which  
1298 are taken from the pure system (Table 5). Dotted coloured lines (Li, Na, K, Mo, Cr) indicate that evaporation temperatures  
1299 are calculated assuming their activity coefficients are constant with temperature (For Li, Na, K calculated at 1673 K, for Mo

1300 and Cr fixed by literature values at 1673 K) and hence uncertain outside of this temperature. In general, caution should be  
1301 exercised in use of evaporation temperatures calculated outside of the experimental range (grey field). Dashed grey lines  
1302 show the  $fO_2$  defined by mineral oxygen buffers (IW = Iron-Wüstite, FMQ = Fayalite-Magnetite-Quartz, MH = Magnetite-  
1303 Hematite).

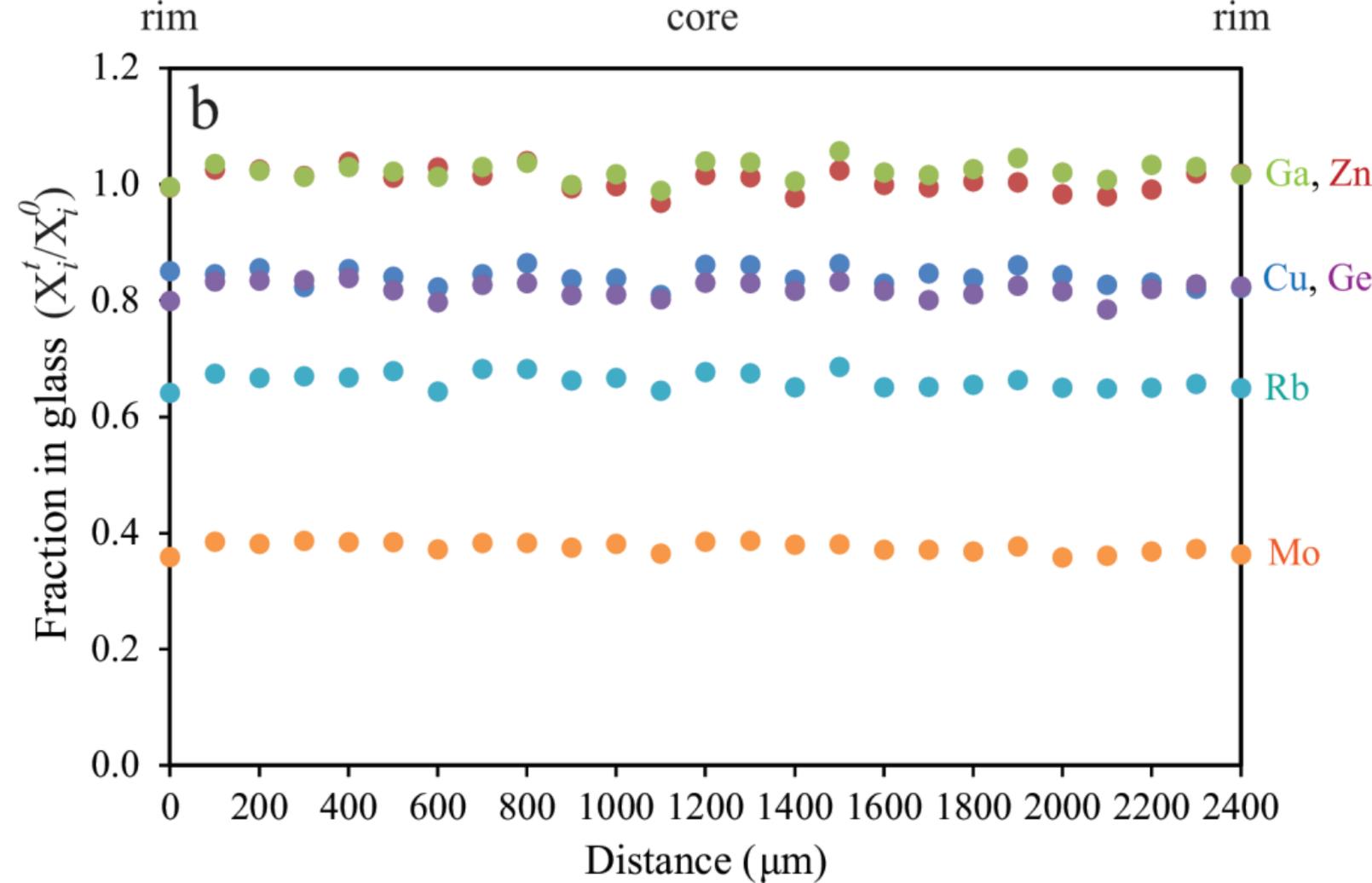
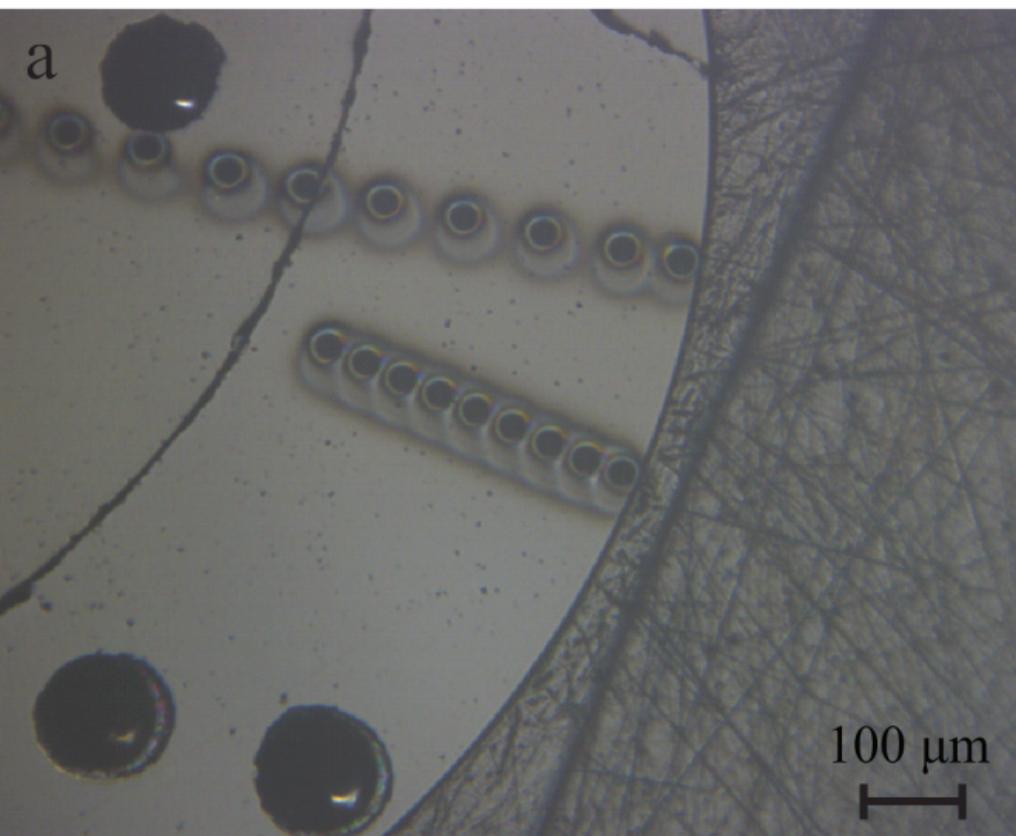
1304 *Fig. 14.* Elemental depletion factors normalised to Mg in a residual ferrobalt melt after Langmuir evaporation at 1 bar  
1305 calculated with eq. 19. Elements are plotted in order of their volatilities from the ferrobalt composition. a) At constant  
1306 relative  $fO_2$  (FMQ buffer) and variable temperature (listed next to lines in K) and b) At constant temperature and variable  
1307 relative  $fO_2$  ( $\Delta$ FMQ listed next to lines). Also plotted are the estimated elemental abundances of lithophile and weakly  
1308 siderophile elements in the Earth's primitive mantle (Palme and O'Neill, 2014; green circles) and the Moon's primitive  
1309 mantle (O'Neill, 1991, Ni et al. 2019; grey circles).



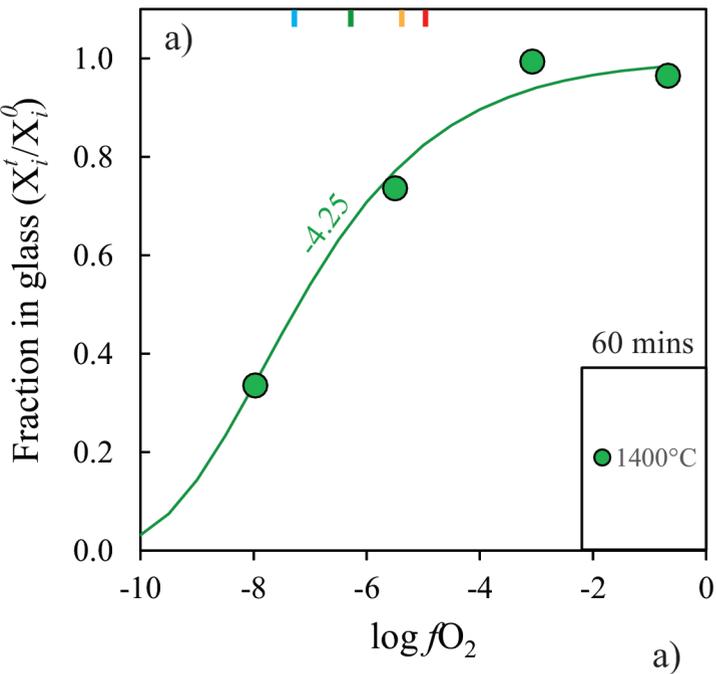
1000  $\mu\text{m}$



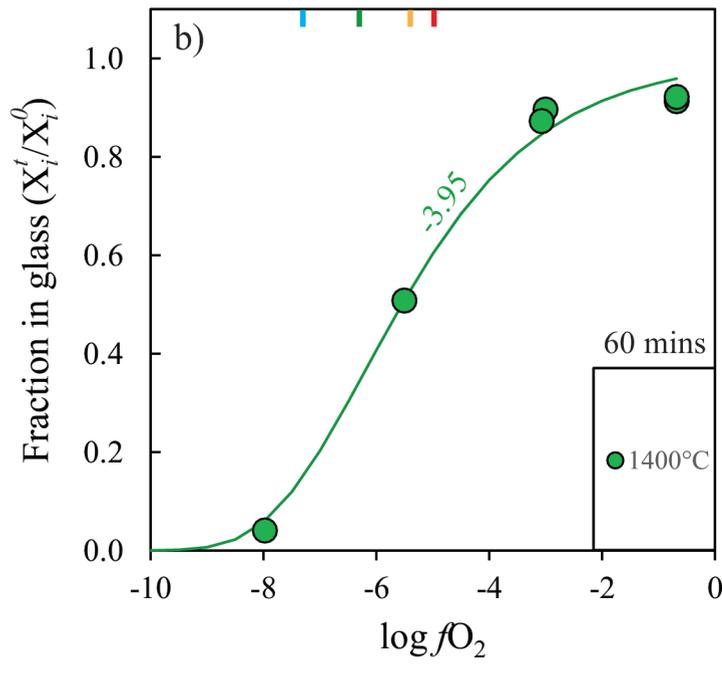
Sample 3M-29/02/16 (1400 °C, 60 mins, air)



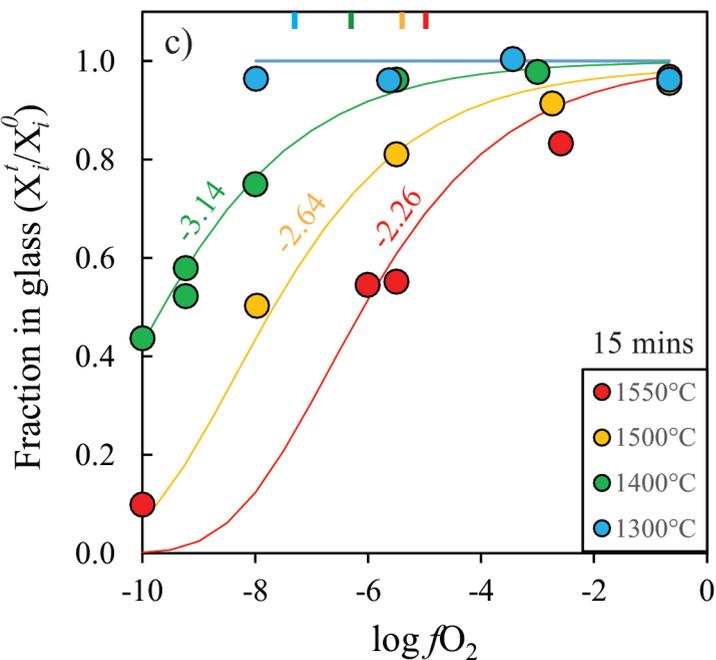
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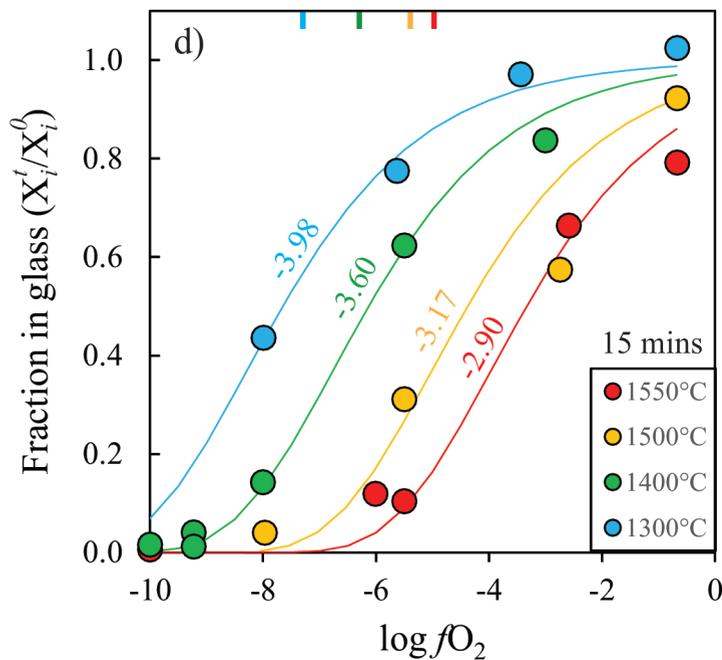
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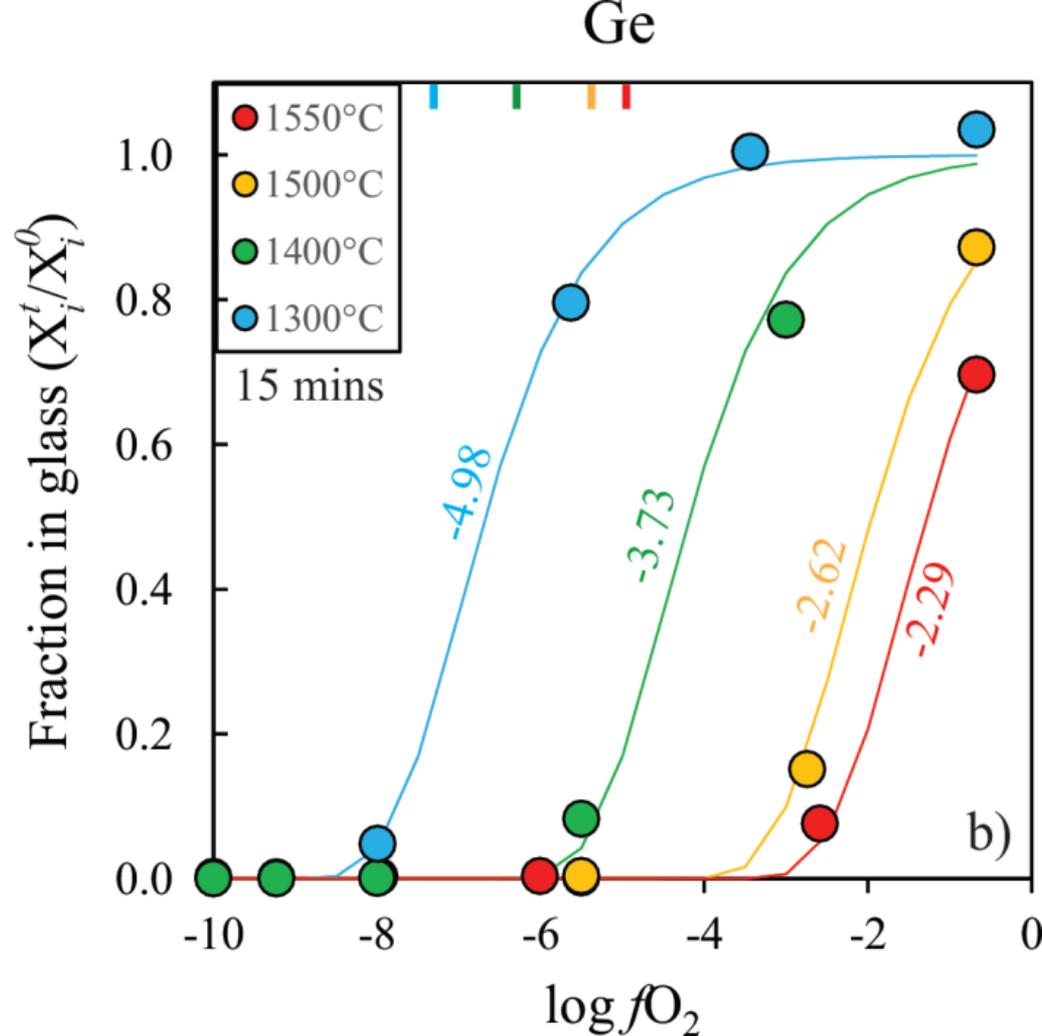
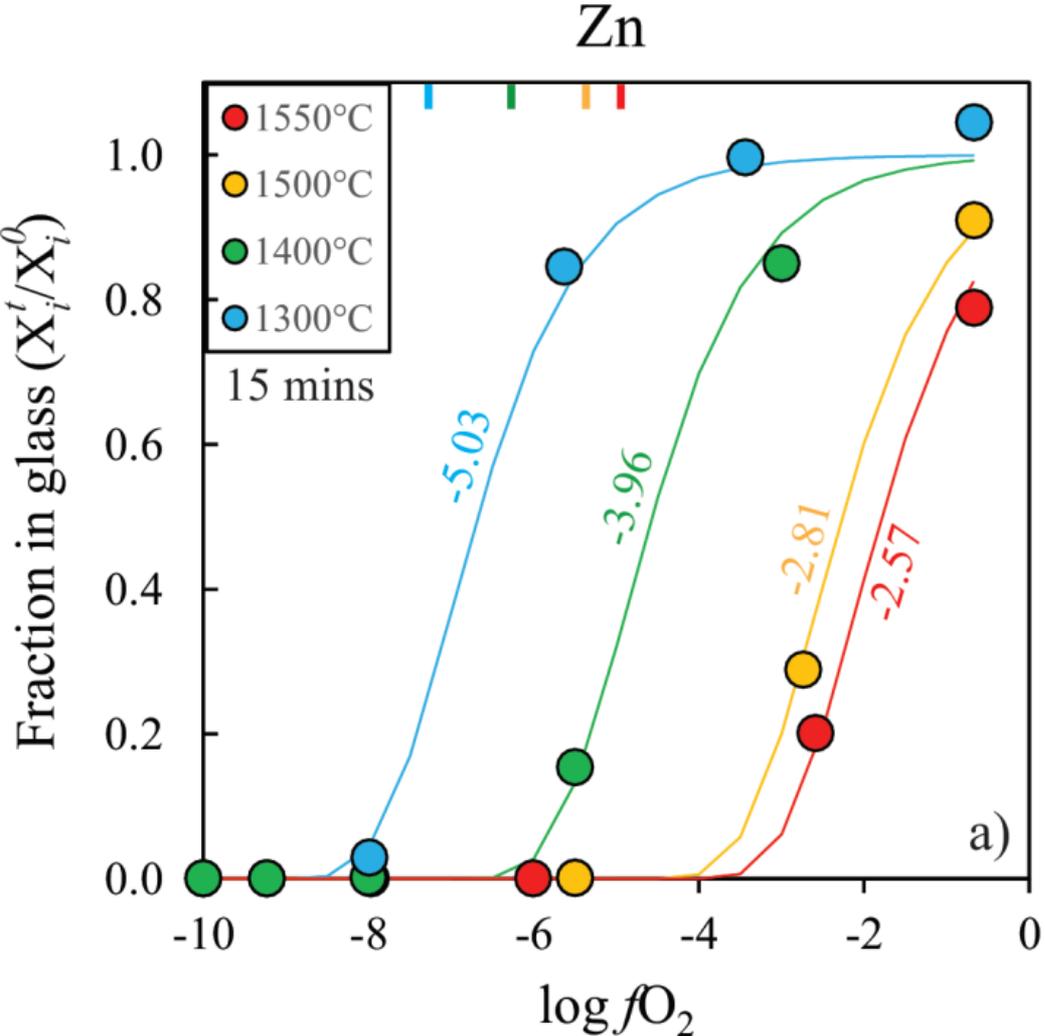


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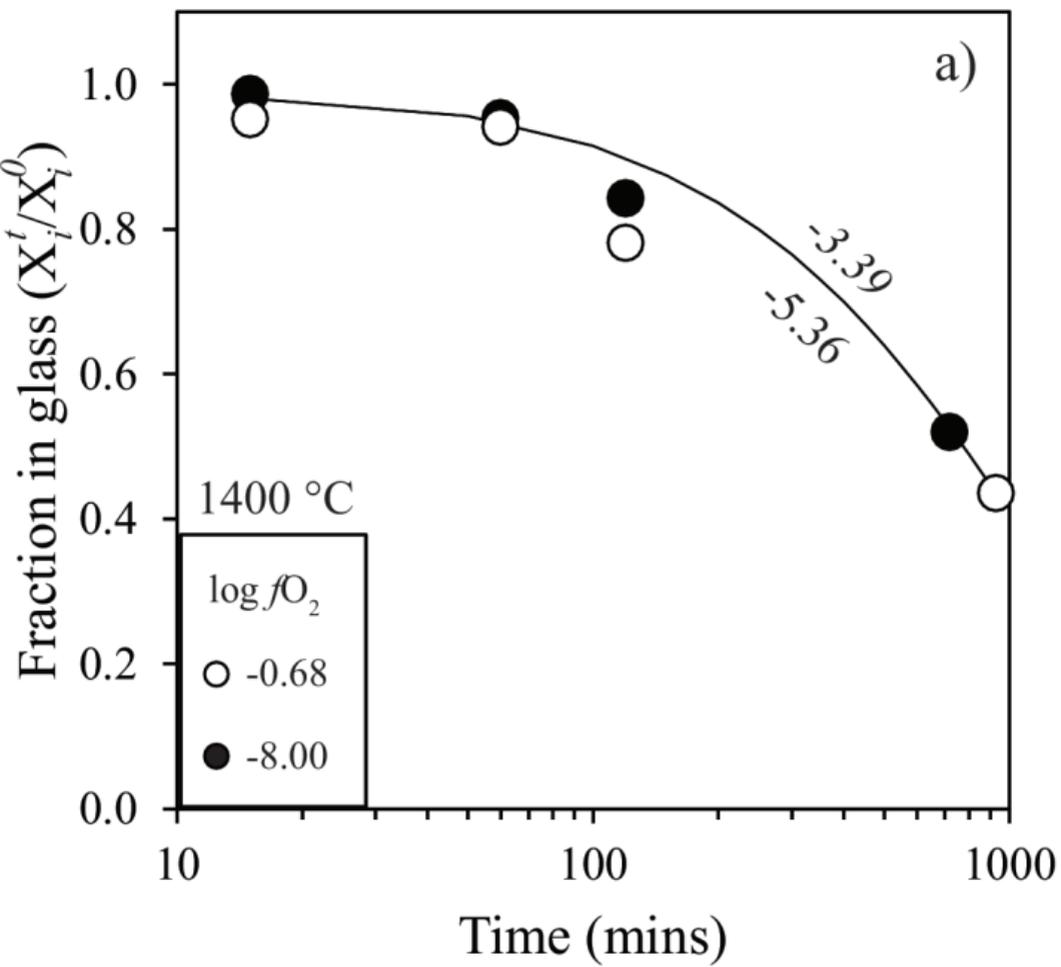


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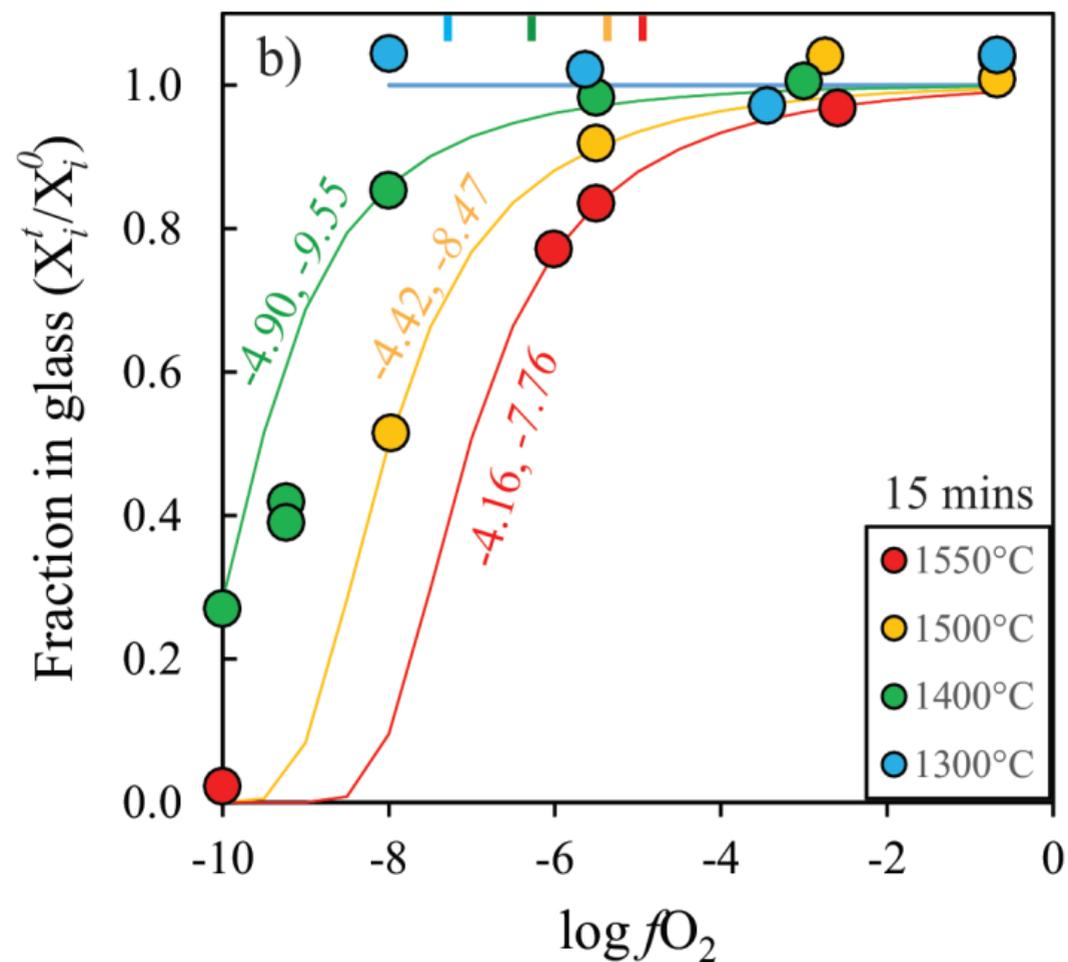




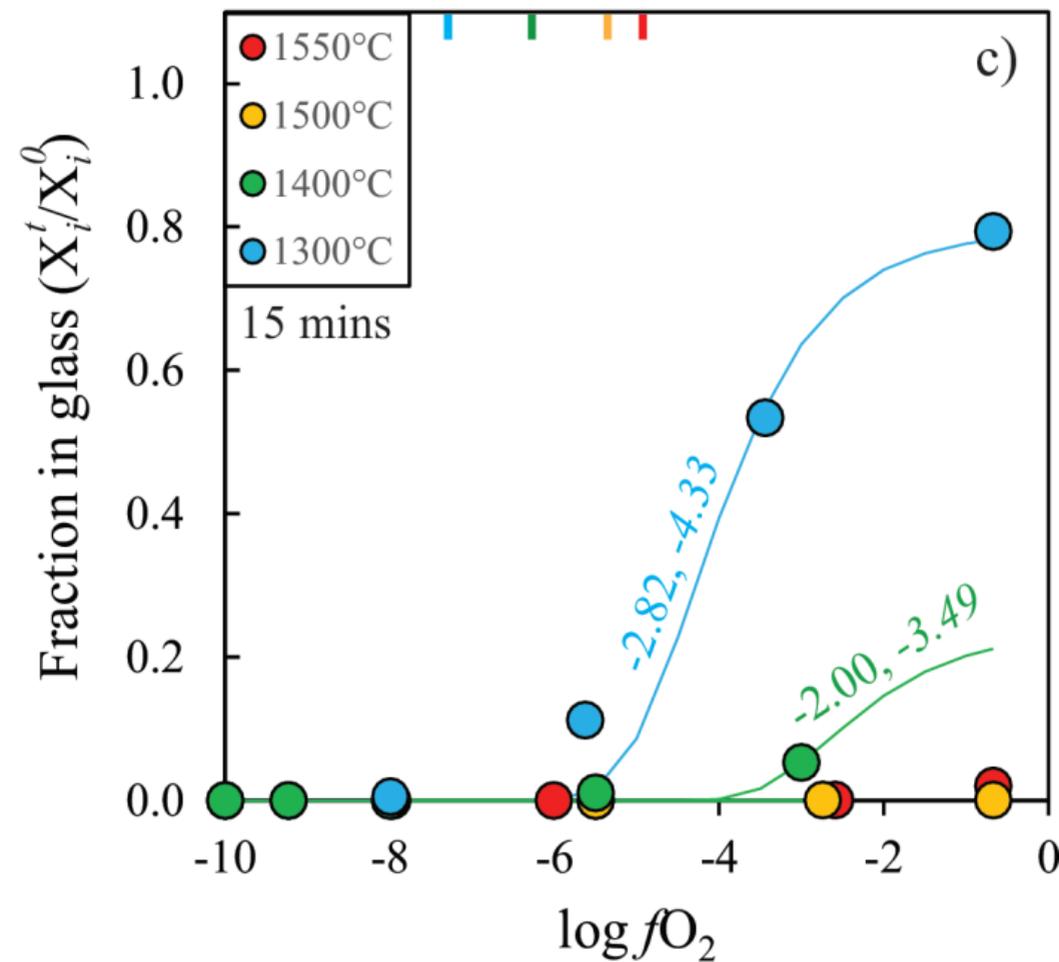
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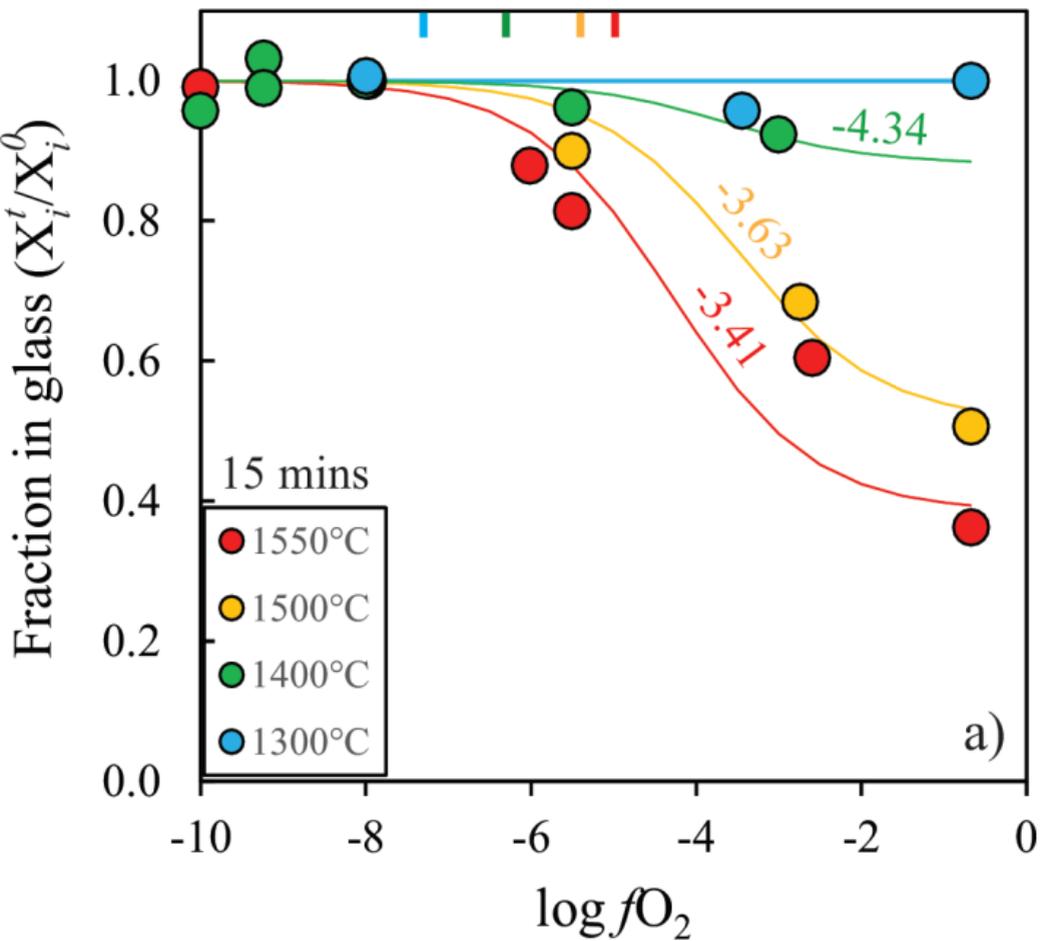
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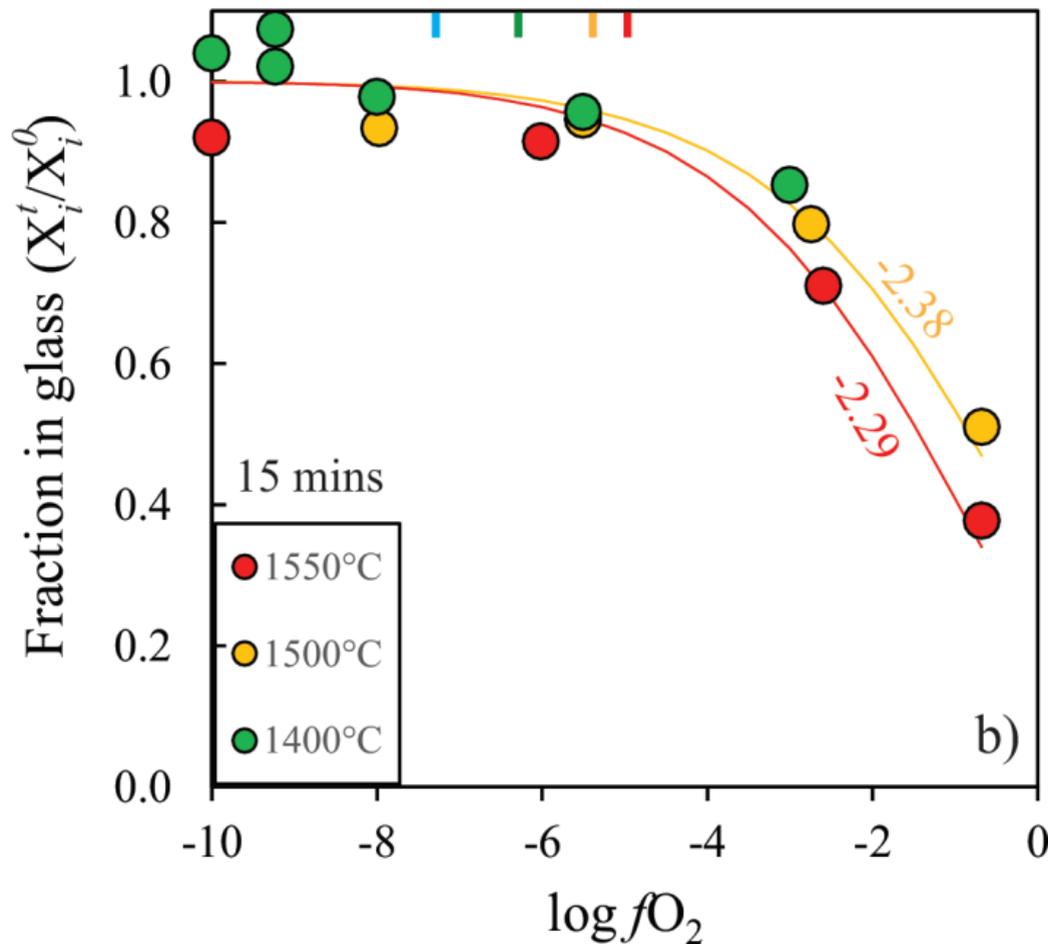
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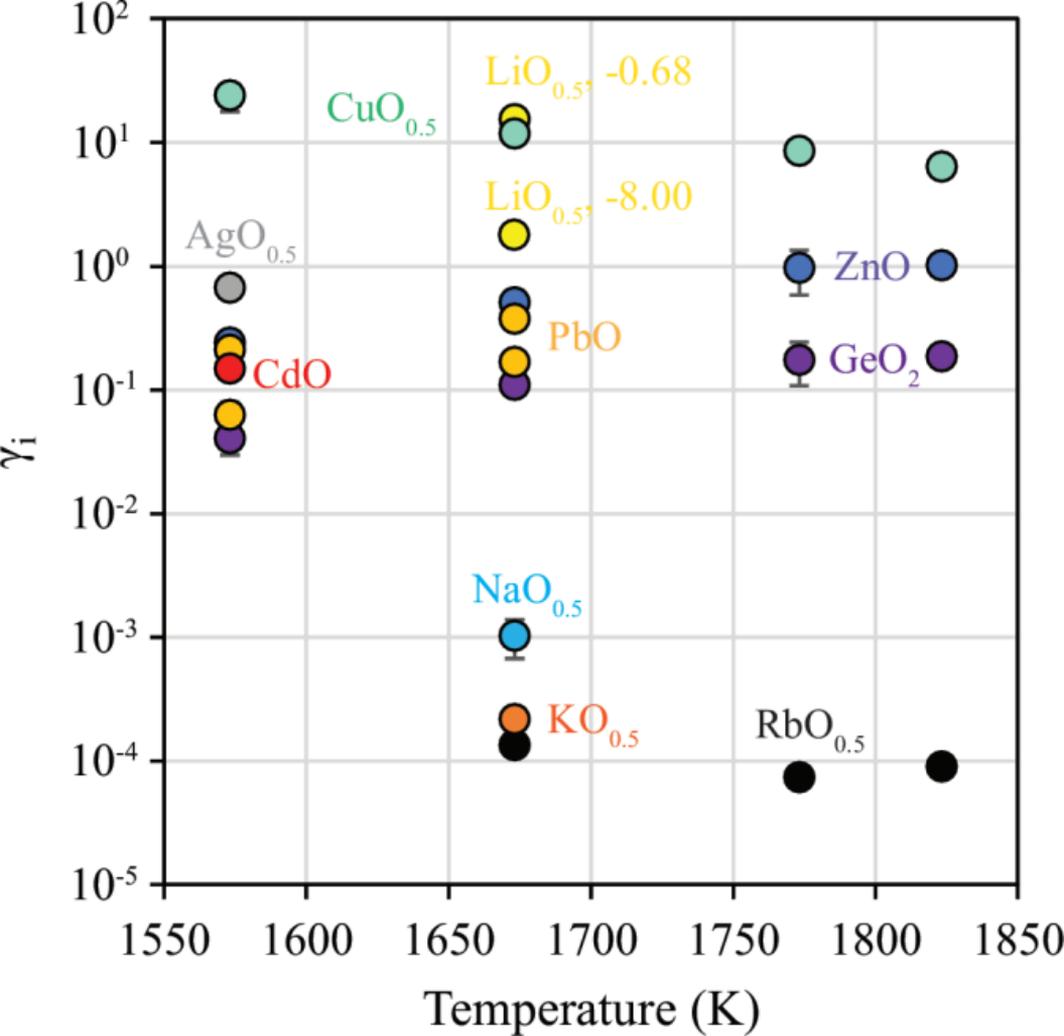


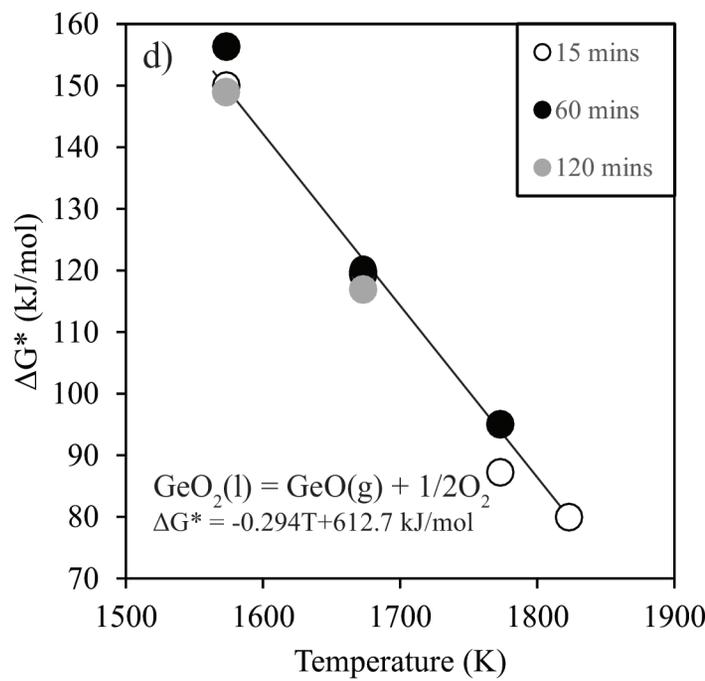
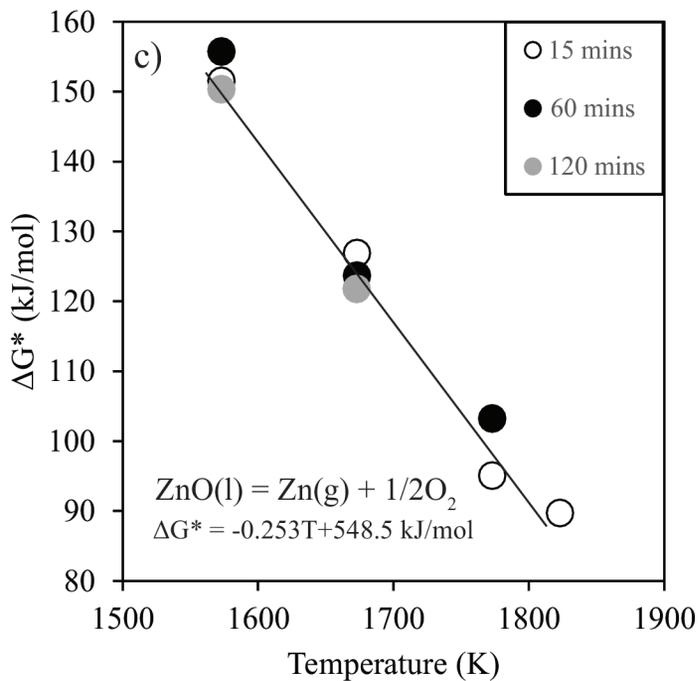
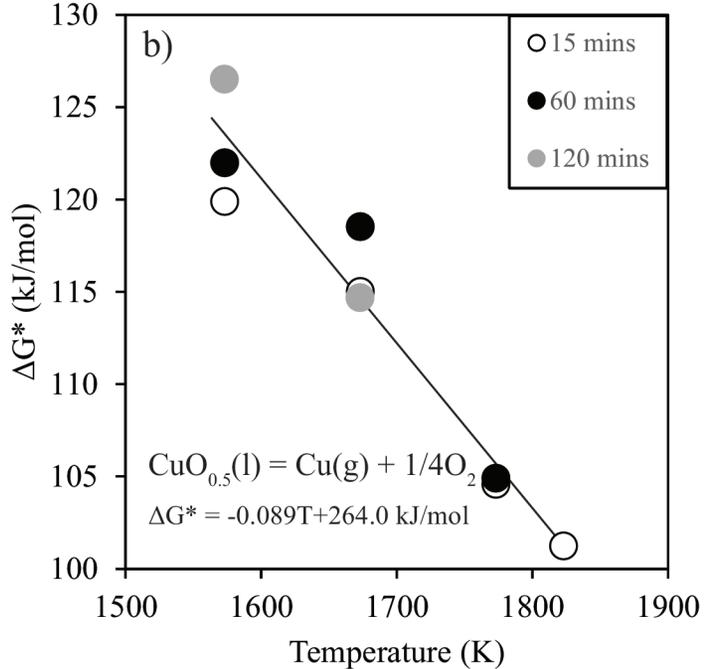
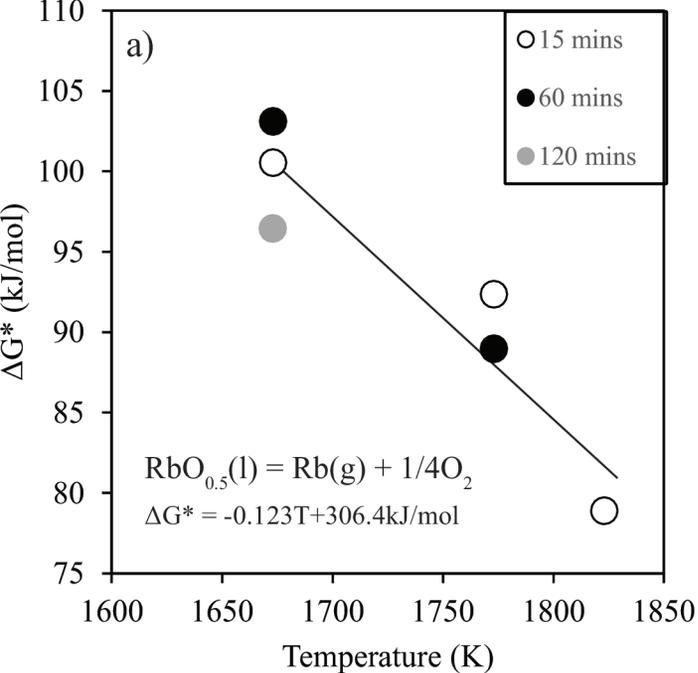
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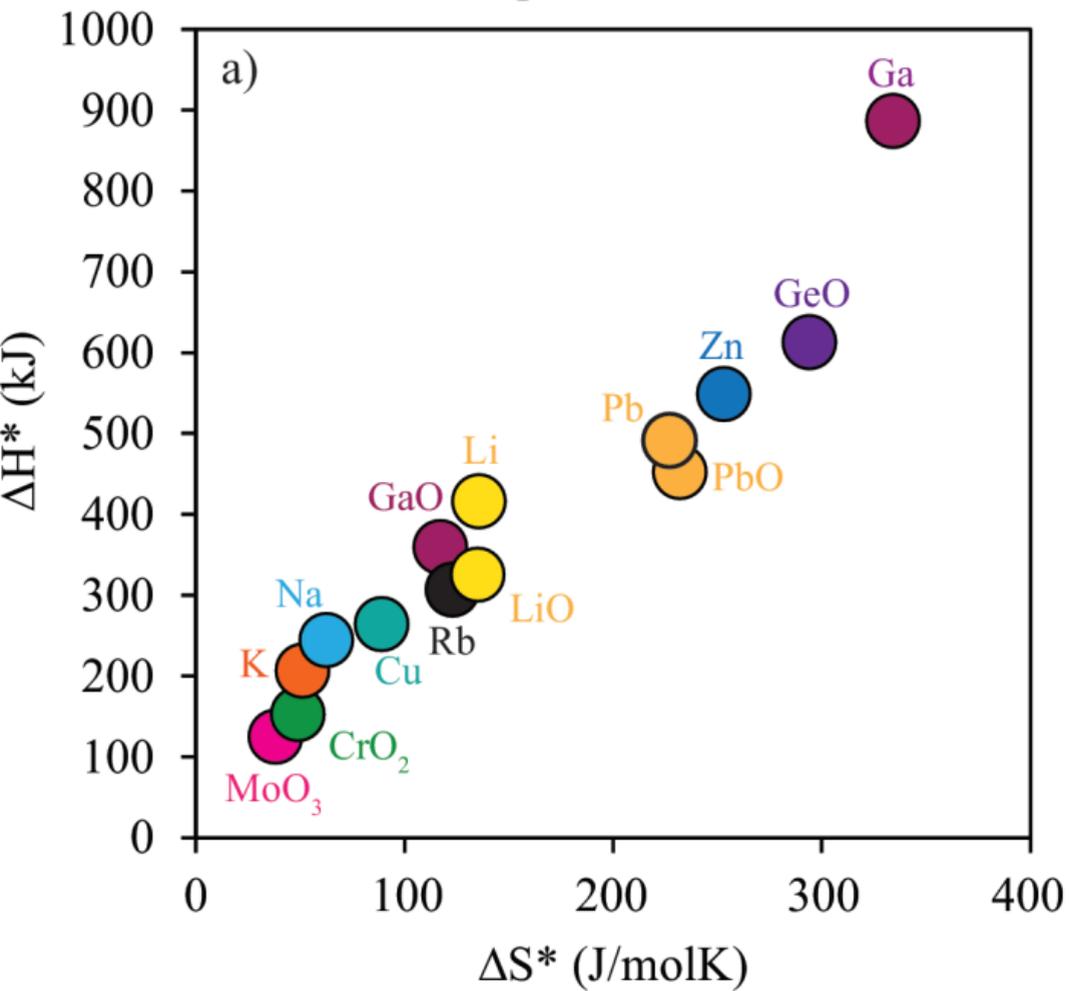
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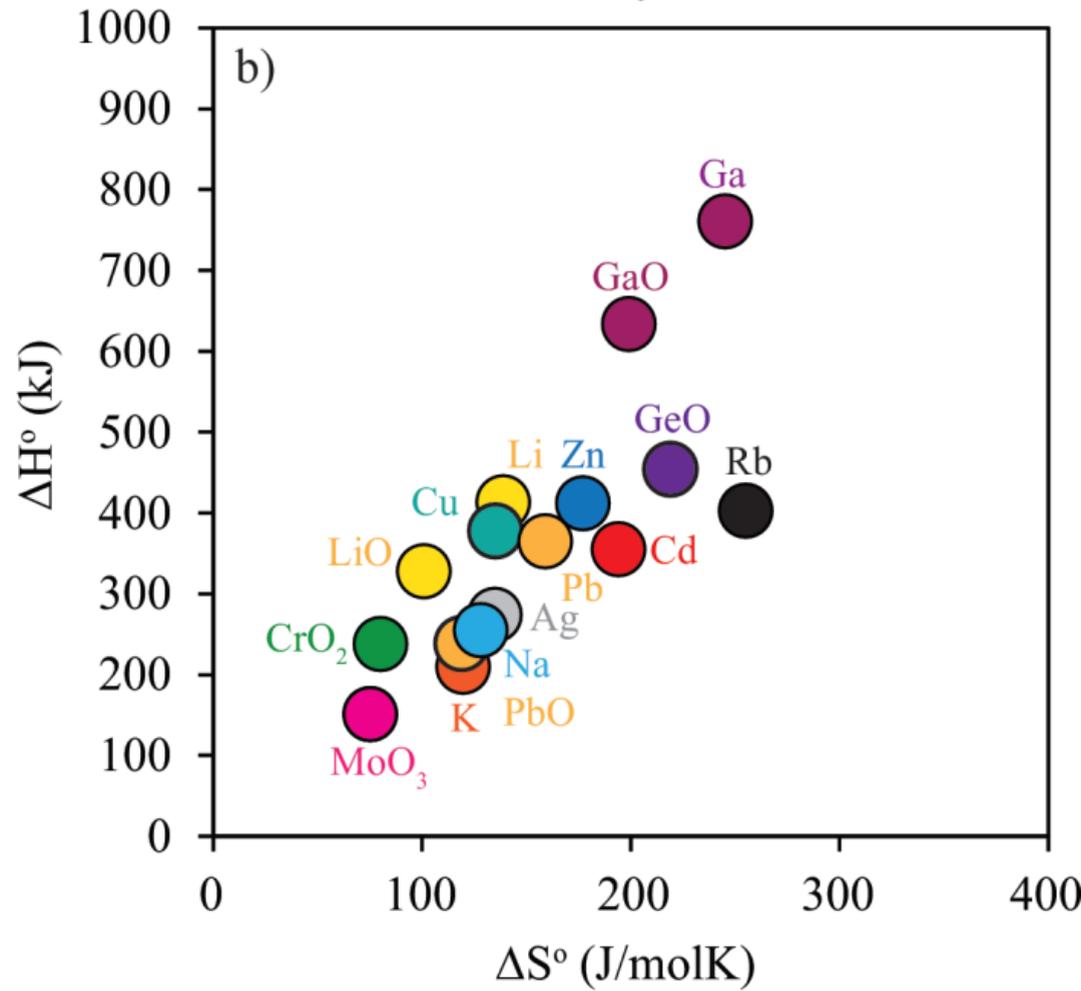


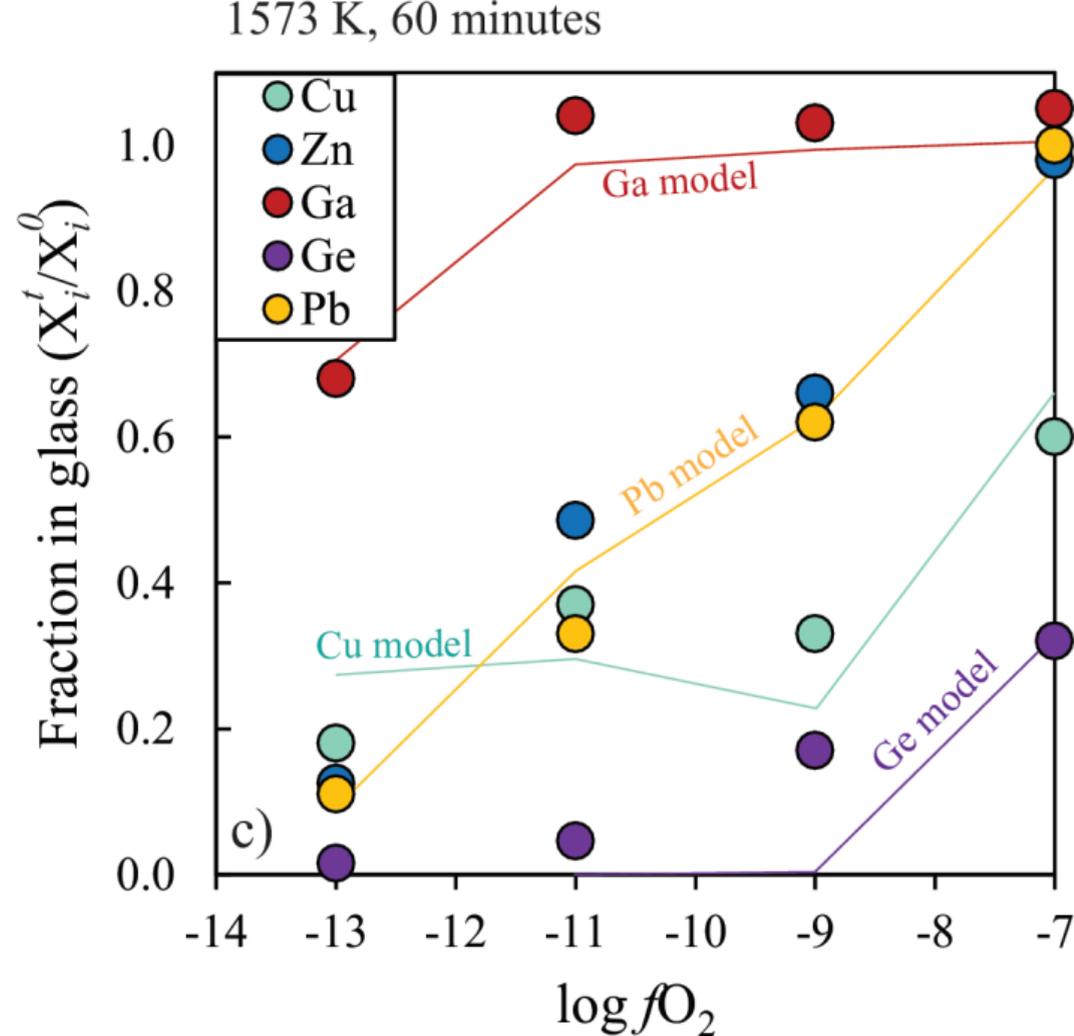
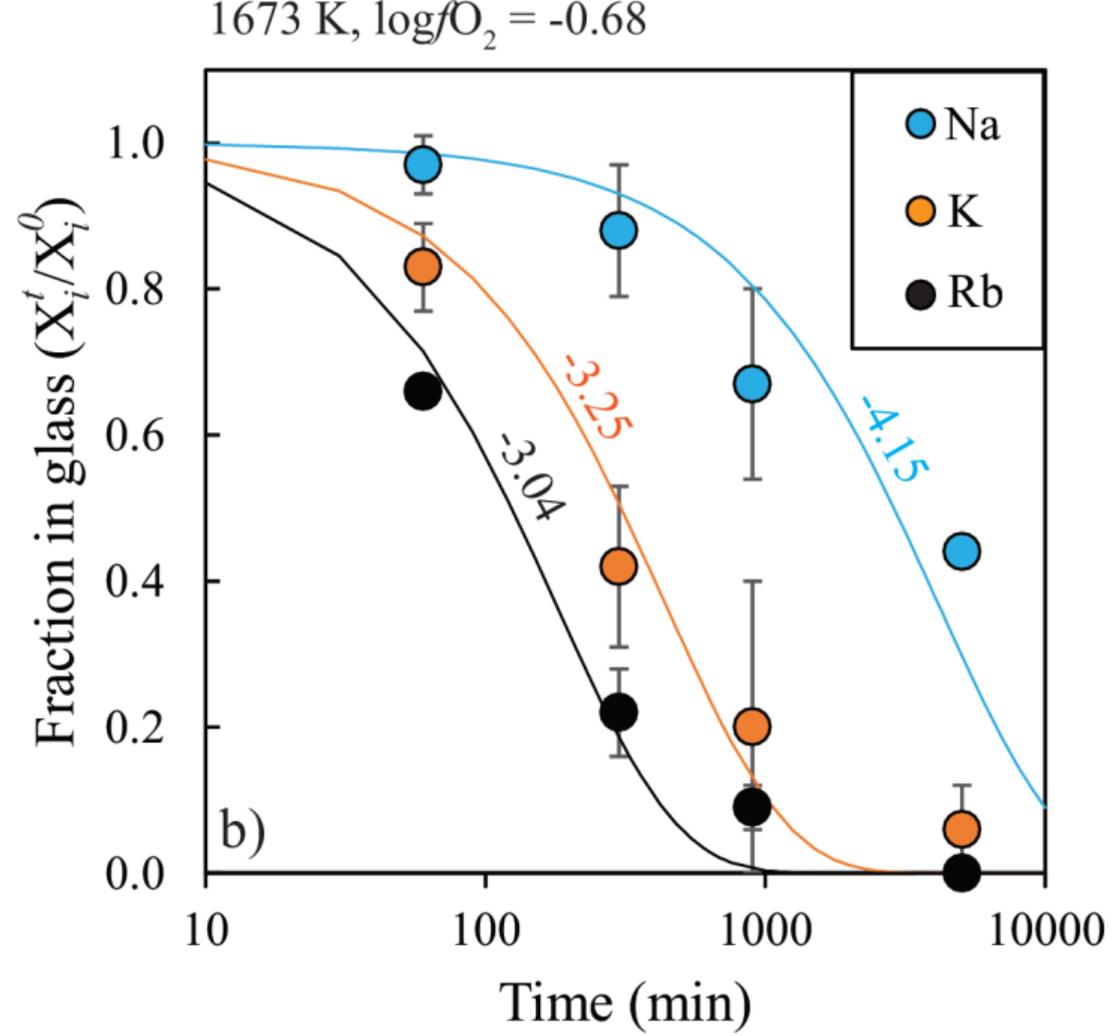
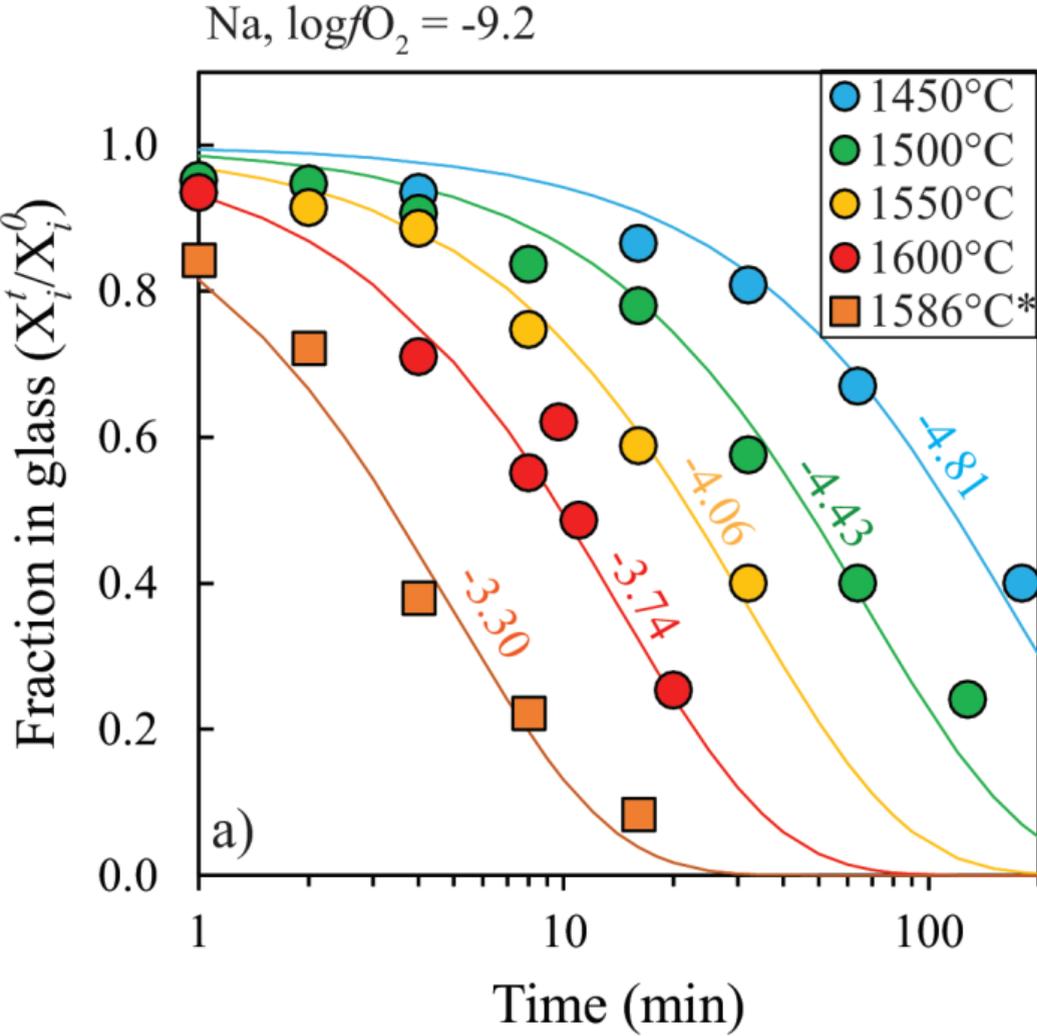


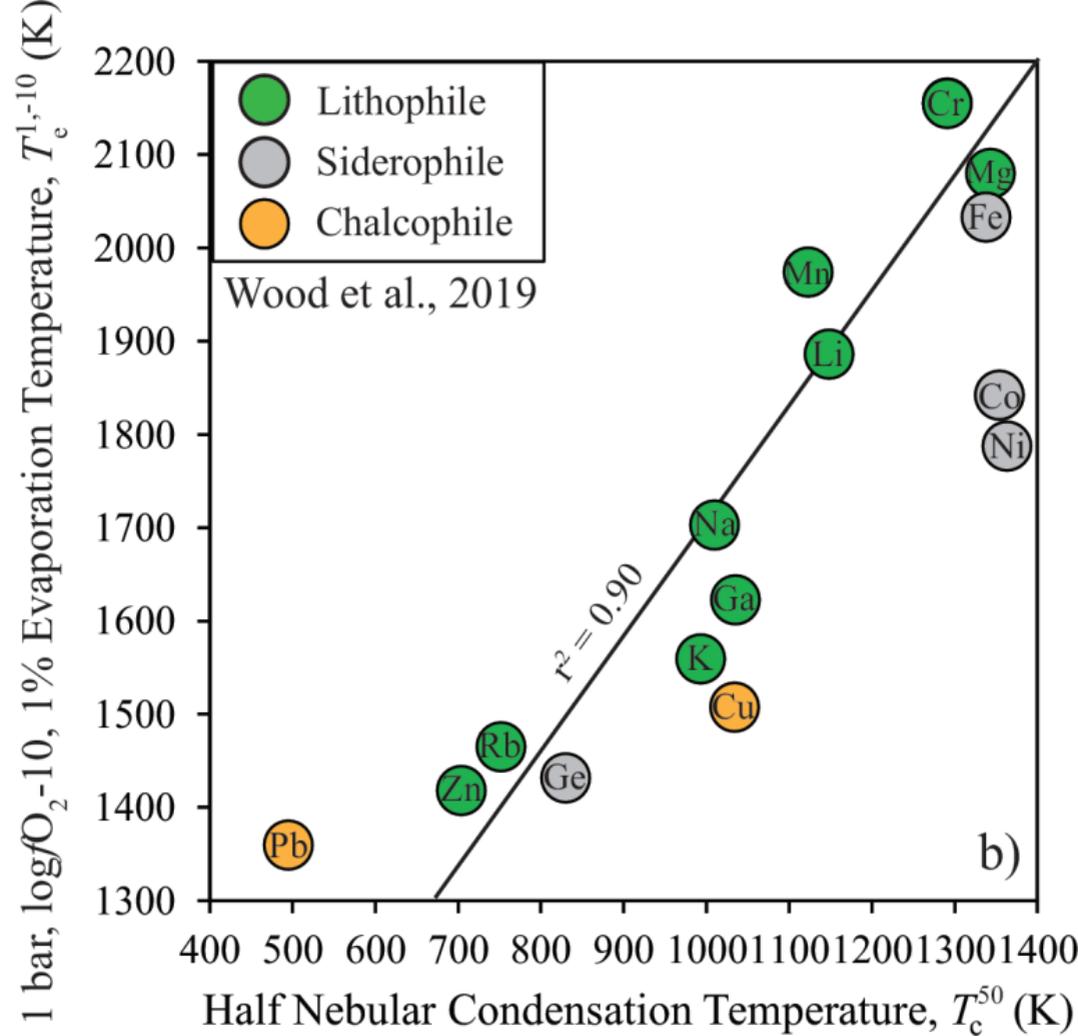
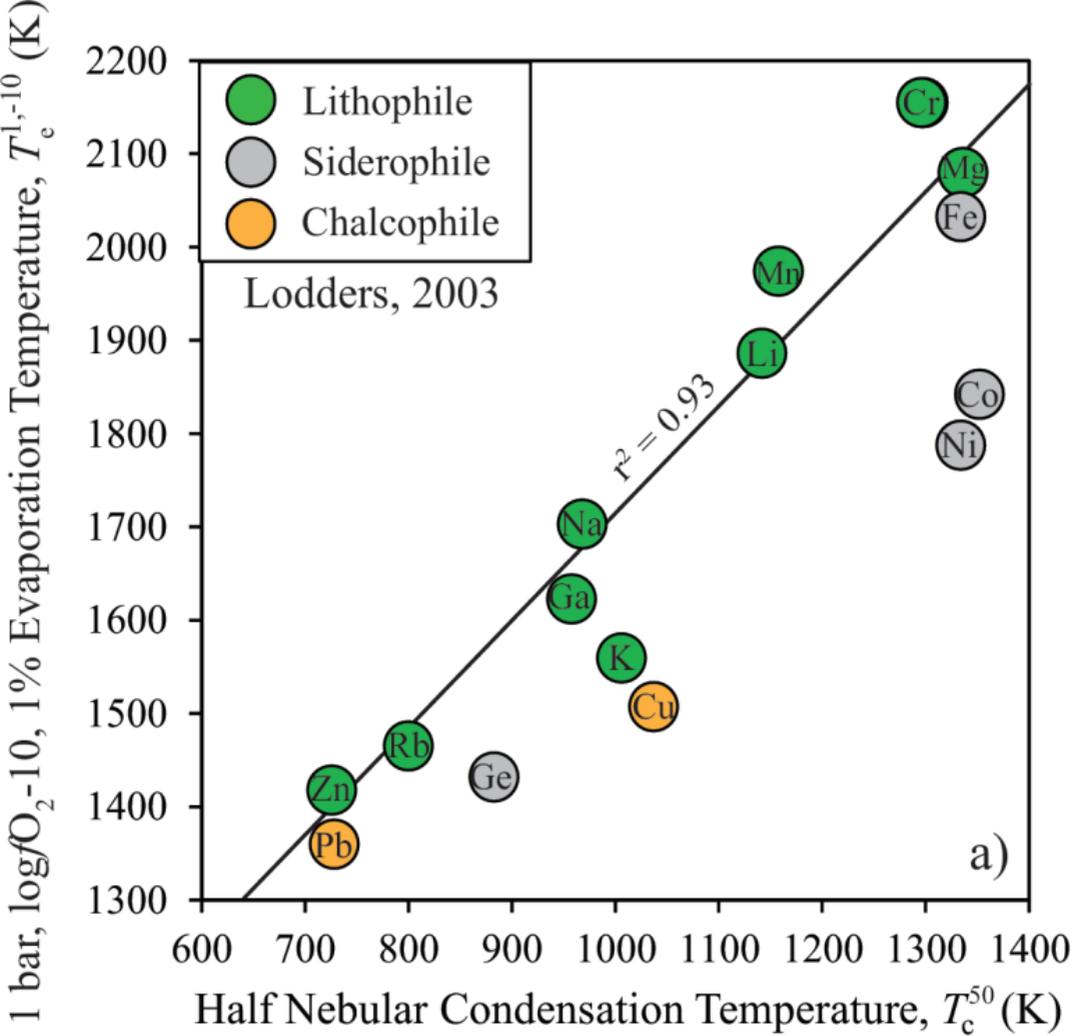
Experimental

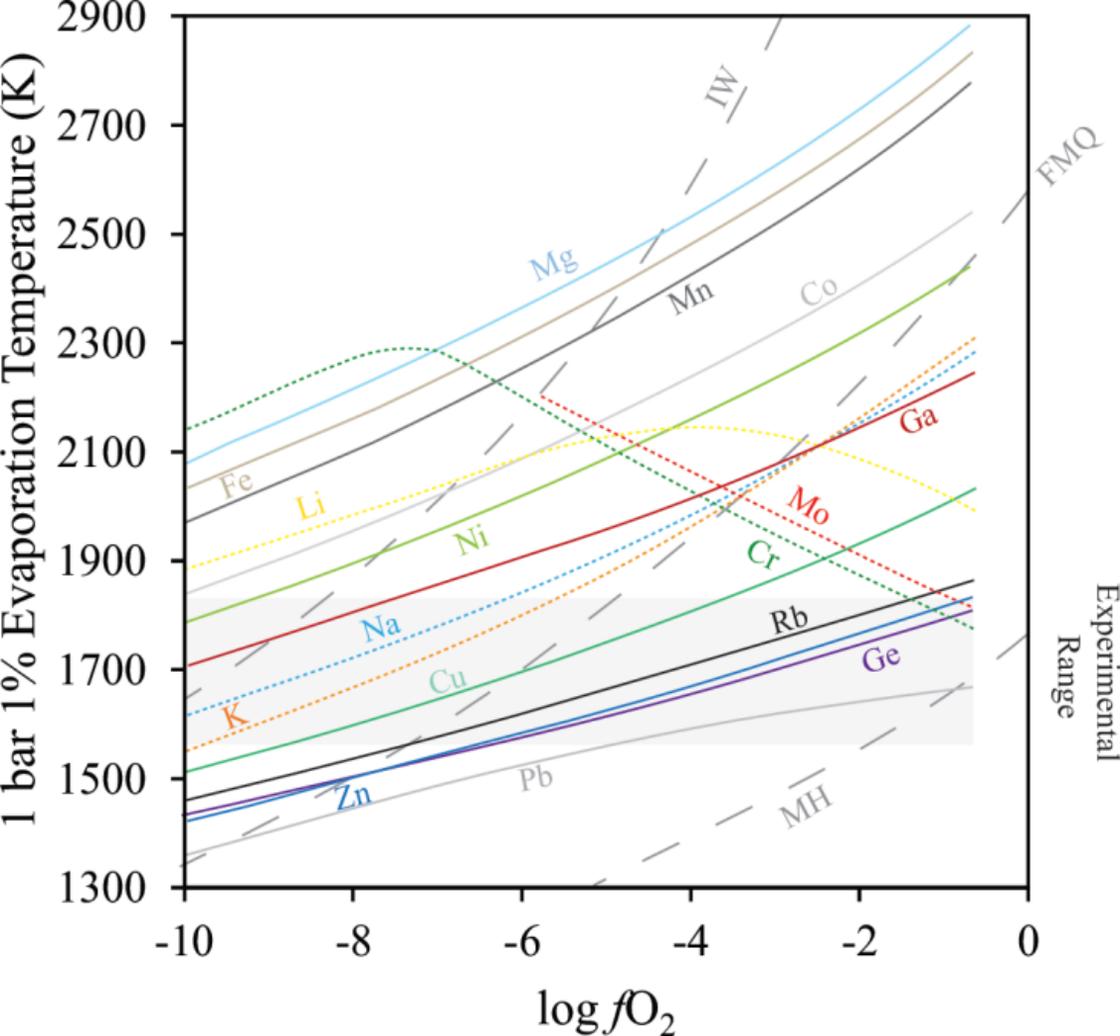


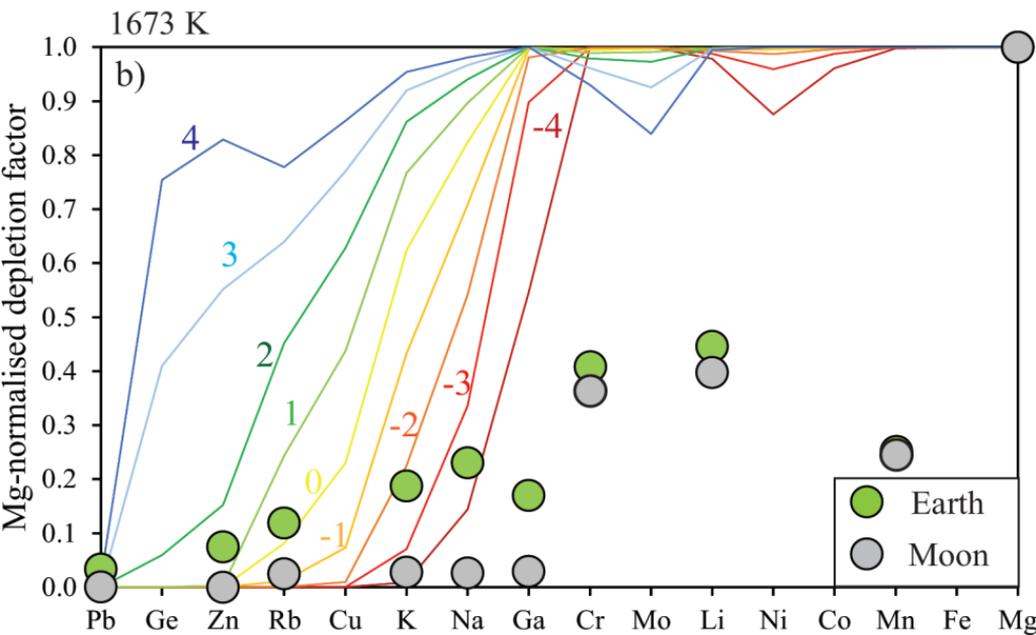
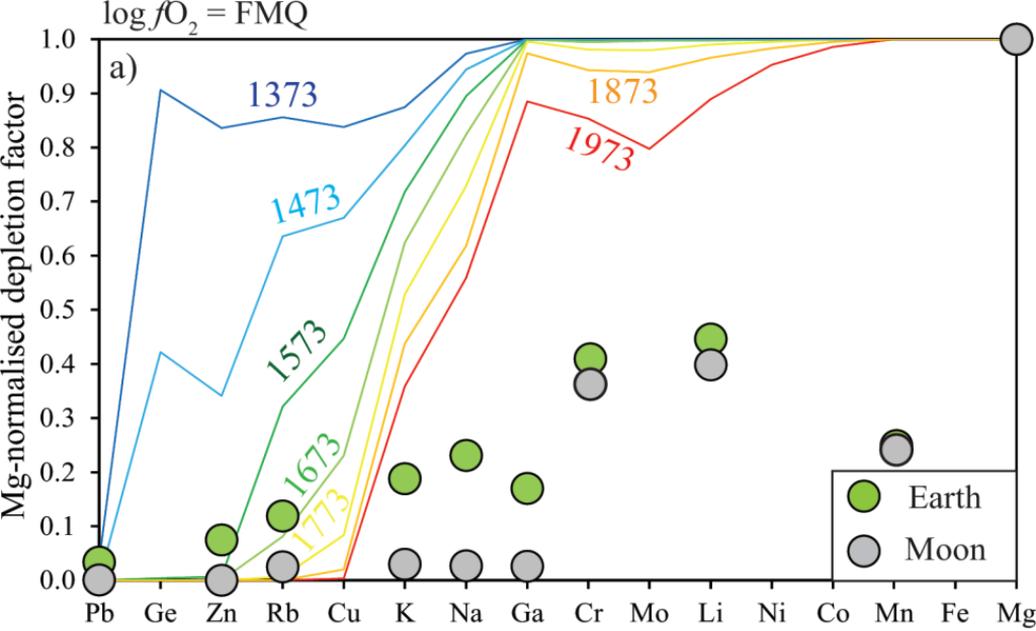
Pure System











**Table 1.** Major (in wt. %) and trace element (in ppm) composition of the starting mixture. The ‘calculated’ column refers to that expected from added weights. The ‘measured’ column refers to EPMA analyses of glasses unaffected by Fe-loss or crystallisation post-experiment (major elements) and solution ICP-MS analyses of the de-carbonated powder pre-experiment (trace elements).

	Calculated	Measured	St. Dev.
wt. %		<i>N</i> = 8	
SiO <sub>2</sub>	40.76	40.60	0.21
Al <sub>2</sub> O <sub>3</sub>	10.52	10.67	0.22
MgO	15.78	15.40	0.23
FeO	16.25	16.26	0.12
CaO	16.69	16.82	0.12
ppm		<i>N</i> = 2	
Li	1008.7	1020.0	17.8
Na	993.4	3252.3	281.3
K	1039.4	944.0	128.0
Sc	970.8	850.8	28.9
Ti	1008.0	1045.0	46.6
V	1019.7	1024.6	32.4
Cr	-	36.8	0.5
Mn	992.4	690.2	3.8
Cu	1009.5	1034.5	49.8
Zn	1015.5	1043.8	51.1
Ga	1019.3	1036.7	23.3
Ge	994.5	1007.7	44.6
Rb	1052.8	1036.1	62.4
Zr	991.9	1118.1	34.8
Mo	1029.0	1044.1	56.6
Ag	994.3	998.2	33.0
Cd	1037.0	991.1	33.2
La	1038.9	969.8	21.2
Gd	1063.3	1060.6	25.2
Yb	1036.2	1111.0	26.4
Pb	1002.7	1078.7	15.5

**Table 2.** Run conditions and LA-ICP-MS trace element data for all experiments. ‘Y’ denotes experiments analysed for 25 µm zoning profiles (‘Profile’) and trace element contents in the wire loop (‘Metal’). Experiments marked ‘\*’ denote repeat experiments.

Run#	T (°C)	t (min)	CO (sccm)	CO <sub>2</sub> (sccm)	logfO <sub>2</sub>	Loop	Profile	Metal	Li	Na	K	Sc	Ti	V	Cr	Mn	Ni	Cu	Zn	Ga	Ge	Rb	Zr	Mo	Ag	Cd	La	Gd	Yb	Pb
2M-15-07-16c	1300	15	-	-	-0.68	Pt	Y		1429.4	6501.2	1245.0	1085.4	1312.4	1098.9	5.5	759.6	-	1024.7	1044.8	1093.8	1034.5	961.7	1088.1	999.9	358.4	448.0	1113.8	1276.0	1273.7	896.2
2M-15-07-16d	1300	15	-	200	-3.44	Pt			1446.9	10376.3	1570.7	1040.7	1196.3	1141.8	10.7	747.0	51.4	971.2	996.1	1020.1	1003.8	1003.2	1184.7	957.2	194.9	84.3	973.9	1125.9	1124.8	478.7
2M-15-07-16g	1300	15	1.8	200	-5.63	Pt			1445.2	13585.8	1868.9	1100.5	1285.4	1270.7	20.1	775.6	-	774.5	845.5	1072.9	795.2	960.3	1193.6	1108.0	5.3	0.2	1055.9	1192.3	1207.0	150.3
2M-15-07-16h	1300	15	24	175	-7.99	Pt			1477.8	11402.1	1798.9	1138.9	1425.6	1412.2	32.7	805.9	40.3	435.6	29.1	1095.9	48.1	963.3	1262.9	1006.2	0.4	0.0	1124.1	1293.8	1296.7	5.1
2M-15-07-16f	1300	15	156	100	-10.10	Pt	Y	Y																						
P11-06-18a*	1300	60	-	200	-3.44	Pt			1121.1	3222.8	1162.0	1023.2	1120.8	1211.7	7.8	709.6	7.0	888.3	981.2	1005.2	876.4	792.8	1228.8	967.6	0.2	0.1	1061.3	1040.4	1073.8	275.0
1M-15-07-16a*	1300	60	-	200	-3.44	Pt			1272.2	6412.8	1358.7	1064.7	1235.9	1113.7	8.1	734.5	8.5	885.1	954.5	1069.0	866.4	782.5	1190.9	972.3	4.1	0.2	1009.0	1164.9	1175.6	244.7
1M-15-07-16b	1300	60	1.9	200	-5.67	Pt			1406.2	15818.1	2075.5	1203.7	1385.7	1403.4	22.2	800.5	112.7	401.1	264.8	1046.1	248.6	589.7	1374.1	975.0	0.3	0.2	1184.5	1358.1	1366.1	1.5
1M-PS6	1300	60	25	180	-8.00	Pt			1201.3	16757.9	2053.3	1184.2	1368.3	1343.1	34.4	782.9	58.1	95.6	10.6	1083.9	21.3	198.7	1252.8	1092.8	0.5	0.1	1087.5	1171.2	1149.3	0.3
3M-18-07-16b	1300	120	-	-	-0.68	Pt			1384.2	7547.0	1011.0	1053.5	1224.3	1015.7	2.8	593.4	24.6	1019.6	1087.6	993.4	1004.0	577.0	1193.4	263.7	0.4	0.0	1019.4	1175.1	1197.6	7.2
2M-18-07-16a	1300	120	-	200	-3.44	Pt			1314.2	8911.1	1495.8	1092.9	1255.8	1294.5	4.7	756.5	46.2	728.5	712.2	1068.0	640.8	983.9	1219.5	765.5	0.2	0.2	1068.6	1211.1	1218.7	15.4
2M-18-07-16c	1300	120	12	188	-7.33	Pt		Y	1405.9	9559.0	1500.9	1149.6	1417.5	1283.4	32.7	721.6	42.6	192.2	2.0	1186.1	4.3	899.1	1341.5	980.3	0.1	0.2	1132.0	1284.3	1284.6	0.0
1M-PS3	1400	15	-	180	-3.07	Pt			1046.6	13784.1	1687.2	1209.1	1276.6	1181.1	30.7	828.4	11.8	837.0	908.1	1055.6	782.0	977.3	1193.7	923.3	3.6	0.1	1028.8	1098.1	1101.8	52.7
1M-PS2	1400	15	5	180	-5.49	Pt			1054.4	10421.8	1504.8	1229.9	1258.3	1188.1	34.4	760.4	5.3	623.3	353.6	1032.1	272.2	961.7	1198.2	962.1	0.7	0.1	1024.4	1101.1	1091.8	10.7
1M-PS4	1400	15	66	133	-8.00	Pt		Y	1084.6	14426.0	1562.7	1240.4	1350.8	1218.0	35.2	833.9	10.5	142.1	1.4	895.7	0.8	749.0	1242.8	1000.4	0.2	0.1	1067.2	1170.6	1167.3	0.1
P09/06/18b*	1400	15	130	65	-9.23	Pt			1199.2	2013.9	732.4	1006.1	1156.0	1179.1	38.7	802.1	13.0	40.5	0.4	439.9	1.2	521.5	1092.2	1031.1	0.1	0.1	1003.8	930.5	947.3	0.0
P09/06/18a*	1400	15	130	65	-9.23	Re			1161.9	1901.2	684.2	1087.0	1180.8	1129.2	36.7	722.0	0.8	11.2	0.3	409.4	0.1	578.5	1126.5	989.7	0.1	0.0	1026.6	978.1	1006.7	0.0
1M-PS5	1400	15	167	33	-10.01	Pt		Y	1110.8	8419.1	1168.0	1177.3	1290.5	1223.5	37.4	851.2	6.9	15.6	0.3	283.2	0.4	436.3	1209.0	957.2	0.2	0.1	1020.5	1096.3	1090.7	0.0
P08-02-17b*	1400	60	-	-	-0.68	Pt			1034.8	3076.2	912.7	1112.2	1188.2	1190.2	9.1	692.7	9.1	840.3	1039.1	1031.2	729.2	677.1	1076.3	467.2	0.1	0.1	1033.8	1001.2	992.6	0.0
3M-29/2/16*	1400	60	-	-	-0.68	Pt	Y		1028.3	5703.4	921.1	1100.3	1084.4	1025.8	11.3	721.4	5.5	816.6	953.7	1028.4	800.6	708.0	1119.2	441.9	0.1	0.1	915.9	992.2	984.1	0.3
1M-2/3/16*	1400	60	-	200	-3.07	Pt			1129.1	10167.2	895.7	1279.7	1273.1	1148.6	28.1	863.9	13.5	695.1	348.0	878.0	214.0	358.6	1232.1	792.1	0.4	2.4	1074.7	1154.5	1178.0	3.4
C18/12/15*	1400	60	0	27	-3.07	Ir			1038.8	3167.7	911.7	1230.0	1346.1	1132.3	29.0	852.5	8.5	833.8	183.4	971.2	115.8	426.7	1090.0	820.8	0.1	0.2	1044.3	1121.8	1110.6	0.4
1M-PS1*	1400	60	5	180	-5.50	Pt		Y	1069.5	9048.0	1363.8	1008.1	1135.3	1194.8	35.6	784.8	5.5	300.5	6.5	930.5	1.6	57.7	1085.8	951.0	0.1	0.1	1037.6	1129.6	1113.6	0.1
P09/06/18c*	1400	60	5.5	195	-5.51	Re			1033.0	2345.0	547.1	1049.5	1135.7	1155.8	36.1	749.3	9.4	327.7	0.4	876.6	0.2	32.2	1011.0	983.2	0.1	0.1	1049.7	951.0	967.6	0.0
C17/12/15a	1400	60	13	27	-7.97	Re			1048.1	1068.8	40.2	1294.5	1418.9	1140.8	35.6	820.4	13.7	13.9	0.3	677.3	0.5	0.3	1499.7	980.2	0.1	0.1	1083.9	1199.7	1193.8	0.0
1M-1/3/16	1400	60	167	33	-10.01	Re		Y	1149.9	3924.1	5.2	1363.5	1396.8	1449.9	38.5	845.8	35.7	6.5	0.8	122.6	4.9	0.1	1132.6	947.5	0.1	0.1	1203.8	1276.6	1276.8	0.0
3M-1/3/16	1400	120	-	-	-0.68	Pt			858.8	20028.4	1102.7	1102.7	1323.2	1258.5	3.6	779.3	76.6	772.6	774.5	1041.6	577.5	368.7	1187.9	9.4	0.1	0.0	1117.6	1219.0	1247.2	0.2

C17/12/15b	1400	120	13	27	-7.97	Re			976.2	950.6	7.7	1223.9	1317.2	1129.1	36.4	754.6	23.6	10.5	0.3	564.1	0.3	0.3	1245.3	857.3	0.2	0.1	1022.5	1110.5	1111.9	0.0
1M-1/3/16b	1400	120	167	33	-10.01	Re	Y		1044.3	1576.5	196.5	1320.6	1385.9	1280.5	36.0	819.9	56.2	4.4	0.2	19.1	2.2	8.3	1896.7	670.2	0.1	0.1	1159.5	1270.7	1275.3	0.0
3M-29/2/16b	1400	930	-	-	-0.68	Pt			479.2	5993.0	541.0	1233.4	1170.0	1149.1	1.3	782.4	9.6	438.9	486.6	1086.2	96.4	113.6	1062.8	10.8	0.1	0.1	1033.7	1108.6	1132.6	0.1
C17/12/15c	1400	720	13	27	-7.97	Re	Y	Y	571.9	32.6	1.1	1308.9	1349.0	1190.2	40.9	843.3	22.7	1.6	0.2	120.1	0.3	0.1	1013.3	718.4	0.1	0.1	1105.7	1196.4	1198.2	0.3
2M-16-07-16e	1500	15	-	-	-0.68	Pt			952.5	7896.9	1199.2	1137.2	1319.0	1148.8	18.4	848.9	105.4	922.3	909.2	1058.2	872.3	955.1	1253.0	506.4	1.4	0.2	1034.3	1194.3	1220.7	0.6
2M-16-07-16a	1500	15	-	200	-2.74	Pt			1217.1	10642.4	1384.8	1130.0	1219.5	1213.4	28.7	742.5	101.2	574.0	288.5	1092.7	151.3	912.9	1185.7	683.8	0.2	0.2	1025.7	1168.3	1191.4	0.5
2M-16-07-16b	1500	15	16	184	-5.50	Pt			1319.4	4959.0	1205.5	1106.7	1238.0	1188.5	34.1	739.9	6.8	311.1	0.5	964.7	3.7	809.7	1155.6	899.5	0.1	0.1	988.5	1134.6	1158.2	0.1
2M-16-07-16c	1500	15	120	80	-7.97	Re	Y		1287.4	4577.0	957.7	1081.0	1247.0	1154.1	33.6	738.1	7.8	39.5	0.2	540.4	2.8	501.9	1155.5	999.5	0.2	0.1	967.9	1117.7	1135.9	0.1
3M-2/3/16	1500	60	-	-	-0.68	Pt			597.3	9378.6	1012.6	1227.5	1210.9	1200.3	3.8	764.0	13.2	570.6	566.3	1079.7	149.7	339.1	1136.7	23.6	0.1	0.6	1032.8	1092.1	1108.4	0.1
2M-17-07-16a	1500	60	-	200	-2.74	Pt	Y		1307.9	5028.1	984.8	1069.1	1239.6	1095.5	21.6	717.7	21.8	372.7	66.1	1096.5	3.9	157.0	1155.0	347.0	0.2	0.2	980.9	1116.5	1136.9	0.1
2M-17-07-16b	1500	60	16	184	-5.50	Pt		Y	1376.6	4711.9	727.7	1082.7	1214.1	1145.4	32.4	760.1	18.8	54.0	0.3	775.1	2.6	27.9	1163.7	609.4	0.1	0.2	991.7	1142.3	1160.1	0.0
2M-17-07-16c	1500	60	120	80	-7.97	Pt		Y	1411.2	1842.0	281.8	1103.9	1312.0	1199.8	34.9	784.9	4.2	10.8	0.2	67.4	1.9	4.8	1158.8	944.1	0.1	0.1	1016.1	1138.9	1153.4	0.1
2M-16-07-16f	1550	15	-	-	-0.68	Pt			580.9	11969.3	1808.5	1137.0	1298.5	1232.4	13.6	801.1	172.5	791.8	768.2	1091.2	696.2	967.6	1189.9	362.0	1.5	0.2	1051.4	1197.7	1212.1	19.9
2M-16-07-16g	1550	15	-	200	-2.59	Pt			621.8	7199.0	1314.1	1149.4	1368.7	1175.1	25.6	825.4	50.3	663.5	251.1	1016.4	76.1	832.3	1240.3	604.2	0.3	0.2	1052.9	1198.4	1217.0	0.5
P11-06-18b	1550	15	25	175	-5.48	Pt			1147.9	2485.5	865.2	1066.8	1123.5	1120.4	34.1	747.4	15.0	103.7	0.5	876.5	1.5	551.3	1057.7	813.9	0.2	0.1	1004.2	964.8	998.6	0.2
2M-16-07-16h	1550	15	42	158	-6.01	Pt	Y	Y	1341.0	4106.7	957.5	1106.0	1239.6	1161.5	32.9	766.4	10.5	138.5	0.4	809.8	3.2	544.6	1201.6	879.0	0.2	0.2	1002.7	1144.9	1162.8	0.0
2M-16-07-16d	1550	15	188	12	-9.56	Re			1361.8	2721.8	480.9	1079.6	1220.5	1108.4	33.1	819.6	5.1	5.7	0.2	22.8	2.3	118.8	1188.0	990.9	0.1	0.1	975.9	1117.6	1128.9	0.0
<i>Blank Runs</i>																														
P28-05-18	1400	15	-	-	-0.68	Pt			0.1	92.1	77.7	0.3	2.0	0.4	1.2	1.3	6.3	1.6	3.0	0.1	0.1	0.1	0.2	0.4	0.1	0.2	0.3	3.1	0.0	1.4
P23-05-18a	1400	60	50	100	-8.00	Re			0.2	45.7	12.1	0.4	1.3	0.3	0.1	1.1	34.5	1.0	0.2	0.4	0.1	0.1	0.2	7.3	0.0	0.0	0.2	4.1	0.0	0.0
P24-05-18a	1500	60	93	60	-8.00	Re			0.3	25.6	1.5	0.3	1.6	0.4	1.1	2.2	119.5	1.4	0.2	2.5	0.1	0.1	0.2	5.9	0.0	0.0	0.3	3.4	0.0	0.0
P24-05-18b	1500	120	93	60	-8.00	Re			0.3	15.6	0.6	0.3	1.7	0.4	1.7	2.2	101.8	0.8	0.2	1.9	0.1	0.0	0.2	10.8	0.0	0.0	0.3	3.9	0.0	0.0

**Table 3.** The  $\log K^*$  values and SD uncertainty and stoichiometries of reaction ( $n$ ) found by non-linear least-squares fit to the experimental data.

Element	Reaction	$n$	$t_0$ (min)	$\log K^*$			
				1573.15 K	1673.15 K	1773.15 K	1823.15 K
<b>Li</b> N	$\text{LiO}_{0.5}(\text{l}) = \text{Li}(\text{g}) + \frac{1}{4}\text{O}_2$	1	0		-5.36±0.05		
<b>Li</b> N	$\text{LiO}_{0.5}(\text{l}) + \frac{1}{4}\text{O}_2 = \text{LiO}(\text{g})$	-1	0		-3.39±0.07		
<b>Na</b> N	$\text{NaO}_{0.5}(\text{l}) = \text{Na}(\text{g}) + \frac{1}{4}\text{O}_2$	1	0		-4.25±0.10		
<b>K</b> N	$\text{KO}_{0.5}(\text{l}) = \text{K}(\text{g}) + \frac{1}{4}\text{O}_2$	1	0		-3.95±0.06		
<b>Rb</b> N	$\text{RbO}_{0.5}(\text{l}) = \text{Rb}(\text{g}) + \frac{1}{4}\text{O}_2$	1	14.4	-4.15	-3.12±0.10	-2.63±0.02	-2.26
<b>Cu</b> N	$\text{CuO}_{0.5}(\text{l}) = \text{Cu}(\text{g}) + \frac{1}{4}\text{O}_2$	1	0	-4.09±0.12	-3.70±0.10	-3.13±0.06	-2.90
<b>Ag</b> N	$\text{AgO}_{0.5}(\text{l}) = \text{Ag}(\text{g}) + \frac{1}{4}\text{O}_2$	1	0	-2.23			
<b>Zn</b> N	$\text{ZnO}(\text{l}) = \text{Zn}(\text{g}) + \frac{1}{2}\text{O}_2$	2	9.0	-5.06±0.09	-3.96±0.09	-2.92±0.17	-2.57
<b>Ge</b> N	$\text{GeO}_2(\text{l}) = \text{GeO}(\text{g}) + \frac{1}{2}\text{O}_2$	2	10.4	-5.04±0.13	-3.70±0.06	-2.71±0.13	-2.29
<b>Cd</b> N	$\text{CdO}(\text{l}) = \text{Cd}(\text{g}) + \frac{1}{2}\text{O}_2$	2	0	-2.48			
<b>Ga</b> N	$\text{GaO}_{1.5}(\text{l}) = \text{Ga}(\text{g}) + \frac{3}{4}\text{O}_2$	3	0		-9.92±0.32	-8.42±0.07	-7.76
<b>Ga</b> N	$\text{GaO}_{1.5}(\text{l}) = \text{GaO}(\text{g}) + \frac{1}{4}\text{O}_2$	1	0		-5.10±0.26	-4.45±0.04	-4.16
<b>Pb</b> N	$\text{PbO}(\text{l}) = \text{PbO}(\text{g})$	0	0	-2.90±0.12	-2.00		
<b>Pb</b> N	$\text{PbO}(\text{l}) = \text{Pb}(\text{g}) + \frac{1}{2}\text{O}_2$	2	0	-4.47±0.19	-3.49		
<b>Mo</b> N	$\text{MoO}_3(\text{l}) = \text{MoO}_3(\text{g})$	0	0	-4.67	-4.34±0.00	-3.64±0.01	-3.41
<b>Mo</b> N	$\text{MoO}_2(\text{l}) + \frac{1}{2}\text{O}_2 = \text{MoO}_3(\text{g})$	-2	0	-2.87	-2.86±0.00	-2.48±0.01	-2.39
<b>Cr</b> N	$\text{CrO}(\text{l}) + \frac{1}{2}\text{O}_2 = \text{CrO}_2(\text{g})$	-2	0		-2.70	-2.40±0.03	-2.29
<b>Cr</b> N	$\text{CrO}_{1.5}(\text{l}) + \frac{1}{4}\text{O}_2 = \text{CrO}_2(\text{g})$	-1	0		-4.96	-4.41±0.03	-4.20

**Table 4.** Evaporation- ( $\alpha_e$ ) and activity coefficients ( $\gamma_i$ ) of melt oxide species. Evaporation coefficients calculated with eq. 6 using activity coefficients shown in the references, activity coefficients calculated with  $\alpha_e = 1$  from eq. 6.

Species		Temperature (K)				
		1573.15	1673.15	1773.15	1823.15	1923.15
ZnO	$\gamma_i$ (this work)	0.24±0.02	0.51±0.13	0.97±0.38	1.01	
	$\gamma_i$ (literature)		0.25 <sup>a</sup>	0.43 <sup>a</sup>	0.58 <sup>a</sup>	
	$\alpha_e$		2.0	2.2	1.7	
RbO <sub>0.5</sub>	$\gamma_i$ (this work)		$1.3 \times 10^{-4} \pm 1.5 \times 10^{-5}$	$7.4 \times 10^{-5} \pm 5.9 \times 10^{-6}$	$9.0 \times 10^{-5}$	
GeO <sub>2</sub>	$\gamma_i$ (this work)	0.04±0.01	0.11±0.01	0.18±0.07	0.19	
CuO <sub>0.5</sub>	$\gamma_i$ (this work)	24.0±6.3	11.8±1.7	8.5±0.1	6.4	4.2*
	$\gamma_i$ (literature)	10±1 <sup>b</sup>				3.5 <sup>c</sup>
	$\alpha_e$	2.4±0.8				1.2
KO <sub>0.5</sub>	$\gamma_i$ (this work)		$2.2 \times 10^{-4} \pm 5.5 \times 10^{-5}$			
	$\gamma_i$ (literature)		$5 \times 10^{-5} - 7 \times 10^{-4}$ , <sup>d</sup>			
	$\alpha_e$		0.3 - 3.4			
NaO <sub>0.5</sub>	$\gamma_i$ (this work)		$1.0 \times 10^{-3} \pm 2.2 \times 10^{-4}$			
	$\gamma_i$ (literature)		$8.4 \times 10^{-4} - 2.2 \times 10^{-3}$ , <sup>e</sup>			
	$\alpha_e$		0.3 - 1.7			
PbO <sup>^</sup>	$\gamma_i$ (this work)	0.06±0.02	0.17			
	$\gamma_i$ (literature)					0.22 <sup>c</sup>
	$\alpha_e$	0.3*	0.8*			
PbO <sup>#</sup>	$\gamma_i$ (this work)	0.21±0.09	0.38			
	$\gamma_i$ (literature)					0.22 <sup>c</sup>
	$\alpha_e$	1.0*	1.7*			
LiO <sub>0.5</sub> (air)	$\gamma_i$ (this work)		1.8±0.2			
LiO <sub>0.5</sub> (-8)	$\gamma_i$ (this work)		15.4±3.1			
AgO <sub>0.5</sub>	$\gamma_i$ (this work)		0.67			
CdO	$\gamma_i$ (this work)		0.15			

a = Reyes and Gaskell, 1983; b = Holzheid et al. 2001; c = Wood and Wade, 2013; d = Hastie et al. 1982; e = Mathieu et al. 2011

<sup>^</sup> = calculated from the reaction  $\text{PbO(l)} = \text{PbO(g)}$

<sup>#</sup> = calculated from the reaction  $\text{PbO(l)} = \text{Pb(g)} + \frac{1}{2}\text{O}_2$

\* extrapolated to 1923.15 K

**Table 5.** Equilibrium thermodynamic data (entropy and enthalpy) for reactions investigated herein (experimental) in addition to those in the metal-oxygen system (pure system).

Element	Reaction	<i>n</i>	# points	Experimental				Pure System		Source
				$\Delta S^*$ (kJ/molK)	$\pm$	$\Delta H^*$ (kJ)	$\pm$	$\Delta S^\circ$ (kJ/molK)	$\Delta H^\circ$ (kJ)	
<i>Experimental</i>										
<b>Li*</b>	$\text{LiO}_{0.5}(\text{l}) = \text{Li}(\text{g}) + 1/4\text{O}_2$	1	1	0.133		413.0		0.139	413.0	1
<b>Li*</b>	$\text{LiO}_{0.5}(\text{l}) = \text{Li}(\text{g}) + 1/4\text{O}_2$	-1	1	0.130		326.3		0.107	326.3	1
<b>Na*</b>	$\text{NaO}_{0.5}(\text{l}) = \text{Na}(\text{g}) + 1/4\text{O}_2$	1	1	0.071		255.0		0.128	255.0	2
<b>K*</b>	$\text{KO}_{0.5}(\text{l}) = \text{K}(\text{g}) + 1/4\text{O}_2$	1	1	0.050		209.5		0.120	209.5	2
<b>Cr*</b>	$\text{CrO}(\text{l}) + 1/2\text{O}_2 = \text{CrO}_2(\text{g})$	-2	4	0.046	0.016	163.1	28.6	0.080	237.6	1, 6
<b>Cr*</b>	$\text{CrO}_{1.5}(\text{l}) + 1/4 \text{O}_2 = \text{CrO}_2(\text{g})$	-1	4	0.085	0.017	301.2	29.1	0.128	414.3	1
<b>Cu</b>	$\text{CuO}_{0.5}(\text{l}) = \text{Cu}(\text{g}) + 1/2\text{O}_2$	1	9	0.089	0.009	264.0	15.7	0.135	377.7	1, 4
<b>Zn</b>	$\text{ZnO}(\text{l}) = \text{Zn}(\text{g}) + 1/2 \text{O}_2$	2	10	0.253	0.011	548.6	19.6	0.177	411.7	3
<b>Ga</b>	$\text{GaO}_{1.5}(\text{l}) = \text{Ga}(\text{g}) + 3/4\text{O}_2$	3	6	0.334	0.026	885.9	45.7	0.245	760.4	3
<b>Ga</b>	$\text{GaO}_{1.5}(\text{l}) = \text{GaO}(\text{g}) + 1/4\text{O}_2$	1	6	0.117	0.015	358.9	24.6	0.199	633.7	3
<b>Ge</b>	$\text{GeO}_2(\text{l}) = \text{GeO}(\text{g}) + 1/2\text{O}_2$	2	10	0.294	0.014	612.7	23.9	0.219	453.8	3
<b>Rb</b>	$\text{RbO}_{0.5}(\text{l}) = \text{Rb}(\text{g}) + 1/4\text{O}_2$	1	6	0.123	0.024	306.4	41.6	0.255	402.4	2
<b>Mo*</b>	$\text{MoO}_3(\text{l}) = \text{MoO}_3(\text{g})$	0	6	0.118	0.016	332.4	16.4	0.120	316.3	1
<b>Mo*</b>	$\text{MoO}_2(\text{l}) + 1/2\text{O}_2 = \text{MoO}_2(\text{g})$	-2	6	0.033	0.004	143.2	7.8	0.075	151.2	1
<b>Pb</b>	$\text{PbO}(\text{l}) = \text{PbO}(\text{g})$	0	3	0.232	0.043	452.1	70.6	0.119	238.0	3
<b>Pb</b>	$\text{PbO}(\text{l}) = \text{Pb}(\text{g}) + 1/2\text{O}_2$	2	3	0.227	0.070	490.9	112.1	0.159	364.7	3
<i>Pure System<sup>#</sup></i>										
<b>Mg</b>	$\text{MgO}(\text{l}) = \text{Mg}(\text{g}) + 1/2\text{O}_2$	2						0.186	666.4	1
<b>Ni</b>	$\text{NiO}(\text{l}) = \text{Ni}(\text{g}) + 1/2\text{O}_2$	2						0.200	597.5	1,5
<b>Fe</b>	$\text{FeO}(\text{l}) = \text{Fe}(\text{g}) + 1/2\text{O}_2$	2						0.183	644.4	1
<b>Mn</b>	$\text{MnO}(\text{l}) = \text{Mn}(\text{g}) + 1/2\text{O}_2$	2						0.173	606.3	1,4
<b>Co</b>	$\text{CoO}(\text{l}) = \text{Co}(\text{g}) + 1/2\text{O}_2$	2						0.192	600.0	1,4
<b>Cr</b>	$\text{CrO}(\text{l}) = \text{Cr}(\text{g}) + 1/2\text{O}_2$	2						0.197	712.6	1,6

1 Chase 1998 ; 2 Lamoreaux and Hildenbrand, 1984 ; 3 Lamoreaux et al., 1987; 4 O'Neill and Pownceby, 1993; 5 Robie and Hemingway, 1995; 6 Toker et al., 1991

\* denotes elements for which  $\log K^*$  was measured at only 1 temperature,  $\Delta S^*$  and  $\Delta H^*$  determined by assuming  $\gamma_i$  remains constant over all temperatures.

<sup>#</sup> pure system elements were calculated assuming  $\gamma_i = 1$  at all temperatures.

<sup>o</sup> enthalpies and entropies of formation for pure system calculated from  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  from T = 1000 to 2000 K

**Table 6.** 1% Evaporation temperatures from silicate melt at 1 bar

logfO <sub>2</sub>	-10		-5		-0.68	
Element	T (K)	±	T (K)	±	T (K)	±
Pb	1360	50	1563	9	1669	6
Ge	1432	9	1612	3	1809	4
Zn	1418	10	1618	5	1843	2
Rb	1465	28	1668	5	1863	16
Cu	1507	9	1746	3	2023	22
K	1548		1867		2290	
Ga	1703	1	1959	17	2239	47
Na	1623		1914		2267	
Li	1886		2092		1976	
Cr	2155		2096	52	1785	4
Mo			2138	41	1816	3
Mg	2080		2445		2883	
Ni	1787		2086		2439	
Fe	2033		2394		2830	
Mn	1974		2339		2783	
Co	1842		2159		2538	