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# 1 **Trace element partitioning in silica-undersaturated alkaline magmatic systems**

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19 **Abstract**

20

21 Alkaline magmatism is an important chemical end-member of magmatic activity that typically  
22 occurs in response to small volume melting of asthenospheric- and/or lithospheric mantle  
23 material in intra-continental settings. Understanding trace element partitioning and phase  
24 equilibria during alkaline magmatism can therefore help provide constraints on intra-continental  
25 geodynamic settings. However, the partitioning of trace elements between alkaline melts and  
26 their dominant equilibrium mineral phases remains poorly constrained. Feldspathoids have  
27 particularly received limited attention with regards to their trace element contents, hampering our  
28 ability to interpret geochemical trends in alkaline magmatic systems. In this study, we performed  
29 a series of 1 atmosphere experiments in a gas-mixing furnace using a variety of highly alkaline  
30 ( $\text{Na}_2\text{O} + \text{K}_2\text{O} = 4.15 - 14.97 \text{ wt.}\%$ ) and silica-undersaturated ( $\text{SiO}_2 = 36.73 - 45.96 \text{ wt.}\%$ ) lava  
31 compositions from Nyiragongo, Democratic Republic of Congo, in order to investigate the  
32 partitioning behaviour of trace elements in minerals from alkaline magmas. Experimental runs  
33 were performed with oxygen fugacity buffered at both QFM (quartz-fayalite-magnetite  
34 equilibrium) and QFM+1 and cover a range of geologically-relevant temperatures (1025 – 1200  
35 °C). The quenched products of these experiments contained leucite, nepheline, melilite,  
36 clinopyroxene, olivine, and rhönite crystals, of which glass-crystal pairs were analysed for rare  
37 earth elements, large-ion lithophile elements, and high-field-strength elements. Leucite and  
38 nepheline host considerable quantities of large-ion lithophile elements but take up negligible  
39 amounts of more highly charged cations. Åkermanitic melilite readily incorporates mono- to  
40 trivalent cations with a preference for light over heavy rare earth elements, but incorporates only  
41 select divalent cations. Rhönite and clinopyroxene have analogous partitioning behaviours, with  
42 a strong preference for heavy over light rare earth elements. Fractionation modelling using the  
43 reported partitioning behaviours can reproduce the 2021 eruption products of Nyiragongo,

44 following 48% fractionation from an olivine-melilitic parental melt composition. Crystallization  
45 of trace-element poor feldspathoid amplifies pre-existing high LREE/MREE ratios of the  
46 parental magma and progressively increase trace element abundances for all but monovalent  
47 cations.

48 **Keywords:** Alkaline magmatism, Partition coefficients, Feldspathoids, Nyiragongo

## 49 **1 Introduction**

50 Modelling of elemental distributions in mineral assemblages is essential to the decryption of  
51 whole-rock compositional trends and magmatic processes as a whole (e.g., Sun and Hanson,  
52 1976; Mittlefehldt and Miller, 1983; Keppler, 1996; Taura et al., 1998; Matzen et al., 2017;  
53 Namur and Humphreys, 2018). However, such modelling requires detailed knowledge of  
54 partition coefficients, which is not always readily available, especially for silica-undersaturated  
55 systems. Here we investigate mineral-melt partitioning for the lavas of the highly alkali-rich,  
56 silica-undersaturated Nyiragongo volcano in the Democratic Republic (DR) of Congo. Samples  
57 from this magmatic system have been reported as unusually enriched in large-ion lithophile  
58 elements (LILE) and light rare earth elements (LREE), although the reason for this remains  
59 uncertain (Hertogen et al., 1985; Platz et al., 2004; Chakrabarti et al., 2009). Quantifying the  
60 behaviour of trace elements during melting and fractional crystallization is essential for  
61 explaining the origin of these enrichments, in particular for discerning between primary  
62 enrichment inherited from the source (Platz et al., 2004; Chakrabarti et al., 2009) and secondary  
63 enrichment driven by fractionation (e.g., Hertogen et al., 1985).  
64 The partitioning behaviour of trace elements between melt and minerals has been studied for  
65 decades (e.g., Jensen 1973; Hart and Dunn 1993; Blundy and Wood 2003; Dubacq and Plunder

66 2018), either through the use of glass/groundmass-mineral pairs in rapidly quenched rocks  
67 (Onuma et al., 1968, 1981; Fujimaki, 1986; Minissale et al., 2019), (Hart and Dunn, 1993;  
68 Dygert et al., 2014), or theoretical methods (Blundy and Wood, 1994; Van Westrenen et al.,  
69 2000; Dubacq and Plunder, 2018). Extensive literature is therefore available on partitioning  
70 behaviour for minerals commonly crystallizing from tholeiitic magmas such as clinopyroxene  
71 (e.g., Skulski et al., 1994; Johnson, 1998; Green et al., 2000; Hill et al., 2011; Bédard, 2014;  
72 Dygert et al., 2014; Shepherd et al., 2022), olivine (e.g., Irving, 1978; Beattie et al., 1991;  
73 Beattie, 1993; Taura et al., 1998; Bédard, 2005; Evans et al., 2008) and plagioclase (e.g., Bédard,  
74 2006; Aigner-Torres et al., 2007; Tepley et al., 2010; Sun et al., 2017; Dygert et al., 2020), but  
75 data remain limited for minerals solely formed from silica-undersaturated magmas (e.g., leucite,  
76 melilite, nepheline). Published partition coefficients between feldspathoids and melt are based  
77 mainly on phenocryst-matrix observations (Onuma et al., 1981; Ewart and Griffin, 1994; Foley  
78 and Jenner, 2004; Arzamastsev et al., 2009; Minissale et al., 2019). While such studies provide  
79 first-order insights, they are frequently influenced by crystal-melt disequilibrium, crystal zoning,  
80 incomplete quenching of the matrix and contamination of analyses by mineral or melt inclusions  
81 leading to anomalous results (Albarede and Bottinga, 1972; Lee et al., 2007). Furthermore, the  
82 few experimental studies performed with compositions crystallizing such minerals sometimes  
83 omitted alkali metals entirely in their starting compositions (Nagasawa et al., 1980; Lundstrom et  
84 al., 2006; Ustunisik et al., 2019), filtering out any potential effect of these elements on the  
85 partitioning behaviour. The frequently reported influence of crystal and melt compositions on  
86 trace element partitioning (Beckett et al., 1990; Dubacq and Plunder, 2018; Beard et al., 2019)  
87 render coefficients derived from such studies potentially unreliable for application to alkali-rich  
88 natural lavas. This hampers geochemical interpretation in active alkali-rich, silica-undersaturated

89 magmatic regions including the circum-Mediterranean region (Lustrino and Wilson, 2007), the  
90 West Antarctic rift system (Kyle et al., 1992; Martin et al., 2013), and the East African rift  
91 system (Platz et al., 2004; Klaudius and Keller, 2006).  
92 In this study, partition coefficients for a variety of minerals common to (per)alkaline magmatic  
93 systems were determined under dry conditions at a pressure of 1 bar. Studied minerals include  
94 leucite ( $\text{KAlSi}_2\text{O}_6$ ), melilite ( $((\text{Ca},\text{Na})_2(\text{Al},\text{Mg},\text{Fe})(\text{Si},\text{Al})\text{O}_7)$ ), clinopyroxene, olivine, nepheline ( $\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$ ) and rhönite ( $((\text{Ca},\text{Na})_2(\text{Mg},\text{Fe}^{2+/3+}, \text{Ti})_6(\text{Si},\text{Al},\text{Fe}^{3+})_6\text{O}_{20})$ ). The relevance of these  
95 partition coefficients was tested for the Nyiragongo volcanic system, allowing for forward  
96 modelling of the trace element evolution of alkaline lavas more generally during fractional  
97 crystallization.  
98

## 99 **2 Nyiragongo volcano**

100 Nyiragongo is an active volcano in the DR Congo, and one of the eight major volcanoes of the  
101 Virunga Volcanic Province (VVP) located in the western branch of the East African Rift system,  
102 generally characterized by the presence of a persistent lava lake in its summit crater (Tazieff,  
103 1949, 1984; Durieux, 2002; Barrière et al., 2022). Nyiragongo is among the most active  
104 volcanoes on Earth (Wright et al., 2015) and threatens the city of Goma, which was impacted by  
105 flank eruptions in 1977, 2002, and 2021, which drained the lava lake system at that time (e.g.,  
106 Pottier, 1978; Komorowski et al., 2002; Barrière et al., 2022). The lava field of Nyiragongo is  
107 also characterised by numerous parasitic cones mostly located at the foot of the main edifice or  
108 along radial fracture zones, some of which erupted explosively (Poppe et al., 2016). The  
109 Nyiragongo volcano is known for the unusual, highly alkaline ( $\text{Na}_2\text{O} + \text{K}_2\text{O} = 6.3 - 13.7 \text{ wt.}\%$ ;  
110 Platz et al. 2004) composition of its main crater lavas (e.g., Sahama 1962; Demant et al. 1994;

111 Platz et al. 2004). The high alkalinity of Nyiragongo's volcanic products is associated with  
112 silica-undersaturation ( $\text{SiO}_2 = 35.7 - 39.0$  wt.%; Barette et al. 2017; Fig. 1), generating some of  
113 the lowest viscosity lavas on Earth (Giordano et al., 2007; Morrison et al., 2020). Magmatism in  
114 the VVP started in the Late Miocene and was related to the doming stage of the development of  
115 the Kivu rift (Pouclet et al., 2016). A compositional transition of the erupted material from sodic  
116 alkaline- to potassic alkaline lavas occurred in the late Pliocene (Pouclet et al., 2016). The exact  
117 nature of the potassic source is still debated, with primary hypotheses focusing on metasomatic  
118 sources of either lithospheric or deep mantle origins (Chakrabarti et al., 2009; Furman et al.,  
119 2015). Nyiragongo itself experienced a transition from more explosive, melilite dominated  
120 magmatism to more nepheline-dominated lavas (Sahama, 1978), which are thought to have  
121 fractionated primarily at shallow levels ( $< 4$  km) (Platz et al., 2004). More olivine-rich  
122 compositions are thought to have crystallized in a magmatic reservoir at 10-14 km depth  
123 (Demant et al., 1994). The lithologies currently exposed at the main Nyiragongo crater are  
124 similar to the composition of the lava lake, and are feldspar-free, leucite-, melilite-, -nepheline-,  
125 oxide-, olivine-, and clinopyroxene-bearing foidites, with a markedly high concentration of  
126 LILE, high-field-strength elements (HFSE), and REE (Hertogen et al., 1985; Platz et al., 2004).  
127 The temperature at the surface of the lake has been measured to be approximately between  $\sim 500$   
128 (lake skin) and  $1000$  °C (Spampinato et al., 2013), whereas crater fountain temperatures are  
129 reported to approach  $1100$ °C (Sahama, 1978), which is the estimated liquidus temperature of the  
130 lava lake material (Tilley and Thompson, 1972). Conversely, the parasitic cones surrounding the  
131 volcano erupt olivine-melilite basalts (e.g., Demant et al. 1994; Platz et al. 2004; Barette et al.  
132 2017), with a maximum reported alkali content of  $\sim 7$  wt.%, and a silica content below 41 wt.%

133 (Barette et al., 2017). Olivine, spinel, clinopyroxene, and melilite are the only minerals present in  
134 these lithologies (Demant et al., 1994; Platz et al., 2004).

### 135 **3 Materials and methods**

#### 136 **3.1 Sampling strategy and starting materials**

137 Nine rock samples from the Nyiragongo volcano were used as starting materials for high-  
138 temperature experiments (Table 1; Fig. 1). Samples were collected during an expedition to the  
139 safely accessible south flank of the volcano organized in the summer of 2017. Samples for this  
140 study were selected to represent the full range of compositions from Nyiragongo. Compositions  
141 A, B, C, and N were collected from the main cone and selected for their large proportions of  
142 leucite (A), melilite (B), and nepheline (C and N). Compositions D, E, F, G, and H were  
143 collected from the parasitic cones surrounding the main edifice (Table 1; Fig. 1) and selected for  
144 being rich in clinopyroxene (D) and olivine (E, F, G, and H). Compositions A to D and N will be  
145 referred to as the low-Mg group (2.09–6.37 wt.% MgO), whereas compositions E-H will be  
146 referred to as the high-Mg group (8.61–21.63 wt.% MgO). This grouping reflects which samples  
147 were run together during each experiment, due to similarity in MgO and alkali content and, by  
148 extension, expected liquidus temperatures (Table 1). Thirty to 50 grams of each sample were  
149 finely powdered at KU Leuven, Belgium. The major element composition of the powders was  
150 measured on lithium-metaborate fused glass discs at the University of Liège using an ARL  
151 PERFORM-X 4200 XRF (Table 1). Samples were dissolved using HF at Utrecht University,  
152 Netherlands, after which trace element contents were analysed using a PerkinElmer NexION



153 2000P ICP-MS (Table 1). Additional details on the XRF and ICP-MS whole-rock analytical  
154 methods are included in Supplementary Materials 2.

### 155 **3.2 Experimental techniques**

156 Experiments were performed at one atmosphere in a GERO HTRV 70-250/18 gas-mixing  
157 furnace at the University of Liège, Belgium. Natural rock samples were ground to below 1  $\mu\text{m}$   
158 grain size using a Pulverisette planetary micro mill. Powders were subsequently homogenized in  
159 a Pulverisette 2 mortar grinder. Experimental runs were performed with oxygen fugacity ( $f\text{O}_2$ )  
160 buffered at either QFM (quartz-fayalite-magnetite) or QFM+1. We used 0.2 mm diameter  
161 platinum loops annealed with 10-12 wt.% Fe for QFM or 7-9 wt.% Fe for QFM+1, added by  
162 electroplating in order to mitigate for iron-loss during experimental runs (Grove, 1981). Loops  
163 were subsequently kept at 1300°C in the furnace flushed with forming gas (95%  $\text{N}_2$ , 5%  $\text{H}_2$ ) for  
164 72 hours to facilitate iron diffusion into the platinum. All low-Mg group compositions were  
165 found to be super-liquidus at 1180°C, whereas the high-Mg group compositions were only super-  
166 liquidus above 1500°C. Powdered samples for all subsequent experiments were mounted on the  
167 loops and pre-heated in a muffle-furnace to super-liquidus temperatures (1180 °C for low-Mg,  
168 1500 °C for high-Mg group) for 2 minutes to make them homogeneous. Such a short run over  
169 the liquidus is not expected to hamper nucleation (Pupier et al., 2008). Samples were placed into  
170 the hotspot of the furnace ( $\Delta T_{\text{gradient}} < 1^\circ\text{C}$  over 5 cm) alongside a calibrated Pt<sub>90</sub>-Rh<sub>10</sub> S-type  
171 thermocouple. Oxygen fugacity in the alumina tube was controlled by a mixture of high-purity  
172 CO and CO<sub>2</sub> gas introduced at the bottom of the furnace. Accuracy was checked with a SIRO<sub>2</sub>  
173 yttria-stabilized zirconia oxygen sensor.

174 Samples were initially kept at super-liquidus conditions (same as muffle furnace) for 2 hours, a  
175 sufficient time to ensure  $fO_2$  equilibration without affecting nucleation (Pupier et al., 2008).  
176 After 2 hours, the temperature was dropped with a constant cooling rate of 2–3 °C/h (below that  
177 of the near-equilibrium cooling rate of Lofgren et al. (2006)) in order to ensure formation of  
178 large enough crystals for LA-ICP-MS analysis. Once these experiments reached the target  
179 temperature, they were left to equilibrate for 2 to 5 days depending on temperature (Table 2).  
180 Two super-liquidus quench experiments (NYA-2 and NYA-21) were also performed in order to  
181 evaluate alkali-loss during the pre-melt in the muffle furnace and the 2-hour super-liquidus stage  
182 in the gas-mixing furnace. No loss of alkalis was observed in these experiments. Losses observed  
183 in the larger set of experiments are listed in Table 2.

### 184 **3.3 Electron microprobe analysis**

185 Electron microprobe analysis (EMPA) of the experimental products was performed at Utrecht  
186 University, Netherlands, using a JEOL JXA-8530F Hyperprobe. Operating conditions were 15  
187 kV for all analyses, using a beam current of 15 nA and 8-10 nA for crystals and glasses,  
188 respectively. A beam size of 10  $\mu\text{m}$  was applied for both crystal and glass measurements in order  
189 to limit diffusion of alkali-metals. On-peak counting times of 20 seconds were employed for all  
190 elements, with off-peak (background) counting times of 10 seconds. Na and K were measured  
191 first in order to minimize the effect of alkali-loss. Primary standardization was performed using  
192 Smithsonian VG-2 (Si, Al for glasses; NMNH 111240-52) and in-house diopside (Si, Mg, Ca),  
193 corundum (Al), synthetic TiO (Ti), hematite (Fe), synthetic  $\text{KTiPO}_5$  (P, K), celestine (Sr), jadeite  
194 (Na), barite (Ba) and tephroite (Mn). Secondary standardization was performed on Smithsonian  
195 VG-2 and A-99 basaltic glasses (NMNH 111240-52 and NMNH 113498-1, respectively),

196 Kakanui augite (NMNH 122142), San Carlos olivine (NMNH 111312-44), ilmenite (NMNH  
197 96189), and microcline (NMNH 143966). Relative errors on major element concentrations  
198 (based on secondary standards) were generally <5% for concentrations above 0.1 wt.%.  
199 Specifically, relative errors for minerals and glasses were up to 1.1% and 0.2% for SiO<sub>2</sub>, 3.0%  
200 and 0.5% for Al<sub>2</sub>O<sub>3</sub>, 7.0% and 0.9% for MgO, 10.4% and 2.8% for TiO<sub>2</sub>, 3.6% and 1.1% for  
201 FeO, 1.5% and 0.1% for CaO, 7.7% and 3.5% for Na<sub>2</sub>O, 0.4% and 3.5% for K<sub>2</sub>O, and 6.1% and  
202 4.2% for MnO at these concentrations. P<sub>2</sub>O<sub>5</sub> was only measured in glasses with a substantially  
203 higher error of 30%, attributed to their low concentrations (<0.38 wt.%).

#### 204 **3.4 Laser-ablation mass spectrometry**

205 LA-ICP-MS analyses of experiments up to NYA-15 were performed at the ALIPP6 facility  
206 (Institut des Sciences de la Terre de Paris; Sorbonne Université, France) using an Analyte G2  
207 UV excimer laser ablation system (wavelength of 193 nm) in parallel with an Agilent 8800 ICP-  
208 MS/MS. Data were acquired with 30 s of ablation, preceded and followed by gas background  
209 measurements. We used a pulse repetition rate of 8 Hz at an energy density of 2.48 J cm<sup>-2</sup>. A  
210 beam diameter of 85 μm was applied for standards, melts and large crystals; for small crystals  
211 (primarily rhönite) the beam diameter was reduced down to a minimum of 25 μm. External  
212 standardization was performed using glass reference material NIST SRM 612, and performance  
213 evaluations were carried out using measurements of standards BIR-1G, BHVO-2G, ATHO-G,  
214 and BCR-2G. Mean relative errors of analysis were estimated to be <10% for concentrations of  
215 >1 ppm, and <20% for concentrations of <1 ppm. Analyses of experiments NYA-16 to NYA-22  
216 were performed at Utrecht University, Netherlands using a ThermoFisher Scientific Element 2  
217 magnetic sector ICP-MS connected to a Geolas 193 nm excimer laser, with a pulse repetition rate

218 of 8 Hz, energy density of 2.7 J cm<sup>-2</sup>, and a beam diameter of 60 μm. External standardization  
 219 was performed using BCR-2G, and an identical set to of standards to those used at ALIPP6 was  
 220 used for performance evaluation (barring BCR-2G), resulting in relative errors of <15% for  
 221 transition and post-transition metals (Zn and Pb, primarily), and <10% for other elements. Laser  
 222 spots were placed at the rims of crystals when crystal size allowed for it, in all other cases the  
 223 core was partially ablated. All resulting data were filtered to remove the potential influence of  
 224 inclusions which were easily spotted by the presence of concentration peaks for some elements  
 225 in measurement spectra.

### 226 3.5 Fitting approach

227 Blundy and Wood (1994) have described the relationship between the partition coefficient ( $D_i$ )  
 228 of a cation with valence  $n$  in a given crystallographic site M with radius  $r_{0(M)}^{n+}$  (in meters\*10<sup>-10</sup>)  
 229 and elastic modulus  $E_{(M)}^{n+}$  (in Pascals\*10<sup>9</sup>; GPa) can be described by the lattice strain model (see  
 230 also Blundy and Wood, 1994; Blundy and Wood, 2003; Wood and Blundy, 2014), following the  
 231 equation:

$$232 \quad D_i = D_{0(M)}^{n+} * \exp \left\{ \frac{-4\pi N_A E_{(M)}^{n+} \left[ \frac{1}{2} r_{0(M)}^{n+} (r_i - r_{0(M)}^{n+})^2 + \frac{1}{3} (r_i - r_{0(M)}^{n+})^3 \right]}{RT} \right\}$$

233 where  $N_A$  is Avogadro's Number, and  $D_{0(M)}^{n+}$  is the strain-compensated partition coefficient of a  
 234 cation of valence  $n$  and radius  $r_{0(M)}^{n+}$ . This equation has been used to approximate the parameters  
 235  $r_{0(M)}^{n+}$ ,  $E_{(M)}^{n+}$ , and  $D_{0(M)}^{n+}$  through a best-fit approach using measured Nernst partition coefficients,  
 236 essentially constructing best-fit Onuma diagrams (Onuma et al., 1968) for cations of a given  
 237 valence in their crystallographic site (e.g., Dalou et al. 2018). However the lattice strain model

238 has been criticized for its erroneous description of the physics behind trace element incorporation  
239 into crystals and for mistakes in the derivation of the governing equation (Karato, 2016; Dubacq  
240 and Plunder, 2018). In particular, elastic parameters retrieved from fitting partition coefficients  
241 with the equations of (Blundy and Wood, 1994, 2003) have little physical meaning.  
242 Nevertheless, the lattice strain model was used in this study for its practical applications and due  
243 to the complexity of currently available alternatives limited to description of partitioning  
244 between melts or between crystals (e.g., Wagner et al., 2017; Figowy et al., 2020). The fitting  
245 procedure was based on a Monte-Carlo approach using 1 million randomly generated parameters  
246 within a given range (0.1 to 50 for  $D_{0(M)}^{n+}$ , 0 to 2500 GPa for  $E_{(M)}^{n+}$ ). Lattice sites for specific  
247 elements were determined based on evaluation of D-value trends with cation size in relation to  
248 the nearest known major element cation sites. Effective ionic radii were derived from Shannon  
249 (1976) and Jia (1991) and the  $r_{0(M)}^{n+}$  range was set per valence and site, limited by the largest and  
250 smallest cations in consideration. Because both sites in leucite only have data on one side of their  
251 strain parabola,  $r_0$  of this mineral was set to a fixed 1.9 Å for the W-site, and 0.39 Å for the T-  
252 site, corresponding to the ideal size of the W-site (Fabbrizio et al., 2008) and size of tetrahedrally  
253 coordinated  $Al^{3+}$ , respectively. For each simulation, the quality of the fit was estimated using a  
254 chi-squared ( $\chi^2$ ) test, after which the best fit was stored. This procedure was repeated 100 times  
255 using D values falling within the  $1\sigma$  range for each element. The mean parameter values among  
256 the 100 best fit simulations were reported with an error defined as the  $1\sigma$  value of the remaining  
257 best ranked simulations for each parameter.

258 In order to compare experimental results with natural glass-crystal pairs, we also applied our  
259 model to literature data. When no temperature was reported, a temperature of 1000 °C was  
260 applied, in accordance with the approximate Nyiragongo lava lake temperature (Sahama, 1978).

## 261 **4 Results**

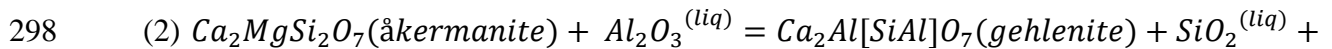
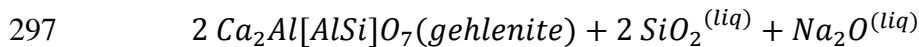
### 262 **4.1 Crystallinity and equilibrium of run products**

263 Fifty-five run products were characterised for major elements and were used to constrain phase  
264 equilibria. Out of those, only thirty-six were characterized for trace element partitioning. This is  
265 because: (1) eight products were not measured because they were run at super-liquidus  
266 conditions (Table 2; Figs 3; 4); (2) five experimental products showed insufficient crystal size  
267 for laser ablation analysis, and four experimental products showed textural evidence for  
268 disequilibrium (e.g., unavoidable significant core-rim zoning, evidence for multi-stage growth,  
269 dendritic crystal forms), or abundance of inclusions in crystals (Table 2). Produced glasses were  
270 clear and homogeneous, with pools of sufficient size for laser ablation analysis. For most  
271 experiments, crystals were distributed homogeneously. However, clustering was observed at  
272 sample edges and around the Pt wire. Mass-balance calculations indicate minimal Fe-loss (< 0.5  
273 wt.%) to the Pt wire. No significant correlation between equilibration temperatures and alkali-  
274 loss was observed within the low-Mg group, but a 5–10 % difference was frequently observed  
275 between the calculated- (based on mass-balance) and initial alkali contents, as measured in the  
276 glasses of super-liquidus runs (Table 2). Experimental products varied in crystallinity between  
277 2% and 80%, increasing steadily with decreasing equilibration temperature and the MgO content  
278 of the residual melt (Table 1; Fig. 3; 4).

### 279 **4.2 Zoning features**

280 Among the experimental run products, clinopyroxene and melilite show signs of zoning in the  
 281 form of core-rim- and sector-zoning, respectively. Clinopyroxene core-rim zoning formed < 10  
 282  $\mu\text{m}$  rims that showed a consistent trend from a Mg-rich core to Fe-rich rims (Fig. 2f). This  
 283 transition was accompanied by a slight decrease in  $\text{Al}^{3+}$  which replaces  $\text{Si}^{4+}$ , interpreted as a  
 284 result of the continuous evolution of the melt during slow crystallization. Such features are not  
 285 uncommon in experimentally derived clinopyroxene (e.g., Dygert et al., 2014; Beard et al.,  
 286 2019). Because the rims were too small for pure LA-ICP-MS measurement, we will refrain from  
 287 further discussing divalent cation partitioning for clinopyroxene. Whereas trivalent and  
 288 tetravalent cations were also moderately affected by these features, their concentrations varied  
 289 within uncertainty limits of the LA-ICP-MS (when measured with a 20  $\mu\text{m}$  spot), and will  
 290 therefore be considered as equilibrated.

291 Melilite sector zoning was a consistent feature in our experimental products, similar to  
 292 previously published literature (e.g., Lundstrom et al., 2006). Zoned crystals are divided into Al-  
 293 rich and Al-poor domains (Fig. 2e). The Al-rich domains are poor in  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{Si}^{4+}$ ,  
 294 indicating that this  $\text{Al}^{3+}$  is introduced in both tetrahedral sites replacing  $\text{Si}^{4+}$  as well as  $\text{Mg}^{2+}$ ,  
 295 presumably through the following substitution mechanisms:



300 Such features have been previously reported in clinopyroxene, wherein the faster growing  
 301 sections are less efficient in rejecting incompatible elements (Lofgren et al., 2006; Welsch et al.,  
 302 2016). For this reason, the Al-enriched sections are filtered out in our results. Due to a general

303 agreement of partitioning data with previously published work (see section 5.1.2), we included  
304 the low-Al zone data.

### 305 **4.3 Phase equilibria and glass compositions**

306 Run products from experiments at QFM+1 crystallized various combinations of leucite,  
307 nepheline, melilite, clinopyroxene, spinel-structured oxides, rhönite, and Ca-phosphate minerals.  
308 Run products from experiments at QFM also included olivine (Table 2). Some samples which  
309 failed to produce crystalline Ca-phosphates instead showed spherical Ca-phosphate inclusions in  
310 late-crystallizing minerals. Crystals with such inclusions were excluded from trace element  
311 analysis, but their observation can help to explain phosphorous deficiencies in mass-balance  
312 calculations.

313 The five compositions of the low-Mg group (Fig. 3) developed differently with temperature,  
314 which resulted in differences in mineral assemblages. However, an overall trend of increasing  
315 melt Na<sub>2</sub>O with differentiation was observed (Fig. 3e), coupled with decreasing FeO (Fig. 3b).  
316 Iron speciation in the glass was calculated using the approach of Putirka (2016) for use in the  
317 calculation of Fe<sup>2+</sup>-Mg exchange K<sub>D</sub> values. Experiments on the high-Mg compositions were  
318 performed at only two temperatures, limiting discussion of major element trends, especially since  
319 these runs only contained olivine and melilite as crystalline products. Detailed compositional  
320 information on a per-experiment basis is provided in Supplementary Material 2.

321

322 **Compositions A, B, C, D, and N:** Descending in temperature from 1180 °C, all low-Mg  
323 compositions started by crystallizing oxides, as evidenced by a continuous decrease in FeO and  
324 MgO (Fig. 3b). The next crystallizing phase on the liquidus varied depending on composition,



325 between leucite (Comp A, C, D), nepheline (Comp N), or melilite (Comp B). For compositions  
326 A, B, and C, these phases were observed to crystallize above 1100 °C (Figs. 3d; 3f), whereas for  
327 compositions D and N, feldspathoids started crystallizing between 1100 °C and 1075 °C (Figs.  
328 3e; 3f). Experiments on composition B at QFM conditions formed olivine in this temperature  
329 interval. Descending further from 1075 °C to 1050 °C, clinopyroxene and (minor) nepheline  
330 crystallized from all compositions, with rhönite appearing in samples of compositions A, D, and  
331 N. Leucite stopped being the dominant crystallizing phase for compositions A and C at this  
332 temperature (Fig. 3f), and clinopyroxene formation dominated composition D samples below this  
333 temperature (Fig. 3d). In the final temperature interval from 1050 °C to 1025 °C, rhönite and Ca-  
334 bearing phosphates crystallized for all remaining compositions. Although having relatively  
335 similar liquidus temperatures, composition B was over 75% crystallized at this point, whereas  
336 composition C was still 75% melt, reflecting their contrasting chemistries and therefore  
337 crystallization paths.

338

339 **Compositions E, F, G, and H:** Between the liquidus (~1250–1500 °C; Table 1) and 1200°C, the  
340 high-Mg group compositions only crystallized olivine, which generated an increase in all oxide-  
341 components other than MgO, FeO (which remained approximately stable), and the alkali oxides,  
342 the latter being related to alkali loss as opposed to crystallization (Fig. 4; Table 2). These trends  
343 were stronger for composition F, corresponding to its higher Mg# ( $[\text{Mg}/(\text{Mg} + \text{Fe}^{2+})]*100$ ) and  
344 liquidus.

345

#### 346 4.4 Major element compositions of the minerals

347 Major element compositions of crystals are summarized below. A complete overview of  
348 representative compositions per experiment is provided in Supplementary Material 1, and a more  
349 extensive discussion is listed in Supplementary Materials 2.

#### 350 4.4.1 *Leucite*

351 Leucite was homogeneous between experiments, following the empirical formula of  
352  $K_{0.92}Na_{0.08}AlSi_2O_6$ , similar to the average formula of  $K_{0.94}Na_{0.06}AlSi_2O_6$  recorded by Platz  
353 (2002). Na substitution for  $K^+$  (0.06–0.12 p.f.u.; 0.91–1.69 wt.%  $Na_2O$ ) in our compositions  
354 correlated with the  $Na^+$ -concentration in the surrounding melt. Trace amounts of  $Fe^{3+}$  (assumed  
355 trivalent based on site filling approach; < 0.03 p.f.u.; < 1.01 wt.% FeO) and  $Ca^{2+}$  (< 0.01 p.f.u.; <  
356 0.22 wt.% CaO) were also found.

#### 357 4.4.2 *Melilite*

358 Melilite compositions were primarily Mg-rich alumoåkermanite  $[(Ca, Na)_2(Al, Mg, Fe^{2+})Si_2O_7]$   
359 (Wiedenmann et al., 2009), including up to 10 mol% gehlenite ( $Ca_2Al_2SiO_7$ ), and with increasing  
360 Na with differentiation from 0.22 Na p.f.u. (2.6 wt.%  $Na_2O$ ) at 1100 °C, to 0.31 Na p.f.u. (3.6  
361 wt.%  $Na_2O$ ) at 1025 °C, with an outlier at 0.37 (4.2 wt.%  $Na_2O$ )(Fig. S2, in Supplementary  
362 Materials 2). The incorporation of  $Na^+$  can be explained by coupled exchange with  $Al^{3+}$  for  $Ca^{2+}$   
363 and  $Mg^{2+}$ , causing a trend towards Na-åkermanite ( $CaNaAlSi_2O_7$ ). All these compositions  
364 overlap with the compositional ranges reported by Platz et al. (2004) and Minissale et al. (2019)  
365 (see Figure S2).

#### 366 4.4.3 *Nepheline*

367 The compositions of nepheline used for trace element analysis (experiment 22N) followed the  
368 empirical formula  $[\square\square_{0.3}K_{0.70}]Na_{2.7}Ca_{0.29}(Mg,Mn,Sr)_{0.01}[Fe^{3+}_{0.1}Al_{3.95}Si_{3.95}]O_{16}$  based on a fixed  
369 16 oxygen basis, reflecting a partially filled A site and minor  $Fe^{3+}$  in the T-site. High Ca-

370 nepheline were also reported by Platz et al. (2004), who indicated up to 2.2 wt.% CaO.  
371 Additional nepheline measurements from other experiments ranged in K-incorporation between  
372 0.28 and 0.64, correlating negatively with the Na content of the melt.

#### 373 4.4.4 Clinopyroxene

374 Clinopyroxene crystals were depleted in SiO<sub>2</sub> (37–45 wt.%, 1.43–1.68 p.f.u.), which was  
375 compensated by <sup>IV</sup>Al<sup>3+</sup>- and Fe<sup>3+</sup>-enrichments (0.28–0.57 and 0.11–0.31 p.f.u., as calculated by  
376 the approach of Lindsley (1983)). The M1 and M2 sites are, in order of descending concentration  
377 per formula unit, filled with Ca<sup>2+</sup> (0.90–0.96), Mg<sup>2+</sup> (0.46–0.69), Fe<sup>2+/3+</sup> (0.23–0.39), Ti<sup>4+</sup> (0.06–  
378 0.20), <sup>VI</sup>Al<sup>3+</sup> (≤ 0.12), Na<sup>+</sup> (0.03–0.07), and Mn<sup>2+</sup> (≤ 0.01), corresponding to Ca-, Mg-, and Al-  
379 rich diopside. These are diopside crystals richer in the CaTiAl<sub>2</sub>O<sub>6</sub> and CaFe<sup>3+</sup>AlSiO<sub>6</sub> components  
380 than is traditionally reported in natural samples (Fig. S3a, in Supplementary Materials 2), but  
381 similar compositions have been previously reported by Gee and Sack (1988).

#### 382 4.4.5 Olivine

383 The forsterite content ( $X_{Mg}^{ol}/(X_{Fe}^{ol} + X_{Mg}^{ol})$ ) of experimentally produced olivine varied between  
384 0.77 and 0.91 (in agreement with the 0.82 to 0.89 range reported by Platz et al. (2004) for  
385 pyroxene nephelinites and alkali olivine basalts). The Fe-Mg partitioning between olivine and  
386 melt ( $K_{D}^{ol-liq} = [(X_{Fe}^{ol}X_{Mg}^{liq})/(X_{Mg}^{ol}X_{Fe2+}^{liq})]$ ) ranged from 0.21 – 0.26 and 0.25 – 0.27 for high-  
387 and low-Mg compositions, respectively.

#### 388 4.4.6 Spinel-structured Oxides

389 Oxide compositions were divided into ulvöspinel, magnetite, and (Mg,Mn)(Al,Fe<sup>3+</sup>)<sub>2</sub>O<sub>4</sub> spinel,  
390 varying primarily on the basis of melt composition but overlapping with the majority of  
391 published data on Nyiragongo volcanic rocks (Fig. S4, in Supplementary Materials 2). The main  
392 compositional variation between samples occurred between magnetite-rich crystals in

393 composition A, C, and D (27–55% Fe<sub>3</sub>O<sub>4</sub>, 17–36% Fe<sub>2</sub>TiO<sub>4</sub>, 21 – 42% Mg(Al,Fe<sup>3+</sup>)<sub>2</sub>O<sub>4</sub>) and the  
394 Mg-spinel-, and ulvospinel- rich crystals in composition B (8 – 34% Fe<sub>3</sub>O<sub>4</sub>, 22 – 46% Fe<sub>2</sub>TiO<sub>4</sub>,  
395 29 – 53% (Mg,Mn)(Al,Fe<sup>3+</sup>)<sub>2</sub>O<sub>4</sub>).

#### 396 4.4.7 Rhönite

397 Rhönite crystals were the primary Ti-rich phases produced, especially at low temperature (<  
398 1050 °C). Their composition depended on the melt composition, with the main variability in the  
399 Fe, Mg, and Ti-bearing site. A compositional range was therefore observed between Mg-rich  
400 rhönite [(Ca<sub>1.8</sub>Na<sub>0.2</sub>)(Mg<sub>3.0</sub>Fe<sup>2+</sup><sub>1.2</sub>Fe<sup>3+</sup><sub>0.8</sub>Ti<sub>1.0</sub>)(Si<sub>3.4</sub>Al<sub>2.3</sub>Fe<sup>3+</sup><sub>0.3</sub>)O<sub>20</sub>], formed in composition B, and  
401 Fe-rich rhönite [(Ca<sub>1.8</sub>Na<sub>0.2</sub>)(Mg<sub>2.0</sub>Fe<sup>2+</sup><sub>1.4</sub>Fe<sup>3+</sup><sub>1.9</sub>Ti<sub>0.7</sub>)(Si<sub>3.0</sub>Al<sub>2.7</sub>Fe<sup>3+</sup><sub>0.3</sub>)O<sub>20</sub>], of compositions A, C,  
402 D, and N.

### 403 4.5 Nernst partition coefficients

404 Crystal/melt partition coefficients are reported for 15 experimental products which produced  
405 inclusion-free crystals of sufficient size without disequilibrium features (see section 4.1) . A  
406 description of the trace element concentrations in minerals is given in Supplementary Material 2.  
407 Minerals not considered for partition coefficients (oxides, Ca-phosphates) were not analysed for  
408 trace elements, and are not discussed further.

#### 409 4.5.1 Leucite

410 Leucite readily incorporated significant amounts of the mono-valent LILE Cs<sup>+</sup> (D<sub>Cs</sub> = 14.2 –  
411 25.1) and Rb<sup>+</sup> (D<sub>Rb</sub> = 7.0 – 13.0), both of which are highly compatible, the degree of  
412 compatibility increasing with cation size (Fig. 5a). Following this trend, the partition coefficients  
413 of divalent Ba<sup>2+</sup> and Sr<sup>2+</sup> also positively correlated with cation size, ranging from incompatible  
414 Sr<sup>2+</sup> (D<sub>Sr</sub> = 0.01 – 0.05) to compatible Ba<sup>2+</sup> (D<sub>Ba</sub> = 0.78 – 2.06). In accordance with their smaller

415 radius, divalent transition metals were found to be incompatible in leucite (Fig. 5a). The  
416 compatibility of all divalent cations increases with temperature.  
417 Trivalent cations were highly incompatible in leucite, with the exception of near-compatible  $\text{Cr}^{3+}$   
418 ( $D_{\text{Cr}} = 1.02 - 2.8$ ). A trend of decreased compatibility with cation size was observed, indicating a  
419 slight preference for HREE over LREE (Fig. 5a). In an extension of the trend formed by HREE,  
420  $\text{Sc}^{3+}$  is only weakly incompatible ( $D_{\text{Sc}} = 0.07 - 0.54$ ).  
421 Tetravalent and pentavalent high field-strength elements (HFSE) are incompatible in leucite  
422 (generally  $D < 0.01$ ) (Fig. 5a). We observe some variation in these elements without a systematic  
423 relationship with temperature, especially Th and U, attributed to the extremely low  
424 concentrations in the mineral (generally  $<0.01$  ppm) closing in on the LA-ICP-MS detection  
425 limit.

#### 426 4.5.2 *Melilite*

427 Monovalent cations were found to be incompatible in melilite, increasing in compatibility from  
428  $\text{Rb}^+$  ( $D_{\text{Rb}} = 0.001 - 0.005$ ) to  $\text{Cs}^+$  ( $D_{\text{Cs}} = 0.004 - 0.07$ ). The same was true for divalent  $\text{Ba}^{2+}$  ( $D_{\text{Ba}}$   
429  $= 0.01 - 0.05$ ), which was found to be slightly more compatible than  $\text{Cs}^+$  (Fig. 5b). In contrast,  
430 divalent  $\text{Sr}^{2+}$  ( $D_{\text{Sr}} = 1.2 - 2.5$ ) and transition metals were found to be (near) compatible (Fig. 5b).  
431 Trivalent cations were almost mildly incompatible in melilite, with the exception of near-  
432 compatible  $\text{Cr}^{3+}$  ( $D_{\text{Cr}} = 0.6 - 2.3$ ). Lanthanides were found to decrease in compatibility from  
433  $\text{Eu}^{3+}$  ( $D_{\text{Eu}} = 0.22 - 0.54$ ) to  $\text{Lu}^{3+}$  ( $D_{\text{Lu}} = 0.03 - 0.08$ ) (Fig. 5b), whereas the larger REE  $\text{La}^{3+}$  ( $D_{\text{La}}$

434 = 0.18 – 0.46) to  $\text{Sm}^{3+}$  ( $D_{\text{Sm}} = 0.19 – 0.48$ ) all showed similar (moderately incompatible)  
435 partitioning behaviour, with compatibility correlating positively with the Na content of melilite.  
436 Highly charged (4+, 5+) cations were incompatible in melilite (Fig. 5b), following a moderate  
437 positive correlation with temperature.

#### 438 4.5.3 *Nepheline*

439 Nepheline was only measured by LA-ICP-MS in experimental products of composition N, due to  
440 small crystal sizes (< 50  $\mu\text{m}$  in diameter) in other compositions. Mono- and divalent trace  
441 element cations were found to all be moderately incompatible ( $1 > D > 0.03$ ) in nepheline. LILE  
442 decreased in compatibility with cation radius, and the mono-valent  $\text{Rb}^+$  ( $D_{\text{Rb}} = 0.68$ ) and  $\text{Cs}^+$   
443 ( $D_{\text{Cs}} = 0.28$ ) were more compatible than the divalent  $\text{Ba}^{2+}$  ( $D_{\text{Ba}} = 0.06$ ).  $\text{Sr}^{2+}$  ( $D_{\text{Sr}} = 0.37$ ) is  
444 located near the peak of the divalent curve, slightly above  $D_{\text{Cs}}$  but less compatible than  $\text{Rb}^+$ .  
445 Partitioning of trivalent cations in nepheline was characterized by a shallow upward slope from  
446 the highly incompatible LREE to HREE range, beyond which  $\text{Sc}^{3+}$  ( $D_{\text{Sc}} = 0.20$ ) and  $\text{Cr}^{3+}$  ( $D_{\text{Cr}} =$   
447 1.14) appeared to be only moderately incompatible.  
448 Tetra- and pentavalent cations were highly incompatible ( $D < 0.01$ ) in nepheline (Fig. 5c),  
449 reflecting the lack of a suitable site for incorporation of these cations.

#### 450 4.5.4 *Clinopyroxene*

451 Trace elements in clinopyroxene of low-Mg compositions could only be measured in  
452 composition D. The large monovalent cations  $\text{Cs}^+$  ( $D_{\text{Cs}} = 0.002 – 0.25$ ) and  $\text{Rb}^+$  ( $D_{\text{Rb}} < 0.02$ )  
453 appeared to be highly incompatible (Fig. 6a) in clinopyroxene.  
454 Partition coefficients of lanthanides increase from the largest cation  $\text{La}^{3+}$  ( $D_{\text{La}} = 0.20 – 0.44$ ) up  
455 to intermediate  $\text{Eu}^{3+}$  ( $D_{\text{Eu}} = 0.76 – 2.15$ ), beyond which partitioning decreased together with  
456 cation size following a shallow slope (Fig. 6a). Scandium was the most compatible ( $D_{\text{Sc}} = 5.38 –$

457 49.03) trivalent cation in the clinopyroxene structure, approximately one order of magnitude  
458 more compatible than the REE.

459 Among the HFSE, only  $Zr^{4+}$  ( $D_{Zr} = 1.51 - 2.91$ ),  $Hf^{4+}$  ( $D_{Hf} = 1.70 - 5.46$ ), and (at low  
460 temperatures)  $V^{4+}$  ( $D_V = 0.61 - 2.65$ ) showed compatible behaviour (Fig. 6a). Thorium ( $D_{Th} =$   
461  $0.05 - 0.20$ ),  $U^{4+}$  ( $D_U < 0.05$ ), and the pentavalent cations were found to be incompatible in  
462 clinopyroxene.

#### 463 4.5.5 Olivine

464 The scarcity of olivine crystals produced in the experiments and the abundance of inclusions in  
465 the crystals resulted in limited trace element data, with less consistent results than for other  
466 silicates.

467 Monovalent cations in olivine were measured at concentrations close to the detection limits,  
468 highlighting their incompatibility but the data is insufficient for further discussion. Divalent  
469 transition metals were observed to be compatible, increasing from  $Co^{2+}$  ( $D_{Co} = 1.64 - 5.74$ ) to  
470  $Ni^{2+}$  ( $D_{Ni} = 2.40 - 31.6$ ), and divalent LILE were highly incompatible (Fig. 6b).

471 In the range of trivalent cations,  $Cr^{3+}$  ( $D_{Cr} = 0.36 - 5.39$ ) was found to have the highest partition  
472 coefficient, and is the only one above unit values, in an upward trend in partition coefficients  
473 starting at the highly incompatible  $La^{3+}$  ( $D_{La} < 0.01$ ; Fig. 6b).

474 Partition coefficients of highly charged (4+, 5+) cations in olivine decrease with radius per  
475 valence (Fig. 6b), but remain highly incompatible ( $< 0.01$ ).

#### 476 4.5.6 Rhönite

477 Despite its common occurrence, analysis of rhönite using LA-ICP-MS has proven difficult due to  
478 its elongated habit and commonly small crystal size ( $< 50 \mu m$  width). Nevertheless, sizeable

479 crystals from experiments 10A, 19B, and 22A provided consistent trace element patterns for  
480 1050 °C (Fig. 6c) reminiscent of the structurally similar melilite and clinopyroxene.  
481 LILE were found to be incompatible in rhönite, decreasing in compatibility in the order of  $\text{Sr}^{2+}$   
482 ( $D_{\text{Sr}} = 0.10 - 0.16$ ),  $\text{Cs}^+$  ( $D_{\text{Cs}} = 0.03$ ),  $\text{Rb}^{2+}$  ( $D_{\text{Rb}} = 0.01 - 0.02$ ), and  $\text{Ba}^{2+}$  ( $D_{\text{Ba}} < 0.01$ ). Divalent  
483 transition metals were instead found to be clearly compatible in rhönite (Fig. 6c).  
484  $\text{Sc}^{3+}$  ( $D_{\text{Sc}} = 4.81 - 8.10$ ) and  $\text{Cr}^{3+}$  ( $D_{\text{Cr}} = 2.69 - 10.2$ ) showed a high compatibility similar to  
485 divalent transition metals, plotting just below  $\text{Ni}^{2+}$  ( $D_{\text{Ni}} = 9.94 - 26.1$ ). Lanthanides instead  
486 followed an increasing compatibility trend from  $\text{La}^{3+}$  ( $D_{\text{La}} = 0.04 - 0.06$ ) to  $\text{Sm}^{3+}$  ( $D_{\text{Sm}} = 0.15 -$   
487  $0.23$ ), with a plateau of partition coefficients observed for  $\text{Eu}^{3+}$  ( $D_{\text{Eu}} = 0.15 - 0.22$ ) to  $\text{Lu}^{3+}$  ( $D_{\text{Lu}}$   
488  $= 0.19 - 0.33$ ).  
489 Rhönite was found to contain abundant HFSE, with a particularly notable preference for the  
490 smaller ions  $\text{Zr}^{4+}$  ( $D_{\text{Zr}} = 0.64 - 0.74$ ),  $\text{Hf}^{4+}$  ( $D_{\text{Hf}} = 1.08 - 1.15$ ),  $\text{V}^{4+}$  ( $D_{\text{V}} = 1.43 - 1.72$ ),  $\text{Nb}^{5+}$  ( $D_{\text{Nb}}$   
491  $= 0.19 - 0.21$ ), and  $\text{Ta}^{5+}$  ( $D_{\text{Ta}} = 0.55 - 0.68$ ), for which the partition coefficients were close to  
492 unity (Fig. 6c). The larger tetravalent cations  $\text{Th}^{4+}$  ( $D_{\text{Th}} < 0.01$ ) and  $\text{U}^{4+}$  ( $D_{\text{U}} < 0.02$ ) were found  
493 to be significantly less compatible, similar to monovalent cations.

## 494 **5 Discussion**

### 495 **5.1 Lattice strain model**

496 The partitioning behaviour for elements of each valence state in each mineral/melt pair was  
497 modelled using a lattice-strain fitting approach (Blundy and Wood 1994; see section 2.5).  
498 Cations were distributed over the available crystallographic sites based on their radius and  
499 charge under the relevant  $f\text{O}_2$  conditions. Fit parameters were then determined for every unique



500 combination of experimental conditions (temperature,  $fO_2$ , composition) on a mineral-by-mineral  
501 basis, a summary of which can be found in Supplementary Material 1. Representative examples  
502 are discussed below.

### 503 5.1.1 Leucite [ $W(T)_3O_6$ ]

504 Leucite has two crystallographic sites in which substitution is viable: the distorted twelve-fold  
505 coordinated W-site occupied by  $K^+$ , and the tetrahedral site normally occupied by  $Al^{3+}$  and  $Si^{4+}$   
506 (Deer et al., 1967; Volfinger and Robert, 1980; Fabrizio et al., 2008). The large ( $> 1.3 \text{ \AA}$ )  
507 mono- and divalent cations occupy the larger W-site, whereas the more highly charged, smaller  
508 cations fall on parabolic curves consistent with partitioning into the T-site, together with  $Al^{3+}$   
509 (Fig. 7). A notable exception to the distribution of cations per valence are the divalent transition  
510 metals, as well as  $Mg^{2+}$ , which form a scattered distribution in logD-cation radius space (here  
511 displayed with 4-fold coordination). This is a consequence of the lack of an energetically  
512 favourable site for these small divalent cation site, resulting in disordered distribution over the 4-  
513 fold site (Fabrizio et al., 2008 and references therein). Highly compatible monovalent ions in  
514 the W-site define a curve which peaks just beyond  $Cs^+$  ( $r_{Cs}^{XII} = 1.88 \text{ \AA}$ ). However, the true  $r_0$   
515 value for this site cannot be fitted due to a lack of data on the far side of the curve, and it is  
516 therefore fixed to  $1.9 \text{ \AA}$ . The  $D_{0(W)}^{1+}$ -value for our experiments varies between 13.3 to 19.1, with  
517 an  $E_{0(W)}^{1+}$  parameter fitted to 31.3 to 35.6 GPa. In line with the findings of Fabrizio et al. (2008),  
518 the divalent W-site curve is shown directly under that of monovalent cations ( $D_{0(W)}^{2+} = 9.6 -$   
519  $15.4$ ), with  $r_0$  fixed to  $1.9 \text{ \AA}$  once again. Outliers were observed for QFM experiments at 1100  
520  $^{\circ}C$ , which plot significantly higher ( $D_{0(W)}^{2+} = 22.7 - 29.8$ ) on account of a lower  $D_{Ca}$  value  
521 which increases the slope of the lattice strain curve. Nevertheless, the  $E_{0(W)}^{2+}$ -value of divalent  
522 cations is uniformly limited to the range of 50.9 to 59.8 GPa. Despite REE commonly

523 substituting for  $\text{Ca}^{2+}$  (e.g., pyroxene), which is mainly found in the W-site of leucite, trivalent  
 524 cations show a pattern of T-site-incorporation (Fig. 7). As before, Onuma diagrams were fixed to  
 525 peak at  $\text{Al}^{3+}$  ( $r_{\text{Al}}^{\text{IV}} = 0.39 \text{ \AA}$ ) considered as the major host of the site. However, the consistently  
 526 incompatible behaviour of trivalent cations in leucite means that  $D_{0(\text{T})}^{3+}$  remains low (0.24 – 1.01).  
 527 This curve has a higher fitted  $E_0$  parameter ( $E_{0(\text{T})}^{3+} = 98 - 173 \text{ GPa}$ ) than the W-site, highly  
 528 influenced by  $D_{\text{Sc}}^{\text{Leucite}}$ . No Onuma curves are constructed for tetravalent cations.  
 529 The same best-fit lattice strain approach applied to previous studies (Francalanci et al., 1987;  
 530 Ewart and Griffin, 1994; Wood and Trigila, 2001; Foley and Jenner, 2004; Fabbrizio et al., 2008;  
 531 Minissale et al., 2019) reveals mostly similar results. Curves constructed from the data of  
 532 Francalanci et al. (1987) were excluded due to anomalously low  $D_{\text{Cs}}^{\text{Leucite}}$  (below  $D_{\text{Rb}}^{\text{Leucite}}$  values  
 533 hampering fitting). The other studies show monovalent partitioning curves in agreement with the  
 534 present study, except for slight variations in  $D_{0(\text{W})}^{1+}$  (Fig. 7). In particular, partition coefficients  
 535 from Minissale et al. (2019) are high ( $D_{0(\text{W})}^{1+} = 21.3 - 26.8$ ) compared to both natural and  
 536 experimental studies from other alkaline systems (Wood and Trigila, 2001; Foley and Jenner,  
 537 2004; Fabbrizio et al., 2008), which provide  $D_{0(\text{W})}^{1+}$  values between 7.1 and 13.0. This  
 538 discrepancy reflects significantly higher  $D_{\text{Rb}}$  (11.0 – 11.1) and  $D_{\text{Cs}}$  (23.0 – 24.6) values in the  
 539 former study, which may be explained through the higher  $^{\text{W}}\text{K}/^{\text{W}}\text{Na}$  ratio in their leucite crystals  
 540 leading to an, on average, larger site (a feature which cannot be evaluated here due to the lack of  
 541 high-r constraints). A similar pattern is found for divalent cations, with the  $D_{0(\text{W})}^{1+}$  values of  
 542 Wood and Trigila (2001), Foley and Jenner (2004), and Fabbrizio et al. (2008) being  
 543 significantly lower than those of Minissale et al. (2019) and our own (Fig. 7). However, this can  
 544 be explained by an elevated  $D_{\text{Ca}}$  value in the latter studies, causing curve flattening despite  
 545 comparable  $D_{\text{Ba}}$  and  $D_{\text{Sr}}$  values, and also explaining the difficulty fitting Ca reported by

546 Fabrizio et al. (2008). Despite a lack of complete sets of trivalent leucite partition coefficients,  
547 data of Fabrizio et al. (2008), Foley and Jenner (2004), and Minissale et al. (2019) agree largely  
548 with our data. Measurements of tetravalent cations in leucite are limited to one sample from  
549 Minissale et al. (2002)'s, falling within error of our results.

### 550 5.1.2 Melilite $[X_2T1(T2)_2O_7]$

551 Substitution in melilite is possible in the eight-fold coordinated X-site which hosts  $Ca^{2+}$  and  $Na^+$ ,  
552 the four-fold coordinated T1-site, which is occupied by  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ , and  $Al^{3+}$  (Smyth and  
553 Bish, 1988; Bindi et al., 2001), and the similarly coordinated T2-site which hosts  $Si^{4+}$  and/or  
554  $Al^{3+}$ . The inclusion of monovalent cations is only observed in the X-site forming a curve that  
555 peaks at radius slightly larger than  $Na^+$  ( $r_{Na}^{VIII} = 1.18 \text{ \AA}$ ,  $r_0^{1+} = 1.23 - 1.27 \text{ \AA}$ ; Fig. 8). Despite  
556  $Na^+$  being a major component in the aluminokermanite structure, partition coefficients for  
557 monovalent cations into this site are moderately low ( $D_{0(X)}^{1+} = 0.53 - 0.71$ ). The site has a  
558 moderate fitted elastic modulus ( $E_{0(X)}^{1+} = 77 - 107 \text{ GPa}$ ). Divalent cations are distributed over  
559 the X- and T1-sites depending on size; with the T1 site incorporating  $Mg^{2+}$  and the transition  
560 metals, and the X-site incorporating the larger alkaline earth metals. T1-site incorporation of  
561 transition metals ( $D_{0(T1)}^{2+} = 1.11 - 3.09$ ) peaks near Ni ( $r_{0(T1)}^{2+} = 0.53 - 0.55 \text{ \AA}$ ;  $r_{Ni}^{IV} =$   
562  $0.55 \text{ \AA}$ ), but is subject to uncertainty resulting from the lack of smaller cations. Divalent cation  
563 incorporation into the X site represents the highest lying curve for melilite ( $D_{0(X)}^{2+} = 4.07 -$   
564  $4.95$ ), peaked by  $Ca^{2+}$  ( $r_{Ca}^{VIII} = 1.12 \text{ \AA}$ ;  $r_{0(M)}^{2+} = 1.07 - 1.14 \text{ \AA}$ ), followed by decreasingly  
565 compatible  $Sr^{2+}$  and  $Ba^{2+}$ . The X-site also hosts the trivalent lanthanide group, with a peak in D  
566 values between  $Pr^{3+}$  and  $Nd^{3+}$  ( $D_{0(X)}^{3+} = 0.28 - 0.48$ ;  $r_{0(X)}^{3+} = 1.11 - 1.12 \text{ \AA}$ ). Slightly elevated  
567  $Al^{3+}$  concentrations, replacing divalent cations in the T1-sites in the Al-rich domains of zoned  
568 crystals promote the incorporation these elements through coupled substitution, but the

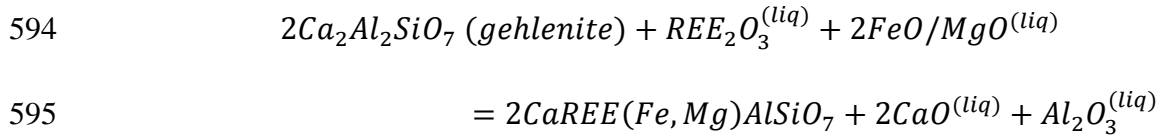
569 corresponding concentration changes are of lower magnitude than inter-crystal variability  
570 combined with errors on LA-ICP-MS measurements. Trivalent cations in the T-sites are limited  
571 to  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Sc}^{3+}$ . Tetravalent cation incorporation in melilite is scarce, with  $\text{Th}^{4+}$  and  $\text{U}^{4+}$   
572 partitioning into the X-site, and  $\text{Ti}^{4+}$ ,  $\text{Hf}^{4+}$ , and  $\text{Zr}^{4+}$  preferring the T-sites. The associated  
573 partitioning curves for the latter have a low  $D_{0(T)}^{4+}$  (0.04 – 0.09), high elastic moduli ( $E_{0(T)}^{4+} =$   
574  $1172 - 1900 \text{ GPa}$ ), and consistent  $r_{0(T)}^{4+}$  of 0.46 to 0.47 Å.

575 A variety of authors have previously studied trace element partitioning into the melilite structure,  
576 some focusing on their presence in calcium-aluminium inclusions (CAIs) in chondritic  
577 meteorites (e.g., Beckett et al. 1990; Lundstrom et al. 2006; Ustunisik et al. 2019), others  
578 carrying out measurements over natural or experimental igneous melilite (e.g Nagasawa et al.  
579 1980; Onuma et al. 1981; Kuehner et al. 1989; Arzamastsev et al. 2009; Minissale et al. 2019).

580 Application of the fitting approach to the available divalent data reveals an overall agreement  
581 with ours, especially with the data from natural samples of Minissale et al. (2019) (Fig. 8). X-site  
582 occupancy parameters for divalent cations are comparable between studies, except for  $D_{0(X)}^{2+}$ ,  
583 which is noticeably lower (1.59 – 1.92) for the gehlenite-rich experimental products of  
584 Lundstrom et al. (2006) and Ustunisik et al. (2019). This is somewhat unexpected given that  
585 gehlenite requires a fully divalent X-site, and the feature is therefore attributed to the melt  
586 composition, given that both studies are performed on CAI melts as opposed to terrestrial ones.

587 A similar pattern is observed for trivalent cation incorporation, wherein  $D_{0(X)}^{3+}$  is significantly  
588 depressed (0.04 – 0.08) in the samples of Beckett et al. (1990), Kuehner et al. (1989), and  
589 Lundstrom et al. (2006). Conversely, REE partitioning in the gehlenite-rich samples of Ustunisik  
590 et al. (2019) appears elevated ( $D_{0(X)}^{3+} = 1.26$ ), with a significantly smaller fitted elastic modulus  
591 ( $E_{0(X)}^{3+} = 81 \text{ GPa}$ ), which is better in line with current views on melilite REE-incorporation

592 (Kuehner et al., 1989). Previous work by Beckett et al. (1990) linked the individual partitioning  
593 of LREE in melilite with the  $X_{\text{geh}}/X_{\text{Ak}}$  ratio, following the reaction:



596 Which indeed explains the high  $D_{0(X)}^{3+}$  values reported by Ustunisik et al. (2019), but fails to  
597 explain the variations between åkermanite-rich compositions, since it does not take sodium into  
598 account, which may greatly affect the X-site of melilite by allowing coupled substitution with  
599 Na. Instead, we observed that a combination of  $X_{\text{Na}}$  (increasing  $E_{0(X)}^{3+}$ ),  $Al^T$  (decreasing  $E_{0(X)}^{3+}$ ),  
600 and temperature (decreasing  $D_{0(X)}^{3+}$ ) most adequately explains the differences between studies.

601 The  $E_{0(X)}^{3+}$  values reported by Minissale et al. (2019) are anomalously high for their crystal  
602 compositions, but this can be explained through large discrepancies in the heaviest HREE (Tm,  
603 Yb, and Lu; all reported at 0.1 ppm, likely close to the detection limit) which artificially flatten  
604 the strain curve.

605 Tetravalent substitution into the T-sites is consistent between our data and those of Minissale et  
606 al. (2019) in terms of site radius and high fitted elastic modulus ( $E_{0(T)}^{4+} = 1572 - 2218 \text{ GPa}$ ),  
607 but has a variable  $D_{0(T)}^{4+}$  (0.22 – 1.03) on account of frequently being controlled by at most three  
608 cations.

### 609 5.1.3 Nepheline [ $AB_3(T1-4)_8O_{16}$ ]

610 Aside from its four tetrahedral sites, nepheline comprises an eight-fold coordinated B-site  
611 primarily occupied by  $Na^+$  and a nine-fold coordinated A-site occupied by  $K^+$ , both of which  
612 may be subject to trace element substitution (Smyth and Bish, 1988; Tait et al., 2003; Antao and  
613 Nicholls, 2018). Dollase and Thomas (1978) described the A-site as only including either a

614 vacancy or charge balancing  $K^+$  (or  $Rb^+$ ,  $Cs^+$ ) ion. Since we report partition coefficients from  
 615 experiment 22N only, lattice parameters are given as single values with associated error based on  
 616 the fitting approach. As was the case for leucite, a lack of data for one side of the parabola  
 617 complicates establishing the monovalent partitioning curve for nepheline. The obtained  
 618 monovalent Onuma diagram forms a near-flat curve, with an elastic modulus ( $E_{0(A)}^{1+}$ ) of  $10 \pm 4$   
 619 GPa. The site's  $r_{0(A/B)}^{1+}$  is larger than  $Na^+$  ( $r_{Na}^{VIII} = 1.18 \text{ \AA}$ ), at  $1.21 \pm 0.01 \text{ \AA}$ . Divalent cation  
 620 incorporation is considered to occur primarily in the B-site. Lattice strain parabola indicate a  
 621 similar optimal site radius to monovalent incorporation, at  $1.23 \pm 0.01 \text{ \AA}$ . The fitted elastic  
 622 modulus for divalent cations is significantly higher, at  $88 \pm 13 \text{ GPa}$ . Whereas lanthanides may  
 623 substitute in the same site as  $Ca^{2+}$ , their distribution in the Onuma diagram suggests an  
 624 unrealistically low  $r_{0(B)}^{3+}$  when using 8-fold coordination (Fig. 9). Instead, T-site incorporation  
 625 appears likely, but the scarcity of the data prohibited constructing partitioning curves.  
 626 Monovalent data from samples of Minissale et al. (2019) plot above our curve, but at a similar  
 627 position ( $1.32 - 1.40 \text{ \AA}$ ). Divalent cation fits are instead heavily influenced by their  $\frac{D_{Ca}}{D_{Sr}}$  ratio, a  
 628 high value of which ( $> 0.8$ ) (e.g., Dawson et al. (2008); this study) indicates an ideal site radius  
 629 slightly smaller than  $r_{Sr}^{VIII}$ , whereas a low ratio ( $< 0.6$ ) such as observed for Larsen (1979) and  
 630 Minissale et al. (2019) implies a larger crystal site ( $1.26 - 1.28 \text{ \AA}$ ) despite a similar fitted elastic  
 631 modulus ( $E_{0(B)}^{2+} = 84 - 92 \text{ GPa}$ ). No concrete controlling mechanism could be inferred due to  
 632 scarcity of available studies.  
 633 Trivalent cations in nepheline have not been thoroughly reported. Larsen (1979) and Minissale et  
 634 al. (2019) provide the only available complete data-sets of REE partition coefficients, the former  
 635 of which reports phenocryst/whole-rock coefficients, and the latter phenocryst/glass partitioning.  
 636 The data of Larsen (1979) is thoroughly clustered around  $D^{3+} = 10^{-2}$  and lacks  $Sc^{3+}$ , and the data

637 of Minissale et al. (2019) provides an image similar to that of our study, but with significantly  
638 higher partition coefficients for MREE to HREE (e.g.,  $D_{Yb} = 0.14$  vs our  $6 - 7 \cdot 10^{-3}$ ). However, it  
639 is noteworthy that the nepheline REE data of Minissale et al. (2019) are scarce, and their HREE  
640 data are close to detection limits.

#### 641 5.1.4 Clinopyroxene [ $M_2M_1(T)_2O_6$ ]

642 Trace element substitution in clinopyroxene is well-documented to occur in the VI-coordinated  
643 M1 and VIII-coordinated M2 sites, (e.g., Wood and Blundy, 1997; Lundstrom et al., 1998;  
644 Neumann et al., 1999; Wood and Trigila, 2001; Hill et al., 2012; Mollo et al., 2016; Bonechi et  
645 al., 2021), the latter of which potentially incorporates the full range of REE. Monovalent cation  
646 partitioning data in this study are insufficient to construct meaningful Onuma curves, and are  
647 therefore excluded. Similarly, divalent partition coefficients are excluded for equilibrium reasons  
648 (see Section 4.2). Among trivalent cations  $Cr^{3+}$  and  $Sc^{3+}$  partition into the smaller M1 site,  
649 whereas the  $REE^{3+} + Y^{3+}$  partition into M2, for which the ideal site radius is close to that of  $Gd^{3+}$   
650 ( $r_{0(M2)}^{3+} = 1.05 - 1.06 \text{ \AA}$ ).  $Lu^{3+}$  and  $Yb^{3+}$  are observed to diverge slightly from this curve,  
651 indicating minor incorporation into the M1-site. No M1-site parabola for this valence could be  
652 constructed on account of  $Cr^{3+}$  and  $Sc^{3+}$  being the only contributing cations. Trivalent M2-site  
653 Onuma curve  $E_0$ -values decrease with temperature (287 – 331 GPa between 1025 and 1075 °C).  
654 M1-site tetravalent trace element incorporation is dictated by  $V^{4+}$ ,  $Ti^{4+}$ ,  $Hf^{4+}$ , and  $Zr^{4+}$ , which  
655 form a tight curve ( $r_{0(M1)}^{4+} = 0.65 - 0.67 \text{ \AA}$ ;  $E_{0(M1)}^{4+} = 1031 - 2060 \text{ GPa}$ ;  $D_{0(M1)}^{4+} = 4.74 -$   
656  $15.17$ ), whereas the M2-site curve is left out due to only being pinned by  $Th^{4+}$  and  $U^{4+}$ . The  
657 investigation of clinopyroxene in alkaline systems has recently received significant attention  
658 (e.g., Beard et al., 2019; Baudouin et al., 2020; Bonechi et al., 2021), allowing for more thorough  
659 comparison between studies. Nevertheless, the high degree of M1-site incorporation of HREE

660 reported by the first two of these authors was not reproduced with our samples, which lack a  
661 significant aegirine component. Meaningful M1-site trivalent strain curves can be constructed for  
662 the data of Larsen (1979), Wood and Trigila (2001), Foley and Jenner (2004), Arzamastsev et al.  
663 (2009), Ambrosio and Azzone (2018), Beard et al. (2019), Minissale et al. (2019), and Baudouin  
664 et al. (2020), among which the data of Ambrosio and Azzone (2018) are in best agreement with  
665 our data (Fig. 10). The samples of Beard et al. (2019) and Baudouin et al. (2020) display  
666 unusually high degrees of REE incorporation into the M1-site, a feature attributed to a  
667 decreasing electrostatic penalty at high aegirine contents (due to  $^{VI}\text{Fe}^{3+}$ ), coinciding with a  
668 decreasing radius of the M1-site (Beard et al., 2019; Baudouin et al., 2020). Trivalent cation  
669 occupancy into the M2-site may consequently be negatively correlated with that of the M1-site  
670 since it performs a charge-compensating role. Nevertheless, data from the experiments of Beard  
671 et al. (2019) still produce significantly elevated M2-site partitioning curves for trivalent cations  
672 (Fig. 10). The same can be said for the data of Wood and Trigila (2001). Those of the remaining  
673 natural studies more often present comparative enrichment of REE in the melt compared to the  
674 crystal. Despite being compositionally unusual, our M2-partitioning data is in line with previous  
675 observations of a link between increased D-values and tetrahedral aluminium (e.g., Hill et al.,  
676 2000; Wood and Trigila, 2001; Sun and Liang, 2012), but needs to be adjusted for silica-  
677 undersaturated cpx-components ( $\text{CaTiAl}_2\text{O}_6$  and  $\text{CaFe}^{3+}\text{AlSiO}_6$ ), since these leave no room for  
678 additional trivalent substitution. The tetravalent partitioning curves constructed from data of  
679 Arzamastsev et al. (2009), Ambrosio and Azzone (2018), and Baudouin et al. (2020) are  
680 comparable to ours, despite our high  $\text{Ca}_2\text{Al}_2\text{SiO}_6$  component which would be expected to  
681 increase the  $D_{\text{HFSE}}$  (Mollo et al., 2016; Ma and Shaw, 2021).



682 5.1.5 Olivine [(M1,M2)<sub>2</sub>TO<sub>4</sub>]

683 The structure of olivine is composed of a single tetrahedral site occupied by Si<sup>4+</sup>, and two  
684 independent six-fold coordinated octahedral sites M1 and M2, of which the latter is slightly  
685 larger (Della Giusta et al., 1990; Zanetti et al., 2004). Larger cations (Ca<sup>2+</sup>, Mn<sup>2+</sup>) tend to  
686 preferentially occupy the M2 site, whereas smaller cations such as transition metals (Ni<sup>2+</sup>, Co<sup>2+</sup>,  
687 Zn<sup>2+</sup>) are more commonly observed to prefer the M1 site. Nevertheless, the similarity in site  
688 radius between M1 and M2 allows for interpretation as if these were a single M-site (Zanetti et  
689 al., 2004). Divalent partitioning curves suffer from a lack of constraints at low ionic radii and  
690 strong dependence on major elements (Fig. 11), on account of which lattice strain parabolas were  
691 not built for this valence. Trivalent cations were typically below detection limits in our olivine  
692 crystals, but when measured display a parabolic pattern peaking at radii smaller than Sc<sup>3+</sup> (0.59 –  
693 0.61 Å;  $r_{Sc}^{VI} = 0.745$  Å). On account of Al being distributed among tetrahedral and octahedral  
694 sites, the trivalent curve is ill-constrained at low radii, leading to a low fitted elastic modulus  
695 ( $E_{0(M)}^{3+} = 167 - 172$  GPa). However, the expected peak of said curve is in general agreement with  
696 the work of Sun and Liang (2013). Tetravalent curves in Onuma diagrams peak at a higher radius  
697 (0.59 to 0.64 Å), with a significantly higher fitted elastic modulus ( $E_{0(M)}^{4+} = 922 - 2136$  GPa).  
698 Identical treatment of data from chemically similar systems (Larsen, 1979; Foley and Jenner,  
699 2004; Minissale et al., 2019) yields comparable patterns. Trivalent partitioning data on olivine  
700 from alkaline systems remain scarce, in part due to the low uptake of REE in the olivine crystal.  
701 Those studies which report sufficient partitioning values to construct complete strain parameters  
702 (Larsen, 1979; Foley and Jenner, 2004) peak near our lower bound estimates ( $r_{0(M)}^{3+} = 0.58 -$   
703 0.59 Å), also with a comparable  $D_{0(M)}^{3+}$  (0.19 – 0.42) in general agreement with olivine from  
704 tholeiitic systems (Zanetti et al., 2004; Evans et al., 2008; Sun and Liang, 2013; Dygert et al.,

705 2020). A complete set of tetravalent cation data was only found in the work of Minissale et al.  
706 (2019), which indicates an ideal radius of 0.64 Å, and a significantly higher value for  $D_{0(M)}^{4+}$  (0.30  
707 vs our 0.01 – 0.05).

#### 708 5.1.6 Rhönite [(X)<sub>2</sub>(Y)<sub>6</sub>(Z)<sub>6</sub>O<sub>20</sub>]

709 The structure of rhönite is identical to that of aenigmatite, hosting nine M-sites and five T-sites,  
710 and is approximated as (X)<sub>2</sub>(Y)<sub>6</sub>(Z)<sub>6</sub>O<sub>20</sub>, in which X, Y, and Z represent the eight-fold, six-fold,  
711 and four-fold coordinated sites, respectively (Kunzmann, 1989, 1999; Bonaccorsi et al., 1990).

712 Substitution is considered to primarily occur in the X- and Y-sites, and for the Z-site to primarily  
713 include Si<sup>4+</sup> and Ti<sup>4+</sup>. Monovalent cation incorporation in rhönite is negligible, as reflected by  
714 our measurements. Divalent cations are distributed over two sites based on size, with alkaline  
715 earth metals and Mn<sup>2+</sup> partitioning into the larger X-site ( $r_{0(X)}^{2+} = 1.03 - 1.08$  Å), and transition  
716 metals partitioning into the smaller Y-site ( $r_{0(Y)}^{2+} = 0.69 - 0.70$ ). Trivalent cations primarily  
717 substitute into the X-site, with the exception of Cr<sup>3+</sup>, Sc<sup>3+</sup>, and the heaviest lanthanides (Tm<sup>3+</sup>,  
718 Yb<sup>3+</sup>, Lu<sup>3+</sup>) which are observed to transition into the Y-site (Fig. 12). The resulting Y-site curves  
719 indicate a site radius close to that of Sc<sup>3+</sup> (0.67 – 0.72 Å;  $r_{Sc}^{VI} = 0.745$  Å), and a high fitted elastic  
720 modulus ( $E_{0(Y)}^{3+} = 559 - 797$  GPa). The trivalent X-site fit has a radius of approximately 1.04  
721 Å, combined with a significantly lower elastic response of 226 to 309 GPa. As with divalent  
722 cations, the Y-site trivalent curve peaks at a significantly higher value ( $D_{0(Y)}^{3+} = 8.56 - 12.72$ ) than  
723 the X-site ( $D_{0(X)}^{3+} = 0.16 - 0.22$ ). Tetrahedral partition coefficient curves adequately agree with the  
724 divalent varieties, with an ideal radius of 0.63 to 0.64 Å for the Y-site, a relatively high value of  
725  $D_{0(Y)}^{4+}$  (3.58 – 5.38) and a high fitted elastic modulus ( $E_{0(Y)}^{4+} = 926 - 1523$  GPa). The X-site  
726 likely hosts Th<sup>4+</sup> and U<sup>4+</sup>, but a strain parabola could not be robustly constructed. Rhönite

727 partitioning has been discussed briefly for experiments by Lofgren et al. (2006), and more  
728 thoroughly for natural samples by Kogarko et al. (2005). The most notable difference between  
729 these studies is found with regards to lanthanides, for which Lofgren et al. (2006) reports  
730 significantly more incompatible behaviour ( $D_{0(X)}^{3+} = 0.05$ ) compared to the  $D_{0(X)}^{3+}$  of 0.58 for the  
731 samples of Kogarko et al. (2005) (Fig. 12). An additional distinction is that whereas the samples  
732 of Lofgren et al. (2006) display HREE partitioning into the Y-site similar to our experimental  
733 products, all HREE in the natural samples of Kogarko et al. (2005) are incorporated into the X-  
734 site. This feature is explained through a lack of  $Fe^{3+}$  in the compositions of the latter study,  
735 causing the electrostatic penalty of introducing REE to be higher, similar to what is observed for  
736 clinopyroxene (Beard et al., 2019; Baudouin et al., 2020). Divalent partitioning into the X-site is  
737 determined by few elements ( $Sr^{2+}$  and  $Ba^{2+}$ ), which results in both studies being within error of  
738 each other. Nevertheless, the data of Kogarko et al. (2005) is also elevated for this valence, and  
739 thus our data corresponds better with that of Lofgren et al. (2006). Tetravalent cation  
740 incorporation is also elevated in these studies, with  $D_{Ti}$  stretching between 6.25 (Kogarko et al.,  
741 2005) and 10.68 (Lofgren et al., 2006), in contrast to our reported range of 3.42 to 5.22.  
742 Insufficient data exists to properly discuss trends for this phase.

## 743 **5.2 Recommended partition coefficients**

744 For use in highly silica-undersaturated, feldspathoid bearing systems we recommend a selection  
745 of partition coefficients listed in Table 3. These partition coefficients are the mean values  
746 reported for each phase at their approximate liquidus temperature in silica-undersaturated ( $\sim SiO_2$   
747  $< 42$  wt.%), alkali-rich ( $\sim Na_2O + K_2O > 6$  wt.%) systems. Though they may well be applicable  
748 to more primitive systems as well as to silica-saturated systems, these coefficients should

749 perform best for compositions and conditions similar to those studied here. We believe that for  
750 the case of silica-undersaturated, alkali-rich, terrestrial volcanic systems, our values take  
751 precedent over those previously reported on account of (a) being derived under controlled  
752 conditions instead of from natural samples, (b) our run products having a clear compositional  
753 overlap with those of natural lavas, and (c) our use of natural starting compositions which are  
754 both silica-undersaturated and alkali-rich, instead of one or the other. We also supply a more  
755 complete range of D-values for a number of phases (3+ in leucite, nepheline), which had so far  
756 been left unreported. Caution is advised when applying partition coefficients for elements of  
757 particularly low abundance in our starting compositions (e.g., transition metals in low-Mg  
758 compositions) to systems more enriched in such elements. Such elements are more subject to  
759 detection limits and rounding errors, and may behave differently at higher abundance. Similarly,  
760 partition coefficients in hydrous systems may vary substantially from those observed in  
761 anhydrous experiments. For more detailed trace element modelling covering a range of  
762 temperatures, we supply our complete dataset in Supplementary Materials 1.

### 763 **5.3 Geological application**

764 The experimentally derived partition coefficients were used to model the behaviour of trace  
765 elements during fractionation processes at Nyiragongo volcano. Specifically, using our newly  
766 established partition coefficients, we determined the degree of fractional crystallization  
767 necessary to reach the composition of the most recent eruptions (Minissale et al., 2022) of  
768 Nyiragongo. Nyiragongo's eruption products are dominated by olivine, clinopyroxene, melilite,  
769 nepheline, leucite, oxides, and apatite. Partition coefficients have been measured for the first five  
770 of these minerals. For oxides and apatite, partition coefficients are available from Minissale et al.

771 (2019), allowing modelling of all major phases in the system. In order to adequately model the  
772 Nyiragongo volcanic system we require a primitive, parental melt composition. Previously Platz  
773 et al. (2004) used an olivine melilite composition retrieved from the Rutoke parasitic cone from  
774 Denaeyer (1972). However, no trace element data is available for this sample, and we have  
775 therefore selected the compositionally similar sample LV1 of Minissale et al. (2022) (MgO =  
776 10.35 wt.%) was thus selected. This sample has Rb and Ba concentrations which appear  
777 anomalously low for their MgO compared to the rest of the dataset (41, **21**, and 116 ppm Rb and  
778 836, **789**, and 1862 ppm Ba corresponding to 17.51, **10.35**, and 5.65 wt.% MgO samples; LV1  
779 shown in bold). These elements were therefore linearly adjusted to lie directly between their  
780 neighbours in terms of MgO (86 ppm Rb, 1457 ppm Ba). A two-step fractionation model was  
781 applied, to account for the contrasting mineral assemblages between samples of the parasitic  
782 cones and those of the main crater complex (e.g., Demant et al., 1994; Platz et al., 2004;  
783 Minissale et al., 2022). The partition coefficients listed in section 5.3 were used, selecting values  
784 for ‘primitive’ compositions (Table 3) for the first fractionation step where possible (only  
785 olivine), and the ‘evolved’ values for the second step. Divalent cation partition coefficients for  
786 clinopyroxene and all D-values for oxides and apatite were derived from the work of (Minissale  
787 et al., 2019).

788 Trace elements were modelled using the step-wise Rayleigh fractionation equation:

789 
$$C_l = C_0 * F^{(D-1)}$$

790 wherein  $C_l$  is the concentration in the liquid after fractionation,  $C_0$  is the concentration in the  
791 parental liquid,  $F$  is the fraction of melt over crystallizing material, and  $D$  is the bulk partition  
792 coefficient of the considered element. The total crystallized fraction was recalculated after each  
793 step. Major elements were concurrently modelled using the following equation:

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$$C_l = (C_0 - 0.01 * C_f) / F$$

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wherein  $C_l$ ,  $C_0$ , and  $C_f$  are the bulk concentrations of a given oxide in the fractionated liquid, starting liquid, and fractionating crystal assemblage, respectively. For the initial fractionation step we used an adjusted fractionating assemblage based on the one used by Platz et al. (2004) consisting of 60% olivine, 15% melilite, and 25% clinopyroxene, consistent with the mineralogical diversity of the Rushayo chain (Demant et al., 1994). Calculating fractionation for this assemblage to the point of 21% crystallization results in a composition comparable to evolved pyroxene nephelinites described by (Platz et al., 2004), which marks the point at which the fractionating assemblage is changed in the model (Fig. 13). In order to constrain the second fractionation assemblage, we performed a using a least-squares fit Monte-Carlo simulation with varying mineral modes (only including locally minerals found in the natural lavas and using both major and trace element concentrations). This meant that the fractionation model was run for 10.000 arbitrarily determined mineral modes, after each of which the mismatch of the resulting composition with the (average of the) Minissale et al. (2019) glass compositions (in % of both major and trace elements) was calculated. Only the assemblage with the smallest mismatch was kept and is reported below. The 2016 glasses were chosen over the newly reported 2021 lavas (Minissale et al., 2022) in order to filter out potential influence of crystal accumulation on compositional data. Indeed, significant differences in trace element compositions reported by various authors for identical eruptive events were found (Fig. 13; 14), likely due to a combination of analytical uncertainties and variable inclusion of phenocrysts in analysed powders. Therefore, the glasses of Minissale et al. (2019) which were analysed by point- instead of bulk-analysis were deemed most trustworthy.

816 The best results were obtained using an assemblage of 20% clinopyroxene, 27% melilite, 19%  
817 nepheline, < 1% leucite, 2% olivine, 25% oxides, and 7% apatite, most likely representing a  
818 combination of pyroxene-nephelinite and melilitite lithologies (Demant et al., 1994). By  
819 continuing fractionation using this assemblage, the 2016 glass composition was reached when  
820 approximately 48% of the starting melt had crystalized (Fig. 13; 14). The resulting composition  
821 adequately matches the 2016 glass compositions in both major and trace element composition,  
822 and has a slightly higher concentration of feldspathoid-incompatible trace elements (e.g.  
823 MREE<sup>3+</sup>) than the 2021 eruptive material (Fig. 13c,d; 14b). Comparison with the 2002 eruptive  
824 material suffers from disagreement between authors, with data from Chakrabarti et al. (2009)  
825 reporting significantly higher trace element contents for a select group of elements (e.g. Ba<sup>2+</sup>,  
826 Yb<sup>3+</sup>, Nb<sup>3+</sup>; Fig. 13b,d,f). Nevertheless, the remaining dataset and those of other authors (Platz,  
827 2002; Minissale et al., 2019), match our calculated composition within a few percent  
828 fractionation. Remaining significant compositional disagreements are for divalent cations,  
829 especially transition metals. This is attributed to a combination of low (near zero) concentrations  
830 as well as to the lack of well-established partition coefficients for these elements in a variety of  
831 phases (also in part due to low concentrations, as well as zoning features).

832 Leucite is notably missing from our modelled fractionation assemblage despite being a major  
833 constituent of the main cone lithologies (e.g., Sahama, 1978; Platz et al., 2004). As a result, the  
834 most LILE-rich compositions in the reported datasets cannot be adequately explained through  
835 simple fractionation (Fig. 13a). Instead we argue that, in line with the interpretations of Platz et  
836 al. (2004), the majority of leucite crystallization appears limited to the lava-lake system, which  
837 leads to accumulation features through floatation (Sahama, 1978), and explains the remaining

838 leucite-rich samples. Simple addition of leucite to our modelled 48% fractionated composition  
839 confirms this (Fig. 13).  
840 Rhönite has not been reported for the Nyiragongo volcanic system and has not been included in  
841 the modelling. However, rhönite may be important in more shallow fractionating alkali systems  
842 such as Cape Verde and the Kaiserstuhl volcanic complex (e.g., Cameron et al. 1970; Kyle and  
843 Price 1975; Grapes and Keller 2010; Mata et al. 2017) where it mimics Na-rich clinopyroxene  
844 partitioning behaviour in terms of REE<sup>3+</sup> (Beard et al., 2019; Baudouin et al., 2020), and forms a  
845 major sink of HFSE<sup>4+</sup>.

## 846 **6 Conclusions**

847 We performed 1 atmosphere gas mixing furnace experiments using alkali-rich, silica-  
848 undersaturated whole-rock compositions from the Nyiragongo volcano to determine partition  
849 coefficients for phases common in alkali-rich magmatic systems. Experiments were carried out  
850 between 1025 °C and 1200 °C with oxygen fugacity buffered to QFM and QFM+1 in order to  
851 investigate the partitioning of trace elements in alkaline magmatic systems.

- 852 - Partition coefficients for trace elements of mono- to pentavalent charges were determined  
853 for leucite, melilite, nepheline, clinopyroxene, olivine, and rhönite at geologically  
854 relevant temperatures. In particular, we present partition coefficients for trivalent to  
855 pentavalent cations in the leucite and nepheline structures.
- 856 - The lattice strain model (Wood and Blundy, 1997) was used to calculate Onuma diagram  
857 parameters in order to allow for extrapolation of trace element partition coefficients.
- 858 - A set of trace element partition coefficients applicable for alkali-rich silica-  
859 undersaturated settings is proposed (Table 3).



- 860 - Fractional crystallization modelling of the Nyiragongo volcanic products using the  
861 reported partition coefficients explains progressive enrichment of light over heavy rare  
862 earth elements. Our results indicate that 48% crystallization from an olivine melilite  
863 basalt composition parental melt reproduces the composition of recent eruptions.
- 864 - Our experiments provide insight into phase equilibria for feldspathoid dominated  
865 magmatic systems at various fractionation stages under anhydrous, low-pressure  
866 conditions.

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## 878 **8 Appendix A. Supplementary Material**

879 Supplementary material associated with this manuscript can be found in the online version. This  
880 includes an overview of all performed experimental runs, including those rejected for analysis,  
881 an overview of all major and trace element data, and an summary of calculated Onuma diagram  
882 parameters for both our own data and those of previous literature. In addition, we supply an  
883 extended discussion on whole-rock geochemical methods, melt compositional evolution and the  
884 trace element compositions of crystallized phases.

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 1231

1232 **10 Tables**

Grouping Sample name	Low-Mg group					High-Mg group				
	A	B	C	D	N	E	F	G	H	
Lithology	Glom- eropor- phyritic			Py- rox- ene-			Oli- vine-	Oli- vine-	Oli- vine-	Oli- vine-
MELTS liquidus	Leu- citite	Melilitite	Leu- citite	Neph- elinite	Nephe- linite	Meli- lite	Meli- lite	Meli- lite	Meli- lite	
(°C)	1236	1475	1233	1182	1198	1221	1558	1201	1184	
wt. %										
SiO <sub>2</sub>	42.50	36.73	45.96	39.43	43.48	38.31	38.78	39.63	41.06	
TiO <sub>2</sub>	2.18	2.85	1.43	3.25	1.53	3.14	1.86	3.53	3.39	
Al <sub>2</sub> O <sub>3</sub>	19.23	12.78	20.66	15.06	23.41	10.47	8.07	11.47	12.25	
Fe <sub>2</sub> O <sub>3</sub>	10.57	12.47	9.18	13.86	7.95	12.75	11.43	13.83	13.05	
MnO	0.21	0.29	0.22	0.27	0.18	0.22	0.20	0.22	0.20	
MgO	2.91	6.37	2.09	4.94	2.30	10.73	21.63	10.00	8.61	
CaO	8.03	17.39	6.02	12.58	6.53	16.08	13.65	15.28	15.06	
Na <sub>2</sub> O	5.87	5.04	6.82	4.41	8.50	2.99	2.36	2.56	2.25	
K <sub>2</sub> O	7.56	4.35	6.95	4.55	6.48	3.06	1.79	2.50	2.35	

P <sub>2</sub> O <sub>5</sub>	1.35	1.97	0.75	1.83	0.81	1.46	1.05	1.03	0.75
LOI	0.63	0.00	1.29	-0.22	1.28	-0.23	-0.30	0.50	0.32
			101.3						
Total	101.05	100.24	7	99.96	102.44	98.97	100.52	100.56	99.30
<i>ppm</i>									
Sc	2.4	12.7	1.6	5.6	2.1	23.6	27	28.5	34.5
V	186	384	49.2	318	117	392	236	405	338.7
Cr	b.d.l.	16.4	b.d.l.	b.d.l.	b.d.l.	388	1227	177	188.7
Co	30.6	36.1	18.6	42.4	19.3	55.9	74.2	51.8	48.1
Ni	21.0	47.4	2.5	25.0	11.1	189.7	701.7	144.5	105.6
Cu	96.5	65.0	13.4	156.1	37.6	100.4	67.5	68.5	69.3
Zn	82.6	91.1	98.4	107.9	77.8	82.8	64.9	84.9	81.5
Rb	294.6	83.7	254.7	112.2	166.5	81.0	43.4	73.7	66.0
Sr	2243	3380	2753	2619	3099	2200	1649	1346	1253.7
Y	27.9	41.2	29.0	35.4	24.3	28.3	22.8	26.9	24.8
Zr	245	345	275	329	229	267	181	280	248.0
Nb	144.6	226.3	231.1	152.5	185.3	114.5	80.8	95.9	79.6
Mo	4.2	1.5	4.4	3.2	5.6	2.7	3.0	2.4	2.0
Cs	4.9	0.70	2.8	1.3	1.7	0.73	0.44	0.74	0.7
Ba	2478	2480	3047	2155	2899	1230	832	1334	1414.1
La	180	281	208	170	199	119	97	102	87.3
Ce	331	518	366	332	347	240	187	207	184.5
Pr	33	50	34	35	33	27	20	23	19.6
Nd	113	174	112	133	110	102	75	88	77.8
Sm	16	25	15	20	15	16	12	14	12.5
Eu	4.4	6.8	4.3	5.5	4.3	4.4	3.2	3.9	3.5
Gd	11	18	10	15	11	12	8.9	11	9.8
Tb	1.3	2.0	1.2	1.7	1.2	1.3	1.0	1.3	1.2
Dy	6.4	9.8	6.1	8.6	5.9	6.3	5.0	6.4	6.2
Ho	1.1	1.7	1.1	1.5	1.1	1.0	0.84	1.1	1.1
Er	3.0	4.5	3.2	3.9	3.0	2.7	2.2	2.8	2.8
Tm	0.38	0.56	0.44	0.48	0.39	0.32	0.27	0.34	0.4
Yb	2.4	3.4	2.9	3.0	2.5	1.9	1.6	2.1	2.2
Lu	0.35	0.50	0.42	0.42	0.37	0.28	0.23	0.30	0.3
Hf	3.7	5.9	4.0	6.1	4.0	5.6	4	7.4	7.1
Ta	45	54	26	16	24	4	10	12	12.9
W	3.0	1.3	2.9	1.7	1.9	1.4	1.5	1.4	1.5
Pb	1.7	5.8	5.2	4.2	5.4	2.7	3.8	2.6	1.8
Th	18	28	24	14	29	9.6	7.6	8.7	8.1
U	6.3	15	10	5.2	16	4.0	2.8	3.7	2.3

1233 *Table 1 Major element oxide and trace element compositions of starting materials for the gas-mixing furnace experiments.*

1234 *MELTS liquidus estimates are reported for QFM conditions using Rhyolite-MELTS 1.0.2 (Gualda et al., 2012).*

Run	Com- posi- tion	T <sub>pre- melt</sub> (°C)	T <sub>Eq</sub> (°C)	Equi- libra- tion time (h)	Cool- ing rate (°C/h)	ΔQFM	log fO <sub>2</sub>	Run products	Na- loss (% of start)	K- loss (% of start)
NYA-4	A	1200	110 0	45.5	3.00	± 1	-8.66	Lc (12), Ox (4), Gl (84)	6.18	4.87
NYA-7	A	1180	105 0	68	3.00	± 1	-9.36	Cpx (10), Lc (19), Neph (5), Ox (6), Rh (<1), Gl (60)	n.d.	n.d.
	B							Mel (34), Ox (10), Wh (<1), Gl (56)	n.d.	n.d.
NYA-8	A	1180	107 5	60	3.00	± 0.8	-9.22	Lc (17), Ox (5), Gl (78)	n.d.	n.d.
	B							Mel (27), Neph (<1), Ox (7), Gl (66)	n.d.	n.d.
	C							Lc (9), Ox (2), Gl (89)	n.d.	0.73
	D							Cpx (19), Lc (7), Ox (5), Rh (3), Gl (66)	3.54	3.39
NYA-9	A	1180	102 5	82.35	3.00	± 1	-9.72	Cpx (23), Lc (24), Neph (14), Ox (6), Gl (33)	n.d.	1.81
	B							Cpx (17), Mel (42), Neph (12), Ox (11), Rh (<1), Wh (<1), Gl (20)	5.80	6.37
	C							Cpx (4), Lc (17), Ox (4), Gl (75)	n.d.	n.d.
	D							Cpx (43), Neph (7), Ox (8), Wh (<1), Gl (42)	7.08	13.11
NYA-10	A	1180	105 0	73	3.00	± 1	-9.36	Cpx (<1), Lc (20), Rh (7), Ox (4), Gl (69)	n.d.	n.d.

NYA-11	B	1180	107 5	75	3.00	± 0	-10.01	Cpx (13), Mel (36), Neph (13), Ox (9), Gl (29)	n.d.	19.38
	C							Lc (12), Ox (2), Rh (5), Gl (81)	n.d.	n.d.
	D							Cpx (32), Lc (9), Ox (7), Wh (2), Gl (50)	n.d.	22.82
	A							Lc (15), Ox (3), Gl (82)	10.07	3.48
NYA-15	B	1180	107 5	163	2.00	± 0.8	-9.22	Mel (30), Neph (7), Ol (2), Ox (7), Gl (54)	n.d.	n.d.
	A							Lc (17), Ox (5), Gl (78)	n.d.	n.d.
	B							Mel (28), Neph (<1), Ox (7), Gl (65)	n.d.	n.d.
	C							Lc (9), Ox (2), Gl (89)	0.89	n.d.
NYA-16	D	1180	110 0		2.00	± 0	-9.66	Cpx (21), Lc (7), Ox (6), Gl (66)	3.76	2.71
	A							Lc (14), Ox (2), Gl (84)	1.24	n.d.
	B							Mel (16), Ox (2), Gl (82)	n.d.	n.d.
	C							Lc (10), Neph (4), Gl (86)	3.54	n.d.
NYA-17	E	1500	120 0	70	2.00	± 0	-8.41	Ol (8), Gl (92)	56.23	61.02
NYA-18		1180	107 5	89	2.00	± 0	-10.01			
	A							Lc (15), Ox (4), Gl (81)	2.12	n.d.
	B							Mel (26), Ol (1), Ox (7), Gl (66)	n.d.	n.d.
	D							Cpx (23), Lc (4), Ox (6), Gl (67)	n.d.	n.d.
NYA-19		1180	105 0		2.00	± 0	-10.36			
	A							Cpx (7), Lc (18), Ox (6), Gl (69)	n.d.	n.d.
	B							Mel (34), Neph (9), Ox (6), Rh (10), Gl (41)	n.d.	n.d.

NYA-20	C	1180	102 5	84	2.00	± 0	-10.72	Lc (17), Ox (2), Gl (81)	9.89	n.d.
	D							Cpx (32), Lc (8), Ox (6), Gl (52)	n.d.	1.58
	B							Mel (40), Neph (8), Ox (7), Rh (13), Wh (<1), Gl (32)	n.d.	n.d.
	C							Cpx (2), Lc (19), Ox (2), Rh (1), Gl (76)	2.36	n.d.
NYA-22	D	1180	105 0	96	2.00	± 0	-10.36	Cpx (39), Ox (7), Rh (<1), Wh (3), Gl (50)	10.62	4.52
	A							Mel (37), Neph (1), Ox (7), Rh (9), Gl (46)	4.59	1.11
	N							Cpx (1), Neph (30), Lc (7), Ox (<1), Rh (5), Gl (57)	2.83	3.09

1235 *Table 2 List of experiments analysed by EMPA and LA-ICPMS. A full table including experiments analysed by EMPA but*  
1236 *rejected for LA-ICMPS are listed in Supplementary Material 1. Numbers in brackets for run products, including glass (Gl), are*  
1237 *volume percentages. Sodium and potassium losses are in percentage relative to the glass compositions from super-liquidus*  
1238 *experimental runs 2 and 21, with the exception of composition N, for which XRF data was used.*

1239  
1240

	Evolved systems (MgO < 10 wt.%)						Primitive compositions (MgO > 10 wt.%)
Temperat ure (°C)	1075	1075	1050	1075	1075	1050	1200
Mineral	Leucite	Melilite	Rhönite	Clinopyroxene	Olivine	Nepheline	Olivine
Cs	17.39 (1.83)	- (-)	0.0255 (0)	0.020 (0.003)	- (-)	0.281 (0.295)	0.921 (0)
Rb	9.23 (0.70)	0.00264 (0.00083)	0.0116 (0.0090)	0.00698 (0.00538)	- (-)	0.676 (0.167)	- (-)
Ba	1.21 (0.17)	0.0356 (0.0035)	0.00583 (0.00479)		- (-)	0.0641 (0.0131)	0.000626 (0)
Sr	0.0264 (0.0048)	1.73 (0.25)	0.137 (0.028)		0.000608 (0.000363)	0.369 (0.099)	0.000168 (0.000096)

Co	0.0152 (0.0181)	1.19 (0.15)	4.23 (0.79)		5.43 (0.29)	0.0403 (0.0067)	2.23 (0.50)
Zn	1.17 (0.57)	0.83 (0.34)	1.08 (0.19)		2.80 (0.62)	0.849 (0.142)	0.13 (0.12)
Ni	0.112 (0.116)	1.22 (0.37)	18.01 (8.22)		31.47 (2.96)	- (-)	6.29 (3.92)
La	0.000942 (0.00103)	0.227 (0.029)	0.0475 (0.0071)	0.349 (0.037)	- (-)	0.00119 (0.00049 1)	0.0000797 (0)
Ce	0.0011 (0.0004)	0.269 (0.031)	0.0732 (0.0104)	0.558 (0.087)	0.000027 5.00 (0)	0.00136 (0.00079 )	0.000241 (0)
Pr	0.000722 (0.00052)	0.285 (0.032)	0.0948 (0.0130)	0.758 (0.081)	0.00152 (0)	0.00128 (0.00083 )	- (-)

Nd	0.00183 (0.00107)	0.289 (0.032)	0.133 (0.019)	0.989 (0.101)	0.00146 (0)	0.00124 (0.00078)	- (-)
Sm	0.00561 (0.00273)	0.251 (0.029)	0.182 (0.036)	1.29 (0.12)	0.00208 (0)	0.00331 (0.00186)	0.00165 (0.00036)
Eu	0.0136 (0.0045)	0.281 (0.030)	0.179 (0.036)	1.30 (0.14)	0.00316 (0)	0.0192 (0.0035)	- (-)
Gd	0.0106 (0.0038)	0.212 (0.028)	0.182 (0.024)	1.43 (0.15)	0.0113 (0)	0.00378 (0.00021)	0.00916 (0)
Tb	- (-)	0.162 (0.020)	0.18 (0.04)	1.36 (0.13)	0.00416 (0)	- (-)	0.00397 (0.00045)
Dy	0.00492 (0)	0.124 (0.019)	0.167 (0.034)	1.28 (0.12)	0.00672 (0)	0.00448 (0.00216)	0.00765 (0.00174)



Y	0.00242 (0.00139)	0.0933 (0.0187)	0.157 (0.037)	1.10 (0.1)	0.0209 (0.0113)	0.00215 (0.00078)	0.00811 (0.00127)
Ho	0.00946 (0.00201)	0.106 (0.020)	0.17 (0.04)	1.18 (0.11)	0.0101 (0.0027)	0.00583 (0.00184)	0.00714 (0.002)
Er	0.00678 (0.00280)	0.075 (0.016)	0.176 (0.052)	1.10 (0.1)	0.0197 (0.0001)	0.00376 (0.00094)	0.014 (0.002)
Tm	- (-)	0.0606 (0.0180)	0.175 (0.072)	1.0 (0.1)	0.0256 (0)	0.00667 (0)	0.0178 (0.0014)
Yb	0.0129 (0)	0.0479 (0.0141)	0.203 (0.047)	0.991 (0.098)	0.0264 (0.0076)	0.00646 (0.00059)	0.0201 (0.0039)
Lu	0.0383 (0.0113)	0.0498 (0.0144)	0.245 (0.069)	1.09 (0.12)	0.0414 (0.0034)	- (-)	0.0361 (0.0058)

Sc	0.181 (0.010)	0.0260 (0.0074)	6.06 (1.71)	17.48 (7.67)	0.304 (0.049)	0.202 (0.034)	0.141 (0.010)
Cr	1.07 (0.57)	0.952 (0.26)	6.24 (3.36)	2.57 (1.26)	3.01 (1.9)	1.14 (0.38)	2.56 (1.58)
Th	0.00236 (0.00123)	0.00468 (0.00142)	0.0114 (0.0040)	0.136 (0.031)	0.000118 (0)	0.000436 (0.00040 8)	0.00155 (0)
U	0.00476 (0.00271)	0.00186 (0.00105)	0.012 (0.010)	0.0224 (0.0093)	0.000524 (0)	0.000748 (0.00088 2)	0.00021 (0.00014)
Zr	0.00197 (0.00095)	0.000542 (0.000514)	0.68 (0.06)	2.26 (0.25)	0.002 (0.00072)	0.000721 (0.00062 0)	0.000518 (0.000211)
Hf	0.0181 (0.0086)	0.0111 (0)	1.11 (0.13)	3.88 (0.70)	0.00769 (0.00309)	0.00316 (0.00074 )	0.00294 (0.00119)

V	0.0132 (0.0040)	0.024 (0.007)	1.57 (0.24)	1.12 (0.09)	0.0119 (0.0022)	0.00381 (0.00134)	0.0147 (0.0011)
Nb	0.00266 (0.00241)	0.000766 (0.000802)	0.20 (0.02)	0.11 (0.02)	0.000369 (0.000434)	0.0014 (0.0020)	0.000186 (0.000043)
Ta	0.00705 (0.00407)	0.00131 (0.00039)	0.588 (0.083)	0.463 (0.083)	0.000494 (0.000161)	0.00115 (0.00054)	0.001 (0.001)

1242 *Table 3 Recommended partition coefficients for main minerals in primitive and evolved systems as indicated by low and high whole-rock MgO. One standard deviation values are*  
1243 *listed in brackets following the recommended coefficient. Zero values for standard deviations indicate that only a single measurement was used to constrain the recommended*  
1244 *value. See Supplementary Material 1 for a more detailed overview.*

## 1245 **11 Figure Captions**

1246 **Fig. 1** Total Alkali-Silica (TAS) diagram including the starting compositions used for all  
1247 experiments. Representative fields of various alkaline magmatic systems are included, with data  
1248 of Nyiragongo, Mikeno and Nyamuragira (Barette et al., 2017), Pico do Fogo (Hildner et al.,  
1249 2012; Eisele et al., 2015), the Eifel (Jung et al., 2006; Tomlinson et al., 2020), Etna (Viccaro et  
1250 al., 2015), Terceira (Mungall and Martin, 1995; Regenauer-Lieb et al., 2015), Mount Morning  
1251 (Martin et al., 2013), and Mount Erebus (Caldwell and Kyle, 1994; Iverson et al., 2014).

1252 **Fig. 2** Representative comparison between rate-cooled (a, c) and isothermal (b, d) experimental  
1253 products, as well as EDX maps of reported zoning features (e,f). Images a-d are false colour  
1254 BSE, with the colours red, blue, yellow, orange, and pink representing clinopyroxene, leucite,  
1255 rhönite, nepheline, and spinel-structured oxide minerals. Melilite (e) and clinopyroxene (f)  
1256 zoning features are displayed through Al-(e) and Fe-(f) EDX maps, respectively, showing sector  
1257 (e) and core-rim (f) zoning features.

1258 **Fig. 3** Evolution of melt composition with equilibrium temperature for the low-Mg compositions  
1259 A, B, C, D, and N. Key trends related to either crystallization of phases or alkali-loss are  
1260 indicated.

1261 **Fig. 4** Evolution of melt composition with equilibrium temperature for the high-Mg  
1262 compositions E, F, G, and H. Key trends related to either crystallization of phases or alkali-loss  
1263 are indicated.

1264 **Fig. 5** Crystal-glass partition coefficients for (a) leucite, (b) melilite, and (c) nepheline. One  
1265 standard deviation errors are displayed for each temperature measurement. Lower bound errors

1266 stretching below  $10^{-5}$  are left out for clarity. For more details see Supplementary Material 1. Note  
1267 that experiments above 1100 °C were performed with High-Mg starting compositions.

1268 **Fig. 6** Crystal-glass partition coefficients for (a) clinopyroxene, (b) olivine, and (c) rhönite. One  
1269 standard deviation errors are displayed for each temperature measurement. Lower bound errors  
1270 stretching below  $1e-5$  are left out for clarity. For more details see Supplementary Material 1.  
1271 Note that experiments above 1100 °C were performed with High-Mg starting compositions.

1272 **Fig. 7** Representative best-fit lattice strain curves for mono- to tetravalent ions in the leucite  
1273 structure for a single set of conditions (listed top left). Ionic radii are for twelve-fold (1+, 2+) and  
1274 four-fold (3+, 4+) coordination taken from Shannon (1976). Four-fold radii are in a large part  
1275 acquired extrapolation, see section 2.5.  $D_0$  values are unit-less,  $E_0$  values are in GPa, and  $r_0$   
1276 values are listed in Å. Open symbols were not considered for the fitting approach. Shaded areas  
1277 and/or lines represent literature data, whereas full opacity lines are from this study. This also  
1278 applies for further figures. Abbreviations for sources of literature curves are as follows: Fab08:  
1279 (Fabrizio et al., 2008), FJ04: (Foley and Jenner, 2004), Min19: (Minissale et al., 2019), WT01:  
1280 (Wood and Trigila, 2001).

1281 **Fig. 8** Representative best-fit Onuma curves for mono- to tetravalent ions in the melilite structure  
1282 for a single set of conditions (listed top left). Ionic radii are for four- (T1-site) and eight-fold (X-  
1283 site) coordination taken from Shannon (1976). Select four-fold radii are acquired through  
1284 extrapolation following the approach by Jia (1991), see section 2.5. Abbreviations for sources of  
1285 literature curves are as follows: Arz09: (Arzamastsev et al., 2009), Beck90 (Beckett et al., 1990),  
1286 Kue89: (Kuehner et al., 1989), Lun06: (Lundstrom et al., 2006), Min19: (Minissale et al., 2019),  
1287 Nag80: (Nagasawa et al., 1980), Onu81: (Onuma et al., 1981), Ust19: (Ustunisik et al., 2019).

1288 **Fig. 9** Representative best-fit Onuma curves for mono- to tetravalent ions in the nepheline  
1289 structure for a single set of conditions (listed top left). Ionic radii are for eight- (B-site), nine- (A-  
1290 site), and four- (T-sites) fold coordination taken from Shannon (1976). Four-fold radii are in a  
1291 large part acquired extrapolation, see section 2.5. Abbreviations for sources of literature curves  
1292 are as follows: Daws08: (Dawson et al., 2008), Lars79: (Larsen, 1979), Min19: (Minissale et al.,  
1293 2019), Onu81: (Onuma et al., 1981).

1294 **Fig. 10** Representative best-fit lattice strain curves for di- to tetravalent ions in the clinopyroxene  
1295 structure for a single set of conditions (listed top left). Ionic radii are for six- (M1-site) and eight-  
1296 (M2-sites) fold coordination taken from Shannon (1976). Abbreviations for sources of literature  
1297 curves are as follows: A&A18: (Ambrosio and Azzone, 2018), Arz09: (Arzamastsev et al.,  
1298 2009), Bau20: (Baudouin et al., 2020), Beard19: (Beard et al., 2019), FJ04: (Foley and Jenner,  
1299 2004), Lars79: (Larsen, 1979), Min19: (Minissale et al., 2019).

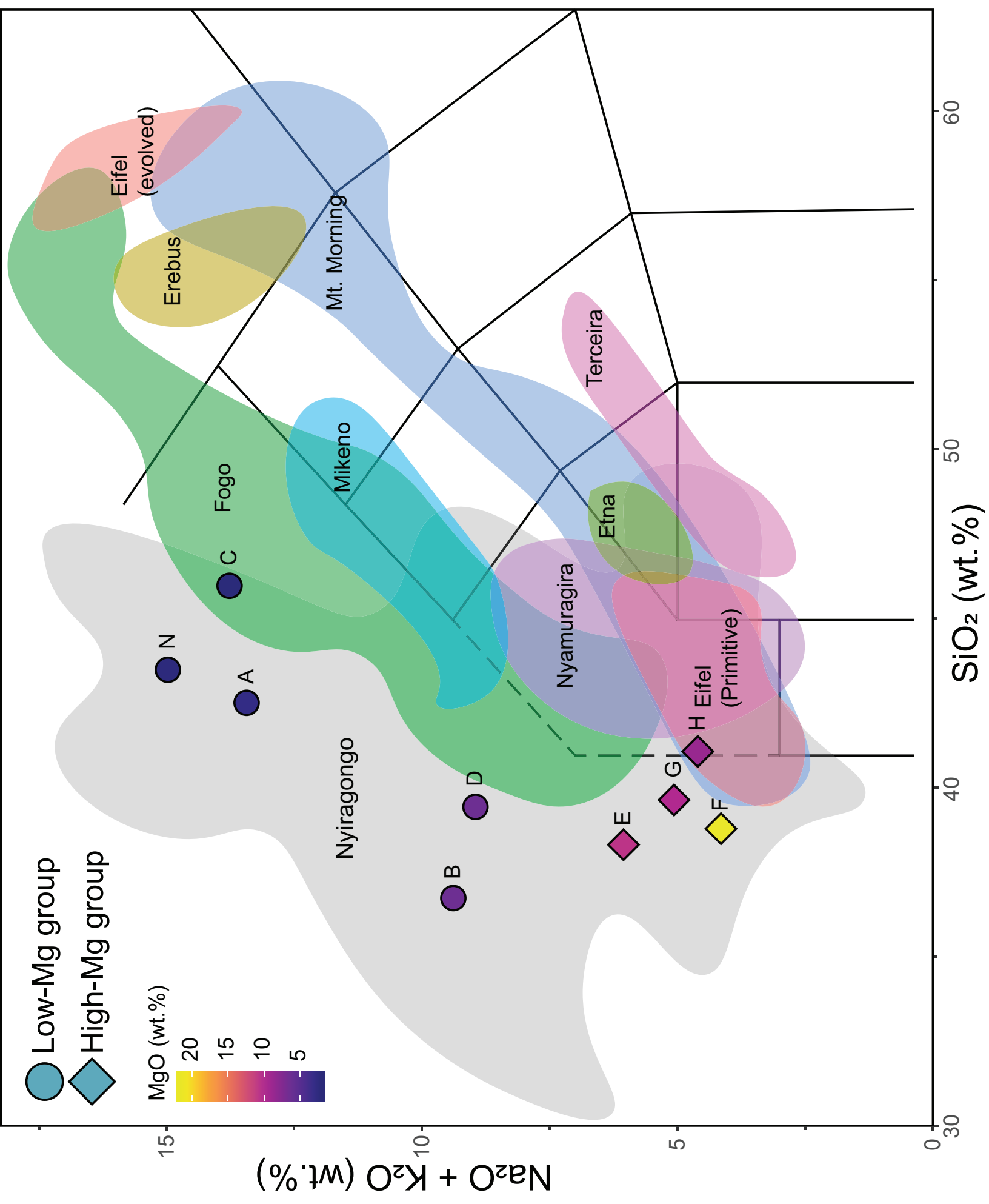
1300 **Fig. 11** Representative best-fit Onuma curves for di- to tetravalent ions in the olivine structure  
1301 for a single set of conditions (listed top left). Ionic radii are for six-fold coordination taken from  
1302 Shannon (1976). Abbreviations for sources of literatures curves are as follows: FJ04: (Foley and  
1303 Jenner, 2004), Min19: (Minissale et al., 2019).

1304 **Fig. 12** Representative best-fit Onuma curves for di- to tetravalent ions in the rhönite structure  
1305 for a single set of conditions (listed top left). Ionic radii are for eight- (X-site), six- (Y-site), and  
1306 four- (Z-site) fold coordination taken from Shannon (1976). Abbreviations for sources of  
1307 literature curves are as follows: Kog05: (Kogarko et al., 2005), Lof06: (Lofgren et al., 2006).

1308 **Fig. 13** Binary trace elements (ppm) vs MgO (wt.%) diagrams comparing modelled  
1309 concentrations with those reported by recent literature. Abbreviations for sources are as follows:  
1310 CH09: (Chakrabarti et al., 2009), Min19: (Minissale et al., 2019), Min22 (Minissale et al., 2022),

1311 PL02: (Platz, 2002), PL04: (Platz et al., 2004). Eruptive material of the 2016 (red triangles) and  
1312 2021 (blue diamonds) eruptions have been highlighted. 10% fractionation arrows are included  
1313 for olivine, melilite, nepheline, and clinopyroxene (cpx) starting from the source composition.  
1314 An additional arrow of leucite addition is listed, with its origin at the 48% fractionation point.  
1315 **Fig. 14** CI-chondrite normalized (a) trace element- and (b) rare-earth element patterns of the  
1316 2002, 2016, and 2021 eruptive materials compared to those resulting from trace element  
1317 fractionation modelling. Icons for different sources are as listed in Figure 13. Only data of the  
1318 2002 (Platz, 2002; Chakrabarti et al., 2009; Minissale et al., 2019), 2016 (Minissale et al., 2019),  
1319 and 2021 (Minissale et al., 2022) eruptions is included here. Normalization values are from  
1320 (McDonough and Sun, 1995).

Figure 1





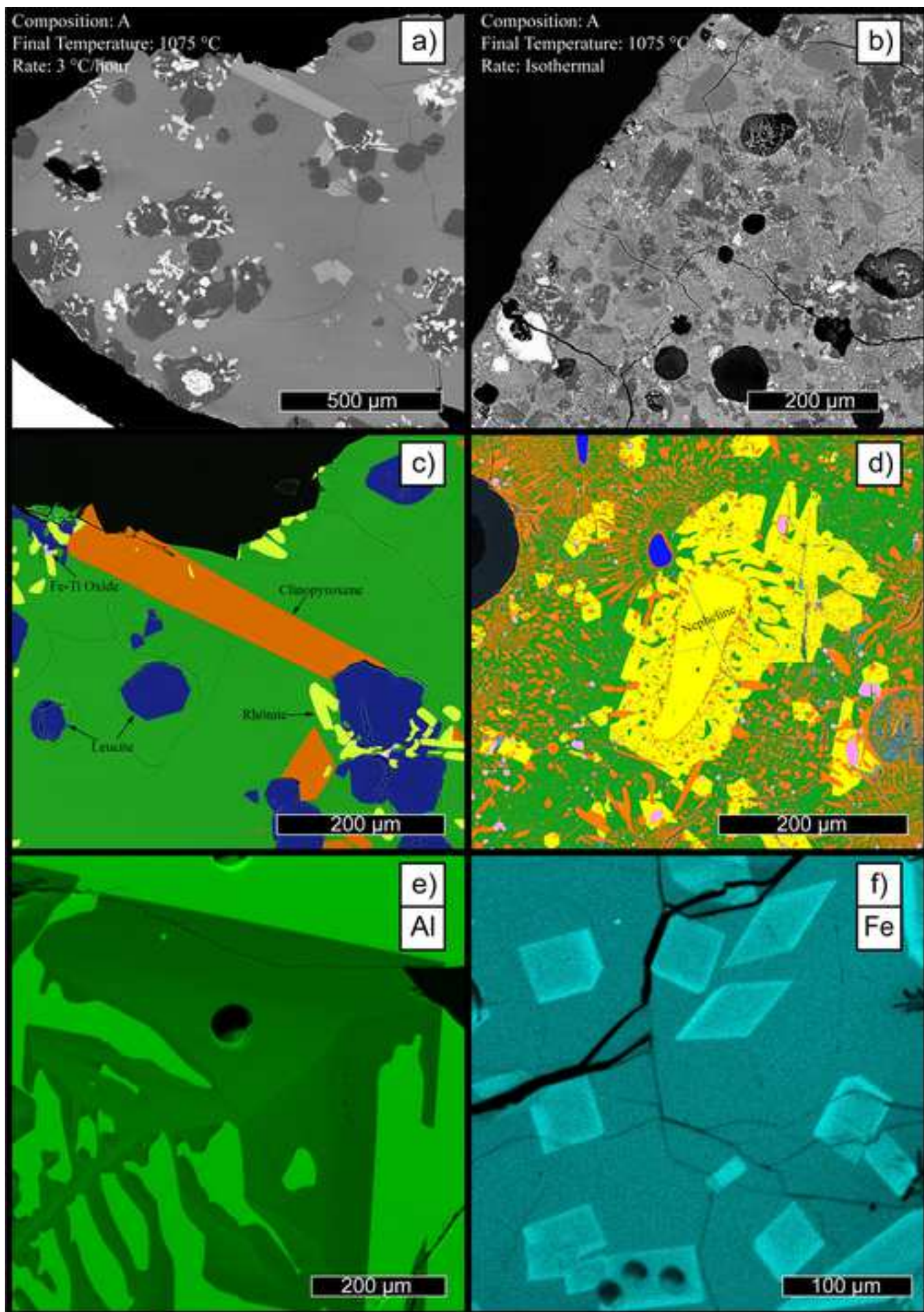


Figure 3

Composition

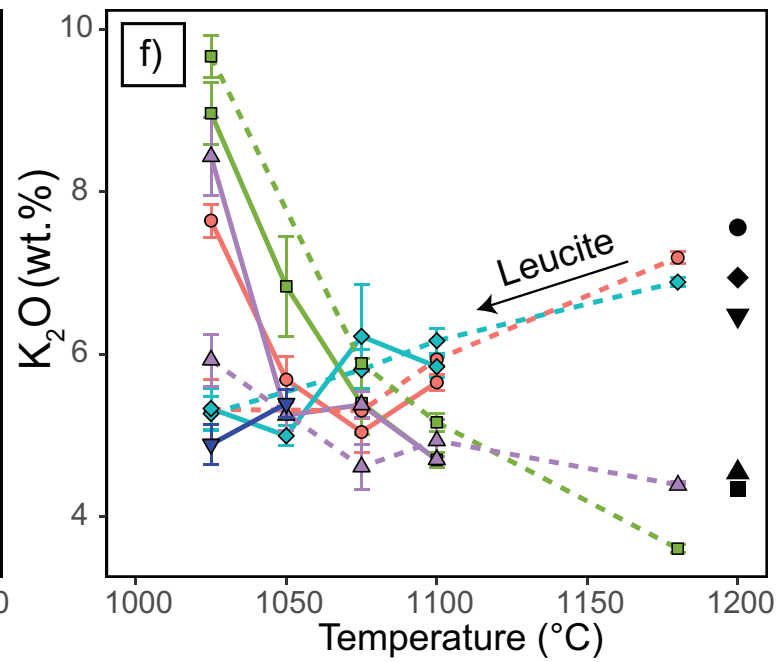
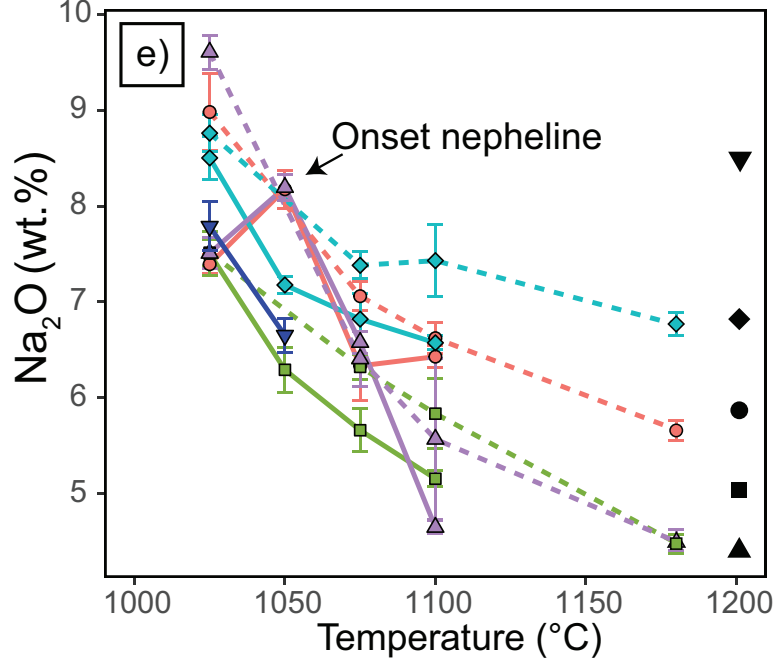
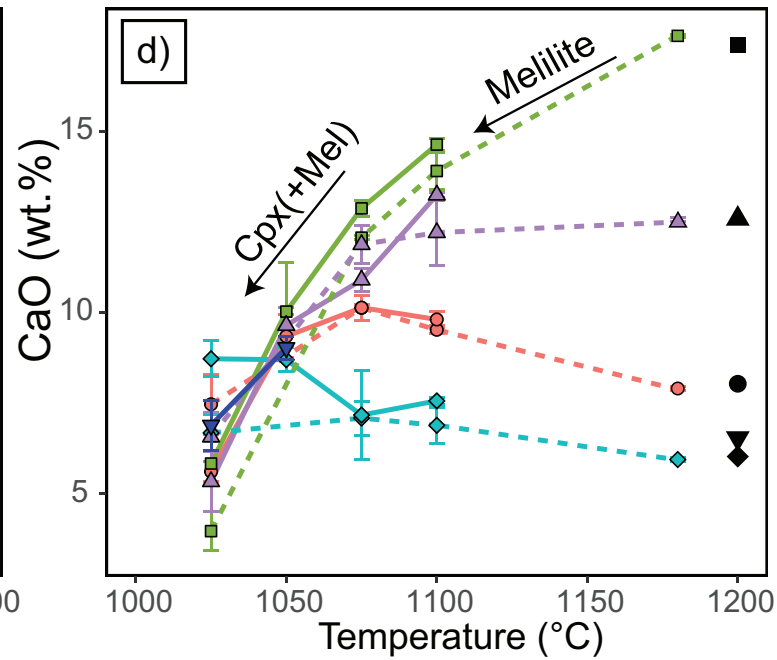
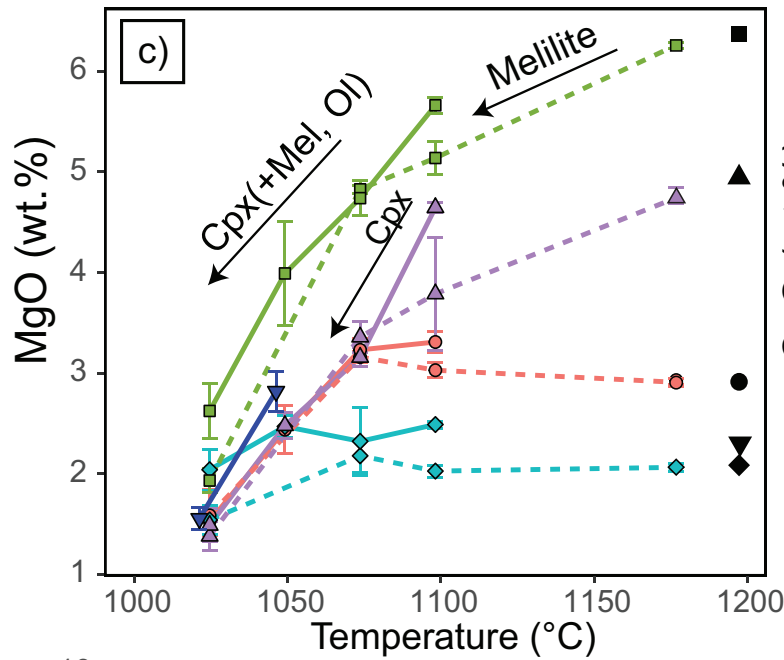
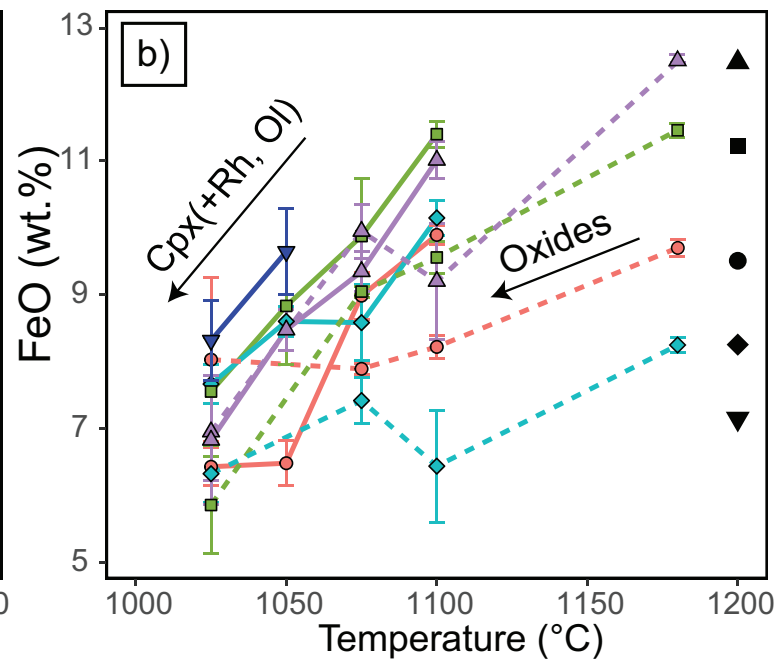
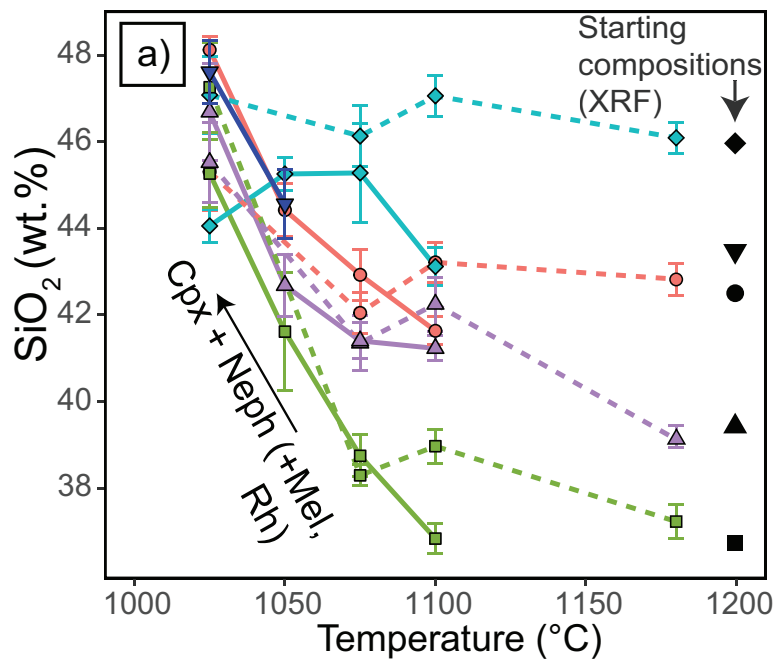
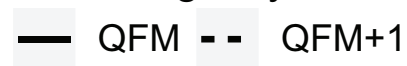
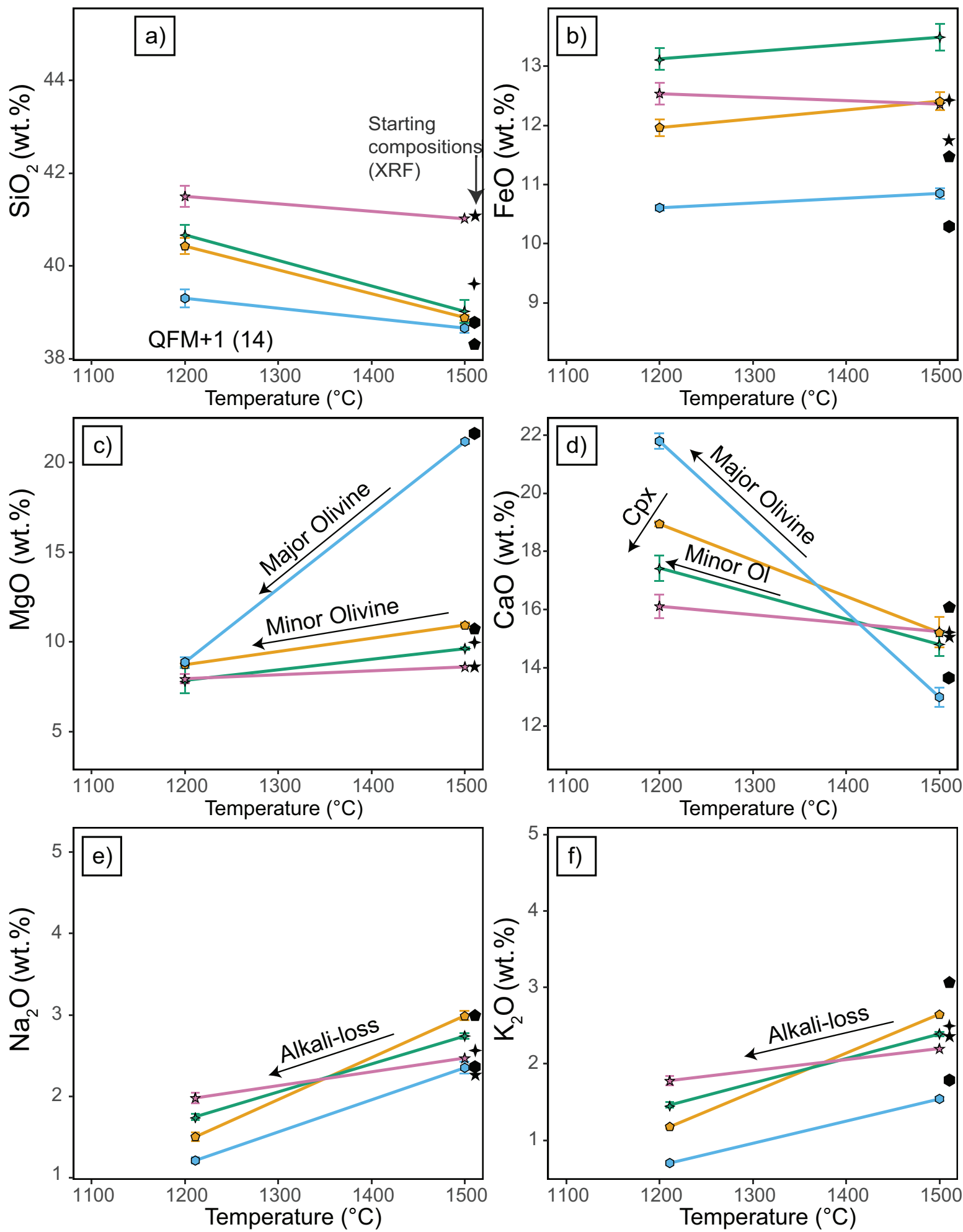
Fugacity [Click here to access Open Peer Review on Figure 3. eps](#)

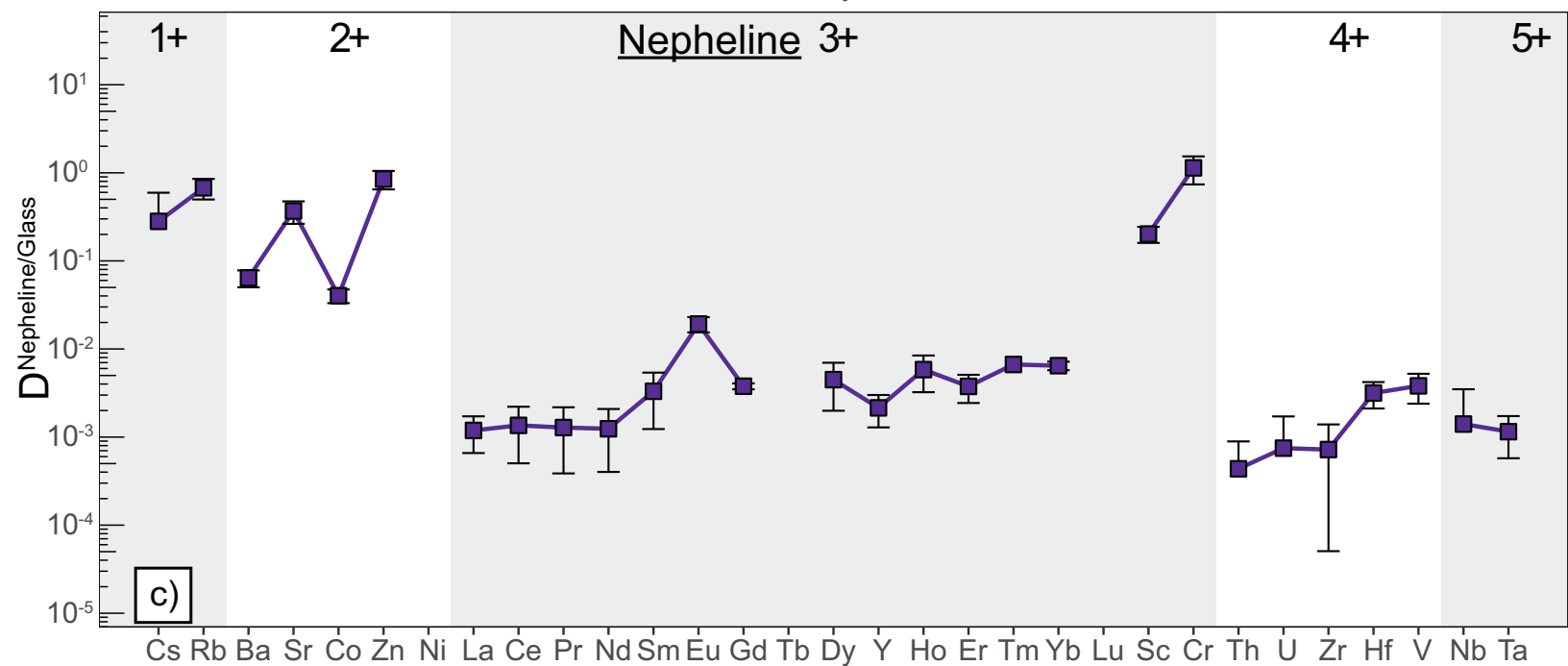
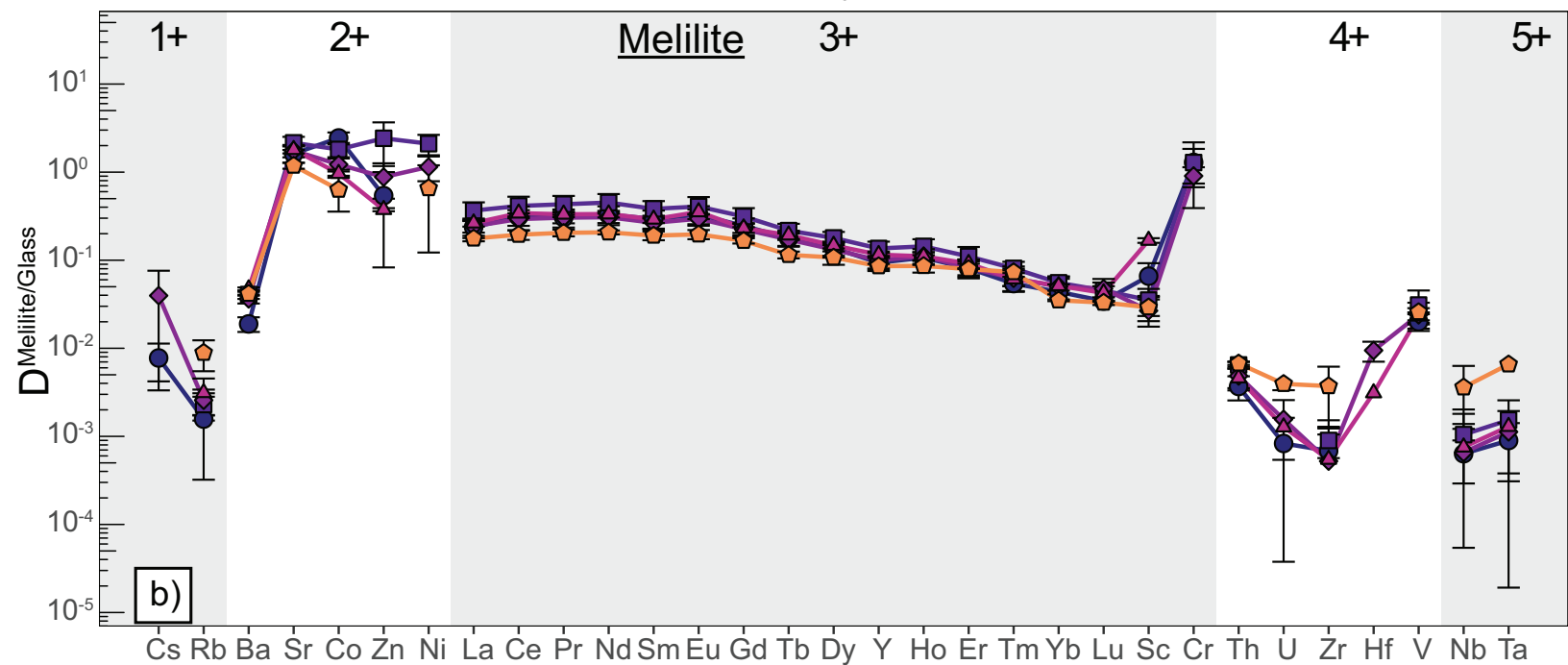
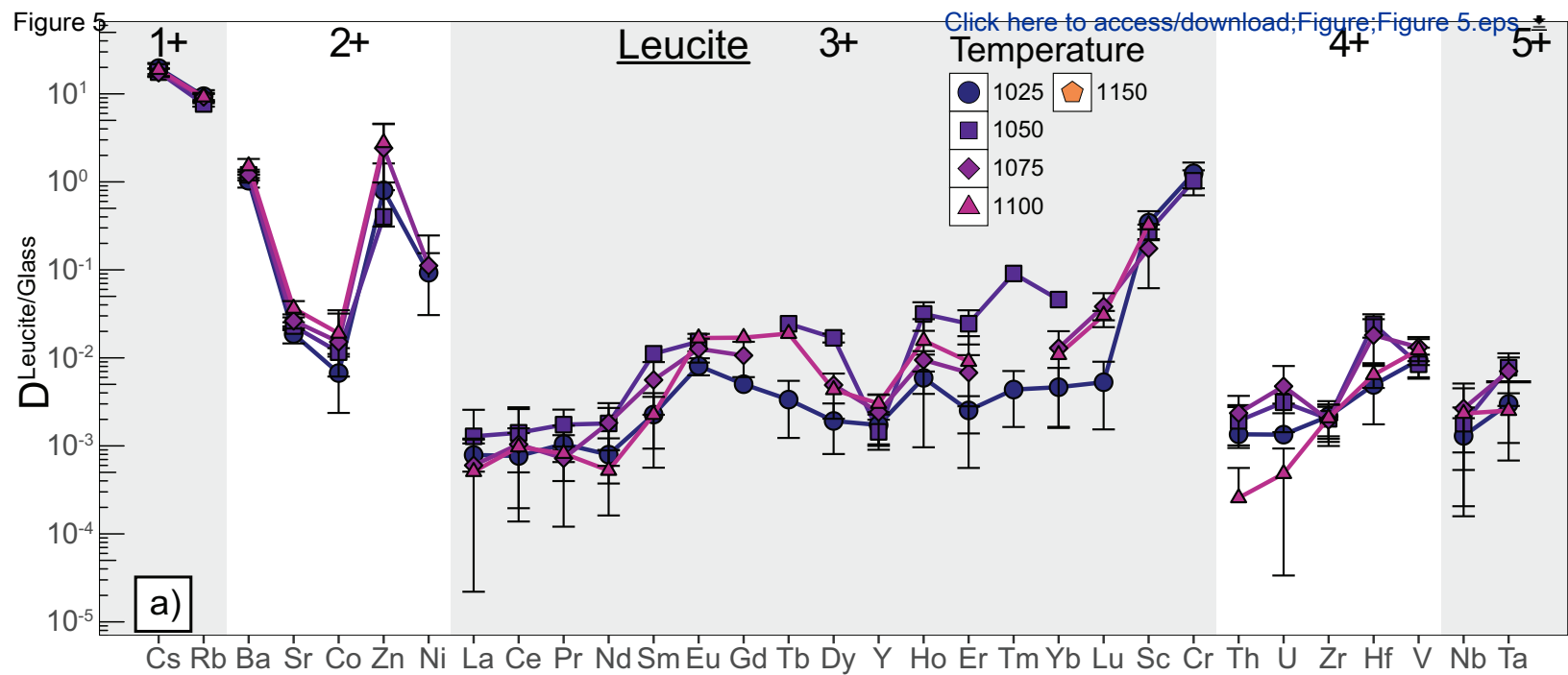
Figure 4

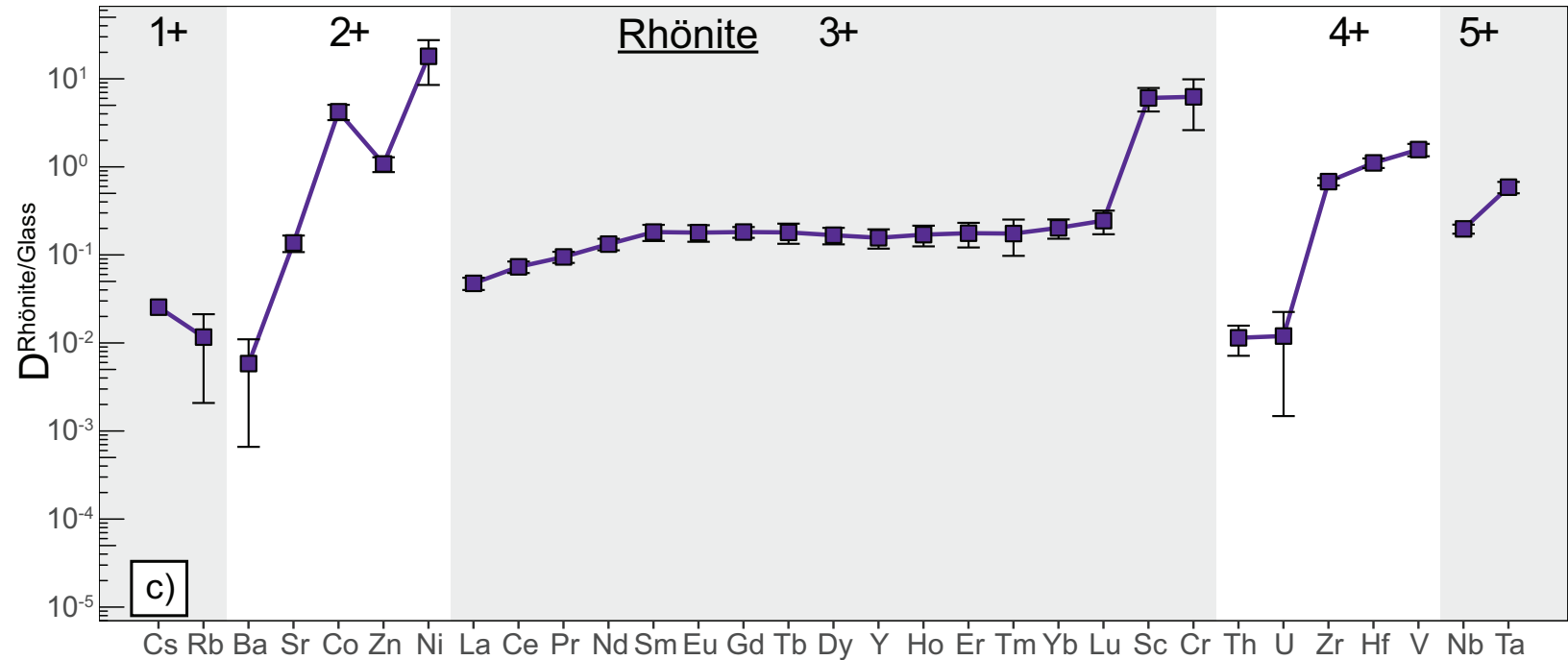
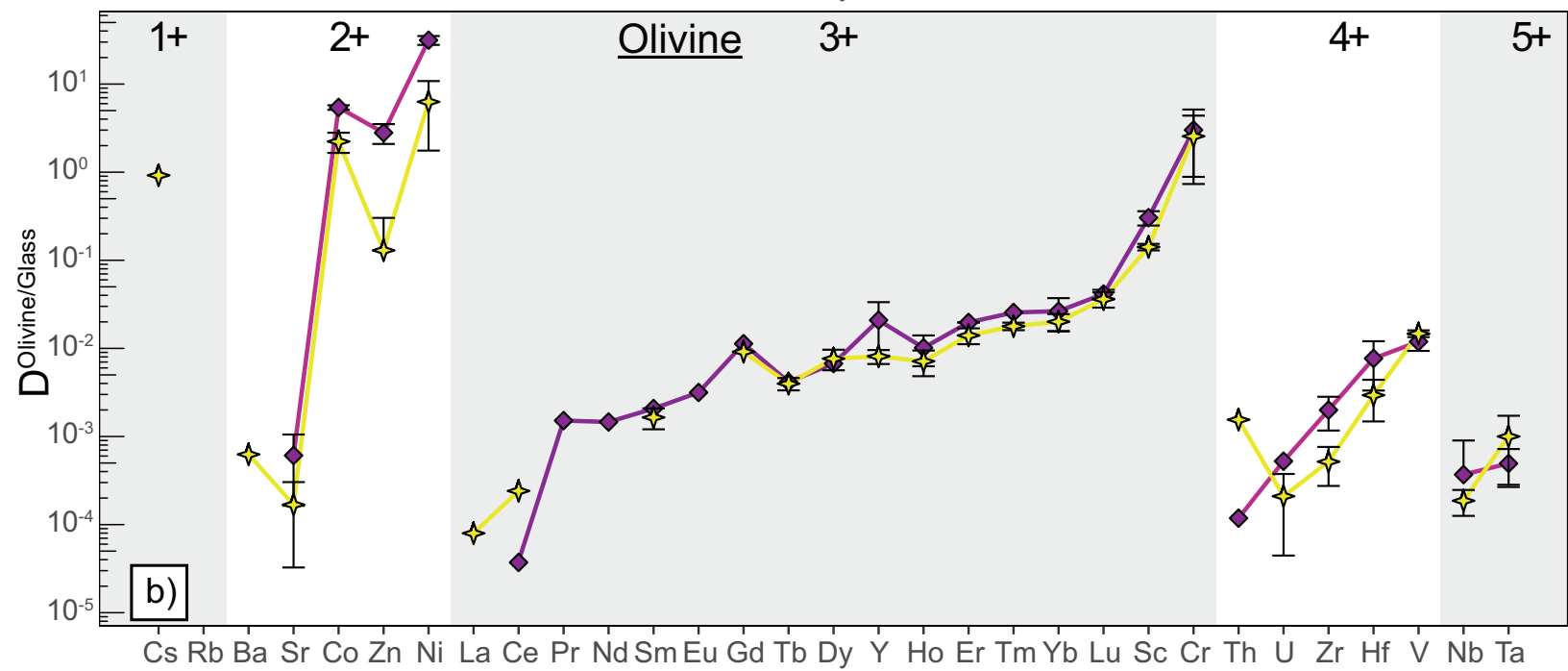
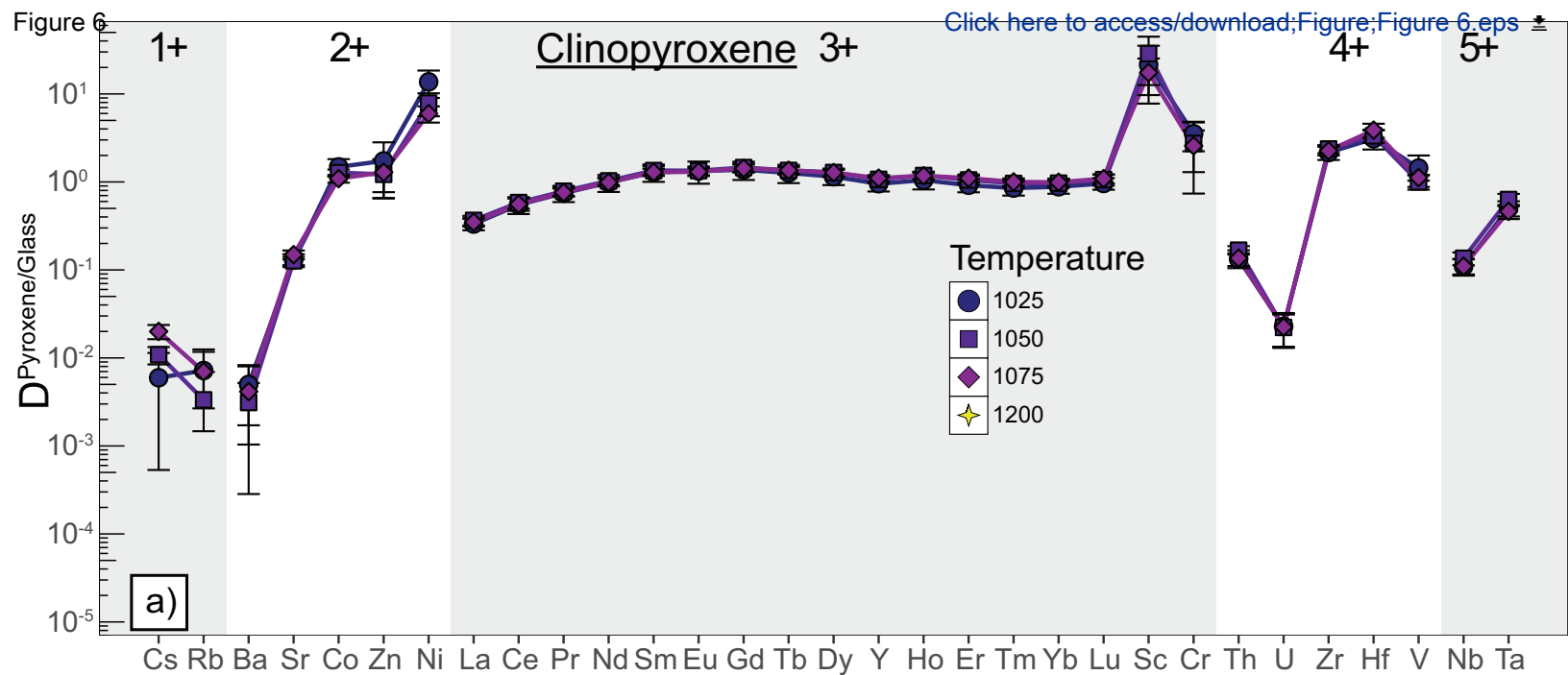
Composition

Fugacity [Click here to access full text; Figure; Figure 4.eps](#)

— QFM







## Leucite-1050°C-QFM-Comp A

- 1<sup>+</sup> Cation
- 2<sup>+</sup> Cation
- ◆ 3<sup>+</sup> Cation
- ▲ 4<sup>+</sup> Cation

$$D_{W}^{1+} = 15.36 \pm 0.79$$

$$E_{W}^{1+} = 33 \pm 0$$

$$r_{W}^{1+} = 1.9 \pm 0 \text{ (fixed)}$$

$$D_{W}^{2+} = 13.20 \pm 1.28$$

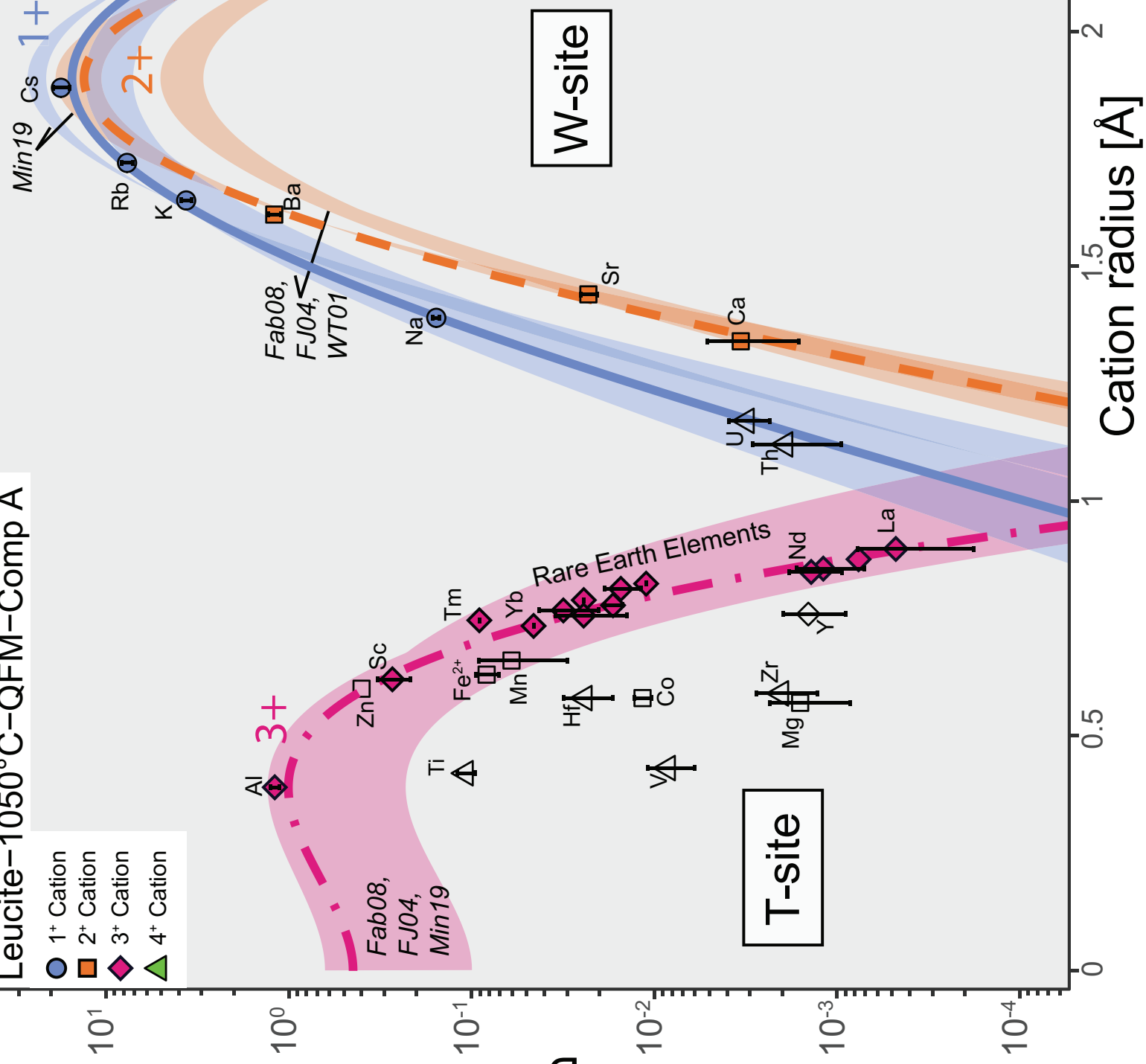
$$E_{W}^{2+} = 53 \pm 2$$

$$r_{W}^{2+} = 1.9 \pm 0 \text{ (fixed)}$$

$$D_{T}^{3+} = 1.01 \pm 0.08$$

$$E_{T}^{3+} = 120 \pm 9$$

$$r_{T}^{3+} = 0.39 \pm 0 \text{ (fixed)}$$

D<sub>Leucite/Glass</sub>

W-site

T-site

Figure 8

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Melilite-1075°C-QFM-Comp B

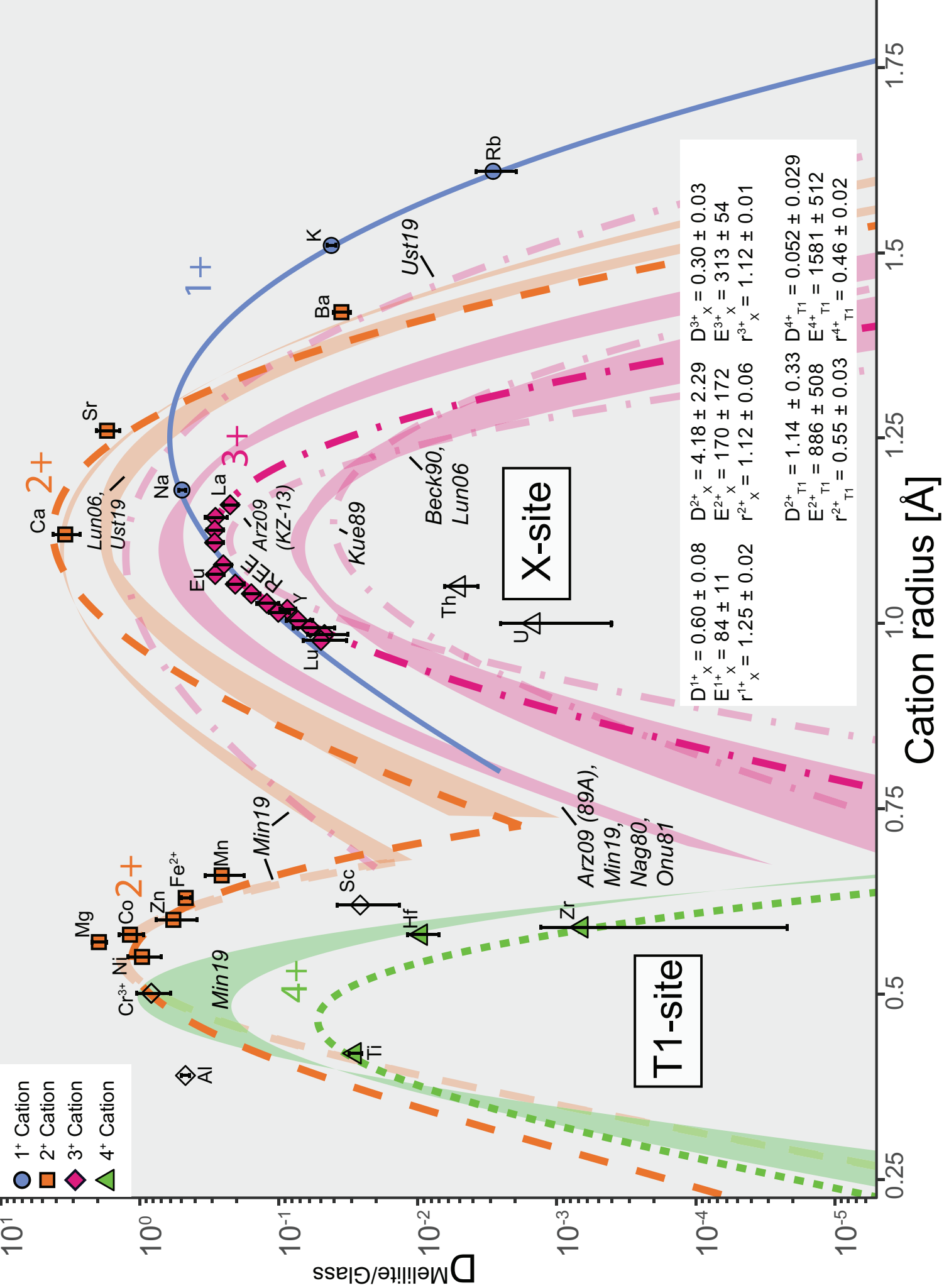
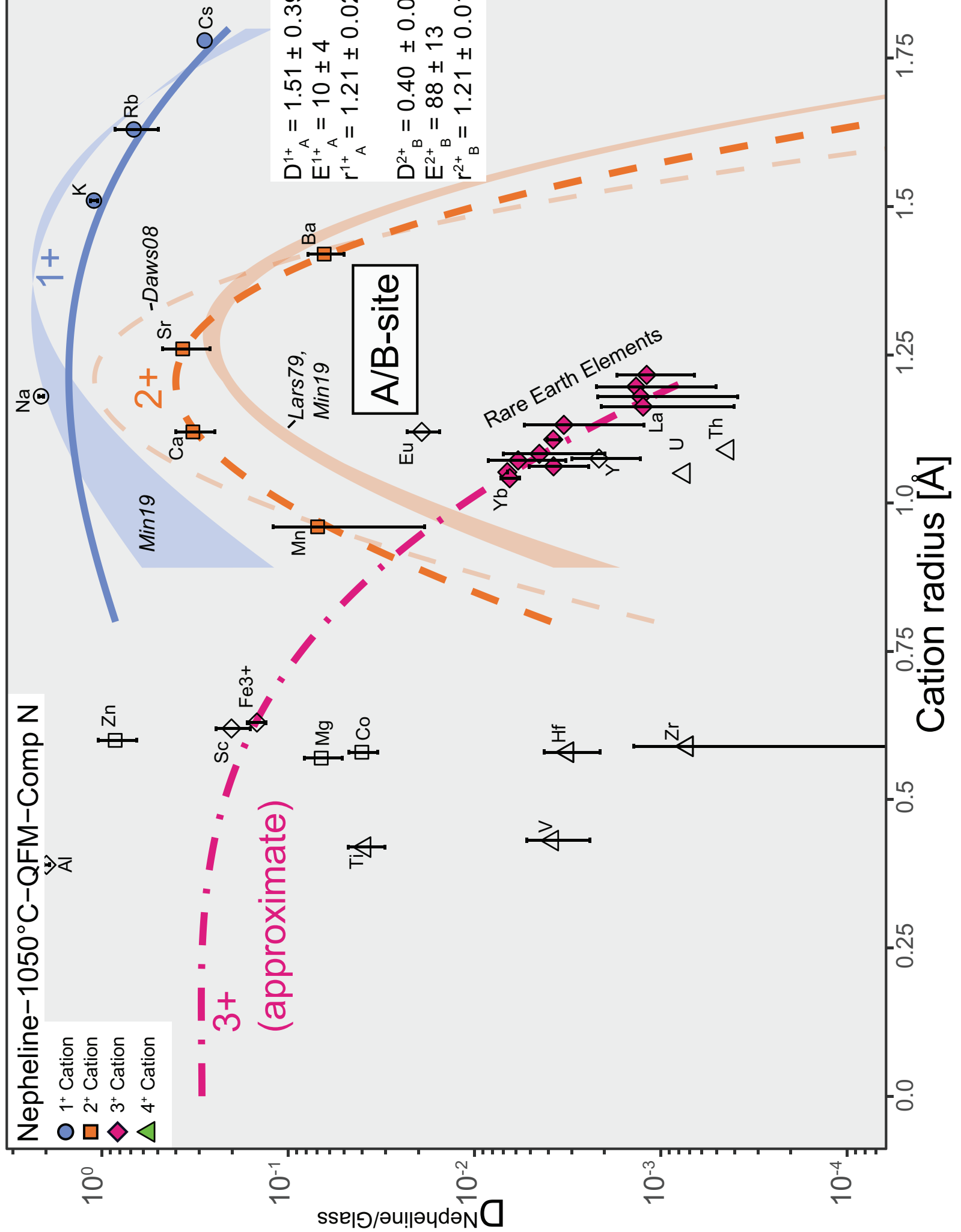
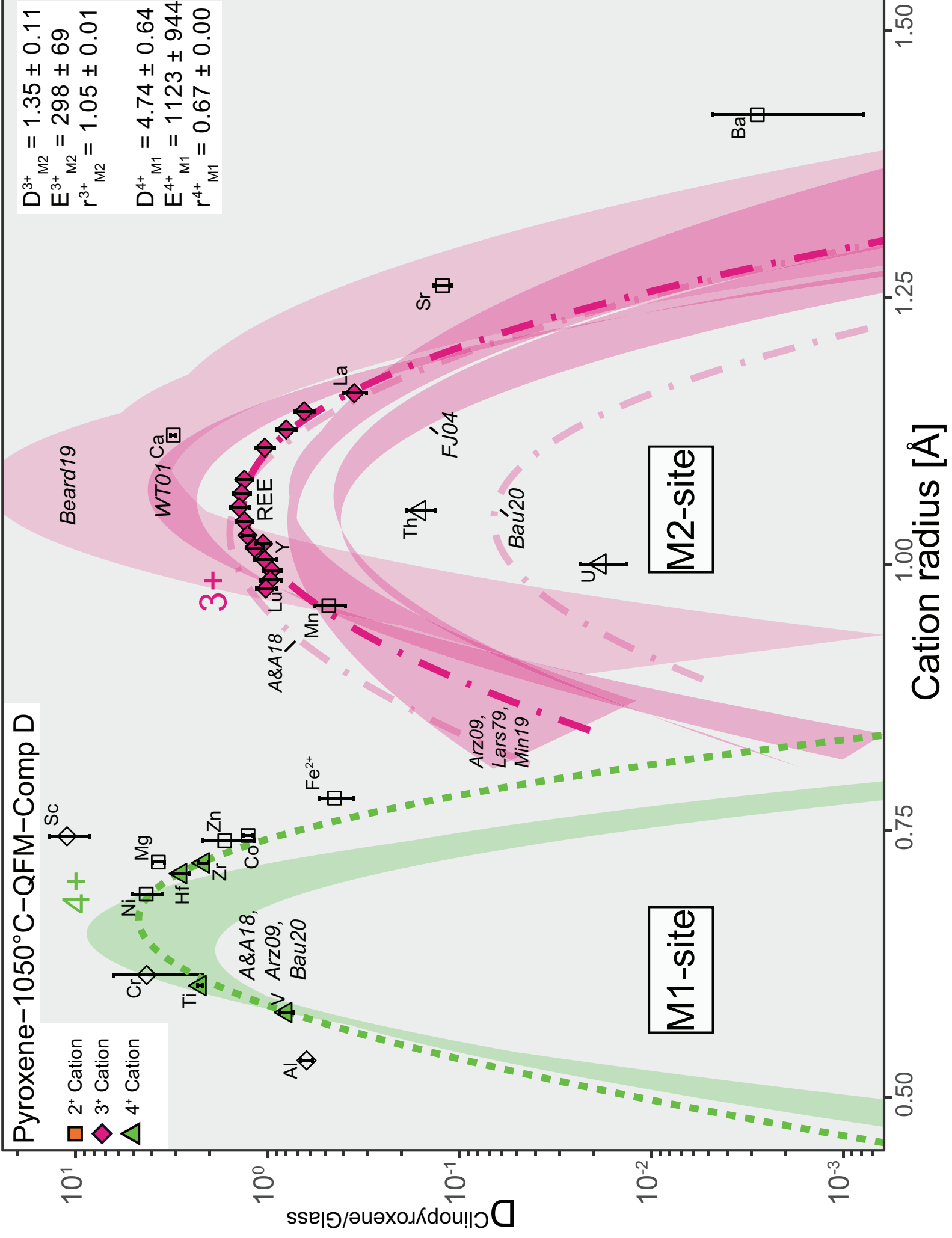


Figure 9

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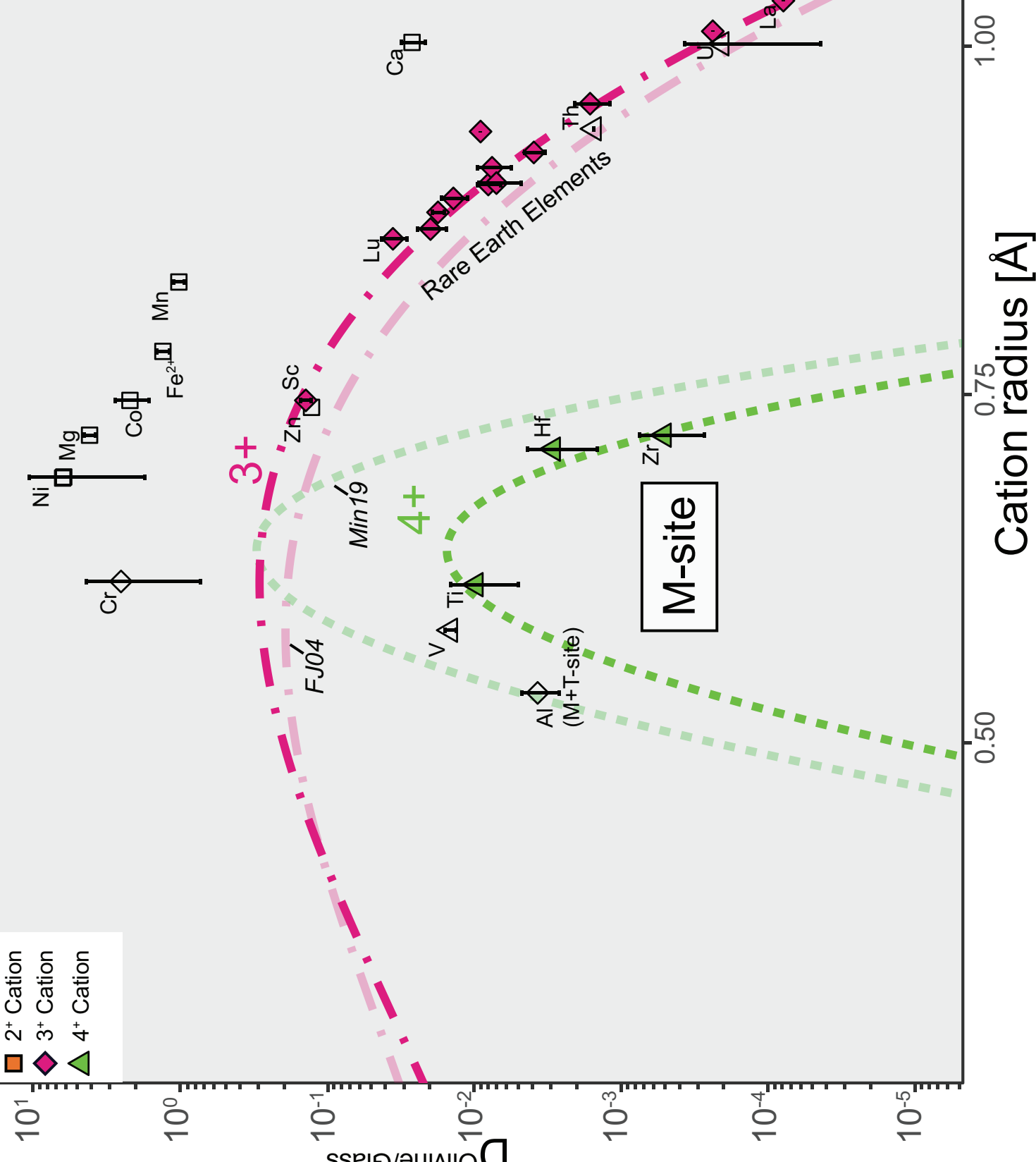




# Olivine-1200°C-QFM-Comp E

- 2+ Cation
- 3+ Cation
- 4+ Cation

$D_M^{3+} = 0.29 \pm 0.10$   
 $E_M^{3+} = 172 \pm 27$   
 $r_M^{3+} = 0.61 \pm 0.04$   
 $D_M^{4+} = 0.02 \pm 0.01$   
 $E_M^{4+} = 2207 \pm 230$   
 $r_M^{4+} = 0.64 \pm 0.00$



Cation radius [Å]

$D_{Olivine/Glass}$

# Rhönite-1050°C-QFM+1-Comp A

Figure 12

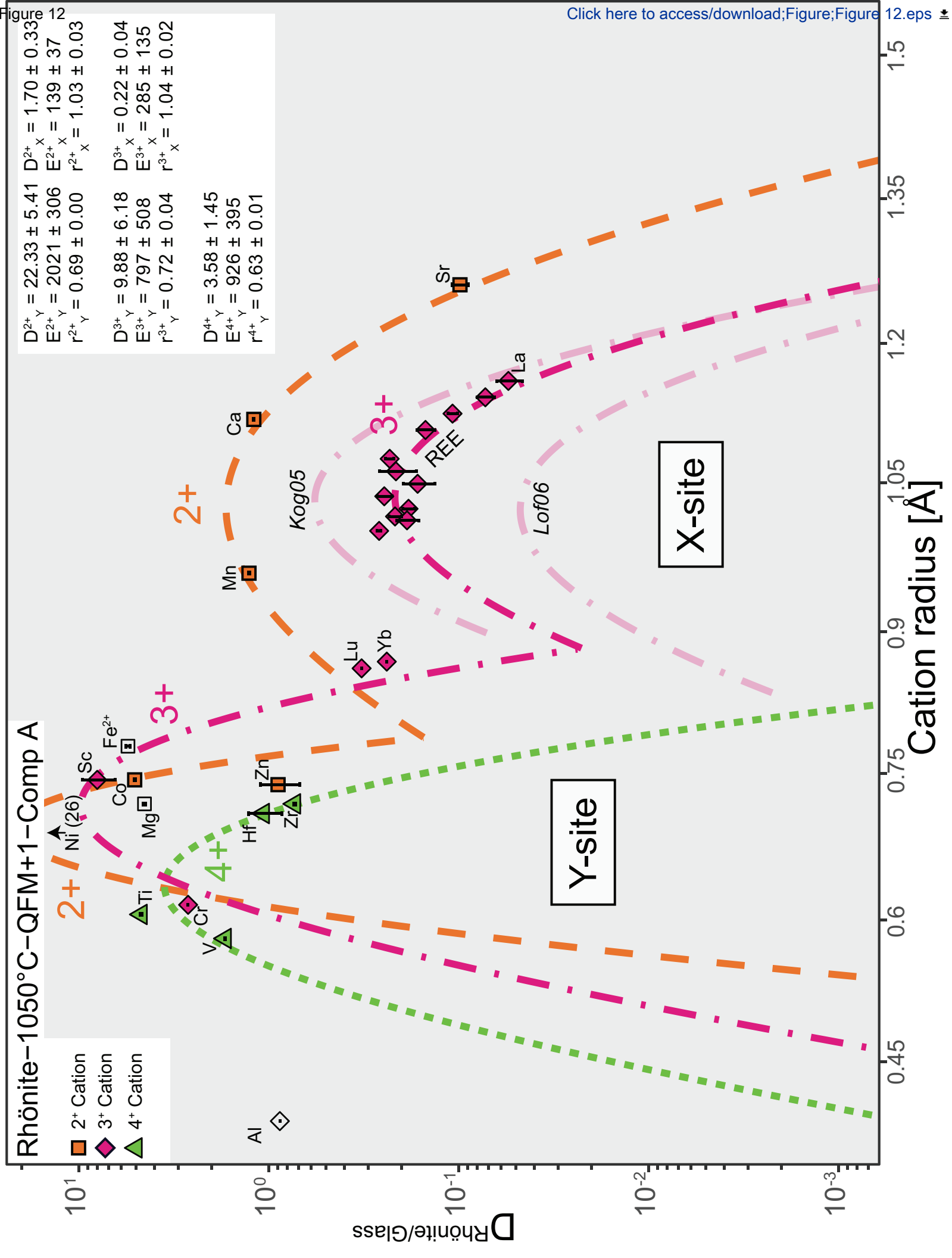
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$D^{2+}_Y = 22.33 \pm 5.41$	$D^{2+}_X = 1.70 \pm 0.33$
$E^{2+}_Y = 2021 \pm 306$	$E^{2+}_X = 139 \pm 37$
$r^{2+}_Y = 0.69 \pm 0.00$	$r^{2+}_X = 1.03 \pm 0.03$
$D^{3+}_Y = 9.88 \pm 6.18$	$D^{3+}_X = 0.22 \pm 0.04$
$E^{3+}_Y = 797 \pm 508$	$E^{3+}_X = 285 \pm 135$
$r^{3+}_Y = 0.72 \pm 0.04$	$r^{3+}_X = 1.04 \pm 0.02$
$D^{4+}_Y = 3.58 \pm 1.45$	
$E^{4+}_Y = 926 \pm 395$	
$r^{4+}_Y = 0.63 \pm 0.01$	

- 2+ Cation
- 3+ Cation
- 4+ Cation

Y-site

X-site



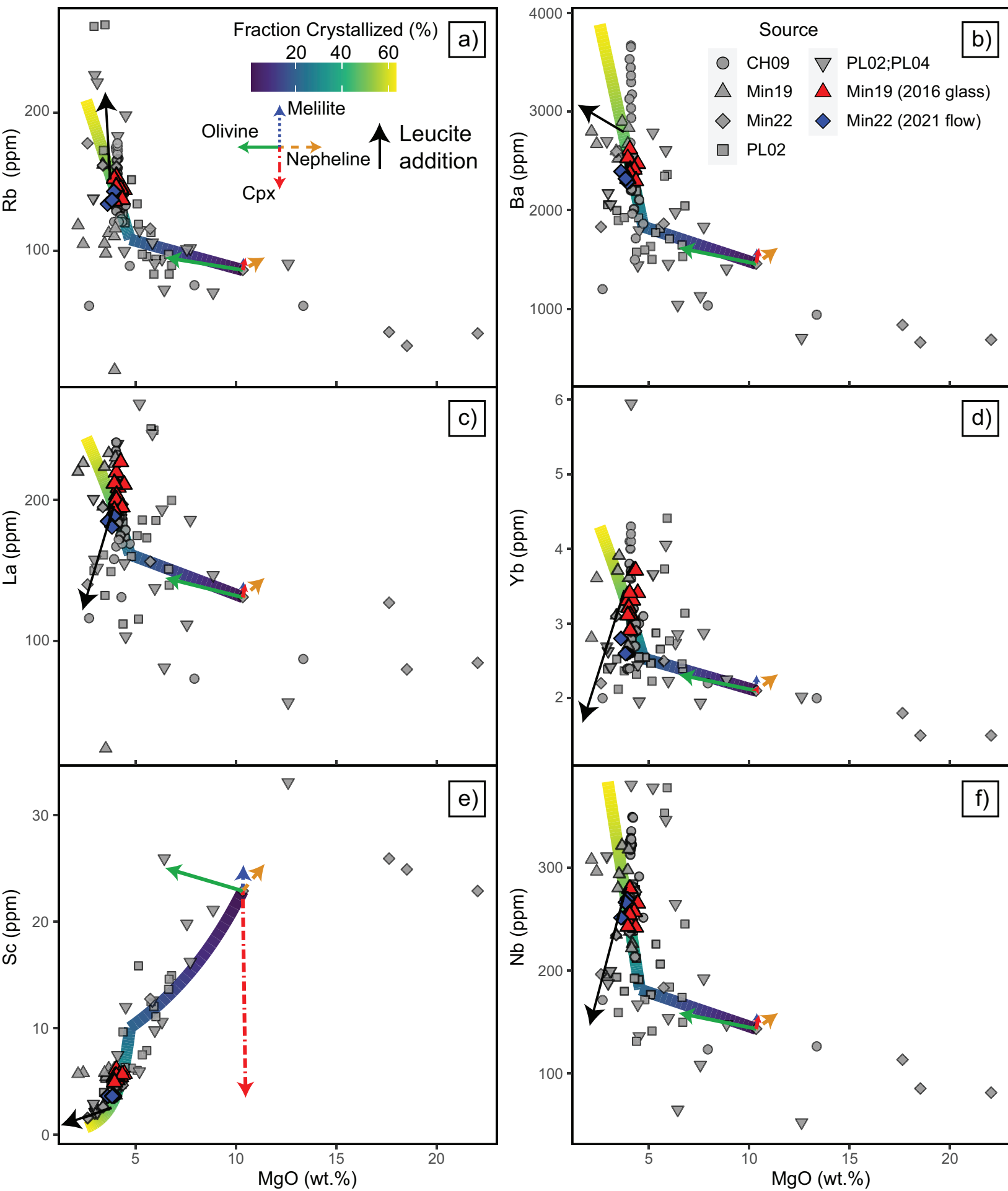
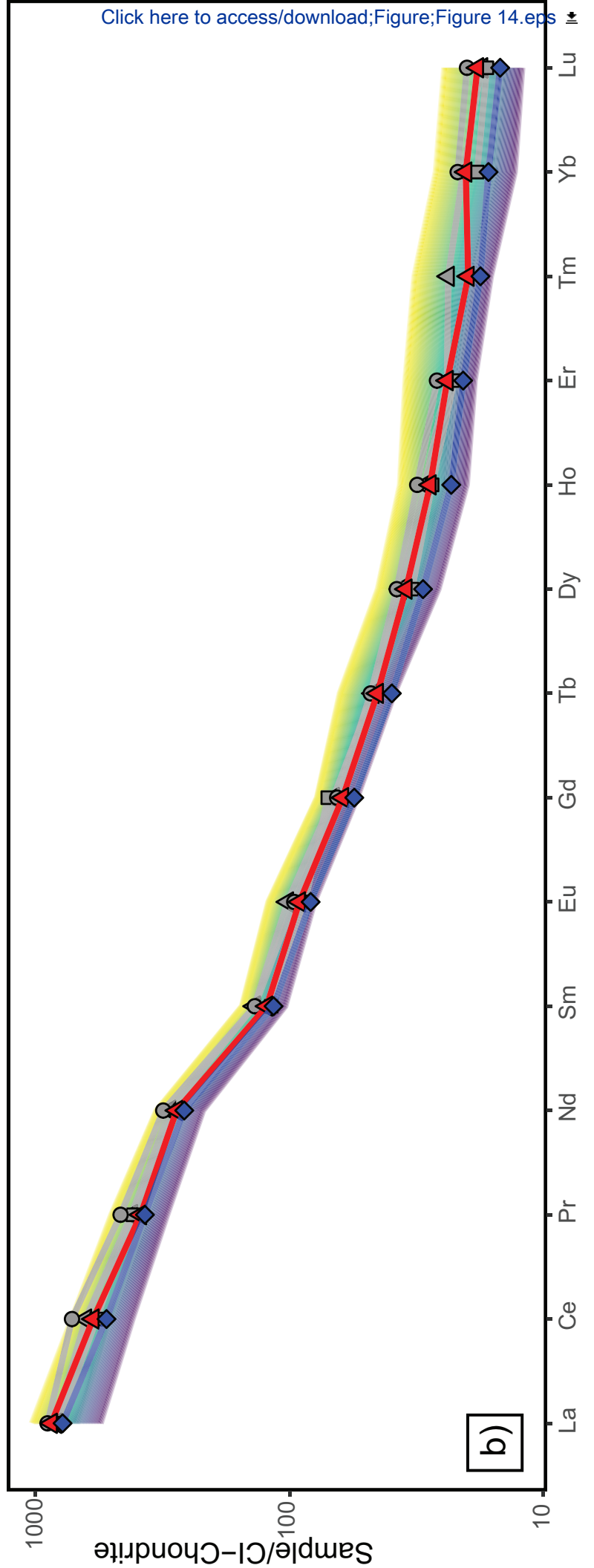
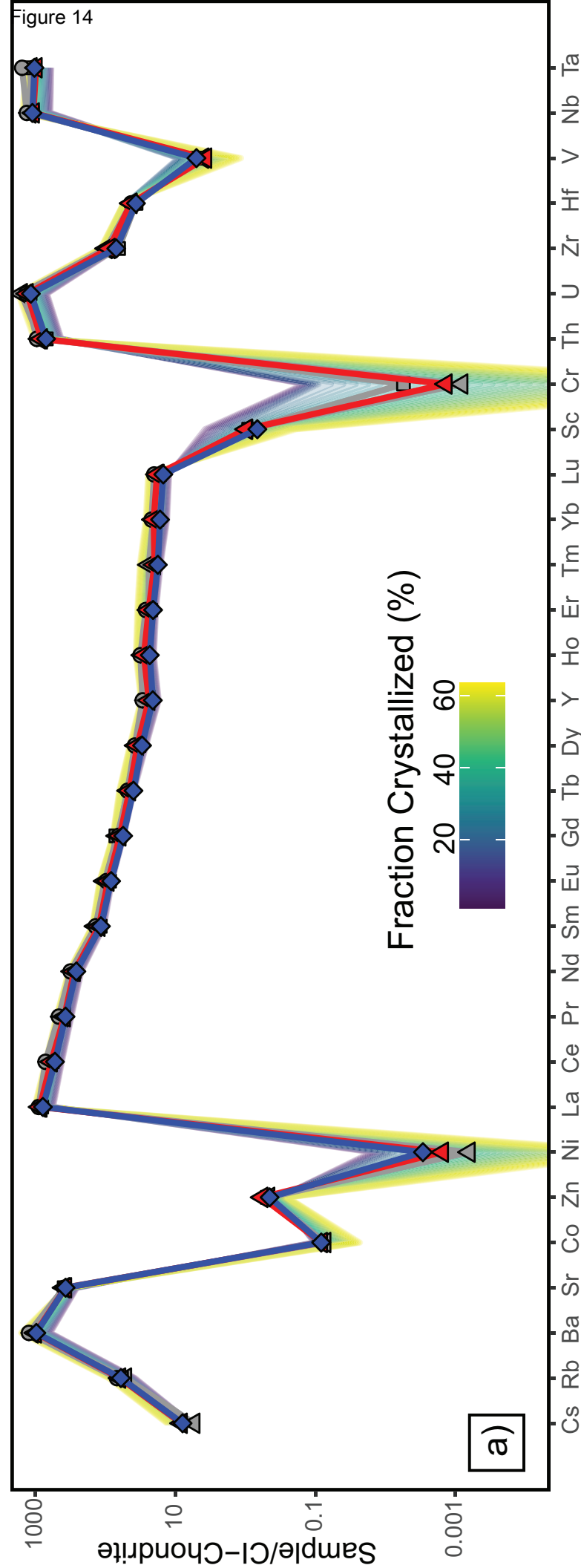


Figure 14

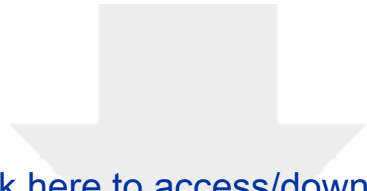


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