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1 Iron and silicon isotope fractionation in silicate melts using first-principles molecular dynamics.

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11
12
13 **ABSTRACT**

14
15 The direct determination of silicate melts iron and silicon isotopes signature remains a major challenge
16 of high-temperature isotope geochemistry. For this reason, melts are often approximated by silicate
17 glasses. Calculation of precise equilibrium Si and Fe isotopes fractionation factors between minerals
18 and melt would indeed allow us to distinguish equilibrium fractionation from diffusion-driven kinetic
19 fractionation involved in the iron and silicon isotopes signatures of Earth and other planets. In this
20 study, we use for the first time, first-principles molecular dynamics based on density functional theory
21 to determine iron and silicon isotope compositions of different silicate melts, namely: iron-rich basalt,
22 iron-depleted basalt, basanite, trachyte and phonolite. The ⁵⁷Fe/⁵⁴Fe reduced partition function ratios
23 (β -factors) of the different melts span over a 1.1 ‰ range at 1000 Kelvin (K) while ³⁰Si/²⁸Si β -factors
24 are much less influenced by the melt composition with a 0.5 ‰ fractionation range at the same
25 temperature. The main parameter controlling iron isotope fractionation in silicate melts having similar
26 iron oxidation state is, after temperature, the average Fe-O bond length. The chemical environment
27 around iron (e.g. Fe-Fe distances) is suggested to contribute to Fe isotope fractionation as well. Silicon
28 isotopes fractionation seems also affected, but to a lesser extent, by its local chemical composition
29 with decreasing Si-Fe distances leading to slightly higher Si β -factor in the melt. From these melts Fe
30 and Si β -factors, a new set of equilibrium fractionation factors between a variety of minerals and melts
31 has been calculated. These new $\Delta^{57}\text{Fe}_{\text{min-melt}}$ and $\Delta^{30}\text{Si}_{\text{min-melt}}$ sets allow us to discuss whether processes
32 such as fractional crystallization, partial melting and diffusion could be responsible for the documented
33 Fe and Si isotopes variations in igneous rocks. Our results suggest that: 1) fractional crystallization may
34 explain at least part of the Fe and Si isotopic evolution during magmatic differentiation, for values up
35 to $\delta^{57}\text{Fe} = 0.65$ ‰ and $\delta^{30}\text{Si} = -0.1$ ‰, respectively, 2) partial melting of the upper mantle can produce
36 the Mid-Ocean Ridge Basalts (MORB) iron isotopes signature. Finally, we calculated that olivine at
37 equilibrium with a basaltic melt could display an iron isotope composition down to -0.1 ‰ for $\delta^{57}\text{Fe}$.
38 Hence, the lower isotopic compositions ($\delta^{57}\text{Fe} < -0.1$ ‰) observed in natural olivines are most likely
39 due to diffusion-driven kinetic fractionation.

40
41
42 **Keywords:** Density Functional Theory (DFT); Silicate melts; Isotope fractionation; Magmatic
43 differentiation

1- INTRODUCTION

Understanding the detailed structural properties of iron-bearing silicate melts as well as the behavior of the constituting cations remains one of the great challenges in geosciences and in the glass-making industry. Many experimental and theoretical studies on melts from simple composition to natural-like melts have been carried out showing that cations could be either network former or network modifier depending on the nature of the cations and their coordination number (CN) that are dependent also of pressure, temperature and redox state of the melt (McMillan, 1984; Oestrike et al., 1987; Stein and Spera, 1996; Gerlach et al., 1998; Rossano et al., 2000; Jackson et al., 2005; Guillot and Sator, 2007b; Guillot and Sator, 2007a; Karki, 2010; Angeli et al., 2011; Bauchy and Micoulaut, 2011; Le Losq et al., 2014; Bajgain et al., 2015; Karki, 2015; Kim et al., 2016; Ghosh and Karki, 2018; Caracas et al., 2019; Solomatova and Caracas, 2019; Ghosh and Karki, 2020; Solomatova and Caracas, 2021). Silicon in melt is mostly four-fold coordinated and acts as the main network former of the melt structure. Despite the fact that silicon could be found as Si^0 in metallic inclusions of meteorites and planetary cores (Poitrasson, 2017), silicon is considered as only tetravalent in the upper mantle and crust of the Earth. Hence, silicon is not redox sensitive in terrestrial melts whereas iron is. Iron in melts has been assessed to behave differently in the melt depending on its redox state (Fe^{2+} or Fe^{3+}). At low pressure, ferric iron is most likely to be four-fold coordinated and acts as a network former, as Al^{3+} , whereas ferrous iron is five to six-fold coordinated and acts as a network modifier (see Mysen, 2006; Mysen and Richet, 2019 and references therein). However, the role of ferrous and ferric iron in melts is still debated as some studies demonstrated that both could be four to six-fold coordinated and therefore they could both act as network modifier (Ghosh and Karki, 2020). Recent study of Ghosh and Karki (2020) displayed indeed that iron redox state has limited impact on the general melt properties. In contrast, the iron spin state has more influence on the structural properties of the melt. Some uncertainties on the behavior of cations in the melt remain and, one of the major unknown so far is the isotopic properties of melts, including those of silicon (^{28}Si , ^{29}Si , ^{30}Si) and iron (^{54}Fe , ^{56}Fe , ^{57}Fe , ^{58}Fe).

Analytical developments and improvements over the past two decades enabled scientists to investigate non-traditional stable isotope fractionation at high-temperature. Several studies carried out on natural and experimental samples have revealed measurable ($> 0.05 \text{ ‰}$) silicon and iron isotopic fractionations in igneous systems: i) Iron and silicon display heavy isotope enrichment during magmatic differentiation, although the trends are different (e.g. Weyer et al., 2005; Williams et al., 2005; Poitrasson and Freydier, 2005; Shahar et al., 2008; Schoenberg et al., 2009; Savage et al., 2011; Sossi et al., 2012; Weyer and Seitz, 2012; Dauphas et al., 2014; Zambardi et al., 2014; Foden et al., 2015; Nebel et al., 2015; Poitrasson and Zambardi, 2015; Gajos et al., 2016; Williams et al., 2018; Li et al., 2020), ii) Oceanic crust (MORB and Ocean Island Basalts (OIB)) displays heavier iron isotope signature than some mantle peridotites (e.g. Williams et al., 2009; Williams and Bizimis, 2014; Konter et al., 2016; Sossi et al., 2016; Nebel et al., 2018), iii) There is significant iron isotopes fractionation, associated to Fe-Mg chemical zoning, within single crystals of olivine (Teng et al., 2011; Sio et al., 2013; Oeser et al., 2015; Collinet et al., 2017a; Sio and Dauphas, 2017; Prissel et al., 2018; Sio et al., 2018; Oeser et al., 2018). The potential processes involved in the documented isotopic variations, such as partial melting (e.g. Weyer and Ionov, 2007; Williams et al., 2009; Sossi et al., 2016; Deng et al., 2019), fractional crystallization (e.g. Schuessler et al., 2009; Sossi et al., 2012; Telus et al., 2012; Foden et al., 2015; Du et al., 2017), diffusion-driven kinetic fractionation (Lundstrom, 2009; Zambardi et al., 2014) or even fluid exsolution during late stage of differentiation (Poitrasson and Freydier, 2005; Heimann et al., 2008; Telus et al., 2012), were then investigated. However, interpretations of these observed isotopic variations are often limited by the lack of available equilibrium fractionation factors between coexisting phases, especially between minerals and silicate melts. Hence, the models used in the literature are under-constrained and precise quantification of the processes involved in Fe and Si isotopic fractionation in igneous rocks is hampered. It became then essential to obtain Si and Fe isotope compositions of various melts in order to quantify the processes associated to the isotopic variations in magmatic settings. By now, only few experimental and in-situ studies were carried out to obtain iron isotope composition of melts, using glasses as a proxy. Dauphas et al. (2014) displayed

96 significant variations in Fe isotope fractionation factors with varying composition of melts.
97 Nevertheless, the mechanisms involved in isotopic fractionation in melts are still under-constrained.
98 The degree of mass-dependent equilibrium fractionation between minerals has been associated to the
99 oxidation state (for Fe; e.g. Polyakov and Mineev, 2000; Dauphas et al., 2014), the bonding
100 environment (i.e. bond length and coordination number; e.g. Sossi and O'Neill, 2017), and the local
101 chemical environments of the atoms of interests (nature and number of the second neighbors; Macris
102 et al., 2015, Rabin et al., 2021). Grant (1954) and Poitrasson and Zambardi (2015) proposed
103 polymerization degree as a key factor influencing the Si isotope fractionation during magmatic
104 differentiation. However, at the mineral scale, this relationship does not seem to be the sole parameter
105 involved (Méheut and Schauble, 2014; Qin et al., 2016; Rabin et al., 2021). The mechanisms listed
106 above could play as well an important role on silicon and iron isotope fractionation in melts.
107

108 To investigate the mechanisms involved in melt isotope fractionation, we have calculated consistent
109 Si and Fe β -factors for various melt compositions using first-principles molecular dynamics (FPMD). In
110 this study, five silicic melt compositions were investigated in order to assess the effect of increasing
111 sodium, iron and silicon contents on the Si and Fe isotope composition of melts at 1 GPa. The pressure
112 effect on isotope fractionation is also explored through a FPMD basalt simulation at 12 GPa. Our
113 calculated Si and Fe β -factors for melts were combined to the set of Fe and Si β -factors of silicate and
114 oxide minerals calculated by Rabin et al. (2021) and Qin et al. (2016) to obtain a full set of equilibrium
115 fractionation factors between minerals and melts of various compositions. These data enable us to
116 discuss the impact of equilibrium fractionation, through different processes such as fractional
117 crystallization and partial melting, on Fe and Si isotopes systematics in igneous contexts.
118

119 2- METHODOLOGY

120 2.1- Modelling approach

121 The structure properties as well as the reduced partition function ratios of each melt were obtained
122 from FPMD simulations based on density functional theory (DFT). All calculations were performed
123 using the Perdew-Burke-Ernzerhof (PBE) parametrized generalized gradient approximation (GGA)
124 functional (Perdew et al., 1996) implemented in the Vienna Ab-initio Simulation Package (VASP; Kresse
125 and Furthmüller, 1996). The interaction between the valence and core electrons were modelled using
126 the projector-augmented wave (PAW) method (Kresse and Joubert, 1999). Plane-wave cutoff of 500
127 meV and Brillouin-zone sampling at Gamma are used. The simulation cell of each system is constrained
128 to a cube (Table 1). The design of the different melt structures in this study was conducted in 3 steps:
129 i) A primary melt structure including 4 compounds (MgO, CaO, Al₂O₃, SiO₂) was generated using
130 classical molecular dynamics (MD) simulations, for few nanoseconds, based on DL-POLY code (Smith
131 et al., 2002) and using empirical potentials proposed by Matsui (1994). ii) Substitution of some Mg
132 atoms by Fe, some Ca atoms by Na or K was then performed in order to reach the desired melt
133 compositions. iii) The structure thereby created was used as starting composition for the FPMD
134 simulations. The structure was first equilibrated at high temperature (well above the melting point, >
135 6000 K) using NVT canonical ensemble (fixed number of atoms N, constant volume V and constant
136 temperature T) and then cooled down to a desired lower temperature (4000 K). A temperature of 4000
137 K was settled in order to preserve the liquid state of the melts during the MD simulations (e.g. Bajgain
138 et al., 2015; Ghosh and Karki, 2018; Caracas et al., 2019). Once the system was at the desired
139 temperature, the isothermal-isobaric ensemble NPT (fixed number of atoms N, constant pressure P
140 and constant temperature T) with variable-cell dynamics was used, for few picoseconds (ps) to
141 optimize the cell parameters of each different melt composition (Table 1). The volume of the melt is
142 indeed a key parameter as the liquid structure is primarily a function of volume, rather than pressure
143 (Karki, 2010). Then, NVT canonical ensembles were used to explore the effect of the various liquid
144 compositions, as well as the pressure effect, on iron and silicon isotopic properties. Both NPT and NVT
145 ensembles used Nosé thermostats (with a Nosé mass-parameter of 3; Nosé, 1984). Each system
146
147

148 contains at least 100 atoms in order to have a simulation cell large enough to calculate equilibrium
149 properties (Karki, 2010). To confirm that 100-atoms simulation cells were sufficient to describe the
150 short- and medium-range properties of the silicate melts, a calculation on a 183-atoms simulation cell
151 was also performed. The duration of the FPMD NVT simulation is also a critical parameter in order to
152 satisfy the ergodicity principles (i.e. the system explores all the possible states of the system, with the
153 same probability as in a liquid, during the simulation time). Therefore, the simulations were carried on
154 for approximately 20 picoseconds in order to acquire representative ensemble at the desired
155 temperature (Bajgain et al., 2015). Analysis of the mean-square displacements (MSD) as a function of
156 time (Allen and Tildesley, 1989) were performed for each temperature-volume-composition condition,
157 in order to confirm that the system stays in the liquid state (Appendix A -Supplementary material, Fig.
158 S1 to S7).

159
160 The mean pressure applied during the simulations is chosen to be around 1 GPa (corresponding to a
161 crustal depth of ~35 km), in order to reproduce the pressure conditions of deep magmatic chambers
162 such as in Montagne Pelée (Pichavant, 2002) or Iceland (Kelley and Barton, 2008). Moreover, partial
163 melting happens at pressures between 1 and 3 GPa (e.g. Bertka and Holloway, 1994). The exact mean
164 pressures of each melt are displayed in Table 1 and more detailed analysis of pressure evolution during
165 the MD simulations are available in the Appendix A - Supplementary material, Fig. S8.

166
167 The melts simulated here are composed of 7 to 8 chemical elements (Na, Ca, K, Fe, Mg, Al, Si, O) in
168 order to reproduce faithfully natural melt compositions. Three calc-alkaline melts (iron-rich (IR) basalt,
169 iron-depleted (ID) basalt and trachyte), and two peralkaline melts (basanite, phonolite) were studied
170 in order to assess the isotopic evolution of the melt through differentiation (increasing SiO₂ content)
171 as well as the effect of alkaline content in the melts on iron and silicon isotopic fractionation. Rhyolitic
172 melt was not modelled in this study, despite being of high interest as it is expected to display heavier
173 iron isotopes composition than basalt (e.g. Dauphas et al., 2014; Roskosz et al., 2022). The low iron
174 content of such melt would require a simulation cell larger than the ones used here, which is out of
175 our calculation capacity. The melts compositions are displayed in Table 2. Ghosh and Karki (2020)
176 showed that iron spin state configuration is a major parameter that influences greatly (> 15 %) the
177 structural parameters of the melt. In our study, iron atoms are set up in high spin-state because it is
178 known that iron is predominantly in high-spin states in glasses and melts at pressures relevant to crust
179 formation (Mysen and Richet, 2019b and references therein). The Hubbard U term was not added to
180 the DFT calculation as previous studies showed that there are no significant changes in terms of Fe
181 local environment and melts properties (spin and valence state) between GGA and GGA+U calculations
182 in liquid systems where Fe is in high-spin state, especially at high temperature (e.g. Karki et al., 2018;
183 Caracas et al., 2019; Solomatova and Caracas, 2019; Ghosh and Karki, 2020). All iron atoms in the melts
184 were set up as Fe²⁺, in order to be closer to natural Fe³⁺/Fe_{tot} composition as MORB displays Fe³⁺/Fe_{tot}
185 of about 0.09 ± 0.2 (Bézos et al., 2021) and OIB of about 0.2 (Cottrell and Kelley, 2014). The Born-
186 effective charge tensors that represent the first-order response of the atomic positions to an electric
187 field, were obtained for iron through VASP in order to control the valence of iron in each melt
188 simulation.

189
190 In addition to melt simulations, first-principles calculations are performed on two silicate minerals
191 (Appendix A - Supplementary material, Table S1), using the same GGA-PBE functional and PAW
192 pseudo-potentials as described above. These silicate minerals, already studied in Rabin et al. (2021),
193 are aegirine (FeNaSi₂O₆) and forsterite (Fe_{0.25}Mg_{1.75}SiO₄). The only purpose of these calculations is to
194 assess the potential bias related to the use of different pseudo-potentials on the Fe and Si β-factors of
195 silicate minerals. This will allow us to provide a more accurate set of fractionation factors between
196 silicate minerals and melts using mineral data from Rabin et al. (2021).

197 198 **2.2- Calculation of equilibrium isotope fractionation factors**

199

200 The equilibrium isotope fractionation factor $\alpha_{(a,b,Y)}$ of an element Y between two phases a and b is
 201 defined as:

$$202$$

$$203 \quad \alpha_{(a,b,Y)} = \frac{\beta_{(a,Y)}}{\beta_{(b,Y)}} \quad \text{Eq. (1)}$$

204 where $\beta(a,Y)$, called β -factor, is the reduced partition function ratio between phase a and a perfect
 205 gas of Y atoms. The usual notation of isotope fractionation, in permil (‰), is written $10^3 \ln \beta(a,Y)$. The
 206 isotope fractionation factor is therefore expressed as $10^3 \ln \alpha(a,b,Y) = 10^3 \ln \beta(a,Y) - 10^3 \ln \beta(b,Y) \approx \Delta_{a-b} =$
 207 $\delta_a - \delta_b$. The notations δ_a and δ_b , used in laboratory studies, represent the isotopic compositions of
 208 coexisting phase a and b and are expressed as, in the case of iron:
 209
 210

$$211 \quad \delta^{57}Fe \text{ (‰)} = \left(\frac{\left(\frac{{}^{57}Fe}{{}^{54}Fe} \right)_{sample}}{\left(\frac{{}^{57}Fe}{{}^{54}Fe} \right)_{standard}} - 1 \right) \times 1000 \quad \text{Eq. (2)}$$

212
 213 The reduced partition function ratios of the melts were calculated in this study using two different
 214 methods referred to as the “snapshot” method and the velocity auto-correlation function, “VAF”
 215 method.
 216

217 2.2.1- The “snapshot” method

218
 219 The molecular dynamics trajectories are constituted of up to 40 000 time-steps ($\Delta t = 0.5$ fs). In order
 220 to obtain the β -factor of each melt, a number of snapshots are extracted from the trajectory, at regular
 221 time interval, large enough to consider the snapshots as independent from each other. Then, each
 222 snapshot structure is relaxed to their equilibrium structure at $T = 0$ K and a finite pressure of 1 GPa,
 223 until the residual forces on atoms are less than 10^{-4} Ry/au, and the residual pressures smaller than
 224 0.002 GPa. Hence, the equilibrated structure does not correspond anymore strictly to a melt but rather
 225 to a glass. The “frozen phonon” approach is then used to determine the dynamical matrix for each
 226 snapshot: 1) Phonopy code (Togo and Tanaka, 2015) is used to generate the 6N (N = number of atoms
 227 in the simulation cell) configurations corresponding to each atomic displacement in the three
 228 dimensions (3N in the positive axis, 3N in the negative axis as it is a glass without symmetry). 2) self-
 229 consistent field (scf) calculations are then performed on each configuration using VASP. 3) Post-
 230 treatment is performed with Phonopy to obtain the dynamical matrix that is subsequently diagonalized
 231 for the two atomic masses of interest in order to obtain the vibrational frequencies for both
 232 isotopologues. The reduced partition function ratio is finally calculated from these vibrational
 233 frequencies (Bigeleisen and Mayer, 1947):
 234
 235

$$236 \quad \beta(a,Y) = \left[\prod_{i=1}^{3N_{at}} \frac{\nu_i}{\nu'_i} \frac{e^{-\frac{h\nu_i}{2k_b T}}}{1 - e^{-\frac{h\nu_i}{k_b T}}} \frac{1 - e^{-\frac{h\nu'_i}{k_b T}}}{e^{-\frac{h\nu'_i}{2k_b T}}} \right]^{1/N} \quad \text{Eq. (3)}$$

237
 238 where, ν_i and ν'_i are the vibrational frequencies of the two isotopologues (the prime symbol refers to
 239 the light isotope of the element Y), identified by a branch index i from 1 to $3N_{at}$; N_{at} is the number of
 240 atoms in the simulation cell containing N atoms of the element Y; h is the Planck constant, k_b is the
 241 Boltzmann constant, and T the temperature (in Kelvin). Equation (3) takes into account that there
 242 should be no isotopic fractionation at the high-temperature limit (i.e. the “Redlich-Teller” rule, Redlich,
 243 1935).
 244

245 In order to obtain accurate and precise Si and Fe β -factors for each melt, “frozen phonon” calculations
 246 were performed on 6 to 10 snapshots per FPMD simulation. The snapshot β -factors are then averaged
 247 in order to obtain a mean β -factor for each melt and the uncertainties associated correspond to the
 248 standard error of the mean β -factor. In this method, the interatomic force constant (F) can be
 249 calculated from the dynamical matrix by averaging the force constants of the atom of interest (Fe or
 250 Si) in the three spatial dimensions x,y,z. The number of snapshots is large enough as shown by the
 251 cumulative mean of the β -factor and Fe force constant (Appendix A - Supplementary material, Fig. S9).
 252

253 The same methodology based on the vibrational frequencies was used to calculate the β -factors of the
 254 two minerals, except that only 3N configurations were generated by Phonopy, because of crystal
 255 symmetry.
 256

257 2.2.2 - The “VAF” method

258
 259 The “snapshot” method described above is a tried-and-tested method, especially for solvated species
 260 (Kowalski and Jahn, 2011; Dupuis et al., 2015; Pinilla et al., 2015; Ducher et al., 2018) but the resultant
 261 β -factor does not strictly correspond to a liquid but rather to a glass as the atomic positions are relaxed
 262 at T = 0 K prior to the calculation of the β -factor. Another approach that allows to keep the
 263 temperature effect and the liquid properties (i.e. configurational disorder as well as possible
 264 anharmonic effects), is a method based on the kinetic energy of the atoms during the simulations
 265 following the thermodynamic perturbation theory (Landau and Lifshitz, 1980) where the β -factor is
 266 expressed as:
 267

$$268 \ln\beta_{AX} = \frac{m - m'}{m} \left(\frac{K}{RT} - \frac{3}{2} \right) \quad \text{Eq. (4)}$$

269
 270 where K is the kinetic energy of the element of interest and can be calculated from the partial
 271 vibrational density of state (VDOS) noted $g(e)$:
 272

$$273 K = \frac{3}{2} \int_0^{e_{max}} E(e/k_B T) g(e) de \quad \text{Eq. (6)}$$

274
 275 In equation 6, e_{max} is the maximum energy of the vibrational spectrum, and $E(e/k_B T)$ is the Einstein
 276 function of the vibrational energy of a single harmonic oscillator at frequency $\nu = e/h$, expressed as:
 277

$$278 \frac{E(e/k_B T)}{k_B T} = \frac{e/k_B T}{\exp(e/k_B T)} + \frac{e}{2k_B T} \quad \text{Eq. (7)}$$

279
 280 Here, the VDOS, $g(e)$, is obtained from the Fourier transform of the velocity auto-correlation function
 281 (VAF) thermodynamically averaged over all atoms (Meyer and Comtesse, 2011):
 282

$$283 g(e) = \int_{-\infty}^{\infty} dt \frac{\sum_{i=1}^N \langle V_i(t) | V_i(0) \rangle}{\sum_{i=1}^N \langle V_i(0) | V_i(0) \rangle} e^{i2\pi\nu t} \quad \text{Eq. (8)}$$

284
 285 where V_i is the velocity of the i-th atom.
 286

287 In this method, the interatomic force constant can also be retrieved from the VDOS, using the following
 288 equation (e.g. Dauphas et al., 2012) :
 289

$$290 \langle F \rangle = \frac{m}{\hbar^2} \int_0^{+\infty} g(e) e^2 de \quad \text{Eq. (9)}$$

291 In this study, the “VAF” method is applied on 10 000 time-steps trajectories (5 ps), enabling us to obtain
 292 2 to 4 β -factors for each melt that are then averaged. Uncertainties are estimated as the 2-standard

293 error of this calculated mean. The “VAF” method was only applied on iron isotopes as iron can be a
294 network modifier, more likely to be affected by the transition liquid-glass (i.e. Fe-O coordination
295 number, Fe-O distance) compared to Si that is a network former.

296
297 The main limitation of using the VDOS to calculate the β -factor of a liquid is the fact that the VDOS
298 display a non-zero value at zero frequency due to diffusion effects. In principle, this diffusive
299 contribution should be removed before calculating the β -factor. Such corrections in complex silicate
300 melts would be difficult to achieve since it would require precise knowledge of the molar volume
301 contribution of each species in the melt. Furthermore, Pinilla et al. (2021) showed that these fluidity
302 effects were negligible in the calculation of equilibrium fractionation factor of iron in liquid $\text{Fe}_{x-1}\text{S}_x$
303 alloys. Therefore, such effects were neglected here.

304
305

306 3- RESULTS

307

308 3.1- Structural melt properties

309

310 The partial radial distribution functions (RDF) of the different atomic species pairs present in the
311 silicate melts were analyzed in order to determine the average interatomic distances as well as the
312 atomic coordination (Appendix A - Supplementary material, Fig. S10 to S16). The atomic coordination
313 (C) for a given species A with respect to another species B can be expressed as:

314

$$315 C_{AB} = 4\pi\rho_B \int_0^{r_{min}} r^2 g_{AB}(r) dr \quad \text{Eq. (9)}$$

316

317

318 where $g_{AB}(r)$ is the partial radial distribution function of the A-B atomic pairs and C_{AB} represents the
319 number of atoms of species B which lie within a spherical region of radius r_{min} centered around the
320 atom of species A.

321

322 The average cation-oxygen distances and CN are displayed in Table 3 and the results are described in
323 Appendix A - Supplementary material (under the heading “The structural properties of the melt”). The
324 results are generally consistent with previous molecular dynamics results performed at high
325 temperature (e.g. Guillot and Sator, 2007a; Bajgain et al., 2015; Ghosh and Karki, 2018; Caracas et al.,
326 2019; Ghosh and Karki, 2020; Feng et al., 2021; Solomatova and Caracas, 2021). The 183-atoms
327 simulation of the basalt_IR displays similar cation-oxygen coordination numbers (difference < 1.8%)
328 and cation-oxygen average bond lengths (difference < 1%) as the 100-atoms simulation (Table 3). This
329 allows us to confirm that 100-atoms simulations are large enough to discuss about the short- and
330 medium-range structural properties and therefore equilibrium isotopic properties.

331

332 Detailed analyses of iron and silicon environment in the different melts were performed by calculating
333 the average distance between Fe or Si and their first cation neighbors as well as the corresponding
334 coordination numbers (Table 4). The iron cationic neighbors are at a distance > 2.9 Å for all elements
335 and all melts, except in iron-rich melts where the average distance between two iron atoms can be as
336 low as 2.25 Å. Silicon is the most represented neighbor with an average Fe-Si coordination number
337 between 3.02 and 4.30. The other elements display a Fe-cation coordination number < 2, except for
338 Fe-Al coordination number in the phonolite (3.09). The silicon cationic neighbors are at a distance > 3
339 Å for all elements and all melts. The silicon close environment is more varied, with no clear preference
340 in term of nature of second neighbors (Si, Al, K). The average number of network formers (Si+Al)
341 around Si are always > 3.8 except for basalt_ID that has an average number of 1.87. This would suggest
342 that iron-depleted basalts (basalt_ID), unlike the other melts, cannot form a proper tetrahedral
343 network. This agrees with Guillot and Sator (2007a) conclusions.

344 The degree of polymerization is an important parameter that is directly associated to the composition
345 of the silicate melts. According to Mysen et al. (1985), a melt can be described in term of degree of
346 polymerization, designated as NBO/T where NBO represents the number of Non-Bridging Oxygen
347 atoms, and T stands for Tetrahedrally coordinated cations representing the network formers (Si and
348 Al in this study). These NBO/T ratios (Table 2) show that the more evolved melts such as trachyte and
349 phonolite (NBO/T = 0.28) are more polymerized than the basaltic melts (NBO/T=1).

350
351 The structural homogeneity of melts can be defined according to glass specialists using a simple
352 parameter characterizing the degree of occupation of the interstitial site $C=M/T$ (Kuryaeva, 2004),
353 where M represents the network- modifiers, and T the network formers. A melt structure is considered
354 homogeneous when $C < 0.27$. The melt heterogeneity is mostly driven by the total concentration of
355 alkali and alkali-earth metals oxides (Kuryaeva, 2004). In this study, melts are heterogeneous,
356 displaying C values ranging between 0.45 for phonolite and 0.67 for the calc-alkaline basalt_IR and
357 basalt_ID. This high degree of occupation of interstices is indeed favorable to individual structural
358 groupings in the melts (i.e. microheterogeneous structure). The heterogeneity of aluminosilicate
359 melts, caused by high content of sodium cations, leads to changes in the properties that are not
360 accounted for in the degree of polymerization calculation. This explains why there is no apparent
361 relationship between NBO/T and the Fe-O coordination number and unclear correlation with Si-O
362 coordination number (Appendix A - Supplementary material, Fig. S17).

364 3.2. Reduced partition function ratios of iron and silicon

365
366 The theoretical reduced partition function ratios have been calculated for iron and silicon. Their
367 temperature dependences are displayed in Fig. 2 as well as their corresponding polynomial fits in Table
368 5. As observed for minerals (Blanchard et al., 2017; Rabin et al. 2021), there is a linear correlation
369 between melt β -factor and their associated average interatomic force constant (Fig. 3). At 1000 K, the
370 $10^3 \ln \beta^{57}\text{Fe}/^{54}\text{Fe}$ for all melts span in a range of ~ 1.1 ‰ and the $10^3 \ln \beta^{30}\text{Si}/^{28}\text{Si}$ are within a range of \sim
371 0.5 ‰ (Fig. 2). The variation of Fe isotope compositions within melts are greater than the one observed
372 in silicate minerals whereas the variation of Si isotope compositions is twice larger in minerals relative
373 to melts (Compare Fig. 2 with Fig. 1 of Rabin et al., 2021). Phonolite, the most evolved peralkaline melt
374 displays the highest iron β -factors followed by the calc-alkaline iron-rich basalt (Basalt_IR) whereas
375 the calc-alkaline iron-poor basalt (Basalt_ID) displays the lowest iron β -factors. On the other hand, the
376 highest Si β -factor is found in trachyte, followed closely by phonolite.

378 3.2.1. "Snapshot" vs "VAF" method.

379
380 The Fe reduced partition function ratios were calculated using two methods: the "VAF" method and
381 the "snapshot" method (See Part 2.2). In the "snapshot" method the β -factors are extrapolated to
382 magmatic temperatures using Eq. (3) using the vibrational frequencies calculated at 0 K and $P = 1$ GPa.
383 On the other hand, β -factors determined by the "VAF" method are extrapolated from the MD run at
384 4000 K and $P \simeq 1$ GPa using Eq. (4). Results show that the "VAF" and "snapshot" methods give similar
385 force constants within uncertainties (Table 6) and therefore β -factors since both quantities are linearly
386 correlated (Fig. 3). This is consistent with the fact that the structures obtained with the "snapshot"
387 method are really similar to the ones from the "VAF" trajectories in terms of bond lengths,
388 coordination number and nature of Fe neighbors. The calculated uncertainties are twice larger with
389 the "VAF" method than using the "snapshot" methods, but uncertainties could be certainly reduced
390 by increasing significantly the duration of the simulations. Concerning phonolite, the discrepancy of
391 force constant between the "VAF" and "snapshot" methods associated to extremely large
392 uncertainties, notably for the former method, make the use of these results more difficult. It is clear
393 that phonolite tends to have heavier Fe isotopic values than the other melts. However, the Fe force
394 constant cannot be clearly quantified. This may be caused by the model itself of the phonolite melt
395 that contains only one Fe atom over the 102-atoms system which reduces significantly statistical

396 sampling. However, outside this exception, the similar Fe β -factors obtained by the “VAF” and the
397 “snapshot” methods allow to conclude that both methods are relevant to determine the isotopic
398 properties of a melt. This conclusion was previously reached by Pinilla et al. (2021) in the case of Fe-S
399 alloys at high pressure and temperature conditions. This also means that potential anharmonic effects,
400 that are at least partially taken in account with the “VAF” method, are negligible considering the
401 uncertainties obtained and that extrapolation of Fe β -factors at high temperature from force constants
402 obtained at low temperature is relevant (e.g. NRIXS and Lamb-Mössbauer measurements; Dauphas et
403 al., 2014; Roskosz et al., 2022). In the discussion and applications parts, the only results that will be
404 considered are the ones obtained from the “snapshot” method for clarity and consistency with Si
405 isotopes results.

406
407

408 *3.2.2 – Fractionation factors between minerals and melts.*

409

410 One of the major issues in determining the processes involved in iron and silicon isotope fractionation
411 during magmatic differentiation is the lack of equilibrium Fe and Si fractionation factors between
412 minerals present at magmatic temperatures (i.e. pyroxene, olivine, oxides...) and their associated
413 melts. In this study, we combine the Fe and Si β -factors of various minerals present in magmatic
414 setting, obtained from first-principles calculation (Rabin et al. 2021) with the present iron and silicon
415 β -factors of the melts in order to obtain a full set of equilibrium fractionation factors between minerals
416 and melts ($\Delta^{57}\text{Fe}_{\text{mineral-melt}}$ and $\Delta^{30}\text{Si}_{\text{mineral-melt}}$). The entire set of Fe and Si equilibrium fractionation factors
417 between minerals and melts, calculated after systematic bias correction (Appendix B- Supplementary
418 Data), is displayed in Table 7.

419

420 It is noticeable that most of the minerals display lighter iron and silicon isotope composition than the
421 different melts at equilibrium (Appendix B - Supplementary material). Only albite, anorthite, quartz
422 and fayalite that display heavier silicon isotopic relative to the different melts. Likewise, aegirine and
423 magnetite display heavier iron isotopic signature than basalt_ID, basanite and trachyte melts. As
424 expected, fayalite, with its low iron force constant ($F = 100 \text{ N/m}$), is the mineral that shows the greatest
425 iron isotope fractionation with the different melts, followed by aegirine, hedenbergite and augite
426 (Appendix B - Supplementary material).

427

428

429 **4- DISCUSSION**

430

431 **4.1 – Iron and silicon environment in the silicate melts.**

432

433 Our results on the iron and silicon structural properties allow us to discuss the iron and silicon
434 environment in the different investigated melt. As mentioned in part 3.1, silicon structural properties
435 are independent of the melt composition whereas iron is sensitive to the compositional change of the
436 melt.

437

438 The nature of the network former in the melt is one of the parameters investigated that have an impact
439 on iron atoms bonding-properties. We observe a linear relationship between Fe-O coordination
440 number and the $\text{Al}/(\text{Si}+\text{Al})$ ratio in melts as described in previous studies (Mysen et al., 2003). Phonolite
441 and basanite display the highest Fe-O coordination numbers that correspond to the highest $\text{Al}/(\text{Si}+\text{Al})$
442 ratio. Peralkaline undersaturated melts are indeed, by definition, depleted in silicon. The increasing
443 aluminum content as network former over silicon results in an increase of the coordination number of
444 all the network modifiers (Table 3) including the part of aluminum acting as network modifier (Fig. 1).

445

446 The iron effective charge in the investigated melts shows little variation (2.28-2.37) that cannot
447 be correlated to systematic changes in coordination number or Fe-O distances (Tables 2 and 3). This

448 agrees with the study of Ghosh and Karki (2020) showing that ferric and ferrous iron can have the same
449 coordination number in melts and that variations of iron effective charge in melts cause no significant
450 change of the structural properties of iron.

451
452 The structural heterogeneity of the melts, defined in part 3.1 as related to the abundance of
453 network modifiers, indicates the potential presence of individual structural groupings that could also
454 induce segregation of cations in the melts. Therefore, it is interesting to look at the nature and
455 distribution of the network modifier cations around iron and silicon (Table 4). Iron tends to favor iron
456 as its closest neighbor in melts when iron concentration is relatively high (basalt_IR, basanite; Table
457 4). The distribution of iron atoms as a next nearest neighbor (NNN) of another iron can be determined
458 by dividing the number of Fe NNN by the total number of its NNN's (i.e. CN_{Fe-Fe}/CN_{Fe-X} , with $X = Fe,$
459 $Ca, Na, Si, Mg,$ and Al , Rossano et al., 2000). In the case of a random distribution of cations in the
460 melt structure, this ratio is only dependent of the melt stoichiometry. For the basaltic melt (basalt_IR),
461 a random cation distribution model predicts a value of 0.1, while our FPMD simulation indicates a value
462 of 0.14. Concerning the basanite melt, a random distribution of iron in the melt corresponds to a value
463 of 0.12. FPMD basanite simulation gives a ratio of 0.14. These results suggest a slight segregation of
464 iron in the basanite and basalt_IR melts. Concerning silicon, unlike iron there is no systematic
465 preferences in term of the nature of second neighbors. The next nearest neighbor of silicon is
466 alternatively silicon itself, aluminum, potassium or even calcium.

467 468 **4.2 – Silicate glasses vs silicate melts.**

469
470 In many experimental studies, glasses are the only proxy for melts. When the melt quenching is fast
471 enough to avoid cation reorganization, then the glass structure associated is most likely to be close to
472 the melt one as observed with the snapshot method. A comparative study of MD simulation and
473 experimental glasses shows that cation-oxygen distances are slightly larger in glasses than in melts
474 even if the structure properties are very similar (Rossano et al., 2000). Feng et al. (2021) exhibited
475 notable structural changes (i.e. density) between the basaltic glass and its molten counterparts,
476 especially at low pressure. Ghosh et al. (2021) also pointed out that the effects of temperature on the
477 Fe-O coordination is not negligible, with a silicate glass at 300 K displaying Fe-O coordination of 4.5
478 whereas melt at 3000 K have a Fe-O coordination of 3.7. In the case of isotopic variation between melts
479 and glasses, this question has not really been assessed. As stated in the methods section, the “VAF”
480 method takes into account all features of the melt system whereas the “snapshot” method involves a
481 relaxation of atomic positions at zero temperature. Both methods give similar β -factors. However, it
482 is noteworthy that this computational structural relaxation does not mimic exactly the quench of a
483 glass that is inevitably slower. Many studies observed that the coordination number of an element is
484 a parameter that will affect its isotopic signature in a material (e.g. Polyakov and Mineev, 2000;
485 Méheut et al., 2009; Sossi and O’Neill, 2017; Rabin et al., 2021). Therefore, it is possible that silicate
486 glasses are not an ideal proxy for melts, as glasses display significantly higher coordination numbers
487 and therefore will underestimate the melts β -factor.

488 489 490 **4.3 – Iron isotope fractionation in melts.**

491 492 *4.3.1 – Parameters controlling Fe isotope fractionation.*

493
494 In silicate minerals, the main parameters involved in iron isotope fractionation, besides temperature,
495 are the oxidation state of iron, i.e. Fe^{3+}/Fe_{tot} (Polyakov and Mineev, 2000; Shahar et al., 2008; Dauphas
496 et al., 2014), the Fe-O bond length, the Fe-O coordination number (Sossi and O’Neill, 2017) and the
497 number and nature of iron second-neighbors (Macris et al., 2015; Rabin et al., 2021). All these
498 parameters are also expected to have an impact on melt iron isotope composition. However, the

499 importance of a parameter over another can change due to the structural differences between melts
500 and minerals. Furthermore, the range of Fe β -factors within those melts is greater than what was
501 observed in silicate minerals (Compare Fig. 2 with Fig. 1 of Rabin et al., 2021).

502
503 The first important observation from these FPMD simulations is that the variations in Fe-O
504 coordination number (from 3.7 to 4.7) does not seem to be correlated to the iron force constants (Fig.
505 4a). Trachyte that has a Fe-O coordination number of 3.74, displays a similar force constant $\langle F \rangle$ (191
506 ± 20 N/m) as basanite (196 ± 13 N/m) that has a Fe-O coordination number of 4.73. The second main
507 observation is the iron force constant dependency on Fe-O distances (Fig. 5a). The basalt_IR has the
508 highest Fe force constant (243 ± 17 N/m) associated to the shorter Fe-O bond length (1.76 \AA). This is
509 consistent with the study of Sossi and O'Neill (2017) that shows that the silicate minerals with the
510 shorter Fe-O bonds tend to be enriched in heavy ^{57}Fe .

511
512 Dauphas et al. (2014), revised by Roskosz et al. (2022), demonstrated that there is a relationship
513 between iron force constant and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ in silicate glasses produced under different level of oxygen
514 fugacity (Fig. 6) with the glasses synthesized under high oxidizing condition displaying the highest Fe
515 force constant. They also demonstrated that Fe^{2+} -glasses ($\log(f\text{O}_2) = -8$) have large variations of iron
516 force constant (from 188 ± 7 up to 251 ± 10 N/m) depending on their SiO_2 content. This range is
517 relatively similar to the one observed in our study (from 171 ± 8 up to 243 ± 17 N/m), however no
518 relationship between SiO_2 content and force constant is observed in our study given the silica range
519 investigated (Fig. 6). In addition, Roskosz et al. (2022) also displayed iron mean force constant
520 variations in Fe^{2+} -rich melts with similar SiO_2 content. Therefore, the variation of Fe force constant in
521 melts with similar Fe^{2+} and SiO_2 content definitely means that iron isotope fractionation within silicate
522 melts cannot be uniquely explained in term of iron redox state or network-former concentration.

523
524 In addition to the lack of relationship between Fe force constant and SiO_2 content, there seems to be
525 no correlation between iron force constant and the melt polymerization parameter NBO/T (Fig. 7a).
526 However, there is a relationship between the Fe-Fe and Fe-Mg distances and iron force constants: a
527 decrease of these distances leads to higher iron force constant (Fig. 8c and d). This explains why
528 basalt_IR and basanite display higher force constant than the basalt_ID and trachyte (Table 6). This
529 suggests that, like for minerals (Macris et al., 2015; Rabin et al., 2021), the melts iron force constant
530 could be influenced by the Fe local environment. However, there is no clear relationship between
531 iron/magnesium concentration in the melts and the iron force constant (Fig. 9). Further investigations
532 are necessary to confirm and quantify the impact of the Fe local environment on the iron force
533 constant. Sodium cations might also play a role on iron isotope fractionation in melts even if there is
534 no direct relationship between Fe-Na distances or Na_2O and iron force constant (Figs. 8, 9). As
535 discussed in part 3.1.2, the content of sodium drives the structural heterogeneity of the melt, enabling
536 the observed segregation of cations around iron atoms. Roskosz et al. (2022) also suggested that melts
537 composition and more precisely the presence of K or Na cations leads to higher force constant. Here,
538 we do not observe a higher force constant in the trachytic melt where the concentration of K and Na
539 is relatively high. The major difference between this study and the one by Roskosz et al. (2022) is that
540 they used simplified melt compositions, therefore the variety of the iron second neighbors was
541 narrowed (Na or K and Fe itself). Furthermore, we display in the present study that neither Na nor K
542 cations are favored as Fe second neighbor in a natural-like melt where the composition is more
543 complex, except the highly alkaline melt (i.e. phonolite). Overall, our theoretical study agrees with
544 Roskosz et al. (2022) on the fact the nature of the cations in the melts, and most likely the nature of
545 the cations surrounding Fe atoms, seems to affect the iron force constant.

546
547 Hence, Fe isotope fractionation in melts appears mainly driven by the Fe-O bond length and by the
548 nature and number of the network-modifier cations around iron atoms.

549
550 *4.3.2 - Comparison between theoretical and experimental data*

551
 552 Dauphas et al. (2014) were the first to provide experimental iron β -factors of silicate terrestrial glasses
 553 of various compositions, as proxy of melts, using Nuclear Resonant Inelastic X-ray Scattering (NRIXS).
 554 In Fig. 6, iron force constant obtained by NRIXS (Dauphas et al., 2014) are compiled with our calculated
 555 ones. The range of iron force constants of their Fe²⁺-basaltic glasses (from 197 ± 8 N/m up to 292 ± 18
 556 N/m) are similar to our calculated iron force constants for Fe²⁺-basaltic melts at 1 GPa (between 171 ±
 557 8 N/m up to 243 ± 17 N/m), although their major element compositions are different. For the most
 558 evolved lavas, our trachyte iron force constant is consistent with that of Dauphas et al. (2014). They
 559 found no major increase in the iron force constant until late stage of magmatic differentiation (~ 70
 560 wt% of SiO₂) for the silica-saturated series. No measurement on silica undersaturated peralkaline
 561 glasses were performed which prevents us to compare our phonolite and basanite iron β -factor. Later,
 562 Prissel et al. (2018) determined iron force constants between 189 ± 9 and 203 ± 11 N/m for their
 563 synthetic lunar glasses using NRIXS that is undistinguishable from Dauphas et al. (2014) estimates for
 564 terrestrial basalts under IW fO₂ conditions (See Fig. 4 of Prissel et al., 2018) and lies within our range
 565 of values for terrestrial basalts. Dauphas et al. (2014) and Prissel et al. (2018) concluded at no Fe
 566 isotope fractionation between forsterite and melts of various planetary composition, including
 567 terrestrial since they have the same force constant. Our calculated fractionation factor between
 568 forsterite and the basalt with low iron content (Basalt_ID) $\Delta^{57}\text{Fe}_{\text{forsterite-basalt_ID}} = -0.01 \text{ ‰}$ at 1500 K agrees
 569 with such a conclusion. However, this study displays a fractionation factor between forsterite and the
 570 basalt with high iron content (FeO = 13.1 wt%) $\Delta^{57}\text{Fe}_{\text{forsterite-basalt_IR}} = -0.15 \text{ ‰}$ at 1500K. If the range of
 571 Fe force constant calculated for the melts is similar to the measured one for glasses (Prissel et al. 2018,
 572 Dauphas et al. 2014), our basaltic melt with high FeO content displays higher iron force constant than
 573 the basalt with elevated FeO contents investigated by Prissel et al. (2018). As we underlined in part
 574 4.3.1, multiple parameters tend to affect the iron force constant of the melts, including differences of
 575 compositions (e.g., the addition of titanium in the glasses studied by Prissel et al. (2018), although
 576 these authors did not see an effect on the Fe force constant). Also, our calculation does not take into
 577 account the possible effect of variable melt fO₂ (Part 2.1). Moreover, our forsterite Fe force constant
 578 calculated by DFT (162 ± 8 N/m) is also lower than the one obtained by NRIXS measurements (197 ±
 579 10 N/m; Dauphas et al. 2014).

580
 581 Other studies mainly focused on inter-mineral iron isotope fractionations (Polyakov and Mineev, 2000;
 582 Shahar et al., 2008; Dauphas et al., 2012; Macris et al., 2015; Roskosz et al., 2015; Sossi and O'Neill,
 583 2017) as measuring iron isotope composition of glasses in equilibrium with minerals is a great
 584 analytical challenge on natural and experimental samples. This is why there is only few data on iron
 585 isotope fractionation factor between silicate melts and minerals. However, $\Delta^{57}\text{Fe}_{\text{mineral-melt}}$ were
 586 assessed empirically in many studies performed on natural samples in order to model fractional
 587 crystallization and other related processes (e.g. Sossi et al., 2012; Sossi et al., 2016; Williams et al.,
 588 2018). Williams et al. (2018) determined a $\Delta^{57}\text{Fe}_{\text{melt-cpx}}$ of 0.15 ‰, based on the observed difference in
 589 mean Fe isotope composition between oceanic basalts and fertile mantle peridotites (Williams and
 590 Bizimis, 2014) with no indication of the temperature dependence. Assuming a temperature of 1000 K,
 591 our calculated $\Delta^{57}\text{Fe}_{\text{Basalt_ID-Augite}}$ and $\Delta^{57}\text{Fe}_{\text{Basalt_ID-Hedenbergite}}$ of about 0.12 ‰ as well as $\Delta^{57}\text{Fe}_{\text{Basalt_ID-Diopside}}$
 592 = 0.08 ‰ are only slightly lower than the empirically determined one. However, looking at iron-rich
 593 basalt, our calculated $\Delta^{57}\text{Fe}_{\text{Basalt_IR-Augite}}$ and $\Delta^{57}\text{Fe}_{\text{Basalt_IR-Hedenbergite}}$ of about 0.42 ‰ as well as our
 594 $\Delta^{57}\text{Fe}_{\text{Basalt_ID-Diopside}} = 0.38 \text{ ‰}$ appear significantly larger than the 0.15 ‰ value proposed by Williams et
 595 al. (2018). Depending on the iron content in the melt $\Delta^{57}\text{Fe}_{\text{cpx-melt}}$ can vary between 0.08 ‰ up to 0.42
 596 ‰ at 1000 K. This is why strong cautions need to be applied when using $\Delta^{57}\text{Fe}_{\text{melt-mineral}}$ to model iron
 597 isotope composition of natural samples. It is important to know the exact chemistry of the bulk rock
 598 and of the minerals, along with the melt fO₂ (see Fig. 6 and Dauphas et al., 2014; Prissel et al., 2018).
 599 The $\Delta^{57}\text{Fe}_{\text{melt-cpx}} = 0.25 \times 10^6/T^2$ used by Sossi et al., (2012) to model fractional crystallization at Red hill
 600 volcano also fits in the calculated range. Our calculated $\Delta^{57}\text{Fe}_{\text{forsterite-basalt_IR}} = -0.15 \text{ ‰}$ at 1500 K agrees
 601 with the $\Delta^{57}\text{Fe}_{\text{ol-melt}}$ of -0.15 ‰ observed by Teng et al. (2008) at magmatic temperature. However,
 602 subsequent in situ Fe isotope measurements from the same group showed that this was essentially a

603 kinetic effect occurring upon magma cooling (see review in Dauphas et al. (2017)). Hence, this
604 comparison with the literature suggest that our calculated values seem to be on the higher end relative
605 to previous field-based and experimental studies (Williams et al., 2018; Prissel et al., 2018) and further
606 investigations will be needed to clarify why.

607

608

609 **4.4 – Silicon isotope fractionation in melts.**

610

611 *4.4.1 – Parameters controlling Si isotope fractionation.*

612

613 The parameters proposed to control silicon isotope fractionation in silicate minerals are Si-O bond
614 lengths, Si-O polyhedron volume (Qin et al., 2016), Si-O coordination number (Méheut et al., 2009;
615 Méheut and Schauble, 2014; Qin et al., 2016), the nature of silicon second neighbors (Rabin et
616 al., 2021), the electronegativity of the surrounding cations (Méheut and Schauble, 2014), and the
617 polymerization degree (Grant, 1954; Poitrasson and Zambardi, 2015) .

618

619 Looking at the melts investigated here, we find that the range of Si isotope β -factors in melts is
620 relatively similar to that observed in silicate minerals, though to the higher end (Fig. 3b), except for
621 fayalite that displays a significantly lower β -factor. The average Si-O bond length and coordination
622 number are similar in all the investigated melts (Table 3). This means that neither Si-O bond length nor
623 Si-O coordination number are responsible for the Si β -factor variation observed in these melts (Fig. 4b
624 and Fig. 5b). This lack of relationship between those parameters and the silicon isotope fractionation
625 were also observed in the silicate minerals investigated in Rabin et al. (2021) that all display a
626 coordination of 4, and an average Si-O bond length of 1.65 Å.

627

628 The melt polymerization has been proposed to be the main factor causing silicon isotope fractionation
629 among bulk igneous rock series (Poitrasson and Zambardi, 2015). At the mineral scale however,
630 polymerization of SiO_4^{4-} tetrahedra did not appear to be the sole parameter influencing Si isotope
631 fractionation in silicates (Méheut et al., 2009; Méheut and Schauble, 2014; Qin et al., 2016; Rabin et
632 al., 2021). In this study, there seems to be a correlation between NBO/T and Si force constant from
633 basalt to trachyte, considering the associated uncertainties (Fig. 7b). However, Phonolite has a Si force
634 constant of 700 ± 15 N/m associated with a NBO/T ratio of 0.28 whereas basalt_ID has a similar Si force
635 constant (695 ± 13 N/m) but a NBO/T ratio of 1 (Fig. 7b). As underlined part 3.1, variable melts
636 composition, generating structural heterogeneities, can blur the potential correlation with the
637 polymerization parameter NBO/T. This scatter is well observed among terrestrial igneous rocks, as
638 opposed to lunar ones with a simpler petrogenetic history, notably in terms of protolith that were
639 likely less varied on the Moon (Poitrasson and Zambardi, 2015). This suggests that in melts displaying
640 structural heterogeneities, the polymerization degree might not be the main parameter influencing
641 silicon isotope composition.

642

643 A limited increase in Si force constants with increasing SiO_2 content, a proxy for magmatic
644 differentiation, can also be inferred (Fig. 10). However, there is no relationship between Si force
645 constant and Si-Si distance (Fig. 11), nor with coordination number. The variation of SiO_2 content (from
646 49.1 to 63.2 wt%) in our simulated melts is relatively reduced. To evidence any strong relationship
647 between Si force constant and SiO_2 content a melt with > 70 wt% silica content would need to be
648 modeled. Silicon force constants are really similar for basalt_ID, basanite and phonolite, with values
649 of 695 ± 13 , 687 ± 8 and 700 ± 15 N/m respectively. This means that increasing alkaline and aluminum
650 content in the melts, that seems to play a role on iron isotope fractionation, has no effect on silicon
651 fractionation (Fig. 10). This also demonstrates that electronegativity differences of the cations
652 constituting the melt ($\chi_{\text{Na}} = 0.93$; $\chi_{\text{Mg}} = 1.31$; $\chi_{\text{Al}} = 1.63$) does not affect the silicon isotope composition
653 of the melts. Silicon is indeed a network former in the melts and silicon structural properties as well as
654 the Si force constant are much less sensitive to melt composition than iron. The only significant

655 variation of Si force constant is between basalt_IR and trachyte with values of 669 ± 11 N/m and 716
656 ± 10 N/m, respectively. Besides the polymerization degree (Fig. 7b), it seems that the major difference
657 between these two melts are the Si-Fe average distance, of about 3.1 \AA for basalt_IR and 2.4 \AA for
658 trachyte (Table 4). The shortest average Si-Fe distance corresponds to the highest Si force constant in
659 the melts (Fig. 11).

660
661 To conclude, the small but significant silicon isotope fractionation in the melts seems to be mainly
662 driven by either the presence of iron as silicon second neighbors and/or the melt polymerization
663 degree. The nature of the melt, whether peralkaline or calc-alkaline, is not influencing the silicon
664 isotope signature. Further studies with a larger range of SiO₂ content would need to be performed in
665 order to assess whether SiO₂ content is affecting or not the Si isotope composition of the melts.

667 4.4.2 - Comparison between theoretical and experimental data

668
669 As for iron isotopes, most studies focused on inter-mineral silicon isotope fractionation (Méheut et al.,
670 2009; Savage et al., 2011; Méheut and Schauble, 2014; Qin et al., 2016) and there are only two studies
671 reporting so far $\Delta_{\text{melt-mineral}}^{30\text{Si}/28\text{Si}}$. Qin et al. (2016) and Deng et al. (2019), used the silicon β -factors of
672 silicate minerals calculated by Qin et al. (2016) in order to assess Si fractionation factors between
673 silicate minerals and different melt compositions. These calculations were performed assuming that
674 silicate melts have Si isotope fractionation factors equal to the weighted sum of those for their
675 normative mineral compositions. Our set of Si isotope fractionation factors as well as the one
676 calculated by Deng et al. (2019) at 1123 K are displayed in Figure 12 (and Table S1 – Appendix B –
677 Supplementary material). Both studies display a similar order for Si fractionation factors with $\Delta_{\text{melt-}}$
678 $\text{diopside}^{30\text{Si}/28\text{Si}} > \Delta_{\text{melt-orthoenstatite}}^{30\text{Si}/28\text{Si}} > \Delta_{\text{melt-olivine}}^{30\text{Si}/28\text{Si}} > \Delta_{\text{melt-anorthite}}^{30\text{Si}/28\text{Si}} > \Delta_{\text{melt-albite}}^{30\text{Si}/28\text{Si}}$. The
679 silicon fractionation factors calculated by Qin et al. (2016) and Deng et al. (2019) are, however,
680 systematically higher than our calculated $\Delta_{\text{melt-mineral}}^{30\text{Si}/28\text{Si}}$, by 0.1-0.2 ‰ for the trachytic melt and by
681 0.4-0.5 ‰ for basaltic (IR) melt. The discrepancies between our calculated silicon fractionation factor
682 between minerals and trachytic melt and the one estimated from Qin et al. (2016) lies within our
683 estimated uncertainties of ≈ 0.3 ‰ at 1123 K. Concerning the basaltic melt, the $\Delta_{\text{mineral-melt}}^{30\text{Si}/28\text{Si}}$ of
684 Qin et al. (2016) is slightly higher than our calculated $\Delta_{\text{mineral-melt}}^{30\text{Si}/28\text{Si}}$ within uncertainties. As a result,
685 Qin et al. (2016) would suggest that olivine and enstatite have a lighter silicon isotope composition
686 than the basaltic melts and that the silicon fractionation factor between the feldspars and the melt is
687 insignificant which is not what is observed in our study (Figure 12). The high Si β -factor of the basaltic
688 melt estimated by Qin et al. (2016) and Deng et al. (2019) is probably due to the high content of
689 feldspars in the composition of the magmatic rocks, mainly in the mesostasis. As a consequence,
690 estimated $10^3 \ln \beta_{\text{melt}}$ is mainly driven by anorthite and albite Si β -factors. From our results, it appears
691 that the melt Si β -factor can hardly be assessed by using the weighted sum of the mineral composition
692 of the melt and their associated Si β -factor, especially for the more mafic ones.

693 694 5- APPLICATIONS

695 696 5.1 – Magmatic differentiation

697 698 5.1.1- Iron isotopes

699
700 Iron isotope fractionation has been widely studied on natural samples in the context of magmatic
701 differentiation. Most of the magmatic series display heavy iron isotope compositions in the most
702 evolved lavas (e.g. Teng et al., 2008; Sossi et al., 2012; Williams et al., 2018), especially with SiO₂
703 content > 70 wt% (e.g. Poitrasson and Freydier, 2005; Schuessler et al., 2009; Zambardi et al., 2014).
704 One of the candidates to explain such isotopic signature is fractional crystallization. However, the
705 impact of fractional crystallization on iron isotope fractionation is still debated. Many studies
706 considered that there is no significant iron isotopic fractionation between Fe²⁺-minerals and the

707 associated melt and that magnetite, an Fe³⁺ oxide, is the main mineral phase driving the iron isotope
708 composition in the lavas. Hence, the evolved lavas should display lighter iron isotopic composition
709 (Shahar et al., 2008). Therefore, fractional crystallization has been discarded as potential candidate to
710 explain the observed heavy iron isotope signature at the last stage of magmatic differentiation
711 (Zambardi et al., 2014). However, Dauphas et al. (2014) displayed the first experimental β -factors for
712 glasses (see section 4.3.2 above) and demonstrated that the heavy isotope signature of evolved melts
713 could compensate for the magnetite crystallization during magmatic differentiation. Thus, fractional
714 crystallization could lead to the heavy $\delta^{57}\text{Fe}$ observed. Besides, Polyakov and Mineev (2000) and Rabin
715 et al. (2021) showed that isotopic fractionation between Fe²⁺-bearing minerals are significant. Taking
716 this into account in fractional crystallization models could reproduce the isotopic trend observed in
717 natural lavas (Rabin et al. 2021). Here, the model produced in Rabin et al. (2021) was modified by
718 replacing the approximated $\Delta^{57}\text{Fe}_{\text{min-melt}}$ (using melt β -factor of Dauphas et al. (2014)), by the $\Delta^{57}\text{Fe}_{\text{min-}}$
719 trachyte calculated in this study (Table 7, Appendix C - Supplementary material -Table E1). Our model
720 shows a smooth increase of $\delta^{57}\text{Fe}$ from 58 wt% SiO₂ to 74 wt% SiO₂ followed by a sharp increase up to
721 0.65‰ (Fig. 13a). This sharp $\delta^{57}\text{Fe}$ increase observed at 74wt% SiO₂ is related to the end of ulvöspinel
722 and magnetite and beginning of ilmenite crystallization (see Appendix C - Supplementary material). If
723 most of the Fe isotope signatures of the evolved lavas and granites (e.g. Poitrasson and Freydier, 2005;
724 Telus et al., 2012; Foden et al., 2015) can be explained by our fractional crystallization model, some of
725 the heaviest iron isotopic signatures observed in some granites ($\delta^{57}\text{Fe} = + 0.9$ ‰; e.g. He et al., 2017;
726 Xia et al., 2017) are however not reproduced by this model. Despite the fact that this is the most
727 constrained fractional crystallization model produced so far, the lack of calculated β -factor for rhyolitic
728 melt could under-estimate the $\delta^{57}\text{Fe}$ of the most evolved melt as rhyolitic melt should have a higher
729 β -factor than trachyte (Dauphas et al., 2014). Overall, from this new model, it is possible to conclude
730 that fractional crystallization may explain at least part of the iron isotope evolution during magmatic
731 differentiation for $\delta^{57}\text{Fe}$ values up to 0.65 ‰.

732 733 5.1.2-- Silicon isotopes

734
735 Silicon isotopes show progressive and systematic enrichment in heavy isotopes during magmatic
736 differentiation (Savage et al., 2011; Zambardi et al., 2014) going from $\delta^{30}\text{Si} = -0.30 \pm 0.05$ ‰ for SiO₂ =
737 47 wt% up to -0.10 ± 0.07 ‰ for SiO₂ = 76 wt% in terrestrial volcanic rocks. Savage et al. (2011) proposed
738 fractional crystallization as the main process involved in silicon isotope fractionation during magmatic
739 differentiation. However, modelling of the effect of fractional crystallization on $\delta^{30}\text{Si}$ along magmatic
740 differentiation performed by Savage et al. (2011) and Zambardi et al. (2014), diverge from the
741 measured silicon isotopic trends (Fig. 13b). This discrepancy can be due to the fact that, besides the
742 effect of magma differentiation, igneous rocks silicon isotope composition also records source
743 signatures, such as a possible heavy seafloor chert contribution for andesites and a light clay
744 contribution for anatectic leucogranites (Poitrasson and Zambardi, 2015). Also, the lack of precise
745 fractionation factor between silicate minerals and melt is a limitation for fractional crystallization
746 modeling. Many studies (Méheut et al., 2009; Méheut and Schauble, 2014; Qin et al., 2016; Rabin et
747 al., 2021) underlined that silicon isotope fractionation between silicate minerals, even at high
748 temperature, are significant. The use of approximated $\Delta^{30}\text{Si}_{\text{min-melt}}$ allowed Qin et al. (2016) to show,
749 through different models, that fractional crystallization is a viable mechanism to explain heavy silicon
750 isotope signatures in the most evolved lavas. Here, we are modelling the effect of fractional
751 crystallization on silicon isotopes using our $\Delta^{30}\text{Si}_{\text{min-trachyte}}$ in order to evaluate this hypothesis (Appendix
752 C - Supplementary material - Table E2). We used the same starting composition in the MCS software
753 as in the model of fractional crystallization for iron isotopes. In this model, silicon isotope evolution is
754 expressed as follow:

$$755$$

$$756 \delta^{30}\text{Si} (\text{melt})_{j+1} = \delta^{30}\text{Si} (\text{melt})_j + \sum_i X_i \times 10^3 \ln \alpha_i (T) \quad \text{Eq. (10)}$$

$$757$$

758 where X_i is the modal proportion of minerals crystallized at each 5°C step. $\delta^{30}\text{Si}_{\text{melt}}$ is the initial $\delta^{30}\text{Si}$ of
759 the melt. In this case $\delta^{30}\text{Si}_{\text{melt}} = -0.22 \text{ ‰}$ for $\text{SiO}_2 = 58 \text{ wt\%}$.

760
761 Our model is in good agreement with the measured silicon isotopic trend in terrestrial lavas (Fig. 13b).
762 The linear trend of our model ($y = 0.0061x - 0.588$) is close to the linear trend measured of the Hekla
763 volcanic suite ($y = 0.0059x - 0.591$; Savage et al. (2011)) and Cedar Butte volcanic suite ($y = 0.0069x -$
764 0.638 ; Zambardi et al. (2014)). The sharp $\delta^{30}\text{Si}$ increase observed in the model at 74wt% SiO_2 is
765 directly correlated to the beginning of quartz crystallization associated with a decrease of anorthite
766 and albite crystallization. Our new set of fractionation factors between silicate minerals and melts
767 allow us to better constrain the fractional crystallization model for the first time. Besides the source
768 effect discussed above, it shows that fractional crystallization may explain the observed heavy silicon
769 isotope signature in the most evolved lavas (Fig. 13b), at variance with the previous interpretation of
770 Zambardi et al. (2014) for the Cedar Butte volcanic suite.

771 **5.2 – Partial melting effect on iron isotopes**

772
773 Previous studies have suggested that mantle-derived melts may show heavier iron isotope signatures
774 compared to their presumed mantle peridotite source rocks (e.g. Williams et al., 2004; Weyer and
775 Ionov, 2007; Williams et al., 2009; Dauphas et al., 2014; Williams and Bizimis, 2014; Sossi et al., 2016;
776 Nebel et al., 2018). The changes in $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ between crystal and liquid due to partial melting has been
777 argued as a key parameter to explain this. The moderately incompatible behavior of Fe^{3+} ($K_d =$
778 $C_{\text{melt}}/C_{\text{solid}} \sim 4.5$; Mallmann and O'Neill, 2009; Cottrell and Kelley, 2011) relative to Fe^{2+} iron ($K_d = 1$;
779 Mallmann and O'Neill, 2009; Davis et al., 2013) suggests that iron isotope fractionation could occur
780 during partial melting of upper-mantle to create oceanic crust. Many studies using different models
781 (i.e. batch-melting, non-modal melting; e.g. Weyer and Ionov, 2007; Williams et al., 2009; Dauphas et
782 al., 2014; Williams and Bizimis, 2014; Sossi et al., 2016), tried to assess whether partial melting of
783 mantle peridotite, through single or numerous stages, could create the heavier isotopic signature of
784 MORB ($0.7 \text{ ‰} < \delta^{57}\text{Fe} < 0.22 \text{ ‰}$; Sossi et al. 2016). However, the role of partial melting on the iron
785 isotope signature of MORB remains debated (e.g. Weyer and Ionov, 2007; Williams et al., 2009;
786 Dauphas et al., 2014; Williams and Bizimis, 2014; Sossi et al., 2016). Many parameters in these partial
787 melting models are well constrained such as the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of MORB ($\text{Fe}^{3+}/\text{Fe}_{\text{tot}} = 0.09 \pm 0.02$; Bézos et
788 al., 2021) and the temperature at depth during mantle melting. One of the main critical parameters is
789 the fractionation factor between the melt and the minerals (olivine, orthopyroxene). A recent study
790 by Dauphas et al. (2014) shows that partial melting is only responsible for one third (0.023 ‰) of the
791 isotopic fractionation between MORB and mantle peridotite. Sossi et al. (2016) proposed a correction
792 of Fe isotope signature of MORB for the effect of olivine early fractionation allowing them to assess
793 whether mantle heterogeneity could be the source of the heavy iron isotope signature of MORB. From
794 this correction, it appears that normal MORB displays a mean $\delta^{57}\text{Fe}$ of $0.10 \pm 0.01 \text{ ‰}$. Sossi et al. (2016)
795 demonstrated then that for an upper mantle $\delta^{57}\text{Fe} = 0.05 \pm 0.01 \text{ ‰}$, a $\text{Fe}^{3+}/\text{Fe}_{\text{tot}} = 0.037$ and a degree
796 of partial melting comprised between 0.1 and 0.2, the MORB iron isotope composition can be
797 reproduced. As mentioned above, the choice of $\Delta^{57}\text{Fe}_{\text{min-melt}}$ is critical in partial melting models. Sossi
798 et al. (2016) applied a $\Delta^{57}\text{Fe}_{\text{min-melt}} = \Delta^{57}\text{Fe}_{\text{ol-melt}} = -0.4 \times 10^6/T^2$ as olivine is the major iron carrier in
799 peridotites before orthopyroxene. At 1500 K, the $\Delta^{57}\text{Fe}_{\text{ol-melt}}$ is about -0.17 ‰ in their models, which is
800 slightly higher, but similar within uncertainties, than our calculated $\Delta^{57}\text{Fe}_{\text{forsterite-basalt_IR}} = \Delta^{57}\text{Fe}_{\text{orthoenstatite-}}$
801 $\text{basalt_IR}} = -0.15 \text{ ‰}$. Our new set of equilibrium isotope fractionation factor between minerals and melts
802 allows us to confirm that normal MORB iron isotopic signature can be explained by 10 to 20 % partial
803 melting of the peridotite mantle as demonstrated by Sossi et al. (2016).

804 **5.3 – Iron isotope intracrystalline diffusion**

805
806
807
808

809 Chemical zoning is commonly observed in phenocrysts (i.e. olivine, pyroxene) of volcanic rocks. This
810 has been interpreted as the result of crystal growth in an evolving melt during magmatic differentiation
811 or/and diffusion-controlled chemical exchange due to the contrast (disequilibrium) between crystal
812 and melt composition (e.g. Teng et al., 2011). In the past few years, studies demonstrated that iron
813 chemical zoning in olivine is mirrored by iron isotope zoning (Teng et al., 2011; Sio et al., 2013; Oeser
814 et al., 2014; Oeser et al., 2015; Collinet et al., 2017; Sio et al., 2018; Oeser et al., 2018). Iron isotopes
815 profiles across olivine display significant variations ($> 1 \text{ ‰}$; Oeser et al., 2015; Oeser et al., 2018) that
816 exceeds potential equilibrium isotope fractionation. Iron isotopes profiles can therefore be used as
817 evidence for the diffusion origin of the chemical zoning in olivine, since the light isotopes (^{54}Fe) diffuse
818 faster than the heavy isotopes (^{57}Fe) (e.g. Richter et al. 2003). Quantifying kinetic isotope effects in
819 minerals and melts from first-principles calculations, as performed in recent studies for other elements
820 (e.g. Luo et al., 2021, 2020; Spallanzani et al., 2022), is beyond the scope of this study. We would
821 require a large simulation cell for the melt with an important number of atoms (N) in order to assess
822 with precision diffusion coefficients for the different elements in our systems, as diffusivity follows the
823 inverse of $N^{1/3}$ dependence (Karki, 2010). However, from our set of iron equilibrium fractionation
824 factors between silicate melts and minerals, we can assess the magnitude of iron isotope fractionation
825 during olivine crystallization over diffusion-driven kinetic isotope fractionation. The net isotope
826 fractionation measured across zoned olivine crystals depends on the rate of crystal growth relative to
827 the rate of chemical diffusion (Sio et al., 2013; Sio and Dauphas, 2017). A fast crystal growth relative
828 to diffusion process would generate olivine zoning driven by crystal growth associated with magmatic
829 differentiation. Some authors (Dauphas et al., 2014; Prissel et al., 2018; Sio et al., 2018), implied that
830 in this case only little isotopic fractionation between mineral and melt is expected as they consider
831 $\Delta^{57}\text{Fe}_{\text{olivine-melt}}$ to be insignificant at magmatic temperature. Alternatively, when crystal growth is slow
832 relative to diffusion, then crystal zoning is induced by diffusive re-equilibration with the evolving melts
833 and higher isotopic variations within the olivine are expected. The lack of fractionation between
834 forsterite and melt was also observed in our study in the case of a basaltic melt with low iron content,
835 basalt_ID, with a $\Delta^{57}\text{Fe}_{\text{forsterite-basalt-ID}} = -0.01 \text{ ‰}$ at 1500 K. Our study shows however that the equilibrium
836 fractionation factors between olivine and a basalt with higher iron content (13.1 wt%) are significant
837 with a $\Delta^{57}\text{Fe}_{\text{forsterite-basalt_IR}} = -0.15 \text{ ‰}$ and a $\Delta^{57}\text{Fe}_{\text{hortonolite-basalt_IR}} = -0.18 \text{ ‰}$ at 1500 K. Therefore, at
838 equilibrium, considering that iron isotope fractionation is exclusively driven by crystal growth process,
839 an olivine may display according to our calculation $\delta^{57}\text{Fe}$ as low as -0.09 ‰ , considering a melt value
840 of 0.09 ‰ (BIR1g, Craddock and Dauphas, 2011; Oeser et al., 2014). Iron isotopes composition lighter
841 than -0.09 ‰ , as observed in in-situ isotopic profiles with olivine rims $\delta^{57}\text{Fe}$ as low as -2.1 ‰ (Oeser et
842 al., 2015), can therefore only be explained by diffusion-driven fractionation (Oeser et al., 2015; Collinet
843 et al., 2017b; Sio and Dauphas, 2017; Prissel et al., 2018).

844
845 Our new equilibrium $\Delta^{57}\text{Fe}_{\text{olivine-basalt_IR}}$ allows us to propose that the low $\delta^{57}\text{Fe}$ signatures observed in
846 olivines can in part be explained by equilibrium fractionation. However, our results also confirm that
847 kinetic diffusion-driven fractionation has a major influence on the iron isotope chemical profiles of
848 olivine as implied by other studies (Teng et al., 2011; Sio et al., 2013; Oeser et al., 2015; Collinet et al.,
849 2017a; Sio and Dauphas, 2017; Prissel et al., 2018; Sio et al., 2018; Oeser et al., 2018). As discussed
850 above in section 5.5.1.1 and underlined by Nebel et al. (2018), although diffusion in olivine can create
851 large isotopic variations at the crystal scale, it is not expected to affect significantly ($> 0.03 \text{ ‰}$) the melt
852 composition during magmatic differentiation as proposed by Lundstrom (2009) and Zambardi et al.
853 (2014).

854 855 **6- Conclusion**

856
857 This study provides, for the first time, equilibrium Fe and Si isotope β -factors of various melts, using
858 first-principles molecular dynamics. We first demonstrated, through comparison of the “snapshot” and
859 “VAF” methods, that both methods are appropriate to study isotope fractionation of melts. Iron, that
860 acts mainly as a network-modifier in the melts, displays significant isotope fractionation among the

861 different compositions of melt. The Fe-O mean coordination number appears not playing a significant
862 role on the observed Fe β -factor variations in melts. The main parameters driving the iron isotope
863 composition in melts is the Fe-O bond length. The chemical environment around iron (i.e. iron second
864 neighbors) is also suggested to contribute to Fe isotope fractionation, as smaller Fe-Fe and Fe-Mg
865 distances leads to higher Fe β -factor values in the melts. Further investigations are necessary in order
866 to confirm this hypothesis. Overall, these results show that significant Fe isotope fractionation is
867 expected without changes of iron redox. On the other hand, silicon isotope fractionation appears to
868 be less sensitive to compositional changes in melts and displays limited isotope fractionation among
869 the different melts. This is most likely due to its network-former role in the melt. Since structural
870 parameters such as Si-O bond length and coordination number remain constant, they do not play a
871 major role on the Si β -factors variation observed in these melts. The silicon isotope compositional
872 variations were also expected to be related to the depolymerization degree (NBO/T; Grant, 1954;
873 Poitrasson and Zambardi, 2015). However, this relationship may be blurred by the high alkaline
874 content of the melts. Silicon β -factors appear to be also driven by its local environment, notably the
875 presence of iron as silicon second neighbors.

876
877 This Fe and Si β -factors of melts allowed us to calculate a consistent set of equilibrium fractionation
878 factors between various minerals and melts. This represents a major step forward in the understanding
879 and quantifying of the processes involved in iron and silicon isotope fractionation in magmatic settings.
880 In this perspective, we used our new $\Delta^{57}\text{Fe}_{\text{min-melt}}$ and $\Delta^{30}\text{Si}_{\text{min-melt}}$ in several models from the literature
881 in order to assess the impact of the addition of more constrained fractionation factors on them. Our
882 results support fractional crystallization as a possible driving process involved in both Si and Fe isotope
883 evolution during magmatic differentiation for the melts chemical range investigated. Our calculated
884 $\Delta^{57}\text{Fe}_{\text{ol-melt}}$ allows us to confirm the model of Sossi et al. (2016) showing that generation of MORB with
885 $\delta^{57}\text{Fe} = 0.1 \text{ ‰}$ can be explained by partial melting of peridotites (with a degree of partial melting
886 comprised between 10 and 20%). This different from nil $\Delta^{57}\text{Fe}_{\text{ol-melt}}$ fractionation factor however
887 contradicts Prissel et al. (2018) conclusions, thus calling for further investigations. We also showed
888 that there is significant iron isotope fractionation between Fe²⁺-bearing minerals and melts. Olivine
889 crystallization at equilibrium could show a $\Delta^{57}\text{Fe}_{\text{olivine-basalt}}$ range from 0 to -0.18 ‰. Our new set of iron
890 fractionation factors can therefore help to quantify the equilibrium fractionation versus the diffusion-
891 driven kinetic fractionation in future iron isotope diffusion models.

892 893 **APPENDIX A. SUPPLEMENTARY MATERIAL**

894 The file includes all the parameters and discussions relative to the structural properties of the melts
895 (including MSDs and RDFs).

896 **APPENDIX B. SUPPLEMENTARY MATERIAL**

897 The file includes the Fe and Si fractionation factors between the different melts and silicate minerals
898 as well as the detailed calculation of the fractionation factors (systematic bias correction).

899 **APPENDIX C. SUPPLEMENTARY MATERIAL**

900 This MS Excel file includes Fe and Si fractional crystallization results and VAF iron beta fractionation
901 factors.

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904
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REFERENCES

- Allen M. P. and Tildesley D. J. (1989) Computer simulation of liquids. *J. Solution Chem.* **18**, 99. Available at: <https://doi.org/10.1007/BF00646086>.
- Angeli F., Villain O., Schuller S., Ispas S. and Charpentier T. (2011) Insight into sodium silicate glass structural organization by multinuclear NMR combined with first-principles calculations. *Geochim. Cosmochim. Acta* **75**, 2453–2469.
- Bajgain S., Ghosh D. B. and Karki B. B. (2015) Structure and density of basaltic melts at mantle conditions from first-principles simulations. *Nat. Commun.* **6**, 1–7. Available at: <http://dx.doi.org/10.1038/ncomms9578>.
- Bauchy M. and Micoulaut M. (2011) Atomic scale foundation of temperature-dependent bonding constraints in network glasses and liquids. *J. Non. Cryst. Solids* **357**, 2530–2537. Available at: <http://dx.doi.org/10.1016/j.jnoncrysol.2011.03.017>.
- Bertka C. M. and Holloway J. R. (1994) Anhydrous partial melting of an iron-rich mantle I: subsolidus phase assemblages and partial melting phase relations at 10 to 30 kbar. *Contrib. to Mineral. Petrol.* **115**, 313–322. Available at: <https://doi.org/10.1007/BF00310770>.
- Bézos A., Guivel C., La C., Fougéroux T. and Humler E. (2021) Unraveling the confusion over the iron oxidation state in MORB glasses. *Geochim. Cosmochim. Acta* **293**, 28–39.
- Bézos A. and Humler E. (2005) The Fe³⁺/ΣFe ratios of MORB glasses and their implications for mantle melting. *Geochim. Cosmochim. Acta* **69**, 711–725.
- Bigeleisen J. and Mayer M. G. (1947) Calculation of Equilibrium Constants for Isotopic Exchange Reactions. *J. Chem. Phys.* **15**, 261–267. Available at: <https://doi.org/10.1063/1.1746492>.
- Blanchard M., Balan E. and Schauble E. A. (2017) Equilibrium Fractionation of Non-traditional Isotopes: a Molecular Modeling Perspective. *Rev. Mineral. Geochemistry* **82**, 27–63. Available at: <https://doi.org/10.2138/rmg.2017.82.2>.
- Bohrson W. A., Spera F. J., Giorso M. S., Brown G. A., Creamer J. B. and Mayfield A. (2014) Thermodynamic model for energy-constrained open-system evolution of crustal magma bodies undergoing simultaneous recharge, assimilation and crystallization: The magma chamber simulator. *Journal of Petrology* **55**, 1685–1717.
- Caracas R., Hirose K., Nomura R. and Ballmer M. D. (2019) Melt–crystal density crossover in a deep magma ocean. *Earth Planet. Sci. Lett.* **516**, 202–211. Available at: <https://doi.org/10.1016/j.epsl.2019.03.031>.
- Collinet M., Charlier B., Namur O., Oeser M., Médard E. and Weyer S. (2017a) Crystallization history of enriched shergottites from Fe and Mg isotope fractionation in olivine megacrysts. *Geochim. Cosmochim. Acta* **207**, 277–297. Available at: <http://dx.doi.org/10.1016/j.gca.2017.03.029>.
- Collinet M., Charlier B., Namur O., Oeser M., Médard E. and Weyer S. (2017b) Crystallization history of enriched shergottites from Fe and Mg isotope fractionation in olivine megacrysts. *Geochim. Cosmochim. Acta* **207**, 277–297.
- Cottrell E. and Kelley K. A. (2014) Redox Heterogeneity of the Mantle Inferred from Hotspots. In *AGU Fall Meeting Abstracts* pp. V23G-02.
- Cottrell E. and Kelley K. A. (2011) The oxidation state of Fe in MORB glasses and the oxygen fugacity of the upper mantle. *Earth Planet. Sci. Lett.* **305**, 270–282. Available at: <http://dx.doi.org/10.1016/j.epsl.2011.03.014>.
- Craddock P. R. and Dauphas N. (2011) Iron and carbon isotope evidence for microbial iron respiration throughout the Archean. *Earth Planet. Sci. Lett.* **303**, 121–132. Available at: <http://www.sciencedirect.com/science/article/pii/S0012821X10008186>.
- Dauphas N., Roskosz M., Alp E. E., Golden D. C., Sio C. K., Tissot F. L. H., Hu M. Y., Zhao J., Gao L. and Morris R. V. (2012) A general moment NRIXS approach to the determination of equilibrium Fe isotopic fractionation factors: Application to goethite and jarosite. *Geochim. Cosmochim. Acta* **94**, 254–275.
- Dauphas N., Roskosz M., Alp E. E., Neuville D. R., Hu M. Y., Sio C. K., Tissot F. L. H., Zhao J., Tissandier

964 L., Médard E. and Cordier C. (2014) Magma redox and structural controls on iron isotope
965 variations in Earth's mantle and crust. *Earth Planet. Sci. Lett.* **398**, 127–140.

966 Davis F. A., Humayun M., Hirschmann M. M. and Cooper R. S. (2013) Experimentally determined
967 mineral/melt partitioning of first-row transition elements (FRTE) during partial melting of
968 peridotite at 3GPa. *Geochim. Cosmochim. Acta* **104**, 232–260. Available at:
969 <http://dx.doi.org/10.1016/j.gca.2012.11.009>.

970 Deng Z., Chaussidon M., Guitreau M., Puchtel I. S., Dauphas N. and Moynier F. (2019) An oceanic
971 subduction origin for Archaean granitoids revealed by silicon isotopes. *Nat. Geosci.* **12**, 774–778.
972 Available at: <http://dx.doi.org/10.1038/s41561-019-0407-6>.

973 Du D. H., Wang X. L., Yang T., Chen X., Li J. Y. and Li W. (2017) Origin of heavy Fe isotope compositions
974 in high-silica igneous rocks: A rhyolite perspective. *Geochim. Cosmochim. Acta* **218**, 58–72.
975 Available at: <https://doi.org/10.1016/j.gca.2017.09.014>.

976 Ducher M., Blanchard M. and Balan E. (2018) Equilibrium isotopic fractionation between aqueous Zn
977 and minerals from first-principles calculations. *Chem. Geol.* **483**, 342–350. Available at:
978 <https://doi.org/10.1016/j.chemgeo.2018.02.040>.

979 Dupuis R., Benoit M., Nardin E. and Méheut M. (2015) Fractionation of silicon isotopes in liquids: The
980 importance of configurational disorder. *Chem. Geol.* **396**, 239–254. Available at:
981 <http://www.sciencedirect.com/science/article/pii/S0009254115000029>.

982 Feng S., Majumdar A., Kuang H., Pan Y., litaka T. and Tse J. S. (2021) A comparative study on pressure-
983 induced structural transformations in a basaltic glass and melt from Ab initio molecular dynamics
984 calculations. *Phys. Chem. Miner.* **48**, 1–14. Available at: [https://doi.org/10.1007/s00269-021-](https://doi.org/10.1007/s00269-021-01165-3)
985 [01165-3](https://doi.org/10.1007/s00269-021-01165-3).

986 Foden J., Sossi P. A. and Wawryk C. M. (2015) Fe isotopes and the contrasting petrogenesis of A-, I- and
987 S-type granite. *Lithos* **212–215**, 32–44. Available at:
988 <http://dx.doi.org/10.1016/j.lithos.2014.10.015>.

989 Gajos N. A., Lundstrom C. C. and Taylor A. H. (2016) Spatially controlled Fe and Si isotope variations:
990 an alternative view on the formation of the Torres del Paine pluton. *Contrib. to Mineral. Petrol.*
991 **171**.

992 Gerlach S., Claußen O. and Russel C. (1998) Self-diffusion of iron in alkali – magnesia – silica glass melts.
993 *J. Non. Cryst. Solids* **226**, 11–18.

994 Ghosh D. B. and Karki B. B. (2020) Effects of valence and spin of Fe in MgSiO₃ melts: Structural insights
995 from first-principles molecular dynamics simulations. *Geochim. Cosmochim. Acta* **279**, 107–118.
996 Available at: <https://doi.org/10.1016/j.gca.2020.03.040>.

997 Ghosh D. B. and Karki B. B. (2018) First-principles molecular dynamics simulations of anorthite
998 (CaAl₂Si₂O₈) glass at high pressure. *Phys. Chem. Miner.* **45**, 575–587. Available at:
999 <http://dx.doi.org/10.1007/s00269-018-0943-4>.

1000 Grant F. S. (1954) The geological significance of variations in the abundances of the isotopes of silicon
1001 in rocks. *Geochim. Cosmochim. Acta* **5**, 225–242. Available at:
1002 <http://www.sciencedirect.com/science/article/pii/0016703754900460>.

1003 Guillot B. and Sator N. (2007a) A computer simulation study of natural silicate melts. Part I: Low
1004 pressure properties. *Geochim. Cosmochim. Acta* **71**, 1249–1265.

1005 Guillot B. and Sator N. (2007b) A computer simulation study of natural silicate melts. Part II: High
1006 pressure properties. *Geochim. Cosmochim. Acta* **71**, 4538–4556.

1007 He Y., Wu H., Ke S., Liu S. A. and Wang Q. (2017) Iron isotopic compositions of adakitic and non-adakitic
1008 granitic magmas: Magma compositional control and subtle residual garnet effect. *Geochim.*
1009 *Cosmochim. Acta* **203**, 89–102. Available at: <http://dx.doi.org/10.1016/j.gca.2017.01.005>.

1010 Heimann A., Beard B. L. and Johnson C. M. (2008) The role of volatile exsolution and sub-solidus
1011 fluid/rock interactions in producing high ⁵⁶Fe/⁵⁴Fe ratios in siliceous igneous rocks. *Geochim.*
1012 *Cosmochim. Acta* **72**, 4379–4396.

1013 Huang F., Wu Z., Huang S. and Wu F. (2014) First-principles calculations of equilibrium silicon isotope
1014 fractionation among mantle minerals. *Geochim. Cosmochim. Acta* **140**, 509–520. Available at:
1015 <http://dx.doi.org/10.1016/j.gca.2014.05.035>.

- 1016 Jackson W. E., Farges F., Yeager M., Mabrouk P. A., Rossano S., Waychunas G. A., Solomon E. I. and
 1017 Brown G. E. (2005) Multi-spectroscopic study of Fe(II) in silicate glasses: Implications for the
 1018 coordination environment of Fe(II) in silicate melts. *Geochim. Cosmochim. Acta* **69**, 4315–4332.
- 1019 Karki B. B. (2015) First-principles computation of mantle materials in crystalline and amorphous
 1020 phases. *Phys. Earth Planet. Inter.* **240**, 43–69.
- 1021 Karki B. B. (2010) First-principles molecular dynamics simulations of silicate melts: Structural and
 1022 dynamical properties. *Theor. Comput. Methods Miner. Phys. Geophys. Appl.* **71**, 355–389.
- 1023 Karki B. B., Ghosh D. B., Maharjan C., Karato S. I. and Park J. (2018) Density-Pressure Profiles of Fe-
 1024 Bearing MgSiO₃ Liquid: Effects of Valence and Spin States, and Implications for the Chemical
 1025 Evolution of the Lower Mantle. *Geophys. Res. Lett.* **45**, 3959–3966.
- 1026 Kelley D. F. and Barton M. (2008) Pressures of crystallization of Icelandic Magmas. *J. Petrol.* **49**, 465–
 1027 492.
- 1028 Kim H. I., Sur J. C. and Lee S. K. (2016) Effect of iron content on the structure and disorder of iron-
 1029 bearing sodium silicate glasses: A high-resolution ²⁹Si and ¹⁷O solid-state NMR study. *Geochim.*
 1030 *Cosmochim. Acta* **173**, 160–180. Available at: <http://dx.doi.org/10.1016/j.gca.2015.10.023>.
- 1031 Konter J. G., Pietruszka A. J., Hanan B. B., Finlayson V. A., Craddock P. R., Jackson M. G. and Dauphas
 1032 N. (2016) Unusual $\delta^{56}\text{Fe}$ values in Samoan rejuvenated lavas generated in the mantle. *Earth*
 1033 *Planet. Sci. Lett.* **450**, 221–232. Available at: <http://dx.doi.org/10.1016/j.epsl.2016.06.029>.
- 1034 Kowalski P. M. and Jahn S. (2011) Prediction of equilibrium Li isotope fractionation between minerals
 1035 and aqueous solutions at high P and T: An efficient ab initio approach. *Geochim. Cosmochim. Acta*
 1036 **75**, 6112–6123. Available at: <http://dx.doi.org/10.1016/j.gca.2011.07.039>.
- 1037 Kresse G. and Furthmüller J. (1996) Efficient iterative schemes for ab initio total-energy calculations
 1038 using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186. Available at:
 1039 <https://link.aps.org/doi/10.1103/PhysRevB.54.11169>.
- 1040 Kresse G. and Joubert D. (1999) From ultrasoft pseudopotentials to the projector augmented-wave
 1041 method. *Phys. Rev. B* **59**, 1758–1775. Available at:
 1042 <https://link.aps.org/doi/10.1103/PhysRevB.59.1758>.
- 1043 Kuryaeva R. G. (2004) Degree of polymerization of aluminosilicate glasses and melts. *Glas. Phys. Chem.*
 1044 **30**, 157–166.
- 1045 Landau L. D. and Lifshitz E. M. (1980) Course of Theoretical Physics. Statistical Physics. Part 1. Pergamon
 1046 5, 544.
- 1047 Li Q. W., Zhao J. H., Wang Q., Zhang Z. F., An Y. J. and He Y. T. (2020) Iron isotope fractionation in
 1048 hydrous basaltic magmas in deep crustal hot zones. *Geochim. Cosmochim. Acta* **279**, 29–44.
 1049 Available at: <https://doi.org/10.1016/j.gca.2020.03.032>.
- 1050 Le Losq C., Neuville D. R., Florian P., Henderson G. S. and Massiot D. (2014) The role of Al³⁺ on rheology
 1051 and structural changes in sodium silicate and aluminosilicate glasses and melts. *Geochim.*
 1052 *Cosmochim. Acta* **126**, 495–517. Available at: <http://dx.doi.org/10.1016/j.gca.2013.11.010>.
- 1053 Lundstrom C. (2009) Hypothesis for the origin of convergent margin granitoids and Earth’s continental
 1054 crust by thermal migration zone refining. *Geochim. Cosmochim. Acta* **73**, 5709–5729. Available
 1055 at: <https://www.sciencedirect.com/science/article/pii/S0016703709004116> [Accessed April 26,
 1056 2019].
- 1057 Luo, H., Karki, B. B., Ghosh, D. B., and Bao, H.: First-principles computation of diffusional Mg isotope
 1058 fractionation in silicate melts, *Geochimica et Cosmochimica Acta*, 290, 27–40,
 1059 <https://doi.org/10.1016/j.gca.2020.08.028>, 2020.
- 1060 Luo, H., Karki, B. B., Ghosh, D. B., and Bao, H.: Deep neural network potentials for diffusional lithium
 1061 isotope fractionation in silicate melts, *Geochimica et Cosmochimica Acta*, 303, 38–50,
 1062 <https://doi.org/10.1016/j.gca.2021.03.031>, 2021.
- 1063 Macris C. A., Manning C. E. and Young E. D. (2015) Crystal chemical constraints on inter-mineral Fe
 1064 isotope fractionation and implications for Fe isotope disequilibrium in San Carlos mantle
 1065 xenoliths. *Geochim. Cosmochim. Acta* **154**, 168–185. Available at:
 1066 <http://dx.doi.org/10.1016/j.gca.2015.01.024>.
- 1067 Mallmann G. and O’Neill H. S. C. (2009) The crystal/melt partitioning of V during mantle melting as a

1068 function of oxygen fugacity compared with some other elements (Al, P, Ca, Sc, Ti, Cr, Fe, Ga, Y, Zr
1069 and Nb). *J. Petrol.* **50**, 1765–1794.

1070 Matsui M. (1994) A Transferable Interatomic Potential Model for Crystals and Melts in the System CaO-
1071 MgO-Al₂O₃-SiO₂. *Mineral. Mag.* **58A**, 571–572.

1072 McMillan P. (1984) Structural studies of silicate glasses and melts-applications and limitations of
1073 Raman spectroscopy. *Am. Mineral.* **69**, 622–644.

1074 Méheut M., Lazzeri M., Balan E. and Mauri F. (2009) Structural control over equilibrium silicon and
1075 oxygen isotopic fractionation: A first-principles density-functional theory study. *Chem. Geol.* **258**,
1076 28–37. Available at: <http://dx.doi.org/10.1016/j.chemgeo.2008.06.051>.

1077 Méheut M. and Schauble E. A. (2014) Silicon isotope fractionation in silicate minerals: Insights from
1078 first-principles models of phyllosilicates, albite and pyrope. *Geochim. Cosmochim. Acta* **134**, 137–
1079 154. Available at: <http://dx.doi.org/10.1016/j.gca.2014.02.014>.

1080 Meyer R. and Comtesse D. (2011) Vibrational density of states of silicon nanoparticles. *Phys. Rev. B -*
1081 *Condens. Matter Mater. Phys.* **83**, 1–6.

1082 Mysen B. O. (2006) The structural behavior of ferric and ferrous iron in aluminosilicate glass near meta-
1083 aluminosilicate joins. *Geochim. Cosmochim. Acta* **70**, 2337–2353.

1084 Mysen B. O., Lucier A. and Cody G. D. (2003) The structural behavior of Al³⁺ in peralkaline melts and
1085 glasses in the system Na₂O-Al₂O₃-SiO₂. *Am. Mineral.* **88**, 1668–1678. Available at:
1086 <https://doi.org/10.2138/am-2003-11-1206>.

1087 Mysen B. and Richet P. (2019a) *Properties of Aluminosilicate Systems., Silic. Glas. Melts, 263-300.*

1088 Mysen B. and Richet P. (2019b) Structure of Iron Silicate Glasses and Melts. *Silic. Glas. Melts*, 403–430.

1089 Nebel O., Sossi P. A., Bénard A., Wille M., Vroon P. Z. and Arculus R. J. (2015) Redox-variability and
1090 controls in subduction zones from an iron-isotope perspective. *Earth Planet. Sci. Lett.* **432**, 142–
1091 151. Available at: <http://dx.doi.org/10.1016/j.epsl.2015.09.036>.

1092 Nebel O., Sossi P. A., Foden J., Bénard A., Brandl P. A., Stammerer J. A., Lupton J., Richter M. and Arculus
1093 R. J. (2018) Iron isotope variability in ocean floor lavas and mantle sources in the Lau back-arc
1094 basin. *Geochim. Cosmochim. Acta* **241**, 150–163.

1095 Nosé S. (1984) A unified formulation of the constant temperature molecular dynamics methods. *J.*
1096 *Chem. Phys.* **81**, 511–519. Available at: <https://doi.org/10.1063/1.447334>.

1097 Oeser M., Dohmen R., Horn I., Schuth S. and Weyer S. (2015) Processes and time scales of magmatic
1098 evolution as revealed by Fe-Mg chemical and isotopic zoning in natural olivines. *Geochim.*
1099 *Cosmochim. Acta* **154**, 130–150. Available at: <http://dx.doi.org/10.1016/j.gca.2015.01.025>.

1100 Oeser M., Ruprecht P. and Weyer S. (2018) Combined Fe-Mg chemical and isotopic zoning in olivine
1101 constraining magma mixing-to-eruption timescales for the continental arc volcano Irazú (Costa
1102 Rica) and Cr diffusion in olivine. *Am. Mineral.* **103**, 582–599.

1103 Oeser M., Weyer S., Horn I. and Schuth S. (2014) High-precision Fe and Mg isotope ratios of silicate
1104 reference glasses determined in situ by femtosecond LA-MC-ICP-MS and by solution nebulisation
1105 MC-ICP-MS. *Geostand. Geoanalytical Res.* **38**, 311–328.

1106 Oestrike R., Yang W. hong, Kirkpatrick R. J., Hervig R. L., Navrotsky A. and Montez B. (1987) High-
1107 resolution ²³Na, ²⁷Al and ²⁹Si NMR spectroscopy of framework Aluminosilicate glasses.
1108 *Geochim. Cosmochim. Acta* **51**, 2199–2209.

1109 Perdew J. P., Burke K. and Ernzerhof M. (1996) Generalized gradient approximation made simple. *Phys.*
1110 *Rev. Lett.* **77**, 3865–3868.

1111 Pichavant M. (2002) Physical conditions, structure, and dynamics of a zoned magma chamber: Mount
1112 Pelée (Martinique, Lesser Antilles Arc). *J. Geophys. Res.* **107**.

1113 Pinilla C., Blanchard M., Balan E., Natarajan S. K., Vuilleumier R. and Mauri F. (2015) Equilibrium
1114 magnesium isotope fractionation between aqueous Mg²⁺ and carbonate minerals: Insights from
1115 path integral molecular dynamics. *Geochim. Cosmochim. Acta* **163**, 126–139.

1116 Pinilla C., De Moya A., Rabin S., Morard G., Roskosz M. and Blanchard M. (2021) First-principles
1117 investigation of equilibrium iron isotope fractionation in Fe(1-x)S_x alloys at Earth's core formation
1118 conditions. *Earth Planet. Sci. Lett.* **569**, 117059.

1119 Poitrasson F. (2017) Silicon Isotope Geochemistry. *Rev. Mineral. Geochemistry* **82**, 289–344. Available

1120 at: <https://doi.org/10.2138/rmg.2017.82.8>.

1121 Poitrasson F. and Freyrier R. (2005) Heavy iron isotope composition of granites determined by high
1122 resolution MC-ICP-MS. *Chem. Geol.* **222**, 132–147. Available at:
1123 <https://linkinghub.elsevier.com/retrieve/pii/S0009254105002615>.

1124 Poitrasson F. and Zambardi T. (2015) An Earth-Moon silicon isotope model to track silicic magma
1125 origins. *Geochim. Cosmochim. Acta* **167**, 301–312. Available at:
1126 <http://dx.doi.org/10.1016/j.gca.2015.07.005>.

1127 Polyakov V. B. and Mineev S. D. (2000) The use of Mossbauer spectroscopy in stable isotope
1128 geochemistry. *Geochim. Cosmochim. Acta* **64**, 849–865.

1129 Prissel K. B., Krawczynski M. J., Nie N. X., Dauphas N., Couvy H., Hu M. Y., Alp E. E. and Roskosz M.
1130 (2018) Experimentally determined effects of olivine crystallization and melt titanium content on
1131 iron isotopic fractionation in planetary basalts. *Geochim. Cosmochim. Acta* **238**, 580–598.

1132 Qin T., Wu F., Wu Z. and Huang F. (2016) First-principles calculations of equilibrium fractionation of O
1133 and Si isotopes in quartz, albite, anorthite, and zircon. *Contrib. to Mineral. Petrol.* **171**.

1134 Rabin S., Blanchard M., Pinilla C., Poitrasson F. and Grégoire M. (2021) First-principles calculation of
1135 iron and silicon isotope fractionation between Fe-bearing minerals at magmatic temperatures:
1136 The importance of second atomic neighbors. *Geochim. Cosmochim. Acta* **304**, 101–118.

1137 Richter F. M., Davis A. M., DePaolo D. J. and Watson E. B. (2003) Isotope fractionation by chemical
1138 diffusion between molten basalt and rhyolite. *Geochimica et Cosmochimica Acta* **67**, 3905–3923.

1139 Redlich O. (1935) Eine allgemeine beziehung zwischen den schwingungsfrequenzen isotoper molekeln.
1140 *Z Phys Chem* **28**, 371–382.

1141 Roskosz M., Dauphas N., Hu J., Hu M. Y., Neuville D. R., Brown D., Bi W., Nie N. X., Zhao J. and Alp E. E.
1142 (2022) Structural, redox and isotopic behaviors of iron in geological silicate glasses: A NRIXS study
1143 of Lamb-Mössbauer factors and force constants. *Geochim. Cosmochim. Acta* **321**, 184–205.
1144 Available at: <https://doi.org/10.1016/j.gca.2022.01.021>.

1145 Roskosz M., Sio C. K. I., Dauphas N., Bi W., Tissot F. L. H., Hu M. Y., Zhao J. and Alp E. E. (2015) Spinel-
1146 olivine-pyroxene equilibrium iron isotopic fractionation and applications to natural peridotites.
1147 *Geochim. Cosmochim. Acta* **169**, 184–199.

1148 Rossano S., Ramos A. Y. and Delaye J. M. (2000) Environment of ferrous iron in CaFeSi₂O₆ glass;
1149 contributions of EXAFS and molecular dynamics. *J. Non. Cryst. Solids* **273**, 48–52.

1150 Savage P. S., Georg R. B., Williams H. M., Burton K. W. and Halliday A. N. (2011) Silicon isotope
1151 fractionation during magmatic differentiation. *Geochim. Cosmochim. Acta* **75**, 6124–6139.
1152 Available at: <http://dx.doi.org/10.1016/j.gca.2011.07.043>.

1153 Savage P. S., Georg R. B., Williams H. M., Turner S., Halliday A. N. and Chappell B. W. (2012) The silicon
1154 isotope composition of granites. *Geochim. Cosmochim. Acta* **92**, 184–202. Available at:
1155 <http://dx.doi.org/10.1016/j.gca.2012.06.017>.

1156 Schoenberg R., Marks M. A. W., Schuessler J. A., von Blanckenburg F. and Markl G. (2009) Fe isotope
1157 systematics of coexisting amphibole and pyroxene in the alkaline igneous rock suite of the
1158 Ilímaussaq Complex, South Greenland. *Chem. Geol.* **258**, 65–77. Available at:
1159 <https://www.sciencedirect.com/science/article/pii/S0009254108002416> [Accessed April 26,
1160 2019].

1161 Schuessler J. A., Schoenberg R. and Sigmarsson O. (2009) Iron and lithium isotope systematics of the
1162 Hekla volcano, Iceland - Evidence for Fe isotope fractionation during magma differentiation.
1163 *Chem. Geol.* **258**, 78–91. Available at: <http://dx.doi.org/10.1016/j.chemgeo.2008.06.021>.

1164 Shahar A., Young E. D. and Manning C. E. (2008) Equilibrium high-temperature Fe isotope fractionation
1165 between fayalite and magnetite: An experimental calibration. *Earth Planet. Sci. Lett.* **268**, 330–
1166 338. Available at: <https://www.sciencedirect.com/science/article/pii/S0012821X08000435>
1167 [Accessed April 26, 2019].

1168 Sio C. K. I. and Dauphas N. (2017) Thermal and crystallization histories of magmatic bodies by Monte
1169 Carlo inversion of Mg-Fe isotopic profiles in olivine. *Geology* **45**, 67–70.

1170 Sio C. K. I., Dauphas N., Teng F. Z., Chaussidon M., Helz R. T. and Roskosz M. (2013) Discerning crystal
1171 growth from diffusion profiles in zoned olivine by in situ Mg-Fe isotopic analyses. *Geochim.*

1172 *Cosmochim. Acta* **123**, 302–321. Available at: <http://dx.doi.org/10.1016/j.gca.2013.06.008>.

1173 Sio C. K., Roskosz M., Dauphas N., Bennett N. R., Mock T. and Shahar A. (2018) The isotope effect for
1174 Mg-Fe interdiffusion in olivine and its dependence on crystal orientation, composition and
1175 temperature. *Geochim. Cosmochim. Acta* **239**, 463–480. Available at:
1176 <https://doi.org/10.1016/j.gca.2018.06.024>.

1177 Smith W., Yong C. W. and Rodger P. M. (2002) DL_POLY: Application to molecular simulation. *Mol.*
1178 *Simul.* **28**, 385–471. Available at: <https://doi.org/10.1080/08927020290018769>.

1179 Solomatova N. V. and Caracas R. (2021) Buoyancy and Structure of Volatile-Rich Silicate Melts. *J.*
1180 *Geophys. Res. Solid Earth* **126**, 1–14.

1181 Solomatova N. V. and Caracas R. (2019) Pressure-Induced Coordination Changes in a Pyrolytic Silicate
1182 Melt From Ab Initio Molecular Dynamics Simulations. *J. Geophys. Res. Solid Earth* **124**, 11232–
1183 11250.

1184 Sossi P. A., Foden J. D. and Halverson G. P. (2012) Redox-controlled iron isotope fractionation during
1185 magmatic differentiation: An example from the Red Hill intrusion, S. Tasmania. *Contrib. to*
1186 *Mineral. Petrol.* **164**, 757–772.

1187 Sossi P. A., Nebel O. and Foden J. (2016) Iron isotope systematics in planetary reservoirs. *Earth Planet.*
1188 *Sci. Lett.* **452**, 295–308. Available at: <http://dx.doi.org/10.1016/j.epsl.2016.07.032>.

1189 Sossi P. A. and O'Neill H. S. C. (2017) The effect of bonding environment on iron isotope fractionation
1190 between minerals at high temperature. *Geochim. Cosmochim. Acta* **196**, 121–143. Available at:
1191 <https://www.sciencedirect.com/science/article/pii/S0016703716305324>.

1192 Spallanzani, R., Koga, K. T., Cichy, S. B., Wiedenbeck, M., Schmidt, B. C., Oelze, M., and Wilke, M.:
1193 Lithium and boron diffusivity and isotopic fractionation in hydrated rhyolitic melts, Contributions
1194 to Mineralogy and Petrology, 177, 74, <https://doi.org/10.1007/s00410-022-01937-2>, 2022.

1195 Stein D. J. and Spera F. J. (1996) Molecular dynamics simulations of liquids and glasses in the system
1196 NaAlSiO₄-SiO₂: Physical properties and transport mechanisms. *Am. Mineral.* **81**, 284–302.

1197 Telus M., Dauphas N., Moynier F., Tissot F. L. H., Teng F. Z., Nabelek P. I., Craddock P. R. and Groat L.
1198 A. (2012) Iron, zinc, magnesium and uranium isotopic fractionation during continental crust
1199 differentiation: The tale from migmatites, granitoids, and pegmatites. *Geochim. Cosmochim. Acta*
1200 **97**, 247–265.

1201 Teng F.-Z., Dauphas N. and Helz R. T. (2008) Iron Isotope Fractionation During Magmatic Differentiation
1202 in Kilauea Iki Lava Lake. *Science (80-.)*. **320**, 1620–1622. Available at:
1203 <http://science.sciencemag.org/content/320/5883/1620.abstract>.

1204 Teng F. Z., Dauphas N., Helz R. T., Gao S. and Huang S. (2011) Diffusion-driven magnesium and iron
1205 isotope fractionation in Hawaiian olivine. *Earth Planet. Sci. Lett.* **308**, 317–324. Available at:
1206 <http://dx.doi.org/10.1016/j.epsl.2011.06.003>.

1207 Togo A. and Tanaka I. (2015) First principles phonon calculations in materials science. *Scr. Mater.* **108**,
1208 1–5. Available at: <http://dx.doi.org/10.1016/j.scriptamat.2015.07.021>.

1209 Weyer S., Anbar A. D., Brey G. P., Münker C., Mezger K. and Woodland A. B. (2005) Iron isotope
1210 fractionation during planetary differentiation. *Earth Planet. Sci. Lett.* **240**, 251–264.

1211 Weyer S. and Ionov D. A. (2007) Partial melting and melt percolation in the mantle: The message from
1212 Fe isotopes. *Earth Planet. Sci. Lett.* **259**, 119–133.

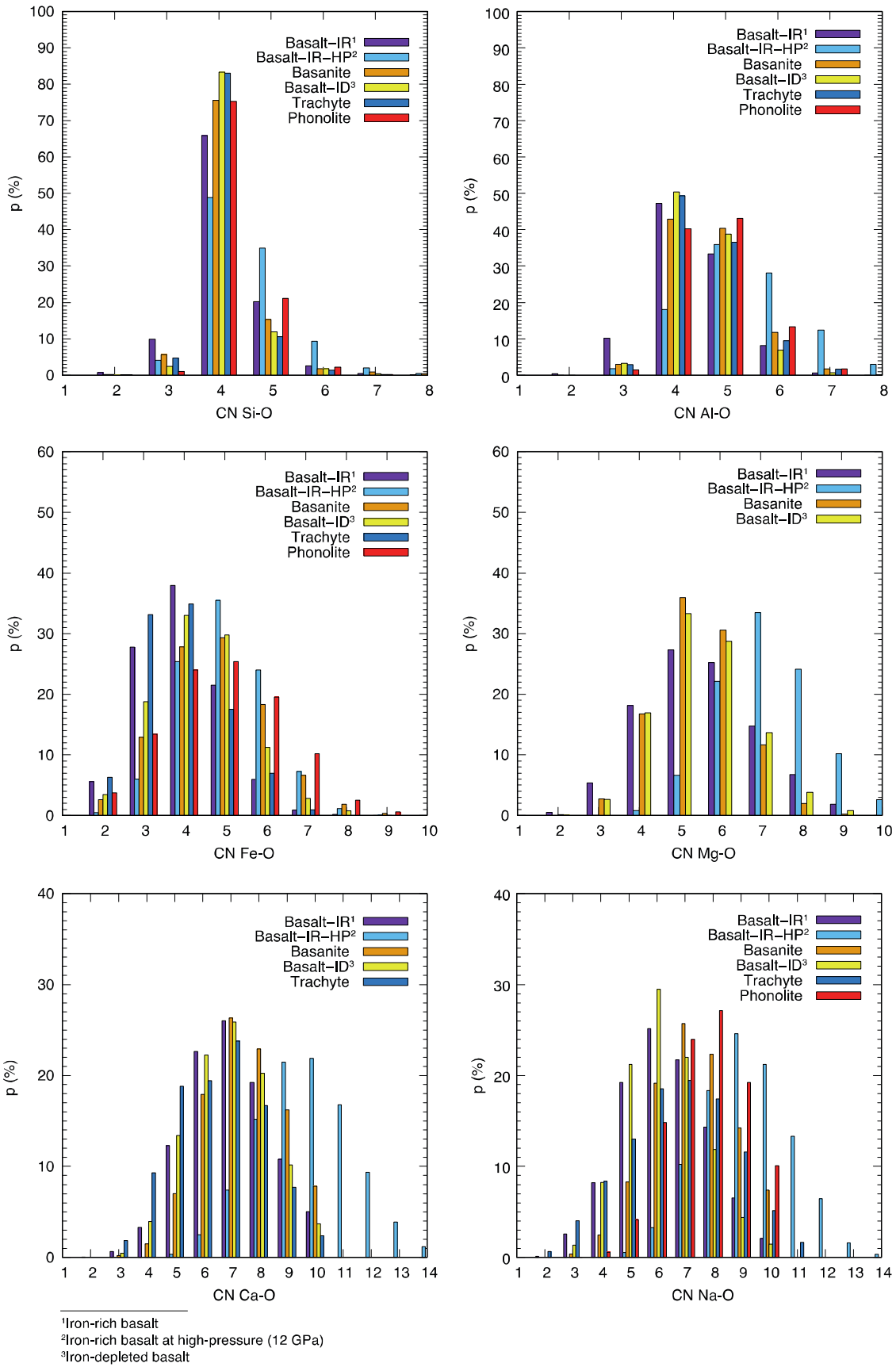
1213 Weyer S. and Seitz H. M. (2012) Coupled lithium- and iron isotope fractionation during magmatic
1214 differentiation. *Chem. Geol.* **294–295**, 42–50. Available at:
1215 <http://dx.doi.org/10.1016/j.chemgeo.2011.11.020>.

1216 Williams H. M. and Bizimis M. (2014) Iron isotope tracing of mantle heterogeneity within the source
1217 regions of oceanic basalts. *Earth Planet. Sci. Lett.* **404**, 396–407. Available at:
1218 <http://dx.doi.org/10.1016/j.epsl.2014.07.033>.

1219 Williams H. M., McCammon C. A., Peslier A. H., Halliday A. N., Teutsch N., Levasseur S. and Burg J.-P.
1220 (2004) Iron Isotope Fractionation and the Oxygen Fugacity of the Mantle. *Science (80-.)*. **304**,
1221 1656 LP – 1659. Available at: <http://science.sciencemag.org/content/304/5677/1656.abstract>.

1222 Williams H. M., Nielsen S. G., Renac C., Griffin W. L., O'Reilly S. Y., McCammon C. A., Pearson N., Viljoen
1223 F., Alt J. C. and Halliday A. N. (2009) Fractionation of oxygen and iron isotopes by partial melting

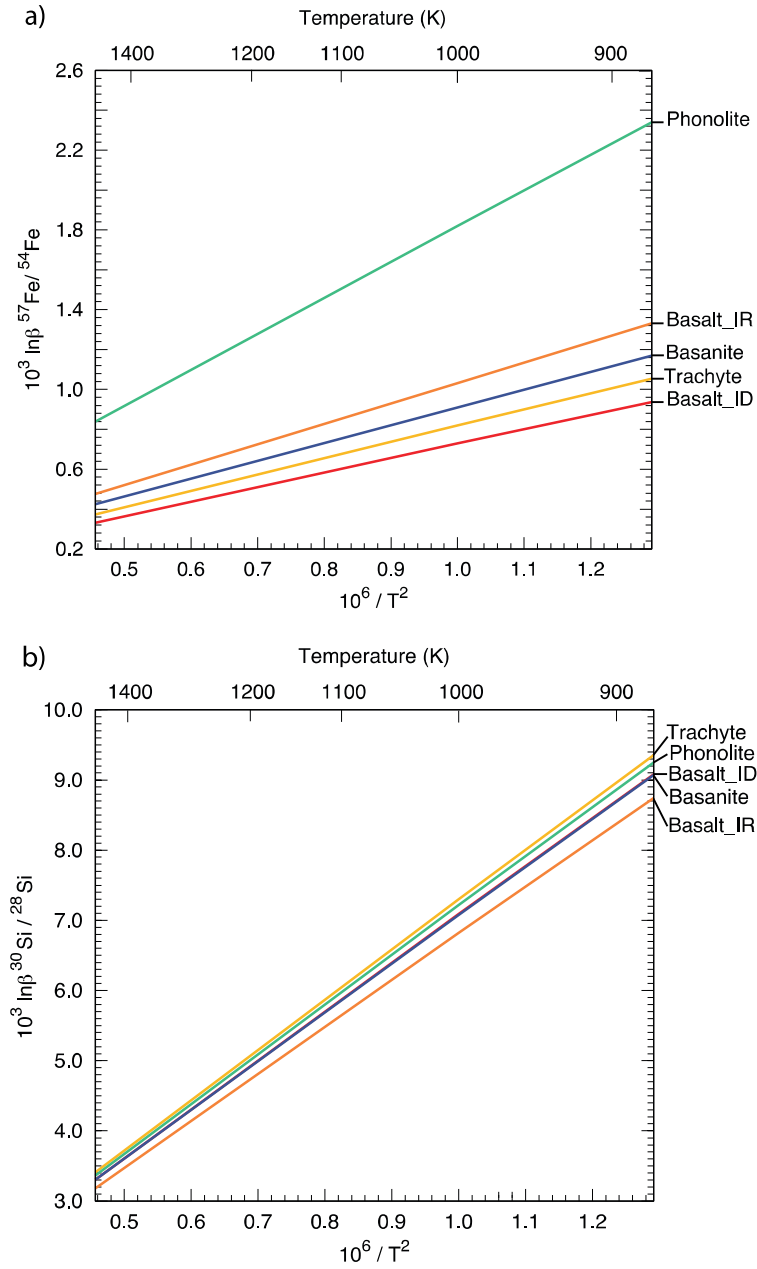
1224 processes: Implications for the interpretation of stable isotope signatures in mafic rocks. *Earth*
1225 *Planet. Sci. Lett.* **283**, 156–166. Available at:
1226 <https://www.sciencedirect.com/science/article/pii/S0012821X0900226X>.
1227 Williams H. M., Peslier A. H., McCammon C., Halliday A. N., Levasseur S., Teutsch N. and Burg J. P.
1228 (2005) Systematic iron isotope variations in mantle rocks and minerals: The effects of partial
1229 melting and oxygen fugacity. *Earth Planet. Sci. Lett.* **235**, 435–452.
1230 Williams H. M., Prytulak J., Woodhead J. D., Kelley K. A., Brounce M. and Plank T. (2018) Interplay of
1231 crystal fractionation, sulfide saturation and oxygen fugacity on the iron isotope composition of
1232 arc lavas: An example from the Marianas. *Geochim. Cosmochim. Acta* **226**, 224–243.
1233 Xia Y., Li S. and Huang F. (2017) Iron and Zinc isotope fractionation during magmatism in the
1234 continental crust: Evidence from bimodal volcanic rocks from Hailar basin, NE China. *Geochim.*
1235 *Cosmochim. Acta* **213**, 35–46. Available at: <http://dx.doi.org/10.1016/j.gca.2017.06.018>.
1236 Zambardi T., Lundstrom C. C., Li X. and McCurry M. (2014) Fe and Si isotope variations at Cedar Butte
1237 volcano; insight into magmatic differentiation. *Earth Planet. Sci. Lett.* **405**, 169–179. Available at:
1238 <http://dx.doi.org/10.1016/j.epsl.2014.08.020>.
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Figure 1 - Population analysis of the cation-oxygen coordination numbers for the different simulated melts.

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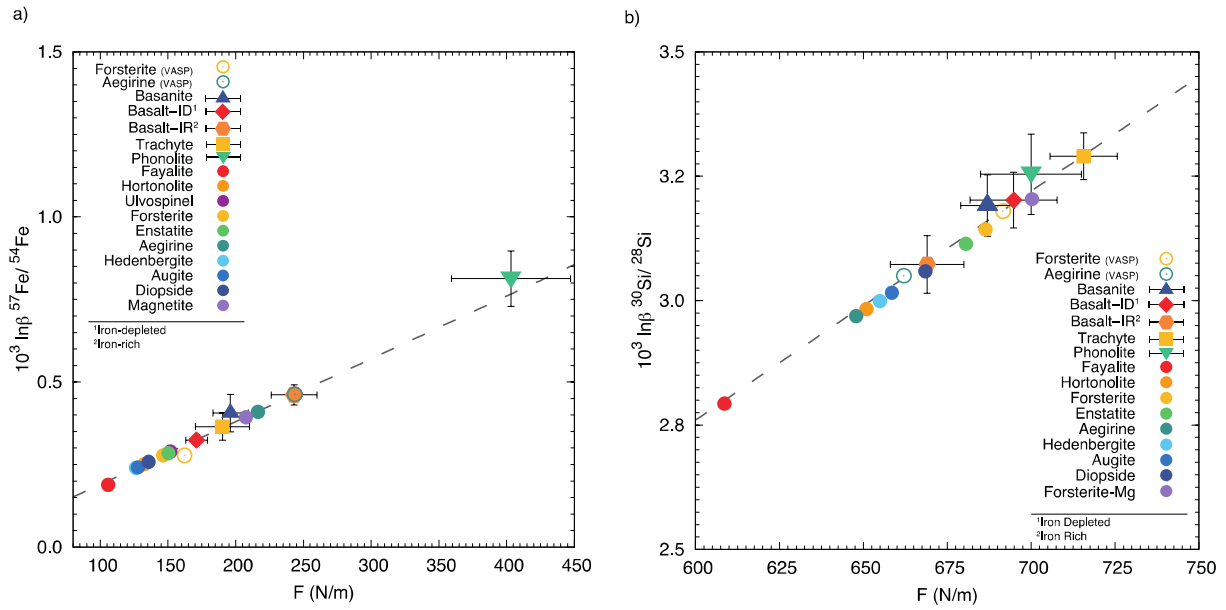
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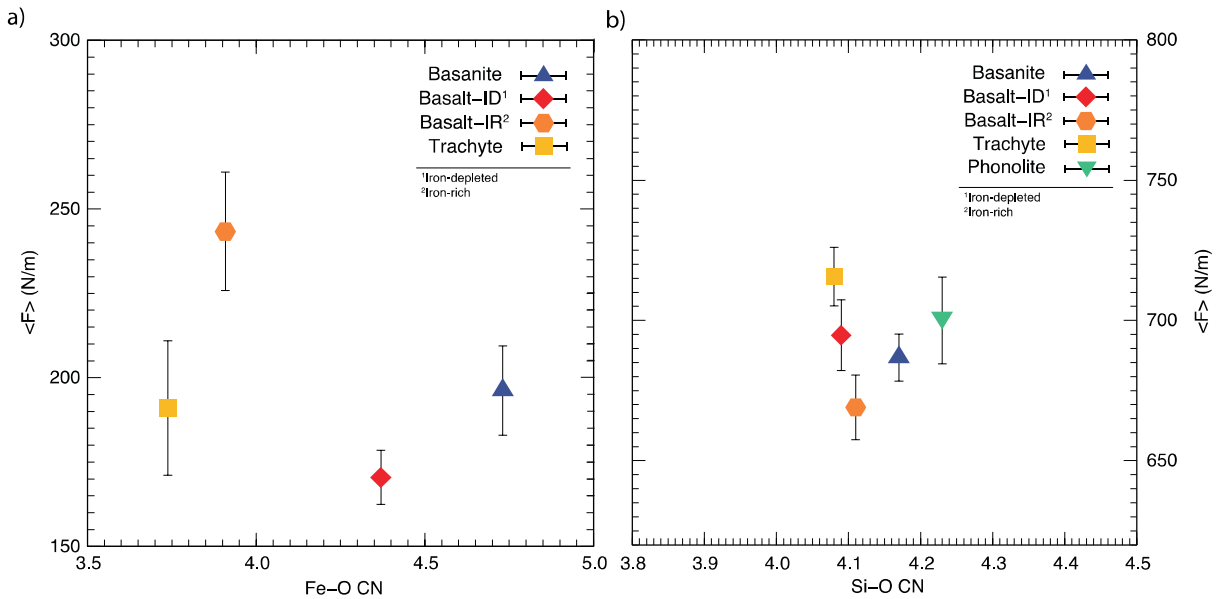
Figure 2 - High-temperature dependence of the reduced partition function ratio for a) iron isotopes and b) silicon isotopes. Basalt_ID and Basalt_IR are the iron-depleted and iron-rich basalt, respectively.

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Figure 3 - $10^3 \ln \beta$ as a function of the average force constant for iron (a) and silicon (b) at $T = 1500K$. Minerals in plain symbols $10^3 \ln \beta$ are taken from the first-principles study of Rabin et al. 2021. The linear fit for iron is $f(x) = 0.0019x$ for melts and minerals. The linear fit for silicon is $f(x) = 0.0046x$ for melts and minerals.



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Figure 4 - Relationship between the average force constant and the average coordination number for Fe (a) and Si (b).

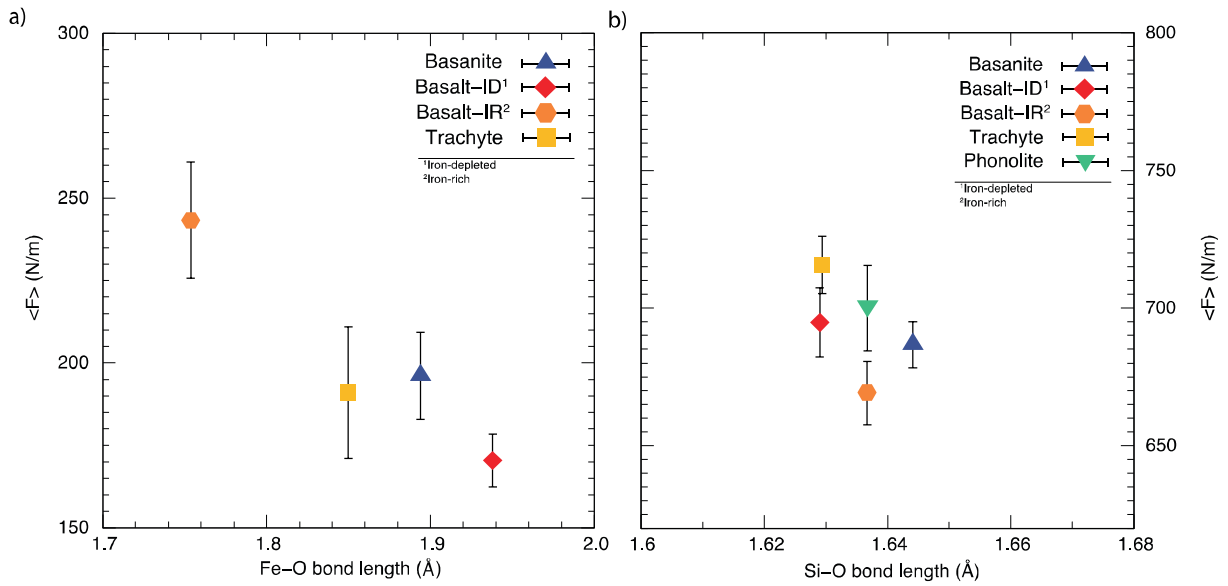


Figure 5 - Relationship between the average force constant and the average bond length for Fe (a) and Si (b).

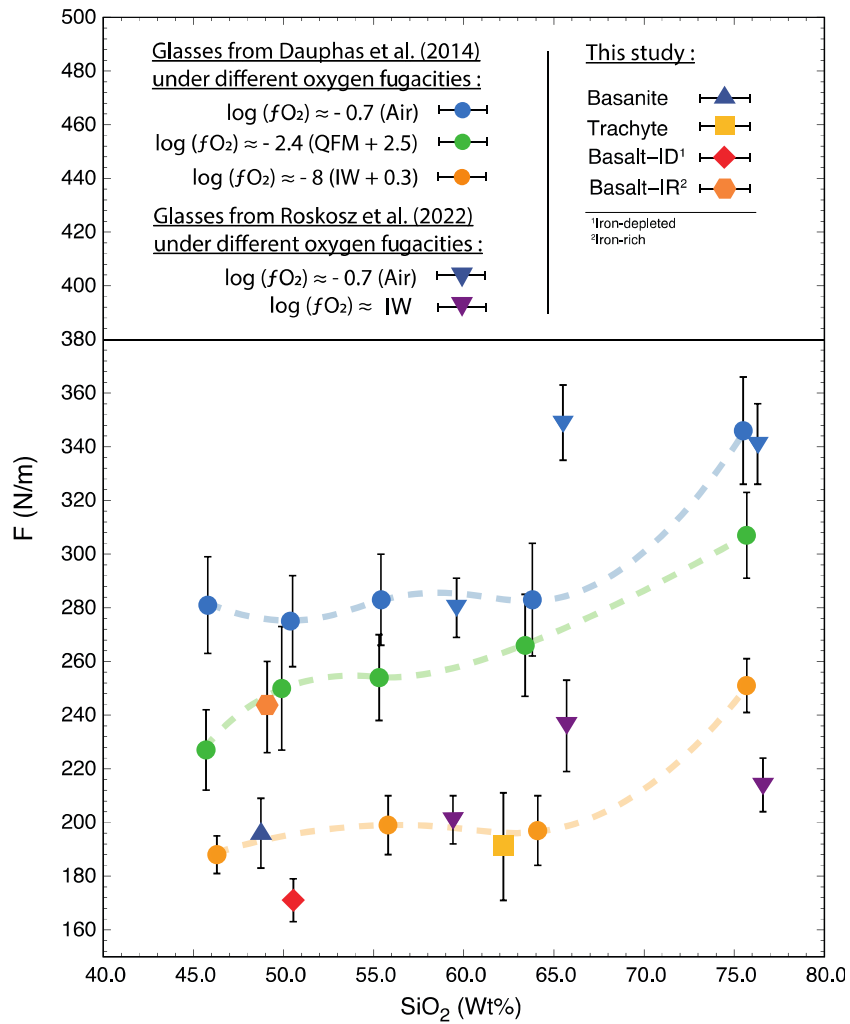
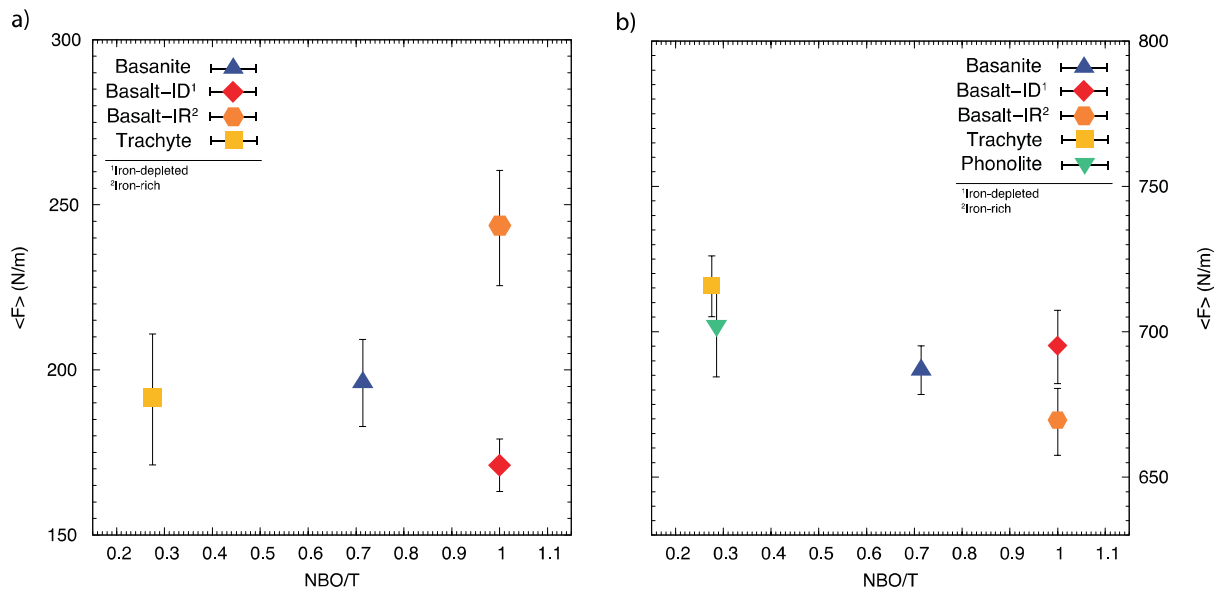
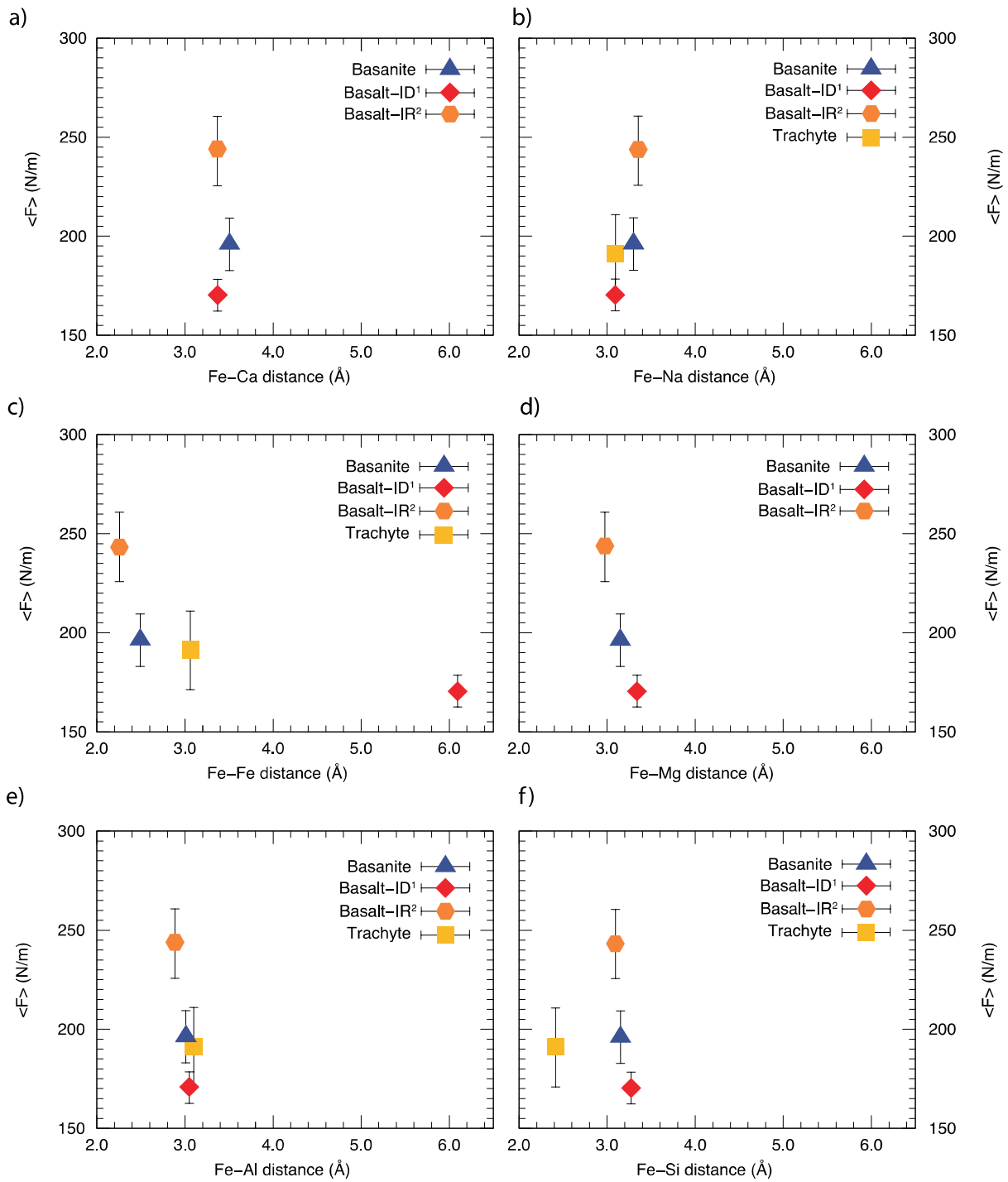


Figure 6 - Comparison of iron force constant of glasses (circles and upside-down triangles) under different oxygen fugacity measured experimentally by Dauphas et al. (2014) and Roskosz et al. (2022) with our calculated iron force constant for the different melts (triangles) versus SiO_2 (in Wt %).



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Figure 7 - Relationship between the degree of polymerization (NBO/T) and the Fe force constant (a) or Si force constant (b) of the melts.



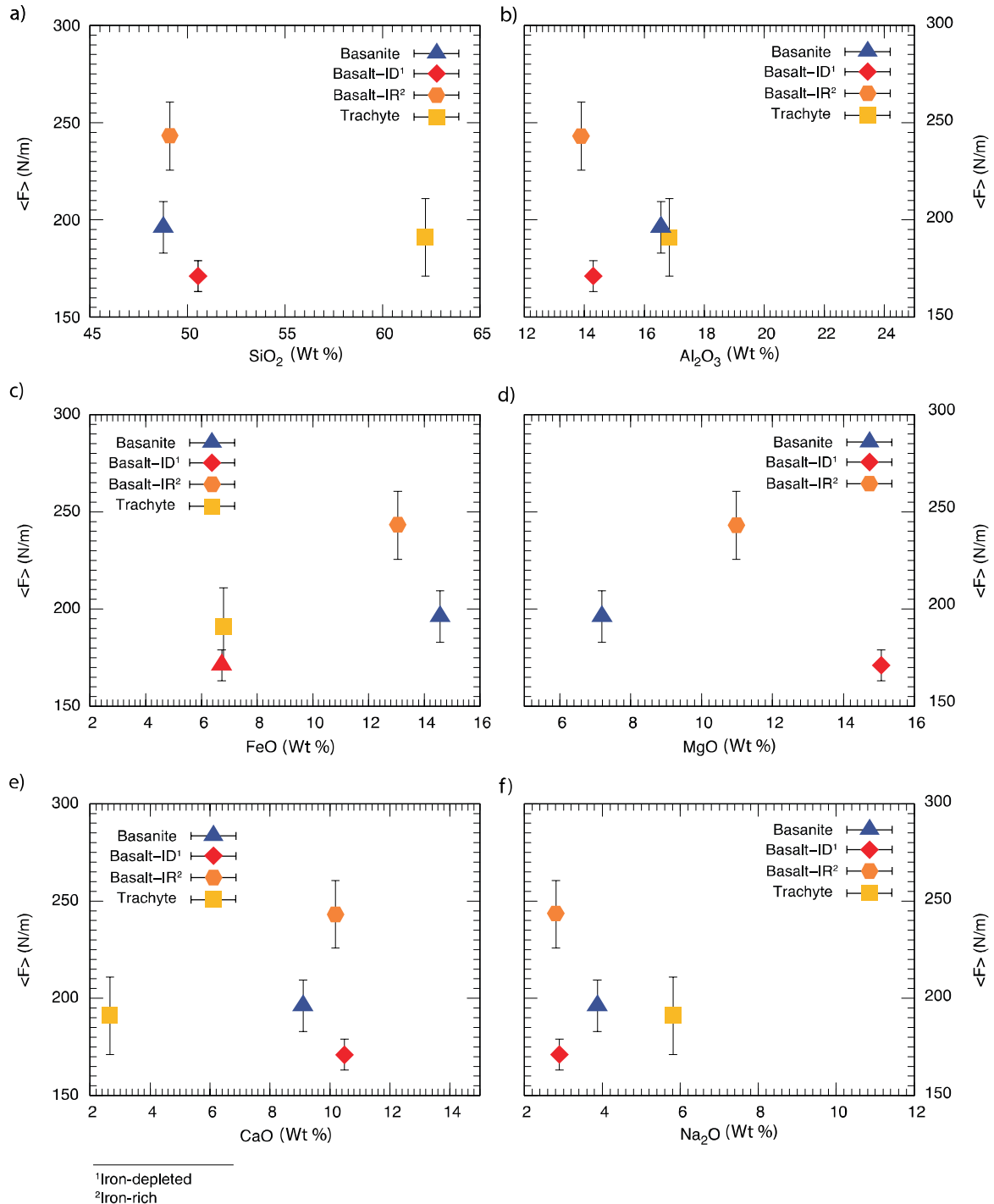
¹Iron-depleted
²Iron-rich

Figure 8 - Relationship between the average Fe-cation distance and the Fe force constant.

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Figure 9 - Relationship between the average iron force constant and the SiO₂ (a), Al₂O₃ (b), FeO (c), MgO (d), CaO (e) and Na₂O (f) content of the melts.

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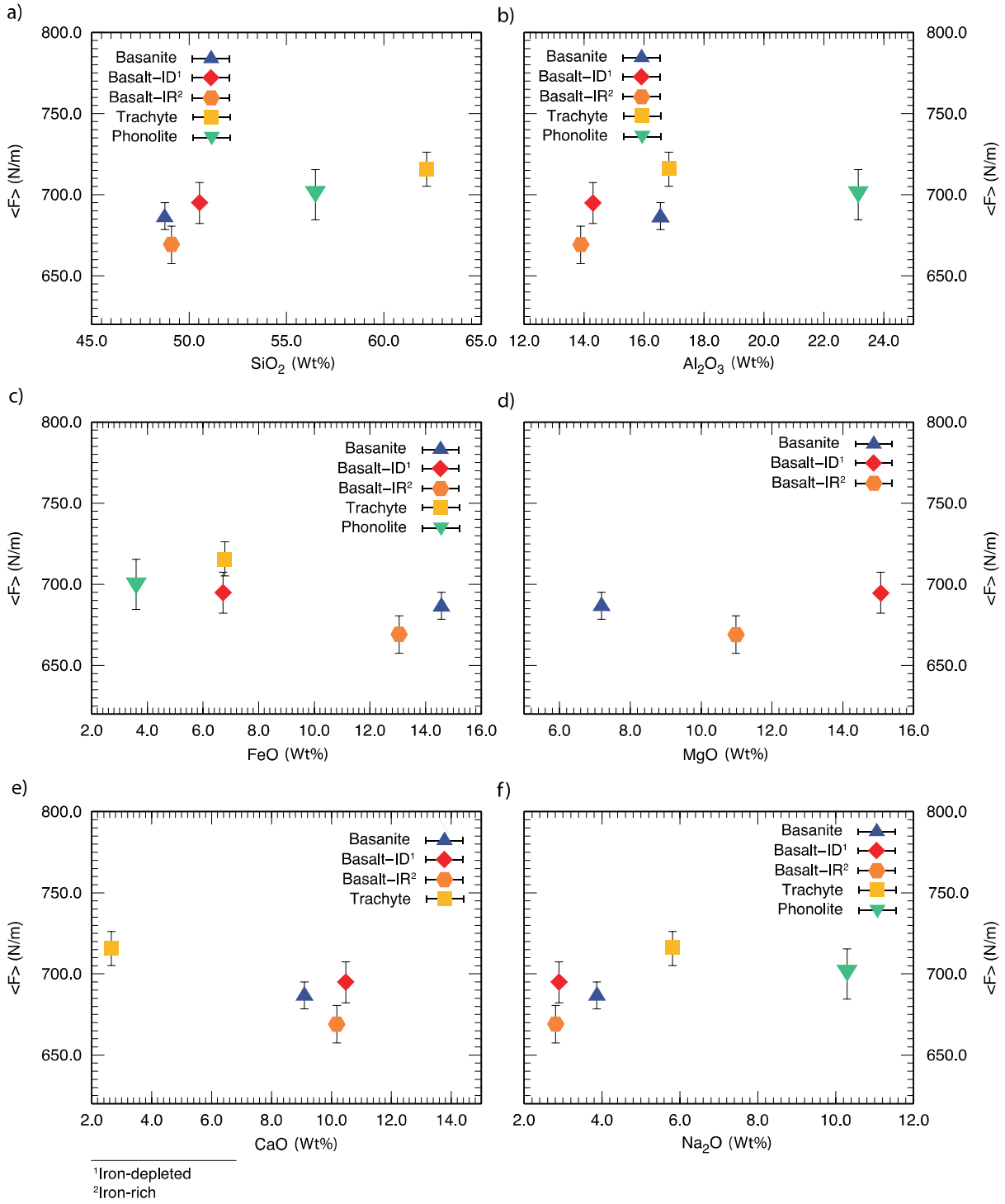
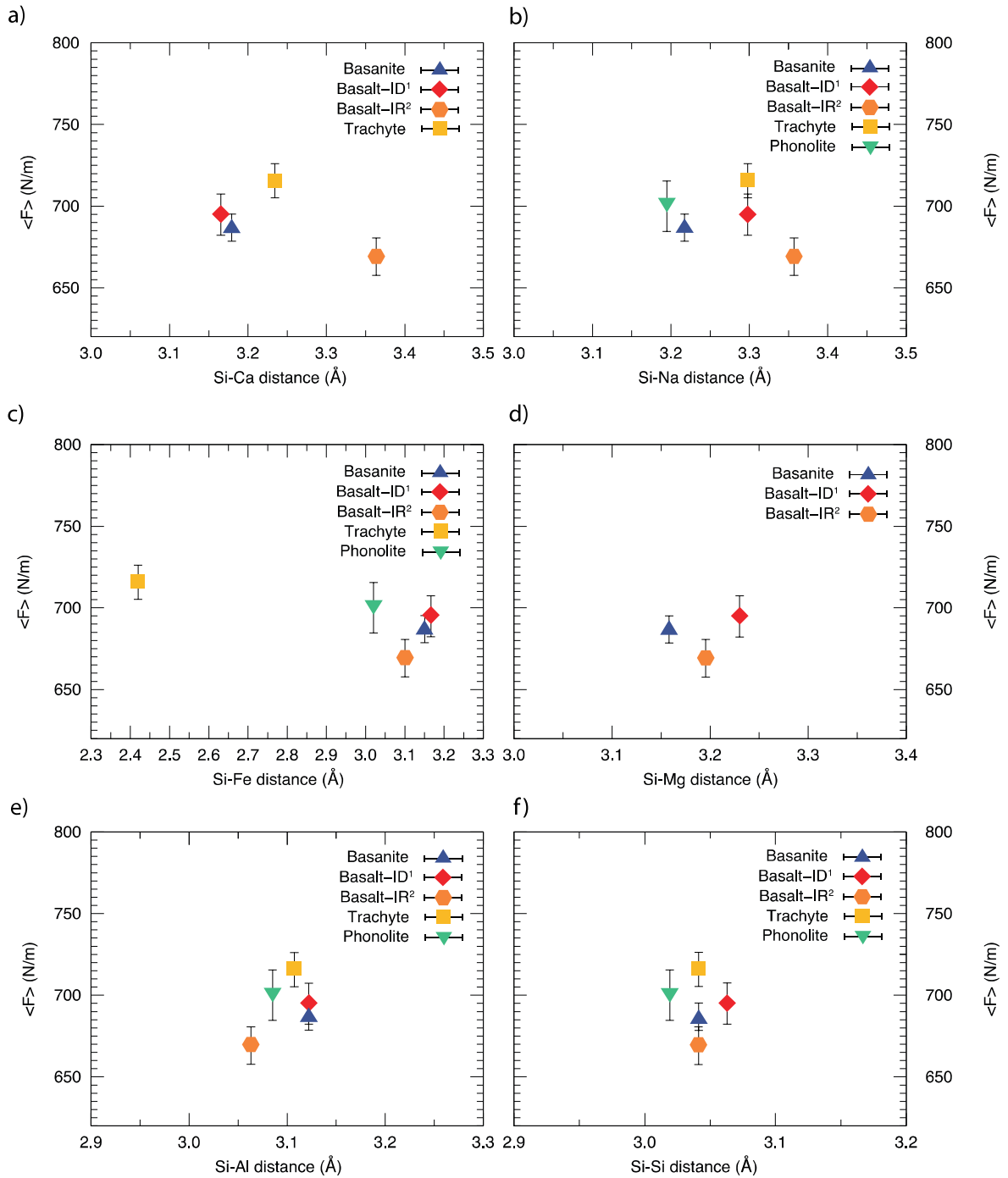


Figure 10 - Relationship between the average silicon force constant and the SiO₂ (a), Al₂O₃ (b), FeO (c), MgO (d), CaO (e) and Na₂O (f) content of the melts.

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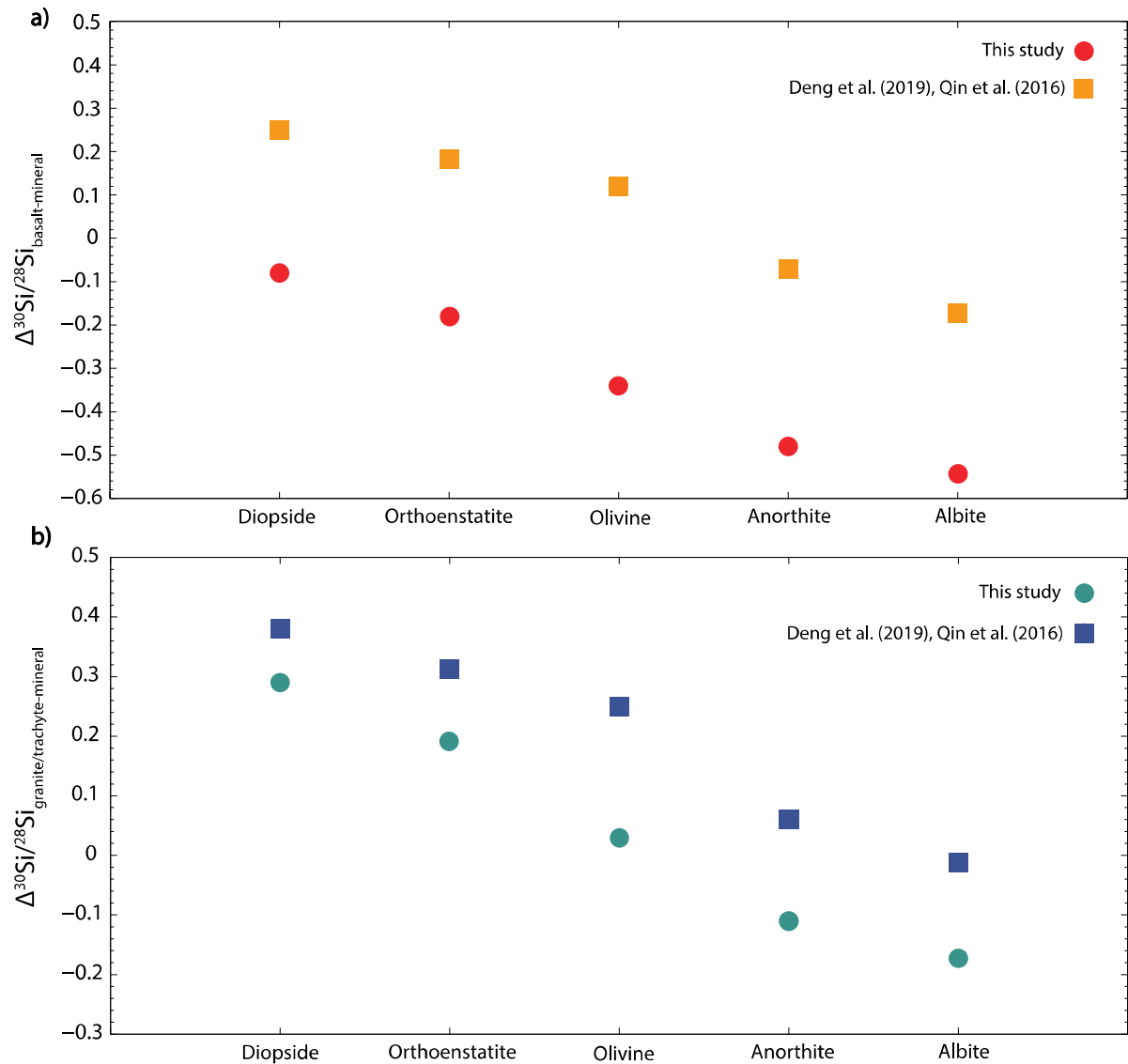


¹Iron-depleted
²Iron-rich

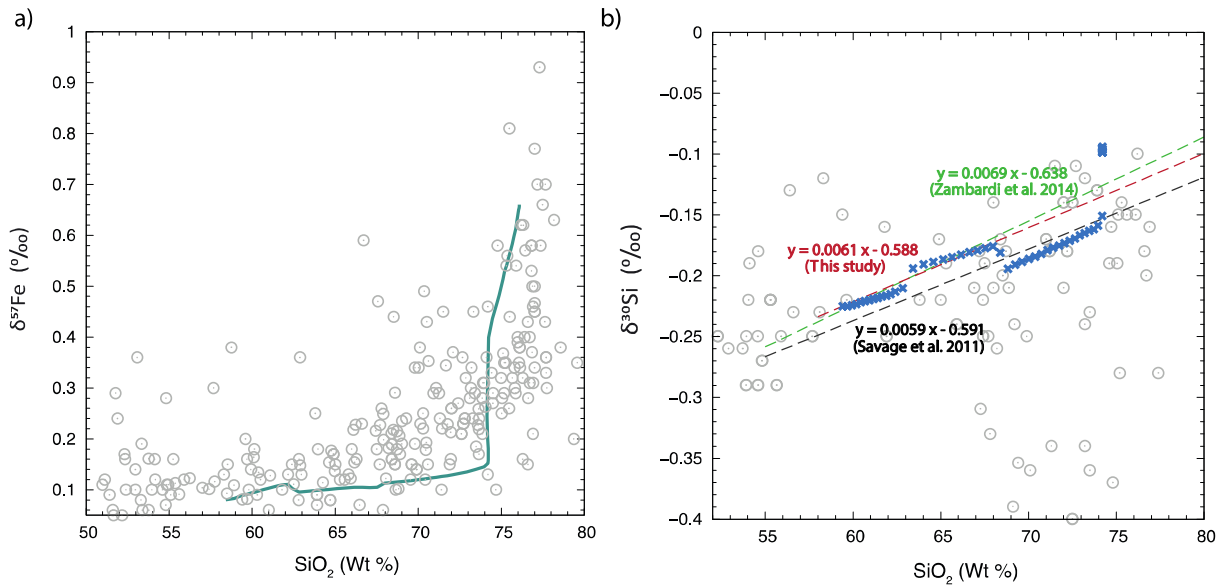
Figure 11 - Relationship between the average Si-cation distance and the Si force constant.

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 1314 Figure 12 - Comparison between $\Delta_{\text{melt-mineral}}^{30\text{Si}/28\text{Si}}$ calculated in this study and the ones estimated in Deng et al.
 1315 (2019) from Qin et al. (2016) at 1123 K. The melt β -factors used correspond to the basalt_IR (this study; red) and
 1316 MORB β -factors (Deng et al. 2019, Qin et al. 2016; orange) in figure a) and to the trachyte (this study; turquoise)
 1317 and the granite (Deng et al. 2019, Qin et al. 2016; dark blue) β -factors in figure b). The minerals corresponding
 1318 to the $\Delta_{\text{melt-mineral}}^{30\text{Si}/28\text{Si}}$ are displayed on the x-axis. Olivine corresponds here to forsterite (Mg_2SiO_4). The $\Delta_{\text{melt-}}$
 1319 $\text{mineral}^{30\text{Si}/28\text{Si}}$ displayed in this figure are also available in Table S1 – Appendix B – Supplementary material.
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1324 Figure 13 - Models of $\delta^{57}\text{Fe}$ (a; blue line) and $\delta^{30}\text{Si}$ (b; dark blue cross) evolution during magmatic differentiation
 1325 : Models were obtained using the MCS software (Bohrson et al., 2014) with starting andesite composition ($\text{SiO}_2 =$
 1326 58.23 , $\text{TiO}_2 = 0.94$, $\text{Al}_2\text{O}_3 = 16.94$, $\text{Cr}_2\text{O}_3 = 0.03$, $\text{FeO} = 7.31$, $\text{MgO} = 3.99$, $\text{CaO} = 7.08$, $\text{Na}_2\text{O} = 3.47$, $\text{K}_2\text{O} = 1.57$, P_2O_5
 1327 $= 0.24$, $\text{H}_2\text{O} = 0.20$) with an QFM buffer (Dauphas et al., 2014). Note that the “jumps” in the models correspond
 1328 to abrupt changes in term of mineralogy during melt differentiation in the MCS software. The grey circles in the
 1329 background correspond to $\delta^{57}\text{Fe}$ (a) and $\delta^{30}\text{Si}$ (b) from the literature (Foden et al., 2015; Poitrasson and Freyrier,
 1330 2005; Savage et al., 2011; Schuessler et al., 2009; Sossi et al., 2012; Telus et al., 2012; Teng et al., 2013; Williams
 1331 et al., 2018; Zambardi et al., 2014, Savage et al., 2012; Poitrasson and Zambardi, 2015; Du et al., 2017; He et al.,
 1332 2017; Xia et al., 2017). The fractionation factor $\Delta^{57}\text{Fe}_{\text{min-melt}}$ ($\Delta^{57}\text{Fe}_{\text{enstatite-trachyte}}$; $\Delta^{57}\text{Fe}_{\text{diopside-trachyte}}$; $\Delta^{57}\text{Fe}_{\text{ulvospinel-}}$
 1333 trachyte ; $\Delta^{57}\text{Fe}_{\text{magnetite-trachyte}}$) and $\Delta^{30}\text{Si}_{\text{min-melt}}$ ($\Delta^{30}\text{Si}_{\text{enstatite-trachyte}}$; $\Delta^{30}\text{Si}_{\text{diopside-trachyte}}$; $\Delta^{30}\text{Si}_{\text{anorthite-trachyte}}$; $\Delta^{30}\text{Si}_{\text{albite-trachyte}}$;
 1334 $\Delta^{30}\text{Si}_{\text{quartz-trachyte}}$) used in these models are displayed in Table 7. The linear trends in b) represent the linear fit of
 1335 bulk rock analyses obtained by Savage et al. (2011) in black and Zambardi et al. (2014) in green from natural
 1336 magmatic rocks analysis as well as the linear trend of our fractional crystallization modelled value (in red).

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	nb atoms	V (\AA^3)	Density ρ (g/cm ³)	Pressure (GPa)	Temperature (K)
Basalt_IR	100	1341.5	1.64	1.1	4000
Basalt_IR_183	183	2489.52	1.39	0.9	4000
Basalt_IR_HP	100	1079.03	1.98	11.7	4000
Basalt_ID	100	1289.51	1.66	0.7	4000
Basanite	110	1366.48	1.78	1.2	4000
Trachyte	104	1355.82	1.68	1.8	4000
Phonolite	102	1248.44	1.82	0.9	4000

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Table 1 - Characteristics of the modeled melts. The pressure given for each melt represents the mean pressure of each FPMD trajectories. The temperature is the target temperature of the FPMD simulations. Basalt_IR_183 and Basalt_IR_HP have the same composition as the iron-rich basalt Basalt_IR with either a larger simulation cell (183 atoms) or a higher pressure (12 GPa). Basalt_ID is the iron depleted basalt.

	<i>Basalt_IR</i>	<i>Basalt_ID</i>	<i>Basanite</i>	<i>Trachyte</i>	<i>Phonolite</i>
<i>SiO₂</i>	49.09	50.54	48.75	62.20	56.48
<i>Al₂O₃</i>	13.89	14.30	16.55	16.83	23.15
<i>FeO_T</i>	13.05	6.72	14.57	6.79	3.60
<i>MgO</i>	10.98	15.07	7.19		0.00
<i>CaO</i>	10.18	10.48	9.10	2.66	0.00
<i>Na₂O</i>	2.81	2.90	3.87	5.81	10.29
<i>K₂O</i>	-	-	-	5.71	6.48
<i>Fe mean valence</i>	2.3	2.37	2.36	2.33	2.28
<i>NBO/T</i>	1	1	0.71	0.29	0.28

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Table 2 - Composition in wt % and degree of polymerization (NBO/T) of the modeled melts as well as the mean valence of iron atoms in the melts that correspond to the Born effective charge calculated in VASP. See Table 1 for sample denomination.

	Ca-O		Na-O		K-O		Fe-O		Mg-O		Al-O		Si-O	
	CN	d(\AA)	CN	d(\AA)	CN	d(\AA)	CN	d(\AA)	CN	d(\AA)	CN	d(\AA)	CN	d(\AA)
Basalt_IR	6.92	2.28	6.55	2.30	-	-	3.91	1.76	5.31	1.99	4.57	1.77	4.11	1.64
Basalt_183	6.88	2.26	6.43	2.28	-	-	3.95	1.78	5.25	1.97	4.49	1.77	4.07	1.64
Basalt_HP	9.53	2.24	9.27	2.24	-	-	5.08	1.80	7.12	1.95	5.45	1.76	4.64	1.64
Basalt_ID	6.95	2.28	6.24	2.35	-	-	4.37	1.94	5.27	1.99	4.59	1.77	4.09	1.63
Basanite	7.48	2.31	7.76	2.30	-	-	4.73	1.90	5.32	1.98	4.75	1.77	4.17	1.64
Trachyte	6.49	2.25	6.80	2.32	10.28	2.68	3.74	1.85	-	-	4.66	1.81	4.08	1.63
Phonolite	-	-	7.71	2.25	11.42	2.65	5.11	1.63	-	-	4.73	1.78	4.23	1.64

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Table 3 - Cation-oxygen coordination number as well as the average cation-oxygen bond length of the modeled melts. See Table 1 for sample denomination.

	Basalt_IR		Basalt_ID		Basanite		Trachyte		Phonolite	
	d(Å)	CN	d(Å)	CN	d(Å)	CN	d(Å)	CN	d(Å)	CN
Fe-Ca	3.37	1.27	3.37	1.13	3.50	1.49	-	-	-	-
Fe-Na	3.35	0.64	3.09	1.14	3.30	0.91	3.09	0.63	3.09	1.27
Fe-K	-	-	-	-	-	-	-	-	3.59	2.07
Fe-Fe	2.25	1.21	6.09	-	2.49	1.24	3.06	-	-	-
Fe-Mg	2.98	1.43	3.34	2.07	3.15	1.05	-	-	-	-
Fe-Al	3.10	1.06	3.05	1.29	3.01	1.79	3.10	1.68	3.17	3.09
Fe-Si	3.09	3.02	3.08	4.06	3.15	4.19	2.97	4.11	3.00	4.30
Si-Ca	3.36	1.30	3.17	1.38	3.26	1.11	3.24	0.37	-	-
Si-Na	3.36	0.76	3.30	0.51	3.22	1.16	3.30	1.17	3.20	2.49
Si-Fe	3.09	0.68	3.10	0.56	3.15	1.21	2.95	0.38	3.02	0.22
Si-Mg	3.20	1.70	3.23	1.80	3.15	1.02	-	-	-	-
Si-Al	3.06	1.30	3.12	0.65	3.12	1.56	3.11	1.42	3.09	1.69
Si-Si	3.04	2.36	3.06	1.22	3.04	2.31	3.04	2.88	3.02	2.81
Si-K	-	-	-	-	-	-	3.58	2.16	3.50	2.80

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1356 Table 4 - Iron-cation and silicon-cation coordination numbers and their corresponding average distance in the
1357 modeled melts. See Table 1 for sample denomination.

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	$10^3 \ln \beta^{57\text{Fe}/54\text{Fe}}$			$10^3 \ln \beta^{30\text{Si}/28\text{Si}}$			
	A	B	Value at 1500 K	A	B	C	Value at 1500 K
Basalt_IR	-0.0059	1.0332	0.461 ± 0.031	0.0028	-0.1474	6.9342	3.073 ± 0.058
Basalt_ID	-0.0035	0.7269	0.324 ± 0.015	0.0031	-0.1569	7.2036	3.202 ± 0.056
Basanite	-0.0061	0.8986	0.406 ± 0.057	0.0031	-0.1578	7.1926	3.191 ± 0.062
Trachyte	-0.0044	0.8178	0.365 ± 0.041	0.0033	-0.165	7.4202	3.290 ± 0.047
Phonolite	-0.0155	1.8063	0.813 ± 0.084	0.0033	-0.1643	7.334	3.254 ± 0.081

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1360 Table 5 - Polynomial fits of the reduced partition function ratios for $^{57}\text{Fe}/^{54}\text{Fe}$ and $^{30}\text{Si}/^{28}\text{Si}$. Polynomial fits use
1361 equation of type $Ax^2 + Bx$ for $10^3 \ln \beta^{57\text{Fe}/54\text{Fe}}$ and $Ax^3 + Bx^2 + Cx$ for $10^3 \ln \beta^{30\text{Si}/28\text{Si}}$ with $x = 10^6/T^2$ for T between
1362 0 and 1500 K. See Table 1 for sample denomination.
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	Fe force constant		Si force constant
	« Snapshot » method	« VAF » method	« Snapshot » method
Basalt_IR	243 ± 17	235 ± 24	669 ± 11
Basalt_ID	171 ± 8	193 ± 19	695 ± 13
Basanite	196 ± 13	196 ± 23	687 ± 8
Phonolite	403 ± 44	290 ± 99	700 ± 15
Trachyte	191 ± 20	159 ± 38	716 ± 10
Basalt_HP	-	269 ± 33	-
Basalt_183	-	222 ± 12	-

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1365 Table 6 - Comparison of the iron average force constants of the melts (in N/m) using either the “snapshot”
1366 method or the “VAF” method as well as the silicon force constants of the melts using the “snapshot” method.
1367 See Table 1 for sample denomination.

	$\Delta_{A-B}^{57}\text{Fe}/^{54}\text{Fe}$			$\Delta_{A-B}^{29}\text{Si}/^{30}\text{Si}$			
	C ₁	C ₂	at 1500 K	C ₁	C ₂	C ₃	at 1500 K
$\Delta_{\text{Aegirine-Basalt_IR}}$	0.0013	-0.0081	-0.003 ± 0.04	$\Delta_{\text{Aegirine-Basalt_IR}}$	-0.0003	0.0128	-0.1088 -0.046 ± 0.15
$\Delta_{\text{Enstatite-Basalt_IR}}$	0.0028	-0.32	-0.142 ± 0.03	$\Delta_{\text{Enstatite-Basalt_IR}}$	0.0001	-0.0029	0.229 0.101 ± 0.16
$\Delta_{\text{Forsterite-Basalt_IR}}$	0.0036	-0.3385	-0.150 ± 0.03	$\Delta_{\text{Forsterite-Basalt_IR}}$	0.0004	-0.0035	0.2951 0.130 ± 0.16
$\Delta_{\text{Augite-Basalt_IR}}$	0.0038	-0.4266	-0.189 ± 0.03	$\Delta_{\text{Augite-Basalt_IR}}$	-0.0002	0.0077	0.0022 0.002 ± 0.15
$\Delta_{\text{Hortonolite-Basalt_IR}}$	0.0039	-0.4042	-0.179 ± 0.03	$\Delta_{\text{Hortonolite-Basalt_IR}}$	-0.0003	0.01	0.074 0.035 ± 0.15
$\Delta_{\text{Hedenbergite-Basalt_IR}}$	0.0043	-0.4329	-0.192 ± 0.03	$\Delta_{\text{Hedenbergite-Basalt_IR}}$	-0.0002	0.0067	-0.0376 -0.015 ± 0.15
$\Delta_{\text{Fayalite-Basalt_IR}}$	0.0047	-0.5601	-0.248 ± 0.03	$\Delta_{\text{Fayalite-Basalt_IR}}$	-0.0007	0.0268	-0.515 -0.224 ± 0.14
$\Delta_{\text{Diopside-Basalt_IR}}$	0.0039	-0.3884	-0.172 ± 0.03	$\Delta_{\text{Diopside-Basalt_IR}}$	0.0004	0.000009	0.1026 0.046 ± 0.16
$\Delta_{\text{Ulvospinel-Basalt_IR}}$	0.0033	-0.3104	-0.137 ± 0.03	$\Delta_{\text{Forsterite-Mg-Basalt_IR}}$	0.0001	-0.0092	0.4385 0.193 ± 0.16
$\Delta_{\text{Magnetite-Basalt_IR}}$	0.0023	-0.0476	-0.021 ± 0.04	$\Delta_{\text{Quartz-Basalt_IR}}$	0.0062	-0.0694	0.7804 0.334 ± 0.17
				$\Delta_{\text{Anorthite-Basalt_IR}}$	0.0059	-0.066	0.7351 0.314 ± 0.17
				$\Delta_{\text{Albite-Basalt_IR}}$	0.0055	-0.0609	0.6467 0.276 ± 0.171
$\Delta_{\text{Aegirine-Basalt_ID}}$	-0.0011	0.2982	0.132 ± 0.03	$\Delta_{\text{Aegirine-Basalt_ID}}$	-0.0006	0.0223	-0.3782 -0.164 ± 0.15
$\Delta_{\text{Enstatite-Basalt_ID}}$	0.0004	-0.0137	-0.006 ± 0.02	$\Delta_{\text{Enstatite-Basalt_ID}}$	-0.0002	0.0066	-0.0404 -0.017 ± 0.16
$\Delta_{\text{Forsterite-Basalt_ID}}$	0.0012	-0.0322	-0.014 ± 0.02	$\Delta_{\text{Forsterite-Basalt_ID}}$	-0.0003	0.006	0.0257 0.013 ± 0.16
$\Delta_{\text{Augite-Basalt_ID}}$	0.0014	-0.1203	-0.053 ± 0.02	$\Delta_{\text{Augite-Basalt_ID}}$	-0.0005	0.0172	-0.2672 -0.115 ± 0.15
$\Delta_{\text{Hortonolite-Basalt_ID}}$	0.0015	-0.0979	-0.043 ± 0.02	$\Delta_{\text{Hortonolite-Basalt_ID}}$	-0.0006	0.0195	-0.3434 -0.149 ± 0.15
$\Delta_{\text{Hedenbergite-Basalt_ID}}$	0.0019	-0.1266	-0.056 ± 0.02	$\Delta_{\text{Hedenbergite-Basalt_ID}}$	-0.0005	0.0162	-0.307 -0.133 ± 0.15
$\Delta_{\text{Fayalite-Basalt_ID}}$	0.0023	-0.2538	-0.112 ± 0.02	$\Delta_{\text{Fayalite-Basalt_ID}}$	-0.001	0.0363	-0.7844 -0.342 ± 0.14
$\Delta_{\text{Diopside-Basalt_ID}}$	0.0015	-0.0821	-0.036 ± 0.02	$\Delta_{\text{Diopside-Basalt_ID}}$	-0.0003	0.0095	-0.1668 -0.072 ± 0.15
$\Delta_{\text{Ulvospinel-Basalt_ID}}$	0.0009	-0.0041	-0.002 ± 0.02	$\Delta_{\text{Forsterite-Mg-Basalt_ID}}$	-0.0002	0.0003	0.1691 0.075 ± 0.16
$\Delta_{\text{Magnetite-Basalt_ID}}$	-0.000056	0.258656	0.115 ± 0.03	$\Delta_{\text{Quartz-Basalt_ID}}$	0.0059	-0.0599	0.511 0.216 ± 0.17
				$\Delta_{\text{Anorthite-Basalt_ID}}$	0.0052	-0.0514	0.3773 0.158 ± 0.17
				$\Delta_{\text{Albite-Basalt_ID}}$	0.0056	-0.0565	0.4657 0.196 ± 0.17
$\Delta_{\text{Aegirine-Basanite}}$	0.0015	0.1265	0.057 ± 0.06	$\Delta_{\text{Aegirine-Basanite}}$	-0.0006	0.0232	-0.3672 -0.159 ± 0.16
$\Delta_{\text{Enstatite-Basanite}}$	0.003	-0.1854	-0.082 ± 0.06	$\Delta_{\text{Enstatite-Basanite}}$	-0.0002	0.0075	-0.0294 -0.012 ± 0.17
$\Delta_{\text{Forsterite-Basanite}}$	0.0038	-0.2039	-0.090 ± 0.06	$\Delta_{\text{Forsterite-Basanite}}$	-0.0003	0.0069	0.0367 0.018 ± 0.17
$\Delta_{\text{Augite-Basanite}}$	0.004	-0.292	-0.129 ± 0.06	$\Delta_{\text{Augite-Basanite}}$	-0.0005	0.0181	-0.2562 -0.110 ± 0.16
$\Delta_{\text{Hortonolite-Basanite}}$	0.0041	-0.2538	-0.112 ± 0.06	$\Delta_{\text{Hortonolite-Basanite}}$	-0.0006	0.0204	-0.3324 -0.144 ± 0.16
$\Delta_{\text{Hedenbergite-Basanite}}$	0.0045	-0.2983	-0.132 ± 0.06	$\Delta_{\text{Hedenbergite-Basanite}}$	-0.0005	0.0171	-0.296 -0.128 ± 0.16
$\Delta_{\text{Fayalite-Basanite}}$	0.0049	-0.4255	-0.188 ± 0.06	$\Delta_{\text{Fayalite-Basanite}}$	-0.001	0.0372	-0.7734 -0.336 ± 0.15
$\Delta_{\text{Diopside-Basanite}}$	0.0041	-0.2538	-0.112 ± 0.06	$\Delta_{\text{Diopside-Basanite}}$	-0.0003	0.0104	-0.1558 -0.067 ± 0.16
$\Delta_{\text{Ulvospinel-Basanite}}$	0.0035	-0.1758	-0.077 ± 0.06	$\Delta_{\text{Forsterite-Mg-Basanite}}$	-0.0002	0.0012	0.1801 0.080 ± 0.17
$\Delta_{\text{Magnetite-Basanite}}$	0.0025	0.087	0.039 ± 0.06	$\Delta_{\text{Quartz-Basanite}}$	0.0059	-0.059	0.522 0.221 ± 0.18
				$\Delta_{\text{Anorthite-Basanite}}$	0.0052	-0.0505	0.3883 0.163 ± 0.18
				$\Delta_{\text{Albite-Basanite}}$	0.0056	-0.056	0.4767 0.201 ± 0.18

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Table 7 - Polynomial fits of iron and silicon fractionation factors between various minerals and melts. Polynomial fits use equation of type $C_1x^2 + C_2x$ for $\Delta^{57}\text{Fe}-^{54}\text{Fe}$ and $C_1x^3 + C_2x^2 + C_3x$ for $\Delta^{30}\text{Si}-^{28}\text{Si}$ with $x = 10^6/T^2$ for T between 0 and 1500 K. The iron and silicon β -factor of minerals were taken from Rabin et al. (2021) for all minerals except quartz, albite and anorthite that were taken from Qin et al. (2016).

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$\Delta_{A-B}^{57\text{Fe}/54\text{Fe}}$				$\Delta_{A-B}^{29\text{Si}/30\text{Si}}$				
A	C ₁	C ₂	at 1500 K	A	C ₁	C ₂	C ₃	at 1500 K
$\Delta_{\text{Aegirine-Trachyte}}$	-0.0002	0.2073	0.092 ± 0.05	$\Delta_{\text{Aegirine-Trachyte}}$	-0.0008	0.0304	-0.5948	-0.258 ± 0.15
$\Delta_{\text{Enstatite-Trachyte}}$	0.0013	-0.1046	-0.046 ± 0.04	$\Delta_{\text{Enstatite-Trachyte}}$	-0.0004	0.0147	-0.257	-0.111 ± 0.16
$\Delta_{\text{Forsterite-Trachyte}}$	0.0021	-0.1231	-0.054 ± 0.04	$\Delta_{\text{Forsterite-Trachyte}}$	-0.0005	0.0141	-0.1909	-0.082 ± 0.16
$\Delta_{\text{Augite-Trachyte}}$	0.0023	-0.2112	-0.093 ± 0.04	$\Delta_{\text{Augite-Trachyte}}$	-0.0007	0.0253	-0.4838	-0.210 ± 0.16
$\Delta_{\text{Hortonolite-Trachyte}}$	0.0024	-0.1888	-0.083 ± 0.04	$\Delta_{\text{Hortonolite-Trachyte}}$	-0.0008	0.0276	-0.56	-0.244 ± 0.15
$\Delta_{\text{Hedenbergite-Trachyte}}$	0.0028	-0.2175	-0.096 ± 0.04	$\Delta_{\text{Hedenbergite-Trachyte}}$	-0.0007	0.0243	-0.5236	-0.228 ± 0.16
$\Delta_{\text{Fayalite-Trachyte}}$	0.0032	-0.3447	-0.153 ± 0.04	$\Delta_{\text{Fayalite-Trachyte}}$	-0.0012	0.0444	-1.001	-0.436 ± 0.15
$\Delta_{\text{Diopside-Trachyte}}$	0.0024	-0.173	-0.076 ± 0.04	$\Delta_{\text{Diopside-Trachyte}}$	-0.0005	0.0176	-0.3834	-0.167 ± 0.16
$\Delta_{\text{Ulvospinel-Trachyte}}$	0.0018	-0.095	-0.042 ± 0.04	$\Delta_{\text{Forsterite-Mg-Trachyte}}$	-0.0004	0.0084	-0.0475	-0.019 ± 0.17
$\Delta_{\text{Magnetite-Trachyte}}$	0.0008	0.1678	0.075 ± 0.05	$\Delta_{\text{Quartz-Trachyte}}$	0.0057	-0.0518	0.2944	0.121 ± 0.17
				$\Delta_{\text{Anorthite-Trachyte}}$	0.005	-0.0433	0.1607	0.063 ± 0.17
				$\Delta_{\text{Albite-Trachyte}}$	0.0054	-0.0484	0.2491	0.102 ± 0.17

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Table 7 – Suite.