

Structural, redox and isotopic behaviors of iron in geological silicate glasses: A NRIXS study of Lamb-Mössbauer factors and force constants

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1	Structural, redox and isotopic behaviors of iron in geological silicate
2	glasses: a NRIXS study of Lamb-Mössbauer factors and force
3	constants
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5	Lamb-Mössbauer factors and force constants for Fe3+ and Fe2+ in
6	silicate glasses from NRIXS and Mössbauer measurements
7	
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34 Abstract

35 We report a combined conventional Mössbauer and synchrotron Nuclear Resonant Inelastic X-ray Scattering (NRIXS) study of a series of glasses of geologically relevant compositions at 36 temperatures ranging from 5 to 1223 K. We show that in materials of mixed Fe²⁺-Fe³⁺ valences, 37 38 the inverse of the Lamb-Mössbauer factor (also called recoil-free fraction) should correlate linearly with the fraction of the conventional Mössbauer peak that can be ascribed to Fe³⁺. 39 Extrapolating this linear relationship to pure Fe³⁺ and Fe²⁺ endmembers yields a ratio for the 40 Lamb-Mössbauer factors C of Fe^{3+} and Fe^{2+} of ~1.21, independent, to the first order, of the 41 42 bulk chemical composition of the glass. We show that the materials studied follow the 43 harmonic approximation up to 1223 K for olivine and 773 K for basaltic glass, allowing us to extrapolate the value of C to different temperatures $C = (1.21 \pm 0.06)^{T/300}$. This calibration 44 is used to correct previous acquired redox ratios, allowing us to estimate the mean force 45 constants of the bonds involving Fe²⁺ and Fe³⁺ in geological glasses. We find a clear correlation 46 between bond strength and iron redox ratio that is secondarily modulated by coordination 47 48 effects in more alkali-rich felsic magmas. By examining synthetic model glasses, we find that the strength of Fe²⁺ bonds is influenced by the presence of network modifiers, more 49 50 particularly K and Na. These observations explain the isotopic behavior of iron during magma differentiation. The refined ratio of Mössbauer factors for Fe²⁺ and Fe³⁺ is used to improve on 51 52 calibrations of iron redox state in geological glasses using XANES spectroscopy.

55 **1. Introduction**

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57 Iron is the most abundant multivalent element in igneous rocks. As such, it plays a 58 unique role for both setting and recording redox conditions in the Earth. Its three valence states Fe⁰, Fe²⁺, and Fe³⁺ coexist within Earth but were partially separated during core 59 60 formation and continental crust extraction. The oxidation state of iron in melts influences 61 many of their properties, notably their rheology, thermal and electrical conductivities, and 62 crystallization behaviors. Moreover, with appropriate thermodynamic calibration, the relative proportions of ferric (Fe³⁺) and ferrous (Fe²⁺) iron can be directly related to oxygen fugacity 63 64 (fO₂) (Kennedy, G.C. 1948), a parameter that greatly influences the nature of volatiles 65 degassed from magmas, thereby shaping the composition of Earth's atmosphere and its 66 evolution through time (Kump et al., 2001; Gaillard et al., 2011; Andrault et al. 2017). Furthermore, the oxidation state of iron in mafic and ultramafic igneous rocks is a window 67 68 into the redox conditions of the mantle (Christie et al., 1986; Canil et al., 1995; Bezos and 69 Humler, 2005; Kelley and Cottrell, 2009; Cottrell and Kelley, 2011; Stolper and Bucholz, 2019, 70 Le Losq et al., 2019). Determining the redox state of iron in natural magmas is therefore 71 central to understanding the redox evolution of the Earth and its constituent reservoirs.

72 A variety of analytical techniques have been used to determine the iron redox ratio $(Fe^{3+}/\Sigma Fe \text{ with } \Sigma Fe = Fe^{2+}+Fe^{3+})$ in minerals and glasses including (but not restricted to) wet 73 74 chemical determinations, Mössbauer spectroscopy and X-ray Absorption Near Edge Structure 75 (XANES) spectroscopy (Neuville et al., 2021). The synchrotron technique of XANES has been 76 increasingly used over the past decade because it has high spatial resolution, data collection 77 is rapid, and the measurements are precise. Very early in the development of this method 78 (e.g. Wilke et al., 2001; 2004, Farges et al., 2004; Giuli et al., 2002), it was found that the pre-79 edge centroid varies only between two endmember values for Fe²⁺ and Fe³⁺ and that the 80 intensity varies with site-symmetry. Therefore, empirical calibration could in principle be unnecessary, as long as the site symmetries of Fe²⁺ and Fe³⁺ are known. This may be the case 81 82 for canonical compositions such as "basaltic glasses" but more exotic natural or synthetic 83 glasses would still require standardization against samples independently calibrated using 84 wet-chemistry redox titration (Bezos and Humler, 2005) or Mössbauer spectroscopy (Berry et 85 al., 2003; Wilke et al., 2005; Cottrell et al., 2009). Specifically, the calibration of XANES entails 86 establishing an empirical relationship between (i) the normalized intensity and centroid position of the pre-edge feature, and (*ii*) the coordination and redox state of iron. Such calibrations were done on a range of synthetic glasses with compositions that matched those encountered in natural settings (Berry et al., 2003; Wilke et al., 2005; Cottrell et al., 2009; Dauphas et al., 2014). In silicate glasses, Cottrell et al. (2009) and Dauphas et al. (2014) consistently found different calibration curves for rhyolitic compositions as compared to basalts, andesites and dacites, presumably reflecting differences in the coordination environment of iron in these glasses.

94 Conversion of Mössbauer data into iron redox ratio is also not straightforward. Zhang 95 et al. (2015) pointed out that previously used data reduction procedures in Mössbauer 96 spectroscopy had ignored the fact that the Lamb-Mössbauer factors (also called recoil-free fraction) of Fe²⁺ and Fe³⁺ in glasses differ significantly. The Lamb-Mössbauer factor (f_{LM}) is the 97 98 probability that a photon with the correct energy will induce a nuclear transition in ⁵⁷Fe 99 without energy loss due to recoil. Zhang et al. (2015) obtained a ratio C = $f_{LM}(\text{Fe}^{3+})/f_{LM}(\text{Fe}^{2+})$ of 1.256±0.153 for andesitic glass based on Mössbauer measurements 100 101 done at various temperatures. The correction in $Fe^{3+}/\Sigma Fe$ ratios for values relevant to 102 terrestrial settings range between ~15 and 25% relative, which is significant. Zhang et al. 103 (2016) corrected Mössbauer data for this difference in Lamb-Mössbauer factors and provided 104 a new set of XANES-Mössbauer calibrations. However, the value of C determined by Zhang et 105 al. (2015) has large uncertainty and was only measured for an andesite glass. It is therefore 106 unclear whether it can be applied to other compositions.

107 XANES and Mössbauer studies also have implications that extend beyond the 108 calibration of spectroscopic approaches used in iron redox determinations. In particular, these 109 techniques can provide clues on the valence state and coordination environment of iron in 110 igneous minerals and melts, which affect iron equilibrium isotopic fractionation (Dauphas et 111 al., 2014; Roskosz et al., 2015; Nie et al., 2020). Dauphas et al. (2014) acquired Nuclear 112 Resonant Inelastic X-ray Scattering (NRIXS) data on the same glasses that they characterized 113 by Mössbauer and XANES. They showed that the chemical bonds involving ferrous iron were 114 characterized by much higher force constants in rhyolite than in less silicic glasses, affecting 115 in turn iron isotopic fractionation during magma differentiation. The peculiar behavior of Fe 116 in rhyolitic glass in XANES (Cottrell et al., 2009, Dauphas et al., 2014) was also found in NRIXS, 117 suggesting that the coordination environment of iron in rhyolitic magmas must be different 118 from that of basaltic, andesitic, or dacitic magmas. A question that remains to be addressed, 119 however, is whether the different force constants of iron bonds in rhyolite could be artifacts 120 of an erroneous $Fe^{3+}/\Sigma Fe$ calibration if the value of *C* differed between rhyolite and other 121 glasses.

122 We use here a multipronged approach to reassess how the composition of glasses 123 affects iron bonding environment and iron redox determinations. New measurements and 124 reevaluations of previously published data allow us to evaluate how iron isotopes could have 125 been fractionated during mantle melting and magmatic differentiation. (i) We report new 126 analyses by conventional Mössbauer spectroscopy at room and low temperatures of the 127 samples previously described in Dauphas et al. (2014). (ii) We determine the ratio C of the 128 recoil-free fractions of ferric and ferrous iron in glasses of basaltic, andesitic, dacitic, and 129 rhyolitic compositions using Lamb-Mössbauer factors derived from NRIXS spectra. (iii) We 130 study three simplified iron-bearing glasses with a silica content similar to rhyolites to 131 understand how silicate melt structure affects the strength of iron bonds. (iv) We report NRIXS 132 measurements of heated basaltic glass and olivine single crystals to evaluate the temperature 133 dependence (or lack thereof) of iron bonds and recoil-free fractions.

134 Our results allow us to revise the calibration of redox determinations by Mössbauer and XANES taking into account the recoil-free fractions of Fe²⁺ and Fe³⁺ in four major groups 135 136 of natural melts (basalts, andesites, dacites and rhyolites). This work also demonstrates that 137 Fe-bonds in olivine and silicate glasses are sufficiently harmonic as to not affect Fe isotope 138 partitioning over a temperature range of several hundreds of degrees. Finally, we show that 139 the large amount of potassium and sodium present in rhyolitic melts leads to a significant 140 increase of the iron force constant compared to basaltic and andesitic melts (at a given redox 141 ratio). This can explain why granites and granitoids tend to have heavy Fe isotopic 142 compositions.

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147 **2.** Experimental and analytical protocols

148 *2.1. Sample synthesis*

149 The samples of basaltic, andesitic, dacitic and rhyolitic compositions were the same as 150 those studied in Dauphas et al., (2014). Simplified potassium-, sodium- and magnesio-calcic 151 ferrosilicate glasses were synthesized for the present study (labeled KS4, NS4 and CMS 152 respectively). The compositions were selected as they allow us to evaluate how the 153 coordination environment of iron is affected by the structure of the silicate melts (Mysen et 154 al., 1980; 1985; Le Losq et al., 2020). The CMS series has a silica content intermediate between andesite and dacite, a NBO/T close to basalts and contains only Mg²⁺ and Ca²⁺ as network 155 156 modifying cations, in proportions that allow these glasses to easily melt and quench (relatively 157 high CaO/MgO ratio). The NS4 and KS4 series have silica contents close to rhyolites (slightly 158 lower though in order to avoid risks of unmixing during the synthesis Richet et al., 2006) and only contain either K⁺ or Na⁺ in order to isolate their effects on the coordination chemistry 159 160 and valence state of iron. Sodic and potassic binary silicate glasses are known to be 161 hygroscopic. A special care was therefore paid to store them in dry conditions. Furthermore, 162 sample surfaces were gently polished before each analytical session. Finally, NRIXS spectra of 163 the reduced KS4 were collected twice on the same sample during two different sessions 164 separated by several months. No changes could be observed indicating that these iron rich 165 potassic glasses did not suffer significant hydration during the course of this study.

All samples analyzed (including KS4, NS4 and CMS) in this study were enriched in ⁵⁷Fe to reduce acquisition time. Glasses were all prepared from mixtures of reagent grade SiO₂, Al₂O₃, CaCO₃, MgO, Na₂CO₃, K₂CO₃, TiO₂, and Fe₂O₃ that were first fired at 300 to 1000 °C. The starting material was melted in air at 1550°C for 1h in a thin-walled Pt crucible and was then finely crushed. Glasses were then remelted for 1h and quenched on a Cu plate.

Final syntheses were performed in vertical gas-mixing furnaces (Gero, CRPG, Nancy, France) using the wire-loop method for natural analogs and CMS glasses. The oxygen fugacity (fO_2) was controlled using CO/CO₂ gas mixtures as detailed in Dauphas et al. (2014). Three nominal oxygen fugacities were applied to the samples at 1550 °C: Log(fO_2)=-0.7 (air), Log(fO_2)=-2.4 (QFM+2.5), Log(fO_2)=-8 (IW+0.3). Limited volatilization was observed during these syntheses as shown in Table 1.

177 The KS4 and NS4 reduced glasses were prepared in a piston cylinder apparatus (LMV, 178 Clermont-Ferrand, France). The reduction was performed in graphite capsules using a nonend loaded piston cylinder in order to avoid large evaporative loss of potassium and sodium.
For those samples, about 80 mg of the glass samples prepared in air were packed in a graphite
capsule (4mm OD) and placed in a salt/pyrex/MgO assembly. Synthesis was done at 1300°C
and 1 GPa for 1h. Strictly speaking, these samples were equilibrated at an unknown fO₂ below
the graphite-CO buffer. For simplicity, we labelled them `IW` just as the most reduced glasses
prepared for each other series.

The chemical compositions of glasses were determined after synthesis with an electron microprobe (Cameca SX100 at the UMET laboratory; University of Lille) operating at 15kV and 15nA beam current. Albite, MgO, Fe₂O₃, orthoclase, wollastonite, MnTiO₃ standards were typically used to calibrate the microprobe. Analyzed glass compositions (Wt%) are summarized in Table 1.

190 In addition to these glass samples, olivine single crystals, enriched in ⁵⁷Fe were 191 synthesized to evaluate whether the strength of iron bonds is affected by temperature. The 192 protocol described in Sio et al. (2018) designed to study iron isotopic diffusion in oriented 193 olivine single-crystal was adapted here. San Carlos olivine single crystals (Fo_{88.8}) were optically 194 selected and cut into roughly oriented parallelepipeds. They were placed in an alumina 195 crucible filled by a mixture of oxides (66 wt% ⁵⁷FeO – 34 wt% MgO) that sintered around the 196 crystals upon heating. This configuration buffered the experiment at low silica activities (a_{SiO2}), 197 which in turns likely affected the Mg-Fe exchange rate through the crystal/oxide interface. 198 Experiments were run at ambient pressure in a Gero furnace at CRPG (Nancy France). A CO-199 CO₂ gas mixture was used to control the oxygen fugacity (f_{O2}), which was set to 1.5 log units 200 below the quartz-fayalite-magnetite (QFM; 72.75% CO2+27.25% CO gas mixture) buffer at 201 1400 °C. The crucible was initially placed in a vertical oven at 1000°C and a gas flow of 300 202 cm³/min to flush the air trapped into the oxide powder for 10 hours. Upon heating, the target 203 temperature of 1400°C was reached in 15 minutes and the flow was decreased to 100 204 cm³/min. Samples were then isothermally annealed for 290 hours. At the end of the 205 experiment, samples were rapidly removed from the hot spot of the furnace and quenched 206 before exposure to air. Recovered samples consisted of single crystals embedded in a loosely 207 sintered black powder. This crust was easily removed after a gentle grinding using silicon 208 carbon abrasives. Crystals were then cut into \sim 150 μ m slices with the help of a wire saw. 209 Samples were deposited on a SEM sample holder and inspected by Scanning Electron 210 Microsopy to check that the oxide crust was completely removed (Fig. 1a).

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212 2.2. Room temperature NRIXS spectroscopy

213 Details on the synchrotron technique of NRIXS are available in Chumakov and Sturhahn 214 (1999); Sturhahn et al. (1995); and Seto et al. (1995). The measurements were performed at 215 beamline 3-ID-B of the Advanced Photon Source (APS) at Argonne National Laboratory. The 216 storage ring was operated in top-up mode with 24 bunches separated by 153 ns. Two 217 Avalanche Photon Diode (APD) detectors positioned at 180° from each other and 218 perpendicular to the incident X-ray beam direction were used. The sample was positioned in 219 between those two detectors. The average energy resolution (full width at half maximum -220 FWHM) was 1.33 meV. The monochromator was tuned from ~ -130 meV to ~+130 meV with 221 a step size of 0.25 meV and a collection time of 2-3 s per step. The number of scans collected 222 per sample depended on its ⁵⁷Fe content and ranged from 2 to 12 scans. The direction of the 223 scans was alternated from low to high energy and vice versa to mitigate the effect of any drift 224 in the instrument response with time.

225 The signal measured is proportional to the phonon excitation probability density 226 function S(E). After elastic peak removal and some normalization, this function can be used to 227 calculate the iron phonon density of states (PDOS) (Sturhahn et al., 1995). The density of 228 states is the energy distribution of network vibration modes. Through statistical mechanics, 229 this distribution relates to the thermodynamics of the sample. A large array of physical 230 properties relevant to the field of mineral physics can be derived from these spectra. Among 231 them, this study particularly focuses on the mean force constant of the bond holding iron in 232 position $\langle F \rangle$, the coefficients in the polynomial expansion of iron reduced partition function 233 ratios used in isotopic geochemistry (β -factors), and the Lamb-Mössbauer factor (f_{LM}). 234 Dauphas et al. (2012) and Hu et al. (2013) showed that the iron reduced partition function 235 ratios used to calculate equilibrium isotopic fractionation between phases could be calculated 236 directly from S(E). At the high temperatures relevant to igneous and metamorphic 237 geochemistry, the fractionation between ⁵⁶Fe and ⁵⁴Fe takes the form,

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$$1000 \ln \beta_{56Fe/54Fe} \simeq 2904 \frac{\langle F \rangle}{T^2},$$
 (1)

239 where *T* is in Kelvin. $\langle F \rangle$ is in N/m and is proportional to the 3rd centered moment of *S*(*E*),

240
$$\langle F \rangle = \frac{M}{E_R \hbar^2} \int_{-\infty}^{+\infty} (E - E_R)^3 S(E) dE, \qquad (2)$$

241 with *M* the mass of ⁵⁷Fe, \hbar is the reduced Planck constant, and E_R is the free recoil energy.

242 When the force constant is higher than 100 N/m, which is the case for Fe-bearing oxides and 243 silicates, equation (1) gives an approximation of the true β -factors with an accuracy of better 244 than 99% down to 300 °C. At lower temperature, a more general equation gives the β -factors 245 through a polynomial expansion in inverse even powers of the temperature,

1000 ln
$$\beta_{56Fe/54Fe} \simeq \frac{A_1}{T^2} + \frac{A_2}{T^4} + \frac{A_3}{T^6}$$
, (3)

where the coefficients A_1 , A_2 , and A_3 can be calculated from the moments of S(E) (Eq. 3 of Dauphas et al., 2012; $A_1 = 2904\langle F \rangle$). The Lamb-Mössbauer factor is the ratio of recoil-free to total nuclear resonant absorption or the probability that a photon with the correct energy will induce a nuclear transition in ⁵⁷Fe without energy loss due to recoil. It is calculated during normalization of the phonon excitation probability density function S(E), and it can also be calculated from the inverse moment of the PDOS g(E) (Sturhahn et al., 1995; Hu et al., 2013; Dauphas et al., 2018).

Data reduction was done with a Mathematica software (SciPhon 1.1.0) described in Dauphas et al. (2018). Its main features are that it calculates all the parameters needed for iron isotope geochemistry, and it propagates all sources of errors (*i.e.*, counting statistics, baseline subtraction, energy scaling) on the derived parameters.

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259 2.3. High temperature NRIXS spectroscopy

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Heating experiments are time consuming and difficult to implement, so we focused on just two compositions. The first one is a basalt glass synthesized in air containing 57% Fe³⁺ and 43 % Fe²⁺ (Dauphas et al., 2014). This mixed valence sample allows us to evaluate whether iron in either oxidation state presents some anharmonic behavior. As discussed below, we did not detect any change in the force constant of iron with temperature, so we did not examine other glass compositions. We also studied olivine single crystals containing pure ⁵⁷Fe as Fe²⁺ prepared as described above.

The samples were heated using a wire-heating furnace (Neuville et al., 2014 and references therein) modified from the design of Mysen and Frantz (1992). The wire-heating system consists of a power supply and Pt wire with a tiny hole pierced in its center. The wire is heated through Joules effect by increasing the electrical current running through it. The relationship between the electrical current and the temperature is calibrated by melting single component phases of known melting temperatures such as NaNO₃ (613 K) and CaSiO₃ (1813
K) (see Neuville and Mysen 1996 for more details). This calibration is done prior to the
beamtime session and melting of the single component phases is optically assessed. Because
the calibration can be affected by gases in the surrounding atmosphere, the temperature is
also measured with a pyrometer during the experiment.

278 All experiments were done under subsolidus conditions in air. Two APD Detectors were 279 used to collect the NRIXS signal (Fig. 1b). The basaltic glass was measured at three 280 temperatures of 300, 558, and 773 K. Olivine was also measured at three temperatures of 281 300, 773, and 1223 K. Before and after measurements, synchrotron Mössbauer spectra were 282 collected at the same beamline to monitor any significant redox or structural evolution. No 283 changes were observed. There were several limitations to the temperature that we could 284 reach. First, force constants can only be measured in solids, so all measurements were 285 subsolidus. For the glass, we stayed below the glass transition temperature to also avoid 286 crystallization. This strict limitation is due to the fact that the signal intensity is proportional 287 to the Lamb-Mössbauer factor of the sample. This factor drops down to 0 at the solid-liquid 288 transition as the fraction of recoil-free iron vanishes. This intensity collapse was used to study 289 melting points of compressed iron and to study local dynamics of Fe species in silicate glasses 290 and melts close to the glass transition temperature (Jackson et al., 2013; Weigel et al., 2010) 291 Second, the Lamb-Mössbauer factor severely decreases when the temperature increases and 292 the multiphonon contribution increases, which makes it difficult to extract useful data from 293 the phonon excitation probability density function (see the result section). For olivine, no 294 useful data could be acquired above 1223 K.

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297 2.4. Conventional and low-temperature Mössbauer spectroscopy

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In order to better characterize reduced samples for which the determination of the redox ratio by conventional Mössbauer spectroscopy is not trivial ($Fe^{3+}/\Sigma Fe<10\%$), the 4 most reduced glasses analyzed in Dauphas et al. (2014) were measured a second time at low temperature (5 and 90 K in the case of the basalt). The basalt prepared in air was also analyzed at 90 K. The three new series of glasses KS4, NS4 and CMS were analyzed at room temperature (Fig. 2). The Mossbauer Spectroscopy measurements were performed in transmission mode using a 305 constant acceleration spectrometer. A fill type liquid Helium cryostat was used for low 306 temperature measurements. The point source was ⁵⁷Co/Pd about 5 mCi. High purity 307 Germanium detector was used for recording the transmitted photons. Data was analyzed 308 using WinNormos commercial program package provided by WissEl Co. The primary purpose 309 of the Mossbauer spectra was to find Fe2+/Fe3+ ratio, and temperature dependence of 310 hyperfine parameters. The line widths used to fit the spectra were wide enough to get a good 311 fit, without invoking gaussian distribution of quadrupole of isomer shift values. Nonetheless, 312 since all spectra were collected in the similar conditions and fits to the data performed in a 313 consistent way, we compare the IS and QS parameters derived from this procedure in the 314 discussion, focusing on the systematic variations observed. 315

316

318 3. Results

319 3.1. Reassessment of redox ratios based on conventional Mössbauer spectra with a special
320 emphasis on reduced glasses

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322 Processing of the data was performed using two to four symmetric lines. In each case, 323 the minimum number of lines required to adjust the fit to the data was preferred. Derived 324 Mössbauer parameters are listed in Table 2. No magnetic ordering (not even a weak long 325 range magnetic correlation) was observed in our spectra down to 5 K. The assignment of some 326 lines is not trivial because they exhibit IS and QS values deviating from the typical ranges 327 covered by ferric and ferrous iron in glasses (Dyar et al., 2006). Similar observations were 328 recently made by Berry et al. (2018). The IS and QS values determined here are comparable 329 to values derived by Berry et al. (2018). In particular, a minor component found in all 'IW' samples with relatively low IS and QS for typical Fe²⁺ (IS close to 1 mm/s, QS close to 1.3 mm/s) 330 331 was also observed by Solomatova et al. (2017) on the same glasses and by Berry et al. (2018). 332 Such signatures were also found earlier by Rossano et al. (1999) on very reduced tektites and attributed to Fe²⁺. We therefore conclude that all the glasses labeled 'IW' (the most reduced 333 334 samples of each series) do not contain measurable amount of Fe^{3+} (i.e. less than 2%).

Turning to simple glasses KS4, NS4 and CMS, we note that at constant oxygen fugacity during melting in air at the same temperature, iron in potassic glasses and in sodium-bearing glasses, is more oxidized than in the CMS glass. This was documented previously in synthetic and natural glasses (*e.g.* Kress and Carmichael, 1988, 1991; Lange and Carmichael, 1989; Moretti, 2005; Borisov et al., 2017). Again, for the samples KS4, NS4 and CMS prepared in reducing conditions of ~IW, no measurable amount of ferric iron could be detected in the Mössbauer spectra.

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343 3.2. NRIXS spectra of simple glasses and derived physical properties

The projected partial densities of states (DOS) collected on simplified glasses are presented in Figure 3 (a, b). A direct comparison with spectra acquired earlier on synthetic natural glasses is also displayed in Figure 3 (c-f). All the physical properties calculated from these data are also tabulated (Table 3). The iron PDOS show significant variations among these glasses at a given oxygen fugacity (Fig. 3 a, b). We first note that the main peak is thinner for reduced than for oxidized glasses. The finest peak is observed for CMS IW, the PDOS of which 350 only displays a broad and weak tail at energy higher than 50 meV. Sample NS4 IW shows a 351 more intense peak at ~65 meV. Such a peak (slightly more intense) is also observed for KS4 352 IW at a slightly lower energy. Turning to oxidized glasses, the main peak at low energy is 353 overall broader for NS4 and KS4 than for CMS. This may essentially be due to the fact that in 354 air, these glasses are overall more oxidized than CMS. Furthermore, a broad peak centered at 355 70 meV (not present in reduced glasses) is observed for all these samples. It is more prominent 356 in KS4 and NS4 than in CMS. This may again be due to the more oxidized nature of these 357 glasses as compared to CMS. This broad peak exhibits a nicely defined shoulder at even larger 358 energy (85 meV) in CMS and NS4 glasses. The KS4 glass does not reveal such a clear shoulder 359 but instead, a broad, intense continuous decay of the signal (Fig. 3a). These peaks (not present 360 in PDOS of reduced glasses) could tentatively be assigned to a ferric iron contribution and to 361 the coordination of sites occupied by iron atoms in the network, as discussed below. Turning 362 to the comparison with natural compositions, the most salient observation is that CMS and 363 tholeiitic basalts have strikingly similar PDOS both for reduced and oxidized glasses (Fig. 3 c, 364 d). Even the subtle variations such as the small peak at 85 meV are found in both simplified 365 and natural glasses. The same similarities are obvious between NS4, KS4 and rhyolites (Fig. 3 366 e,f). This has strong implications in terms of structural role of iron as seen by NRIXS as 367 discussed below. For instance, aluminum has no influence on the iron coordination chemistry 368 since simplified glasses do not contain any aluminum.

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370 3.3. Spectroscopic determination of the Lamb-Mössbauer factors

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372 Zhang et al. (2015, 2016) made the case that the recoil-free fractions differ for Fe²⁺ and 373 Fe³⁺. The Lamb-Mössbauer factor can be precisely quantified using NRIXS data. It can either 374 be calculated from the phonon excitation probability density function *S*(*E*) or the partial PDOS 375 g(E) (Dauphas et al., 2018 and references therein). Table 4 summarizes all the f_{LM} extracted 376 from the samples studied here together with the values derived for previous measurements 377 of basaltic, and esitic, dacitic, and rhyolitic glasses by Dauphas et al. (2014). This factor varies 378 from a glass to the other and seems to exhibit some weak compositional dependences with 379 optical basicity, silica content, redox state (See Supplementary Online Material). These 380 correlations are clearly multivariate and may also correlate with bulk properties such as Debye 381 sound velocity and compressibility because all these properties are dominated by the position

and intensity of the first main peak of PDOS. A multivariate ACP analysis could eventually
shade some interesting lights on these entangled correlations but this would need a much
larger database.

385 As the most reduced samples of each series only contain Fe²⁺, the recoil-free fraction 386 for ferrous iron is directly determined. This is not true for ferric iron because even the most 387 oxidized samples of each series contain significant amounts of ferrous iron. To estimate f_{LM} 388 for Fe³⁺, one can examine how f_{LM} correlates with Fe³⁺/ Σ Fe on a range of glasses synthesized under different oxygen fugacities, and then extrapolate the correlation to a Fe³⁺/ Σ Fe of 1. The 389 390 difficulty with this approach is that the Fe³⁺/ΣFe estimated by Mössbauer depends on the ratio C of the Lamb-Mössbauer factors of Fe³⁺ and Fe²⁺, noted f_3 and f_2 respectively (C= f_3/f_2). For 391 392 each glass composition series (basalt, and esite, dacite and rhyolite) f_{LM} was plotted against 393 'raw' redox ratios determined by conventional Mössbauer spectroscopy at 300 K as the ratios 394 of the areas of the spectral lines for ferric and ferrous iron. For all series of glasses, a linear 395 correlation was observed between the apparent redox ratios and f_{LM} . We therefore assumed 396 in the following that, at the first order, f_{LM} of intermediate glasses containing both ferric and 397 ferrous irons could be described as a linear mixture of two endmembers for ferric and ferrous 398 iron (again noted f_3 and f_2 respectively).

We therefore assume that the f_{LM} value of a given glass is given by a linear combination of the end-members f_2 and f_3 ,

401

$$f_{LM} = x_3 f_3 + (1 - x_3) f_2, \tag{4}$$

402 where $x_3 = \text{Fe}^{3+}/\Sigma\text{Fe}$ is the fraction of Fe³⁺ in total iron. The absorption areas of Mössbauer 403 lines produced by Fe³⁺ and Fe²⁺ (S_3 and S_2 respectively) are related to the abundances of the 404 ions ($N_{\text{Fe}3+}$ and $N_{\text{Fe}2+}$) and to the recoil-free fractions of each ion at a given temperature, 405 according to,

407 where $C=f_3/f_2$. If we note $s = S_3/(S_3 + S_2)$ the ratio of the surface areas of the peaks 408 of Fe³⁺ relative to the total area of the Mössbauer spectrum, we can combine Eqs. 4 and 5 to 409 establish the following relationships,

410
$$\frac{1}{f_{LM}} = \frac{1-s}{f_2} + \frac{s}{f_3}$$
, (6)

 $S_3/S_2 = C \frac{N(Fe^{3+})}{N(Fe^{2+})} = C \frac{x_3}{1-x_3}.$

411
$$\frac{1}{f_{LM}} = \frac{1}{f_2} + \frac{1}{f_2} \left(\frac{1}{C} - 1\right) \delta.$$
 (7)

These equations show that if we plot $1/f_{LM}$ measured by NRIXS against *s* measured by conventional Mössbauer, the points should define a straight line of slope $1/f_3 - 1/f_2 =$ $1/f_2(1/C - 1)$ and of intercepts $1/f_2$ at s = 0 and $1/f_3$ at s = 1. In Fig. 4, $1/f_{LM}$ is presented against *s* for all synthetic glass samples. The slope and intercept of the best-fit lines were calculated and then f_2 , f_3 , and *C* were derived. Uncertainties on these values were estimated by bootstraping the residuals from the best-fit line. For each glass composition, the results are compiled in Table 4.

2hang et al. (2015) obtained a *C* value of 1.256 ± 0.153 for andesite. Our estimate for approximately the same composition is 1.171 ± 0.026 , which is in good agreement with the value that they propose but of much higher precision. Furthermore, our data suggest that a single value of *C* (1.21 ± 0.06) could be used to correct Mössbauer data collected at room temperature (~300K) on the entire range of glasses studied here (from simple ternary glasses such as NS4 and KS4 to analogues of natural glasses). With this correction in hand, we reappraise below the XANES *vs.* Mössbauer and the <F> *vs.* redox calibrations.

426

427 3.4. High-T NRIXS spectra and physical properties of basalt glass and olivine

428

The NRIXS spectra for basaltic glass synthesized in air and olivine were acquired over a range of temperatures. The PDOS are plotted in Fig. 5 and the derived parameters are compiled in Table 5. For olivine at 1223 K, the Lamb-Mössbauer factor derived from the data is ~0.23. This means that S(E) contains a large multiphonon contribution and under these circumstances, we were unable to calculate a reliable PDOS. We were also unable to calculate many of the parameters that derive from both g(E) and S(E), including the force constant of iron bonds. We only report in Table 5 the data that are deemed to be reliable.

The PDOS of basaltic glass containing 57% Fe³⁺ and 43% Fe²⁺ does not change when 436 437 the temperature increases from room temperature (300K) to 773 K. Expectedly, the Lamb-438 Mössbauer factor decreases from 0.685 to 0.375. The thermal agitation associated with this 439 temperature increase is associated with increases in the mean square displacement from 440 0.0071 to 0.0184 Å², internal energy/atom from 29.9 to 68.3 meV, kinetic energy/atom from 441 15.0 to 34.1 meV. The mean force constant on the other hand does not change significantly, 442 staying at ~290 N/m at all temperatures. This constancy of the force constant is expected for 443 a harmonic system. For basaltic glass in air, Dauphas et al. (2014) had previously reported values of 0.668, 0.0076 Å², 30.1 meV, 15.0 meV, and 292 N/m, for the Lamb-Mössbauer factor,
mean square displacement, internal energy, kinetic energy, and force constant, respectively,
which are all in excellent agreement with the value reported here (Table 5).

447 The three olivine measurements at 300, 300, and 773K yield variable PDOS. We believe 448 that these differences are not due to temperature but rather to crystal orientation of the 449 olivine single crystals that were measured as the largest difference is between the two PDOS 450 acquired at 300K (Fig. 5). We indeed find that the two olivine PDOS at 300K, although very 451 different in their shapes, yield similar values for the Lamb-Mössbauer factor (0.757 vs. 0.769), 452 mean-square displacement (0.00523 vs. 0.00493 Å²), internal energy (28.67 vs. 29.15 meV), 453 kinetic energy (14.33 vs. 14.57 meV), and force constant (202 vs. 245 N/m). These values are 454 also very similar to our previous room temperature NRIXS measurement of olivine (0.766, 0.00499 Å², 28.87 meV, 14.43 meV, 197 N/m for the same parameters; Dauphas et al., 2014). 455 456

- 458 **4. Discussion**
- 459
- 460 4.1. Harmonic or anharmonic behavior of iron in basaltic glass and olivine
- 461

462 To apply the results from NRIXS experiments performed at room temperature to 463 geological settings, the assumption is often made that the bonds are harmonic, meaning that 464 the interatomic potential varies with the square of atomic displacement. Under this 465 assumption, the force constant of iron bonds measured at room temperature can be used 466 directly to calculate equilibrium isotopic fractionation between coexisting phases at any 467 temperature (Dauphas et al., 2012). Anharmonicity must however be present at some level as 468 it is one of the main mechanism responsible for thermal expansion. For example, the volume 469 of forsterite expands by 8% when the temperature is increased from 300 to 2300 K (Bouhifd 470 et al., 1996) and no expansion would be present if the bonds were perfectly harmonic. If the 471 bonds are perfectly harmonic, then the force constant of those bonds should not vary with 472 temperature. Conversely, anharmonicity in interatomic potentials would be manifested as an 473 apparent variation of the force constant of the iron bonds as temperature changes and the 474 potential is explored over a range of interatomic distances. For example, Hu et al. (2013) 475 considered an anharmonic potential V including a quartic term,

476

$$\frac{\partial^2 V}{\partial z^2} = K + Az + \frac{B}{2}z^2,\tag{8}$$

477 where z is the atomic displacement, K is the spring constant, and B is the anharmonic term. 478 They showed that for such a potential, the apparent mean force constant $\langle F \rangle$ given by the 479 third moment of the NRIXS measurements will be,

480

$$\langle F \rangle = K + \frac{B}{2} \langle Z^2 \rangle, \tag{9}$$

481 where $\langle z^2 \rangle$ is the atomic mean square displacement, which can be derived from NRIXS spectra using the equation $\langle z^2 \rangle = -\ln(f_{LM})/k^2$ with k the angular wavenumber (see Dauphas et al., 482 483 2017 and references therein for details). In Fig. 6, the apparent force constant $\langle F \rangle$ is presented against $\langle z^2 \rangle$ for basalt glass and olivine crystals measured at different temperatures. No 484 485 measurable variation in the force constant of Fe can be resolved even when the mean square 486 displacement increases by a factor of ~2.6. For the force constant, temperatures up to 773 K 487 (500 °C) were investigated. The mean square displacement increases more or less linearly with 488 temperature, which imply that although the temperature investigated do not reach those 489 encountered in igneous systems, they are sufficient to rule out the presence of large 490 anharmonic effects for the force constant. It is therefore reasonable to use iron force 491 constants measured at room temperature to calculate equilibrium isotopic fractionation 492 between melts and minerals at temperature relevant to igneous systems. Further work is 493 nevertheless needed to ascertain whether harmonicity holds up to the temperature of silicate 494 melts where there is the most chance to detect anharmonic behavior. Because the Lamb-495 Mössbauer factor decreases with increasing temperature, it is not possible to test for 496 anharmonicity beyond the temperatures investigated here and another approach such as 497 first-principle calculations (Pinilla et al., 2021) should be used.

The temperature dependence of the Lamb-Mössbauer factor was also studied. Under the harmonic approximation, the Lamb-Mössbauer factor is expected to change with temperature following (Dauphas et al. 2018 and references therein),

501
$$\ln f_{LM} = -\frac{k^2 \hbar^2}{M} \int_0^{+\infty} \frac{1}{2E} \coth\left(\frac{E}{2k_B T}\right) g(E) dE,$$
 (10)

502 with \hbar the reduced Plank constant and M the mass of the nuclear resonant isotope. For x503 approaching 0, $coth(x) \sim 1/x$ so at high temperature the above equation is extrapolated as:

504
$$ln f_{LM} \simeq -k^2 \frac{d\langle z^2 \rangle}{dT} T$$
 (11)

To first order, f_{LM} should exponentially approach zero as the temperature increases. To test this behavior, the values measured at high temperature are compared with the predicted evolution using Eq. 10 and taking the lowest temperature PDOS, g(E) to calculate the value in the integral (Fig. 7). The decrease of the Lamb-Mössbauer factor f_{LM} is found to be well accounted for by the harmonic approximation.

510 The temperature dependence of C was also investigated within the harmonic 511 approximation. The PDOS of Dauphas et al. (2014) were used to calculate how the f_{LM} values 512 of the basalt, and esite, dacite, and rhyolite glasses synthesized with different $Fe^{3+}/\Sigma Fe$ ratios 513 should change with temperature based on their room temperature PDOS measurements. At 514 each temperature, the values of C were calculated by extrapolating the computed f values to 515 Fe³⁺/ Σ Fe ratios of 0 and 1. As shown, C starts from C = 1 at T = 0, and increases with T (Fig. 516 7). A simple parametric formula is proposed to account for this dependence. For that purpose, 517 a Debye PDOS with a cutoff energy E_D was considered

518
$$g(E) = 3E^2/E_D^3; E \le E_D,$$
 (12)

519
$$g(E) = 0; E > E_D.$$
 (13)

520 With this assumption, the Lamb-Mössbauer factor f_{LM} can be written according as,

521
$$\ln f_{LM} = -\frac{k^2 \hbar^2}{M} \int_0^{E_D} \coth\left(\frac{E}{2k_B T}\right) \frac{3E}{2E_D^3} dE.$$
 (14)

522 At high temperature, Eq. 14 can be approximated using Taylor expansion (This

523 approximation was tested numerically and found to be valid above 150 K) and thus,

524
$$\ln f_{LM} \simeq -\frac{k^2 \hbar^2}{M} \int_0^{E_D} \left(\frac{2k_B T}{E} + \frac{E}{6k_B T}\right) \frac{3E}{2E_D^3} dE,$$
 (15)

525 which can be further simplified to:

$$\ln f_{LM} \simeq -\frac{k^2 \hbar^2}{M} \left(\frac{3k_B T}{E_D^2} + \frac{1}{12k_B T} \right).$$
(16)

527 If we now consider that Fe^{2+} and Fe^{3+} have Debye cutoff energies of $E_{D,Fe^{2+}}$ and $E_{D,Fe^{3+}}$, it 528 follows from Eq. 16 that:

529
$$\ln C = \ln \frac{f_{LM,Fe^{3+}}}{f_{LM,Fe^{2+}}} \simeq -\frac{k^2 \hbar^2}{M} \left(\frac{1}{E_{D,Fe^{3+}}} - \frac{1}{E_{D,Fe^{2+}}} \right) 3k_B T,$$
(17)

530

526

531 The value of *C* can then be parameterized as (with θ a constant),

532

$$C = e^{\theta T}, \tag{18}$$

with θ a constant. The Debye model predicts a linear relationship between ln*C* and *T*, which is verified in figure 7 (a near linear relationship that goes through the origin is observed). For geological glasses, $C = (1.21 \pm 0.06)^{T/300}$, where the uncertainty is given as 1σ .

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- 537

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4.2. Determination of 'true' redox ratios and reassessment of a distinct XANES-Mössbauer calibration for rhyolitic glasses

541 The accuracy of the determination of redox ratios from Mössbauer spectra depends 542 on several assumptions and parameters. An important parameter is the ratio of the recoil-free fractions of Fe³⁺ and Fe²⁺ ions (f_3 and f_2 respectively), which represent the fractions of 14.4 543 544 keV X-rays interacting resonantly with the ⁵⁷Fe ions through a nuclear transition. The absorption areas of Mössbauer lines produced by Fe^{3+} and Fe^{2+} (S₃ and S₂ respectively) are 545 546 indeed related to the abundances of the ions (N_{Fe3+} and N_{Fe2+}) and to the recoil-free fractions 547 of each ion at a given temperature, according to Eq.5, where $C=f_3/f_2$, the recoil-free fraction, 548 related to the mean-square atomic displacement. As mentioned above, the standard 549 assumption is to consider that C=1 (e.g. Mysen and Virgo, 1985; Dyar et al., 1987; Jayasuriya 550 et al., 2004; O'Neill et al., 2006; Rossano et al., 2008; Cottrell et al., 2009; Borisov and 551 McCammon, 2010; Berry et al., 2018). This simplification is in part justified because some 552 comparisons between uncorrected room-temperature Mössbauer measurements and redox 553 ratios determined by other methods have found good agreement with wet chemical 554 determinations (Mysen and Virgo, 1985; Dingwell, 1991; Magnien et al., 2004, Wilke et al., 555 2005). However, some discrepancies have also been found (e.g. Righter et al., 2013).

556 As recoilless interactions depend on bond strengths and are affected by network vibrations, the values of f_i have no reason to be the same for Fe³⁺ and Fe²⁺ in minerals and 557 558 glasses. The recoil-free fraction has been determined experimentally from a determination of 559 the Debye temperature derived from the change of the isomer shift (IS) with temperature 560 (Niemantsverdriet et al., 1984b; De Grave et al., 1985; Dyar et al., 2012). Chen and Yang (2007) 561 and Zhang et al. (2015) used another method based on the temperature-dependence of the ratios of Fe³⁺ and Fe²⁺ Mössbauer lines. All these approaches are indirect and time-consuming. 562 563 For this reason, available data for C for glasses of geological interest is very limited. Studies of 564 silicate minerals have found values of C at room temperature ranging from \sim 1.0 in biotite 565 (Bancroft and Brown, 1975) to 1.4 in garnet (Woodland and Ross, 1994; Dyar et al., 2012), but 566 typical values are closer to 1.2 (De Grave and Van Alboom, 1991). To our knowledge, the only 567 study on glasses focused on two andesitic glasses (Zhang et al., 2015). They found values of 568 1.151 ± 0.118 and 1.256 ± 0.0153 for the two samples that they analyzed. Zhang et al. (2016) 569 also proposed a C-value of 1.124 for rhyolite glass, from a comparison between room 570 temperature Mössbauer and wet chemistry data from Cottrell et al. (2009).

571 Our experimental data significantly expand this database for glasses to encompass 572 basalt, andesite, dacite and rhyolite. Indeed, the Lamb-Mössbauer factor is a direct output of 573 the processing of NRIXS data (Table 3; Dauphas et al., 2014). We therefore used newly 574 acquired NRIXS spectra (KS4, NS4 and CMS) and previously published data (Dauphas et al., 575 2014) to derive experimental values of C for a complete array of geologically relevant glass 576 compositions (Table 4). As presented before compositional effects are very limited. Within 577 analytical uncertainties a single value of C (1.21±0.06) captures the behavior of iron in 578 tholeiitic basalts, andesites, dacites and rhyolites (Table 4). This value encompasses the 579 previously estimated values for andesite from Zhang et al. (2015; 2016). Our result therefore 580 confirms the conclusion of Zhang et al (2015) that conventional Mössbauer without correction 581 for the difference in Lamb-Mössbauer factors of ferrous and ferric iron overestimates Fe³⁺/ΣFe 582 of glasses. We further demonstrate that the correction that needs to be applied is not

583 dependent on the glass composition to the first order.

The Fe³⁺/ Σ Fe reported by Dauphas et al. (2014), as well as most literature data, were not corrected for the difference in Lamb-Mössbauer factors between Fe²⁺ and Fe³⁺ and are therefore presumably offset by up to 20% relative to the true values. We have therefore reevaluated those data by applying a correction using our new estimates of *C*. The corrected Fe³⁺/ Σ Fe and force constants of the Fe²⁺ and Fe³⁺ endmembers are compiled in Table 4.

589 Our results also confirm that there is a significant difference in the XANES vs. 590 Mössbauer calibration between rhyolite on one hand and basaltic compositions on the other 591 hand (Cottrell et al., 2009; Dauphas et al., 2014). In order to illustrate this difference, we have 592 compiled available data from the literature. As conditions of XANES data collection vary from 593 one study to another, the energy of the centroid of the pre-edge feature cannot be compared 594 directly. Strictly speaking, the background treatment induces the largest error in the whole 595 data processing and makes the transfer of centroid values from one study to another almost 596 impossible, unless it can be checked on model compounds. However, as a first order 597 approximation, assuming an inter-laboratory consistent redox determination by Mössbauer 598 spectroscopy or wet chemistry, we have rescaled all available data (see figure captions for 599 more details). Our compilation demonstrates that most natural glasses define a single trend 600 in centroid energy vs. redox state, with the notable exception of rhyolites that define a 601 separate line (Fig. 8). Zhang et al. (2016) proposed that this feature, noted by Cottrell et al. 602 (2009) and Dauphas et al. (2014), may at least in part be caused by different C-values for 603 basalts, andesites and rhyolites. Our results invalidate this hypothesis. Instead, they sustain 604 our initial claim (Dauphas et al., 2014) that redox state of rhyolitic glasses cannot be quantified 605 from XANES spectra using the basalt glass calibration. Fiege et al. (2017) proposed that a single 606 curve could account for both mafic and felsic glasses. We note that their calibration does not 607 include data for highly reduced rhyolitic compositions that exhibit the largest discrepancy 608 relative to the "basaltic" calibration line (Fig. 8). Therefore, this calibration is only valid when 609 $Fe^{3+}/\Sigma Fe > 0.3$ as pointed out by Fiege et al. (2017), where the compositional dependence is 610 smaller. Their calibration curve is quite uncertain (the envelope of the 95% confidence interval 611 for the prediction is large), which stems in part from the assumption that composition has no 612 significant effect on the calibration. Here, we have included their data in Figure 8. Their data 613 for rhyolite are in excellent agreement with ours (and those of Cottrell et al., 2009). It is of 614 note that their data for andesites and dacites also plot on the same "rhyolitic" calibration line

(black dotes following the blue curve on Figure 8). This is at odd with our dataset where andesites and dacites plotted on the "basaltic" line. There are therefore some ambiguities concerning these intermediate compositions that may need further investigation. Still, based on the two parametric equations describing the fit to the data (Fig. 8), we propose that a robust calibration of XANES to derive redox ratios of rhyolitic glasses (and possibly andesitic and dacitic ones) is achieved by applying an offset to the basalt regression curve of the form

621

$$\Delta E = 0.37 \cdot (\text{Fe}^{3+}/\Sigma\text{Fe})^2 - 0.78 \cdot (\text{Fe}^{3+}/\Sigma\text{Fe}) + 0.39, \qquad (19)$$

622 where ΔE is the centroid energy difference in eV.

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- 624 625

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4.3. The structural origin of the high force constant of iron in reduced rhyolitic glasses

Dauphas et al. (2014) used force constants measured in glasses with diverse $Fe^{3+}/\Sigma Fe$ 627 628 to extrapolate the force constants to $Fe^{3+}/\Sigma Fe = 0$ and 1, and thus infer the force constants of 629 the pure Fe^{2+} and Fe^{3+} end-members. With our revised data of $Fe^{3+}/\Sigma Fe$, we reappraise how 630 iron redox state in magmas influences Fe isotopic fractionation. In Fig. 9, we plot the force 631 constants of iron bonds as a function of the corrected Fe³⁺/ Σ Fe. From these, we estimate that 632 the force constants of iron Fe²⁺ and Fe³⁺ are 193±7 and 364±23 N/m for basalt, andesite, dacite 633 glasses (these samples form a single trend), and 250±11 and 382±31 N/m for rhyolite 634 respectively. For comparison, Dauphas et al. (2014) had obtained force constants of 199±15, 635 351±29, 240±13, and 385±24 N/m for the same sample sets, which is similar to the values that we derive here with the corrected Fe^{3+}/Σ Fe ratios. We therefore confirm the finding of 636 637 Dauphas et al. (2014) that rhyolite glasses define a different trend than other samples. The 638 force constant of Fe²⁺ in rhyolite is higher than those of Fe²⁺ in basalt, andesite, and dacite, 639 whereas the force constants of Fe^{3+} in all compositions are indistinguishable.

640 The measurements made on the simple glass compositions help refine the structural and chemical origin of the peculiar behavior of Fe²⁺ in silicic magmas (Fig. 9). While the (Ca, 641 642 Mg)-rich glass (CMS) has a force constant identical to those measured in basaltic glasses, a 643 significant increase of <F> is observed in Na- and K-rich glasses. Furthermore, the force 644 constant of the reduced KS4 glass matches the values observed for rhyolites, while NS4 has 645 an intermediate <*F*> value (Fig. 9). This suggests that the control on the force constant may be 646 related to the nature of the network-modifying cations present in the glass. Silica content may 647 also potentially have an effect as seen by the weak correlations presented in the

648 supplementary material. However, we note in this respect that NS4 contains more silica than 649 KS4 but still has a much lower <F> (only slightly higher than those of dacite and andesite). This 650 suggests on the contrary that the silica content does not, per se, explain the higher force 651 constant of Fe²⁺ in rhyolitic and alkali-rich glasses. Aluminum also typically plays pivotal and 652 complex structural roles in silicate glasses and melts. A salient result of our study is to 653 demonstrate that as far as NRIXS can tell, aluminum does not modify the structural role of 654 iron (reduced and oxidized): simple Al-free glasses have strictly similar PDOS to Al-rich natural 655 counter-parts. Finally, the fact that the highest force constant is found for glasses containing 656 potassium as the dominant cation suggests that the ionic radius of the alkali cation has a direct 657 effect on the force constant of iron.

658 A possible interpretation is that the large radius of K⁺ (and Na+) lowers the average oxygen coordination number of Fe²⁺. This interpretation is sustained by the detailed analysis 659 660 of PDOS of simplified and natural compositions (Fig. 3). From the reduced CMS to reduced 661 NS4 and KS4, the overall PDOS becomes broader with an increasing number of peaks and 662 shoulders, this could be consistent with an increased number of iron environments at constant 663 redox ratio. When ferric iron is introduced in the structure (i.e. sample prepared in air), the 664 PDOS becomes even broader indicating also an increased number of iron geometries including IV-fold coordinated Fe³⁺ at around 85 meV (Fig. 3). Assuming that CMS IW is dominated by VI-665 and V-fold coordinated Fe²⁺, as generally proposed for basic glasses (e.g. Jackson et al., 2005, 666 667 Wilke et al., 2005; 2007, Le Losq et al. 2020), the Na-K substitution for Ca-Mg would trigger an 668 increase of the fraction of IV-fold coordinated ferrous iron, at the expense of VI-fold 669 coordinated iron and an overall decrease of the iron coordination number. This interpretation 670 is furthermore consistent with XANES data and Mössbauer spectra. Though it is not possible 671 to provide an average coordination number from our experimental results, we note that the 672 normalized integrated pre-edge intensity (see the calibration of XANES spectra published in 673 Le Losq et al., 2020) of the reduced rhyolite is 0.1975 whereas other similarly reduced glasses, 674 intensities are comprised between 0.1816 and 0.1876 (Dauphas et al., 2014). Based on the 675 coordination plot developed by Wilke et al. (2001) and adapted by LeLosq et al. (2020), these 676 values imply that reduced rhyolite contains significant amount of IV-fold coordinated Fe²⁺ 677 whereas other compositions contain Fe²⁺ in mixed V-fold and VI-fold coordinated iron. The fit 678 to Mössbauer data also suggests that the overall coordination number of reduced rhyolite 679 glass is lower than in other glasses (Fig. 10). Three lines were typically used to fit self680 consistently the data for the reduced glasses (IW series). Interestingly, these lines define 3 681 clusters within narrow ranges of IS and QS. It is tempting to attribute these lines to three 682 different sites occupied by ferrous iron (Fig. 10). From basaltic to rhyolitic glasses, each of 683 these sites show a systematic decrease of both IS and QS that may suggest a systematic 684 change of iron site symetries. We interpret the cluster exhibiting the lowest IS and QS to IVfold Fe²⁺ following a previous suggestion made on the similar samples by Solomatova et al. 685 686 (2017). The two other lines may be characteristic of V- and VI-fold sites or of another IV- and 687 a V-fold sites. The presence of a component, with low IS and QS, attributed to a four-fold 688 coordinated ferrous iron agrees with the interpretations of Rossano et al. (1999) of mössbauer 689 spectra of highly reduced tektites but also with Jackson et al., 2005; Solomatova et al. (2017) 690 and Berry et al. (2018). Most structural studies based on K-edge XANES have concluded that 691 Fe²⁺ in silicate glasses was mostly in V-fold coordination (e.g. Wilke et al., 2005; Giuli et al., 692 2012; Fiege et al., 2017). Our conclusion slightly tempers this interpretation yet it does not 693 contradict the fact that the V-fold coordination of ferrous iron dominate over other coordinations. Still, a significant amount of Fe²⁺ could actually occupy IV-fold coordinated sites 694 695 in silica-rich potassic and sodic glasses.

696

698 **5. Concluding remarks**

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700 At equilibium, heavy isotopes are concentrated in the strongly bonded structural sites 701 (Bigeleisen and Mayer, 1947; Schauble, 2004; Blanchard et al. 2017). The force constant can 702 be influenced by several factors, notably the coordination number and geometry, redox state, 703 and second neighbors (e.g. Blanchard et al. 2017, Rabin et al., 2021). In the case of Fe isotopes 704 in igneous systems, oxygen fugacity has been shown to have a clear effect (Dauphas et al., 705 2014; Roskosz et al. 2015, Sossi and O'Neill, 2017). The effect of pressure was also pointed out 706 (Shahar et al. 2016, Liu et al. 2017), influenced in part by spin transitions (Yang et al., 2019), 707 though direct manifestation in nature of these effects are still elusive. Our study highlights the 708 effect of iron coordination change at constant valence state. Decreasing the average 709 coordination number of Fe²⁺ (from basalts to rhyolites) leads to a significant strengthening of 710 the Fe-O bonds (observable from XANES, conventional Mössbauer spectroscopy and NRIXS) 711 with $\langle F \rangle$ increasing from 193 to 250 N/m. This variation would be equivalent to a change in 712 the oxidation state of Fe in a basalt from Fe³⁺/ Σ Fe =0 to 0.33. It is a major driver of Fe isotopic 713 fractionation during magmatic differentiation, explaining heavy isotopic compositions 714 measuring in granitoids (Poitrasson and Freydier, 2005; Heimann et al., 2008; Telus et al., 715 2012; Sossi et al., 2012; Dauphas et al., 2014, Rabin et al. 2021).

716 In this study, we have for the first time combined NRIXS and conventional Mössbauer spectroscopy to determine the Lamb-Mössbauer factors of Fe²⁺ and Fe3⁺ in a variety of silicate 717 718 glasses of geological relevance. The same approach could be applied to other solid solutions where Fe²⁺ and Fe³⁺ can coexist (*e.g.*, garnet, biotite, Fe,Ti-oxides, clinopyroxene). Our 719 approach yields a ratio between the recoil-free fractions of Fe^{3+} and Fe^{2+} of 1.21±0.06 (1s.d.) 720 721 that can be applied to convert conventional Mössbauer spectra into $Fe^{3+}/\Sigma Fe$ in basalt, 722 andesite, dacite, and rhyolite. We confirm that XANES-Mössbauer calibrations should consider 723 some compositional specificities, notably in rhyolite with redox ratios (Fe³⁺/ Σ Fe) lower than 724 0.3. This unique behavior of rhyolites in XANES is also found in the form of high force constants 725 of Fe²⁺, high normalized integrated XANES pre-edge intensity and low IS and QS in Mössbauer 726 spectra in rhyolite glass. These observations may point to a fraction of the total Fe²⁺ being IV-727 fold coordinated in rhyolite, as opposed to other compositions were Fe²⁺ is mostly in V- and 728 VI-fold coordination. The structural control on this coordination anomaly is the high 729 potassium/sodium content of rhyolites rather than the high silica or alumina content. We also

730 show that Fe-bonds in basalt and glass behave harmonically even at elevated temperature 731 relevant to metamorphism/crustal igneous systems. The use of room temperature spectroscopic measurements to document high temperature geochemical equilibrium is thus 732 733 valid as long as no major phase transition are crossed. The question of the representativity of 734 solids (glasses or crystals) as proxies for liquids is still open but is obviously beyond the scope 735 of this study. Yet, we note that recent first-principle calculations demonstrate that a 736 congruent melting of a molten alloy would not lead to a significant change in the reduced 737 partition function ratios (Pinilla et al., 2021). A similar study needs to be carried for silicates 738 and melts of geological relevance.

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749 **7. References**

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1043 Table 1: Glass compositions determined by EMPA (Wt%) (Dauphas et al. 2014; this study)

Name	SiO2	AI2O3	FeO	CaO	MgO	Na2O	K2O	TiO2
Tholeitic Basalt Air	45.8	14.5	7.7	11.2	18.0	1.3	0.0	0.9
Tholeitic Basalt Int	45.7	14.4	7.7	11.3	18.1	1.5	0.1	0.8
Tholeitic Basalt IW	46.3	14.5	7.6	11.4	18.3	1.0	0.1	0.9
Basalt Air	50.5	16.7	7.6	12.7	9.4	1.9	0.0	1.0
Basalt Int	49.9	16.6	7.6	12.6	9.3	2.2	0.0	1.0
Andesite Air	55.4	16.1	7.0	6.9	8.1	3.3	1.5	0.8
Andesite Int	55.3	16.1	7.1	7.1	8.3	3.2	1.5	0.8
Andesite IW	55.8	16.3	7.0	7.2	8.3	3.0	1.4	0.8
Dacite Air	63.8	14.9	4.5	4.8	4.3	3.9	2.5	0.7
Dacite Int	63.4	14.9	4.6	4.8	4.3	3.8	2.5	0.7
Dacite IW	64.1	14.9	4.5	4.7	4.2	3.9	2.5	0.7
Rhyolite Air	75.5	10.5	4.1	0.0	0.0	5.0	4.6	0.0
Rhyolite Int	75.7	10.4	4.1	0.0	0.0	5.3	4.7	0.0
Rhyolite IW	75.7	10.4	4.1	0.0	0.0	4.5	4.5	0.0
CMS air	59.6	0.0	6.6	20.7	11.4	0.0	0.0	0.0
CMS IW	59.4	0.0	6.9	20.5	11.5	0.0	0.0	0.0
KS4 Air	65.5	0.0	8.3	0.0	0.0	0.0	25.9	0.0
KS4 IW	65.7	0.0	8.2	0.0	0.0	0.0	25.5	0.0
NS4 air	76.3	0.0	11.2	0.0	0.0	12.4	0.0	0.0
NS4 IW	76.6	0.0	10.9	0.0	0.0	11.9	0.0	0.0

1047 Table 2: Isomer shifts (IS), quadrupole splitting (QS) and associated standard deviation, all in

1048 mm/s, of the components used to fit the ⁵⁷Fe Mössbauer spectra presented in Figure 2.

Commite				Reduced (IV	V)		Oxidized (Air)								
Sample		IS	IS err	QS	Qs err	band area	IS	IS err	QS	Qs err	band area				
	site #1	1.016	0.000	1.877	0.000	62.8	0.267	0.001	0.968	0.002	78.2				
NS4	site #2	0.646	0.001	1.623	0.001	19.5	1.076	0.003	1.820	0.005	21.8				
	site #3	1.388	0.001	1.671	0.001	17.7									
KEA	site #1	1.007	0.001	1.605	0.007	54.8	0.262	0.001	0.852	0.001	79.2				
K34	site #2	1.051	0.001	2.221	0.003	45.2	1.031	0.003	1.952	0.006	20.8				
CNAS	site #1	1.162	0.001	1.928	0.001	67.5	0.568	0.002	1.060	0.004	54.4				
CIVIS	site #2	0.815	0.001	1.814	0.001	32.5	0.856	0.002	2.657	0.003	40.1				
							1.614	0.005	1.887	0.007	5.5				
	site #1	1.170	0.002	2.048	0.009	47.5	0.510	0.023	1.424	0.007	40.0				
The laitie Decelt at 00	site #2	1.083	0.004	1.391	0.013	26.4	1.135	0.007	2.062	0.007	40.1				
Indientic basait at 90	site #3	1.209	0.002	2.680	0.010	26.2	0.200	0.015	1.449	0.008	14.5				
	site #4						1.577	0.009	1.967	0.012	5.5				
	site #1	1.180	0.002	2.049	0.012	42.1									
Tholeitic Basalt at 5	site #2	1.107	0.006	1.369	0.020	28.7									
	site #3	1.225	0.003	2.703	0.014	29.2									
	site #1	1.165	0.003	1.977	0.013	46.3									
Andesite at 90K	site #2	1.214	0.004	2.614	0.017	27.4									
	site #3	1.075	0.007	1.317	0.018	26.3									
Desite at 00%	site #1	1.165	0.002	1.952	0.009	45.9									
Dacite at 90K	site #2	1.0/1	0.005	1.293	0.015	27.1									
	site #3	1.220	0.003	2.609	0.011	27.0									
	site #1	1.155	0.001	1.897	0.005	46.4									
Rhyolite at 90K	site #2	1.046	0.002	1.162	0.007	34.3									
	site #3	1.211	0.002	2.615	0.005	19.3									

1054 Table 3: Compilation of parameters derived from NRIXS spectra collected at room 1055 temperature on simple model glasses. The data reduction was done using the SciPhon 1056 software (Dauphas et al. 2018).

	6145 4VB			Char Inv			KEA AID											
	CMSAIR			CIVIS IW 477.00			K34 AIR 470 50			450.50	170.26	450.67	476.00	450.00	N54 IV	V 477.52		
Total energy range:	-157.52	to	1/6.41	-158.64	to	1/7.28	-157.91	to	1/6.50	-160.60	to	1/8.36	-158.67	to	1/6.88	-159.03	to	1/7.52
Energy cutoff (left and right in mev):	61	and	32	49 and 29		57	and	22	80	and	36	59	and	25	6/ and 41			
Baseline subtracted:	initial 2005 04		4 445 03	linear	0.000.04	2 425 02	linear	6 335 64	5 055 05	linear	2 405 04	4 045 00	linear	7 205 04	linear			
a=	1.51E-03	±	7.05E-04	1.44E-03	*	8.63E-04	2.42E-03	±	6.32E-04	5.86E-05	±	3.49E-04	1.81E-03	±	7.30E-04	1.16E-03	±	6.30E-04
b=	6.4/E-01	±	9.91E-02	8.53E-01	±	1.26E-01	5.74E-01	±	8.93E-02	4.03E-01	±	4.75E-02	7.1/E-01	±	1.03E-01	6.23E-01	±	8.80E-02
Input temperature (K):	302			302			302			300			302			302		
Temperature from detailed balance (K):	309			304			311			295			322			311		
From S																		
lamb-mossbauer factor from S:	0.6794	±	0.0014	0.6302	±	0.0012	0.6570	±	0.0015	0.5510	±	0.0026	0.6598	±	0.0015	0.5756	±	0.0017
Mean square displacement <z^2> from S (A^2):</z^2>	7.25E-03	±	2.89E-05	8.66E-03	±	2.69E-05	7.88E-03	±	3.10E-05	1.12E-02	±	6.52E-05	7.80E-03	±	3.19E-05	1.04E-02	±	4.01E-05
Internal energy/atom from S (meV):	29.81	±	0.64	28.77	±	0.60	30.69	±	0.66	29.07	±	0.72	30.59	±	0.69	28.97	±	0.63
Kinetic energy/atom from S (meV):	14.90	±	0.32	14.38	±	0.30	15.34	±	0.33	14.53	±	0.36	15.29	±	0.35	14.48	±	0.32
Force constant from S (N/m):	280	±	11	201	±	9	349	±	14	236	±	17	341	±	15	214	±	10
beta-value coefficients from S																		
1000 In beta 56Fe/54Fe=A1/T^2+A2/T^4+A3/T6 (T in K)																		
A1:	7.994E+05	±	3.196E+04	5.737E+05	±	2.488E+04	9.953E+05	±	3.925E+04	6.742E+05	±	4.886E+04	9.724E+05	±	4.169E+04	6.118E+05	±	2.727E+04
A2:	-7.22E+09	±	7.18E+08	-4.75E+09	±	6.21E+08	-1.02E+10	±	9.95E+08	-6.30E+09	±	1.38E+09	-9.86E+09	±	1.09E+09	-4.42E+09	±	5.57E+08
A3:	1.81E+14	±	3.30E+13	1.36E+14	±	3.21E+13	2.75E+14	±	5.15E+13	1.91E+14	±	7.05E+13	2.72E+14	±	5.74E+13	9.18E+13	±	2.35E+13
1000 In beta 56Fe/54Fe=B1 <f>/T2-B2<f>^2/T^4 (T in K)</f></f>																		
B1:	2853			2853			2853			2853			2853			2853		
B2:	67104			81050			59210			75976			59604			74524		
From g																		
lamb-mossbauer factor from g:	0.6701			0.6259			0.6402			0.5289			0.6459			0.5532		
Mean square displacement <z^2> (A^2):</z^2>	7.51E-03			8.79E-03			8.37E-03			1.20E-02			8.20E-03			1.11E-02		
d <z^2>/dT (A^2/K):</z^2>	2.34E-05			2.76E-05			2.63E-05			3.85E-05			2.57E-05			3.55E-05		
Critical temperature (K):	801			679			714			488			729			528		
Resilience (N/m):	59			50			53			36			54			39		
Internal energy/atom from g (meV):	29.83			28.77			30.73			29.17			30.63			29.03		
Kinetic energy/atom from g (meV):	14.91			14.39			15.37			14.59			15.32			14.52		
Vibrational entropy (kb/atom):	1.12			1.26			1.04			1.22			1.05			1.25		
Helmholtz free energy (meV):	0.67			-4.09			3.66			-2.34			3.38			-3.39		
Vibrational specific heat (kb/atom):	0.88			0.91			0.85			0.89			0.85			0.90		
lamb-mossbauer factor at T=0 from g:	0.9072			0.8954			0.9100			0.8914			0.9101			0.8917		
Kinetic energy/atom at T=0 from g (meV):	7.51			6.30			8.41			6.79			8.32			6.55		
Force constant from g (N/m):	280			201			349			237			341			215		
beta-value coefficients from g																		
1000 ln beta 56Fe/54Fe=A1/T^2+A2/T^4+A3/T6 (T in K)																		
A1:	7.996E+05			5.739E+05			9.955E+05			6.749E+05			9.728E+05			6.124E+05		
A2:	-7.23E+09			-4.75E+09			-1.02E+10			-6.32E+09			-9.88E+09			-4.43E+09		
A3:	1.83E+14			1.37E+14			2.78E+14			1.93E+14			2.75E+14			9.26E+13		

1062Table 4: Redox ratios (as determined from conventional Mössbauer spectroscopy at 300K,1063data from Dauphas et al., 2014) and corrected for the recoil-free fractions of ferrous and ferric1064irons), Lamb-Mössbauer factors and force constants calculated from NRIXS spectra and C1065derived from the same spectra. The values of *f2, f3,* and C were obtained by combining NRIXS1066and conventional Mössbauer data (see text for details).

Sample "Raw" redox ratio			f	LΜ	1		f2		f3				С		Corrected	<f> (</f>	'N/	m)			
tholeitic basalt IW	0	±	0.02	0.5956	±	0.0016										0.00	±	0.03	188	±	7
tholeitic basalt INT	0.4	±	0.02	0.6527	±	0.0026	0.5954	±	0.0056	0.7676	±	0.0159	1.289	±	0.036	0.34	±	0.07	227	±	15
tholeitic basaltAIR	0.54	±	0.02	0.6784	±	0.0025										0.48	±	0.06	281	±	18
basalt INT	0.32	±	0.02	0.6330	±	0.0029	0 5047	-	0.0115	0 7225	-	0.0105	1 222		0.056	0.28	±	0.09	250	±	23
Basalt AIR	0.57	±	0.03	0.6666	±	0.0027	0.3947	I	0.0115	0.7555	-	0.0195	1.235		0.056	0.52	±	0.08	275	±	17
Andesite IW	0	±	0.02	0.5967	±	0.0016	0.5968			0.6978						0.00	±	0.03	199	±	11
Andesite Int	0.35	±	0.02	0.6289	±	0.0018		5 ±	0.0038		±	0.0101	1.169	±	0.023	0.32	±	0.08	254	±	16
Andesite AIR	0.55	±	0.02	0.6482	±	0.0018										0.51	±	0.05	283	±	17
Dacite IW	0	±	0.02	0.5765	±	0.0028		3 ±	0.0041	0.6672						0.00	±	0.03	197	±	13
Dacite INT	0.32	±	0.02	0.6104	±	0.0026	0.5793				±	0.0095	1.152	±	0.022	0.29	±	0.08	266	±	19
Dacite AIR	0.59	±	0.02	0.6242	±	0.0029										0.56	±	0.05	283	±	21
Rhyolite IW	0	±	0.05	0.5342	±	0.0021			0.0043		±	0.0076	1.202		0.022	0.00	±	0.03	251	±	10
Rhyolite INT	0.51	±	0.03	0.5740	±	0.0027	0.5304	±		0.6374				±		0.46	±	0.08	307	±	16
Rhyolite AIR	0.73	±	0.03	0.6078	±	0.0023										0.69	±	0.06	346	±	20
NS4 IW	0	±	0.02	0.5756	±	0.0017	0 5756	+	0.0040	0 6000	-	0.0067	1 106		0.017	0.00	±	0.03	214	±	10
NS4 AIR	0.78	±	0.02	0.6598	±	0.0015	0.5750	-	0.0040	0.0882	-	0.0007	1.190	-	0.017	0.75	±	0.04	341	±	15
KS4 IW	0	±	0.02	0.5510	±	0.0026	0 5510	+	0.0041	0 6024	+	0.0066	1 257	+	0.018	0.00	±	0.03	236	±	17
KS4 AIR	0.79	±	0.02	0.6570	±	0.0015	0.5510	' ±	0.0041	0.0924	I	0.0066	1.257	1 I	0.018	0.75	±	0.04	349	±	14
CMS IW	0	±	0.02	0.6302	±	0.0012	0 6 2 0 2		0.0041	0 7201	001	0.0098	1.143	±	0.019	0.00	±	0.03	201	±	9
CMS AIR	0.58	±	0.02	0.6794	±	0.0014	0.0302	Т	0.0041	0.7201	Т					0.55	±	0.05	280	±	11

- 1072 Table 5: Parameters derived from NRIXS analyses of olivine (100%Fe²⁺) and basaltic glass
- 1073 synthesized in air (57%Fe³⁺+43%Fe²⁺) for different temperatures. Only partial results are
- 1074 presented for the 1223K olivine measurement because of the large mutiphonon contribution
- 1075 at high temperature.
- 1076

Temperature (f) the set of the s		Basalt air		Basalt air		Basa	Basalt air		rine	0	ivine	Olivi	ine	Oli	vine
Value: accluication (5) 0.00 0.008 ± 0.000 0.007 ± 0.000 0.077 ± 0.000 0.0093 ± 0.0000 0.0193 ± 0.0000 0.0193 ± 0.0000 0.0193 ± 0.0000 0.0193 ± 0.0000 0.0193 ± 0.0000 0.0193 ± 0.0000 ± 0.0193 ± 0.0000 ± 0.0193 ± 0.0000 ± 0.0193 ± 0.0000 ± 0.0193 ± 0.0000 ± 0.0193 ± 0.0000 ± 0.0193 ± 0.0000 ± 0.0193 ± 0.0000 ± 0.0193 ± 0.0000 ± 0.0193 ± 0.0000 ± 0.0193 ± 0.0000 ± 0.0193 ± 0.0000 ± 0.0000 ± 0.019 ± 0.0000 ± 0.019 ± 0.0000 ± 0.019 ± 0.0000 ± 0.019 ± 0.0000 ± 0.019 ± 0.0000 ± 0.019 ± 0.0000 ± 0.019 ± 0.0000 ± 0.018 ± 0.0000 ± 0.018 ± 0.0000 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018 ± 0.018	Temperature (K)	3	00	55	8	7	73	30	00		300	77	3	12	223
Lamb-Modely factor from 5 0.052 i 0.079 i 0.000 0.0171 i 0.0000 0.0171 i 0.0100 0.0171 i 0.0100 0.0100 0.0101 i 0.0100 0.0101 i 0.0111 <	Values calculated from S(E)														
	Lamb-Mössbauer factor from S	0.685	± 0.002	0.508	0.003	0.375	0.002	0.757 ±	0.003	0.769	± 0.003	0.476 ±	0.004	0.226	± 0.007
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Mean square displacement $\langle z^2 \rangle$ from S (Å ²)	0.00711	± 0.00004	0.01271 ±	0.00009	0.01842	0.00009	0.00523	0.00005	0.00493	± 0.00005	0.01395 ±	0.00013	0.02790	± 0.00047
Kinetic energy/atom from S (mov) 14.40 z 0.32 14.37 0.45.77 0.46 33.42 0.47.77 0.46 33.42 0.47.77 0.46 33.42 0.47.77	Internal energy/atom from S (meV)	29.91	± 0.71	50.23	1.44	68.26	1.64	28.67	0.72	29.15	± 0.91	67.65 ±	1.82	105.80	± 2.80
fore	Kinetic energy/atom from S (meV)	14.96	± 0.36	25.12	0.72	34.13	0.82	14.33	0.36	14.57	± 0.46	33.82 ±	0.91	52.90	± 1.40
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Force constant from S (N/m)	298	± 16	276	23	291	31	202	15	245	± 30	181 ±	38		
D00/h0 ² Fe/ ^A fe/ _A /f ⁴ +A/f ⁴ (T in K) Image: Constraint of the fe/ ^A set of the fe/ ^A s															
A_ Split Spl	$1000\ln(b^{56} \text{ Fe})^{54} \text{ Fe})=A_1/T^2 +A_2/T^4 +A_3/T^6$ (T in K)														
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	A ₁	8.512E+05	± 4.635E+04	7.877E+05	6.427E+04	8.292E+05	8.857E+04	5.763E+05	4.182E+04	6.998E+05	± 8.419E+04	5.171E+05 ±	1.080E+05		
A 1.66+.3 1 2.42+.3 2.76+.3 2.76+.4 2.76+.4 2.76+.4 2.76+.4 2.76+.4 2.76+.4 2.76+.4 2.76+.4 2.76+.4 2.76+.3 2.85+.3 0 0 B1 285 0.675 0.765 0.765 0.765 0.765 0.765 0.765 0.765 1.805.05 1.805	A ₂	-7.4E+09	± 1.0E+09	-5.4E+09 ±	1.1E+09	-6.8E+09 ±	2.4E+09	-3.5E+09 ±	7.0E+08	-7.7E+09	± 2.5E+09	-1.7E+09 ±	1.9E+09		
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	A ₃	1.6E+14	± 4.2E+13	7.6E+13 ±	3.3E+13	1.2E+14	1.1E+14	6.7E+13	2.1E+13	2.7E+14	± 1.2E+14	7.5E+12 ±	5.8E+13		
h_1 283 7911 48845 1 <th1< th=""> <th1< th=""> 1</th1<></th1<>	1000ln(beta56Fe/54Fe)=B1 <f>/T2-B2<f>^2/T^4 (T in K)</f></f>														
b, 63910 5983 64907 6862 79161 48845 Lamb-Mostbauer factor from g 0.679 0.595 0.367 0.756 0.768 0.473 Lamb-Mostbauer factor from g 0.679 0.0027 0.0128 0.0180 0.00525 0.00495 0.10405 Mean square displacement c2 from g(Å') 0.00727 0.01283 0.0180 0.00525 0.00495 0.10405	B1	28	53	28	53	28	53	28	53	2	853	285	53		
Value sclutted from g(f) value sclutted from g(h) value sclutted from g(h) value sclutted from g(h) 0.579 0.579 0.575 0.756 0.768 0.473 0 0 Mean square displacement <2^ > from g(h^2) 0.00727 0.01283 0.01880 0.00525 0.00495 0.01405 1 0 1 0 <td>B₂</td> <td>63</td> <td>910</td> <td>599</td> <td>83</td> <td>649</td> <td>907</td> <td>68</td> <td>562</td> <td>7</td> <td>9161</td> <td>488</td> <td>45</td> <td></td> <td></td>	B ₂	63	910	599	83	649	907	68	562	7	9161	488	45		
Lamb-Mossbauer factor from g 0.679 0.505 0.367 0.766 0.768 0.473 Image of the set of the	Values calculated from g(E)														
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Lamb-Mössbauer factor from g	0.6	579	0.5	05	0.3	867	0.7	'56	0	.768	0.47	73		
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Mean square displacement $\langle z^2 \rangle$ from g (Å ²)	0.00	0727	0.01	283	0.01	L880	0.00	525	0.0	0495	0.014	405		
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	d <z<sup>2>/dT (Å²/K)</z<sup>	2.20)E-05	2.22	-05	2.35	E-05	1.60	E-05	1.4	9E-05	1.805	-05		
Resilience (N/m) 62 59 86 93 77 Internal energy/tom from g (meV) 15 25 34 14 15 34 Vibrational entropy (klytom) 1.08 1.64 1.97 1.12 1.10 2.04 Vibrational entropy (klytom) 2.12 -22.850 62.61 -0.28 0.76 66.8.55 <td< td=""><td>Critical temperature (K)</td><td>8</td><td>53</td><td>84</td><td>5</td><td colspan="2">797</td><td>11</td><td colspan="2">1175</td><td>258</td><td>104</td><td>11</td><td></td><td></td></td<>	Critical temperature (K)	8	53	84	5	797		11	1175		258	104	11		
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Resilience (N/m)	e	3	6	2	59		86		93		77			
Kinetic energy/atom fom g (meV) 15 25 34 14 15 34 9 What on all entropy (kb/atom) 1.08 1.64 1.97 1.12 1.10 2.04 2 What on all entropy (kb/atom) 0.212 -28.50 -62.61 -0.28 0.76 -66.35 1 What on all specific heat (kb/atom) 0.97 0.96 0.98 0.90 0.89 0.98 0.98 0.91 0.91 0.92 0.91 0 1 Inabm-mossbale factor at To from g (meV) 7.81 7.69 7.74 6.73 7.09 6.55 1 1 Force constant from g (N/M 29 277 291 202 245 181 1 1 1000m(b ⁶⁵ Fe/ ⁴⁴ Fe)=A ₁ / f ⁴ +A ₂ / f ⁴ +A ₃ / f ⁴ (T in K) 517969 7.74 6.73 700143 517969 1 1 1 A ₁ 851630 756734 770143 517969 1.666409 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 </td <td>Internal energy/atom from g (meV)</td> <td>3</td> <td>0</td> <td colspan="2">50</td> <td>6</td> <td>8</td> <td colspan="2">29</td> <td colspan="2">29</td> <td colspan="2">68</td> <td></td> <td></td>	Internal energy/atom from g (meV)	3	0	50		6	8	29		29		68			
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Kinetic energy/atom from g (meV)	1	.5	25		34		14		15		34			
Heimholtz free energy (meV) 2.12 -28.50 -62.61 -0.28 0.76 -68.35 -68.35 Vibrational specific heat (kb/atom) 0.87 0.96 0.98 0.90 0.89 0.90 0.89 0.93 0.91 0.92 0.91 0.91 0.92 0.91 0.91 0.92 0.91 0.92 0.91 0.91 0.91 0.91 0.91 0.91 0.91 0.91 0.91 0.91 0.91 0.91 0.91	Vibrational entropy (kb/atom)	1.	08	1.64		1.97		1.12		1	10	2.0	4		
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Helmholtz free energy (meV)	2.	12	-28.50		-62.61		-0	-0.28		0.76	-68.35			
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Vibrational specific heat (kb/atom)	0.	87	0.96		0.	0.98		90	(0.89	0.9	8		
Kinetic energy/atom at T=0 from g (meV) 7.81 7.69 7.74 6.73 7.09 6.55 Image: constant from g (N/m) Force constant from g (N/m) 298 277 291 202 245 181 Image: constant from g (N/m) 1000n(b ⁵ Fe/ ⁴ Fe)=A ₁ /T ² +A ₂ /T ⁴ +A ₃ /T ⁶ (T in K) 7.99 6.55 181 Image: constant from g (N/m) 1 1 1 A ₁ 851630 789786 830871 576734 700143 517396 1 1 A ₂ -7.41E+09 -5.50E+09 -6.83E+09 -3.55E+09 -7.75E+09 -1.66E+09 1 Input basity (g/cc) 1.61E+14 8.59E+13 1.25E+14 6.99E+13 2.80E+14 5.36E+09 - Input basity (g/cc) 2.78 2.78 2.78 3.43 3.43 3.43 3.43 1 1 p-wave velocity (m/s) 3897 ± 127 3566 ± 79 3511 ± 58 4924 ± 254 5367 ± 208 4405 ± 167 1 1 p-wave velocity (m/s) 3897 ± 127 3566 ± <td>lamb-mossbauer factor at T=0 from g</td> <td>0.</td> <td>91</td> <td colspan="2">0.91</td> <td>0.</td> <td>91</td> <td>0.</td> <td>91</td> <td colspan="2">0.92</td> <td colspan="2">0.91</td> <td></td> <td></td>	lamb-mossbauer factor at T=0 from g	0.	91	0.91		0.	91	0.	91	0.92		0.91			
Force constant from g (N/m) 298 277 291 202 245 181 Image: constant from g (N/m) 1000/nt/5 ⁶ Fe/ ⁵⁴ Fe)=A ₁ /T ² +A ₉ /T ⁴ +A ₉ /T ⁶ (T in K) Image: constant from g (N/m) I	Kinetic energy/atom at T=0 from g (meV)	7.	81	7.69		7.	7.74		73	7.09		6.55			
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Force constant from g (N/m)	2	98	27	7	291		202		245		181			
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$															
A1 88 1630 789786 830871 576734 700143 517396 6 A2 $-7.41E+09$ $-5.50E+09$ $-6.88E+09$ $-3.55E+09$ $-7.75E+09$ $-1.66E+09$	1000ln(b ⁻⁰ Fe/ ⁵⁴ Fe)=A ₁ /T ⁺ +A ₂ /T ⁺ +A ₃ /T ⁰ (T in K)														
A2 -7.41 ± 09 -5.50 ± 09 -6.83 ± 09 -3.55 ± 09 -7.75 ± 09 -1.66 ± 09 -1.66 ± 09 A3 -1.61 ± 14 8.59 ± 13 1.25 ± 14 6.99 ± 13 -7.75 ± 09 -1.66 ± 09 -1.66 ± 09 Input density (g/c) -7.75 ± 09 -7.75 ± 09 -1.66 ± 00 -1.66 ± 00 -1.66 ± 00 -1.66 ± 00 Input density (g/c) -7.75 ± 09 -7.75 ± 09 -7.75 ± 09 -7.75 ± 09 -7.75 ± 09 -7.75 ± 09 -1.66 ± 00 -1.66 ± 00 Input bulk modulus (GPa) 2.78 2.78 3.43 3.43 3.43 3.43 3.43 -1.66 ± 00 -1.66 ± 00 Debye velocity (m/s) 3897 \pm 127 3566 ± 79 3511 ± 58 4924 ± 254 5367 ± 208 4405 ± 167 -1.66 ± 00	A ₁	851	.630	789	786	830	871	576	734	70	0143	5173	396		
Ag 1.61E+14 8.59E+13 1.25E+14 6.99E+13 2.80E+14 5.35E+12 Implement of the stress of the s	A ₂	-7.41	LE+09	-5.50	E+09	-6.83	E+09	-3.55	E+09	-7.7	'5E+09	-1.668	E+09		
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	A ₃	1.61	E+14	8.598	+13	1.25	E+14	6.99	E+13	2.8	0E+14	5.35E	+12		
Input balk modulus (SPa) 2.78 2.78 3.43	to such allow the distance	2	70		0	2	70	2	12				2		
Input bit modulus (ora) 100 <th< td=""><td>Input density (g/cc)</td><td>2.</td><td>/8</td><td>2.1</td><td>8</td><td>2.</td><td>78</td><td>3.</td><td>43</td><td>-</td><td>1.43</td><td>3.4</td><td>-3</td><td></td><td>_</td></th<>	Input density (g/cc)	2.	/8	2.1	8	2.	78	3.	43	-	1.43	3.4	-3		_
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Input bulk modulus (GPa)	2807	+ 127	25.66	70	2511	5	4024	254	5267	+ 209	10	167		
p-wave velocity (m/s) 7210 2 76 7011 440 5365 136 7455 110 7015 110 swave velocity (m/s) 3466 ± 121 3162 ± 75 3139 ± 155 4449 ± 2439 ± 198 3957 ± 159 0.27 0 0.23 0.24 0.27 0 0.25 0.24 0.27 0 0.24 0.27 0 0.24 0.27	n wave velocity (m/s)	3697	± 12/	3000 3	19	5011 3	20	74524	100	9307	± 208	4405 ±	10/		
Sware velocity (in/s) 3400 [1] 121 3132 [1/3 3439 [1/22 4433 [1/35 3337 [1/35 1335	p-wave velocity (m/s)	e velocity (m/s) 7210 ±			40	2120	50	1455	242	4920	± 100	7073 ±	110		
Comparison 1000in(b) at 300 K 8.76 2.48 1.37 6.06 7.20 0.86 0 from A ₁ -A ₃ g coefficients (%s) 8.77 2.48 1.37 6.05 7.08 0.86 0 from K ₁ -K ₃ g coefficients (%s) 8.77 2.48 1.37 6.07 7.21 0.86 0 from k ₁ -K ₃ g coefficients (%s) 8.72 2.48 1.37 6.05 7.08 0.86 0	Poisson ratio	0400	35	0 :	. , , , , , , , , , , , , , , , , , , ,	0 0	31	4449	- <u>-</u> 22	4039	120	3537 ±	7		
Image: None of the strength of the stre	Comparison 1000In(b) at 300 K	0.	55	0.2	,,	0.	J1	0.	<i>LL</i>			0.2	.,		
Image: Second Se Second Second Seco	from AA. S coefficients (‰)	8	76	2.4	18	1.	37	6.	06	-	.20	0.8	6		
Interim and a second	from A ₄ -A ₂ g coefficients (‰)	8	77	2.	18	1	37	6	6.07		.21	0.0	6		-
One (and (and (and (and (and (and (and (and	from kinetic energy from S (‰)	8	72	2.	18	1	37	6	05	1 -	7.08		-		
	from kinetic energy from g (‰)	8	77	2.	- 1	1	44	6		1 -	.10	0.0	7		

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Figure 1: (a) SEM micrograph (BSE mode) of a section of a recovered ⁵⁷Fe-doped olivine single crystal. The lighter grey upper part of the crystal was in contact with the isotopically labelled FeO-MgO oxide mixture during thermal annealing. It was therefore slightly enriched in FeO and labelled in ⁵⁷Fe. The small white zones present around the crystal (mainly on the left upper surface) are small patches of this oxide mixture. This indicates imperfectly prepared samples. In this case, additional grinding was preformed to remove any trace of such oxide mixture. (b) Experimental setup used during HT in-situ NRIXS measurements (see text for details).



- **Figure 2:** Mössbauer spectra of simplified glasses and natural analogs. The data collection was
- 1095 carried out at temperature varying from 5K to 300 K.



- Figure 3: Partial density of states of simplified glasses collected at room temperature and presented against spectra collected on glasses of natural compositions (From Dauphas et al., 2014).



- 1115Figure 4: Inverse of Lamb-Mössbauer factor of studied glasses derived from NRIXS spectra as1116a function of the fraction of the Mössbauer peak surface area that can be ascribed to Fe^{3+} 1117divided by the total Mössbauer peak $[S_{Fe3+}/S_{tot}=S_{Fe3+}/(S_{Fe3+}+S_{Fe2+})]$. The errors of $1/f_{LM}$ are1118smaller than the data points and hence not plotted in the figure.



1122 Figure 5: Iron PDOS of basaltic glass synthesized in air and olivine at 300, 558, and 773 K. The 1123 PDOS of the basaltic glass remains completely unchanged when the temperature increases. 1124 The PDOS of the olivine crystal differ between the different temperature acquisitions but this 1125 most likely reflects differences in crystal orientations between the runs rather than true 1126 changes in the PDOS with temperature. Note that one olivine crystal was measured at 1223 K 1127 but the Lamb-Mössbauer factor was low (~0.226) and as a result, the calculated PDOS shows 1128 large negative excursions and is unreliable. For that temperature, we therefore only report 1129 data that we deem to be reliable (Table 5).

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1133 Figure 6. Assessment of the harmonicity of iron bonds in basaltic glass (red filled circles) and 1134 olivine (orange filled circles). The green filled circle correspond to a second spectrum of olivine 1135 collected at ambient condition but in a very different orientation (See fig. 5). If the interatomic 1136 potential departed significantly from harmonic behavior, we would expect the force constant 1137 of iron bonds to change as the temperature and mean square displacement increase. For a 1138 quartic potential, the correlation would be linear (see text for details). As shown, the slope of 1139 the correlations defined by the data points are zero within uncertainties (-568±3045 for 1140 olivine; -4865±4662 for basaltic glass), meaning that the data are close to harmonic up to the 1141 temperatures of 773 K investigated. Therefore, it is justifiable to use force constants measured 1142 at room temperature to calculate the equilibrium isotopic fractionation of iron in 1143 metamorphic rocks and possibly igneous rocks. Further work is needed to test whether 1144 structural changes in liquids or anharmonicity in liquid/solid in the solidus/liquidus region 1145 induces changes in iron bonds relative to glasses.





Figure 7: Values of In*C* as a function of temperature for Tholeitic basalt, basalt, andesite, dacite, and rhyolite. The dashed line is the average of In*C* of all five glass compositions. (b) Lamb-Mossbauer factor of basalt (grey) and olivine (red) as functions of temperature. The points are experimental determinations of Lamb-Mossbauer factors at certain temperatures and the curves predict the variation of Lamb-Mossbauer factors as a function of temperature based on PDOS of the basalt and olivine at room temperature. The olivine datum at 1223 K is discrepant as explained in the text, and was discarded.

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1159 Figure 8: Data compilation of rescaled energies of the centroid of the pre-edge feature as a 1160 function of the corrected redox ratios determined by Mössbauer spectroscopy. Presented 1161 data are for basalts, andesites, dacites and rhyolites published in Cottrell et al. (2009), 1162 Dauphas et al., (2014), Zhang et al. (2015-2016), Fiege et al. (2017, here only data collected at 1163 APS for simplicity, data from ANKA being consistent but shifted in energy as explained by 1164 authors) and Berry et al., (2018). In all cases, uncorrected redox ratios were used. A uniform 1165 correction using our average C-value of 1.196 was then applied to all Mössbauer data. The 1166 energies of the centroid provided by Berry et al. (2018) and by Fiege et al. (2017) were 1167 empirically rescaled such that basaltic glasses from the different studies exhibiting similar 1168 Mössbauer-derived redox ratios plot on a single line. In practice, a constant correction of +1 1169 eV was applied to the dataset of Berry et al. (2018) and of +0.46 eV to the dataset of Fiege et 1170 al. (2017). No further correction had to be applied to account for compositional variations 1171 among basalts, andesites, dacites and rhyolite. Data for rhyolites are from Cottrell et al., 1172 (2009), Dauphas et al., (2014) and Fiege et al., (2017). A typical error of ±0.022 eV for the 1173 centroid energy and 0.02 for the redox ratios determined by Mössbauer spectroscopy are reported here. Parametric fits to the data have the form: $\Delta E = -0.82 \cdot (Fe^{3+}/\Sigma Fe)^2 + 1.97 \cdot$ 1174 $(Fe^{3+}/\Sigma Fe) + 7112.39$ for the rhyolites and $\Delta E = -1.19 \cdot (Fe^{3+}/\Sigma Fe)^2 + 2.75 \cdot (Fe^{3+}/\Sigma Fe)^2$ 1175 1176 Σ Fe) + 7212 for other compositions. These fits take into account the physical limitations 1177 provided by Westre et al. (1997) and Wilke et al. (2007) and therefore, the trend of centroid end at ca. 7112 eV as observed on Fe²⁺ model compounds and in accordance with multiplet 1178 1179 theory as well as crystal field splitting by optical spectroscopy.

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1184 Figure 9: Reappraisal of the iron force constants in variably oxidized synthetic silicate glasses 1185 (Dauphas et al., 2014). Basalt, andesite, dacite, and rhyolite glasses define linear arrays that can be extrapolated to $Fe^{3+}/\Sigma Fe = 0$ and $Fe^{3+}/\Sigma Fe = 1$ to estimate the force constants of Fe^{2+} 1186 and Fe³⁺, respectively. Basalt, andesite, and dacite define a single correlation that gives force 1187 constants of 193 \pm 7 and 364 \pm 23 N/m for the Fe²⁺ and Fe³⁺ end-members, respectively. 1188 1189 Rhyolite defines a different correlation that gives force constants of 250 ± 11 and 382 ± 31 N/m for the Fe²⁺ and Fe³⁺ end-members, respectively. The regressions were calculated using 1190 the Isoplot software. Uncertainties are 95% confidence intervals. Data for simplified glasses 1191 also demonstrate that potassium (and sodium to a lower extent) has a strong effect on the 1192 1193 force constant of Fe²⁺.





1196 Figure 10: Mössbauer parameters (Isomer shift, IS and Quadrupole splitting, QS) for reduced 1197 glasses. Fit to the data were performed with three Lorentzians. These three lines define three 1198 clusters of parameters. In each cluster, data define trends from basalt to rhyolite (from high 1199 IS-QS to low IS-QS). The effect of acquisition temperature is also seen for the basaltic glass for 1200 which data were collected at 5 and 90K.







200

150 ±

0.0

0.2

0.4 Fe³⁺/SFe

0.6



0.50 ± 0.0

0.2

0.4 Fe³⁺/SFe

0.6