

1. Experimental and analytical procedure

Starting compositions

We synthesized a series of Fe-rich haplo-basalt (HB) glasses based on the natural Adirondack-class Humphrey basalt from Gusev Crater, Mars (1) as well as a haplo-MORB (B14) and a haplo-andesite (A05) based on the compositions of Armstrong et al. (2) and Zhang et al. (3), respectively. We mixed pre-dried spectroscopically pure SiO_2 , Al_2O_3 , MgO , CaCO_3 , Na_2CO_3 , and K_2CO_3 reagents. The mixtures were decarbonated by slow heating ($3^\circ\text{C}/\text{min}$), then fused in air for 2 h at 1400°C in platinum crucibles in a 1 atm furnace. Melts were quenched to glass in water, then crushed and ground in PULVERISETTE agate jars to produce a fine 1–2 μm powder. After decarbonation of the glass powder, Fe was added as Fe_2O_3 powder. The Fe-bearing mixtures were then reduced in a Nabertherm furnace at 900°C and $\log f_{\text{O}_2} = -14$ for 48 h. Finally, nitrogen was introduced as Si_3N_4 powder to yield charges of 0.2 and 0.8 wt% N in the starting material. By varying the amount of Si_3N_4 added to the starting compositions, we were able to change (but not control) the sample f_{O_2} , since Si_3N_4 has a strong reducing effect (1). $\text{Si}_3^{14}\text{N}_4$ was synthesized by Si nitridation using flowing N_2 in a Nabertherm 1 atm furnace. Except for the haplo-MORB sample, starting mixes were spiked in ^{15}N using $\text{Si}_3^{15}\text{N}_4$ synthesized by Leonova et al. (4). The starting materials were loaded into graphite capsules, chosen to ensure reducing conditions and to provide a source of C in the experiments.

Experimental procedure

Experiments were designed to equilibrate graphite-saturated basaltic melts with Fe-C-N alloys over a range of redox conditions ($\Delta\text{IW} -0.5$ to $\Delta\text{IW} -3$) to determine metal-silicate N fractionation. Experiments were performed in a 3/4-inch piston cylinder at 1 GPa and 1400°C for 6 h at the Laboratoire Magmas et Volcans (Clermont-Ferrand, France). Run temperature was controlled to within $\sim 1^\circ\text{C}$ of the set point using W95Re5/W74Re26 thermocouples. Power output was monitored during the runs to ensure no temperature drift. Before decompression, the power to the furnace was cut and the experiment was quenched rapidly ($\sim 50^\circ\text{C}/\text{s}$).

Samples were mounted in epoxy resin and polished individually to limit ^{15}N contamination between samples. They were then removed from the resin and pressed into high-purity indium metal mounts (as recommended for water analysis) and carbon coated for electron microprobe analysis. Raman analyses were performed before carbon coating to avoid interference from carbon vibrational bands.

Electron probe microanalysis (EPMA)

Major element compositions were analyzed with a CAMECA SX5 at CAMPARIS Centre at Sorbonne Université (Paris, France). For silicate glass analyses, we used an accelerating voltage of 10 kV and a 10 nA beam defocused to 10 μm . Diopside glass (Si, Ca, Mg),

43 orthoclase (Al, K), albite (Na), and pure Fe were used as standards. For metal alloys, we used
 44 a 10 kV accelerating voltage and a focused 40 nA beam. Pure Fe and Pt were used as metal
 45 standards. The major element compositions of silicate glasses are presented in Table S1, and
 46 those of metal alloys in Table S2.

47
 48 **Table S1.** Major element compositions (wt%) of glasses determined by EPMA.

Sample	n_{EPMA}	SiO ₂	Al ₂ O ₃	MgO	CaO	K ₂ O	FeO	Na ₂ O	Total
HB01	7	68.7 ± 0.3	8.3 ± 0.4	8.2 ± 0.5	2.4 ± 0.2	0.53 ± 0.06	1.6 ± 0.2	5.3 ± 0.2	95.0 ± 1.2
HB05	4	46.4 ± 0.2	9.1 ± 0.2	10.0 ± 0.3	6.1 ± 0.1	0.74 ± 0.03	22.1 ± 0.6	3.7 ± 0.2	98.2 ± 1.0
HB15	7	61.4 ± 0.4	6.7 ± 0.1	8.0 ± 0.3	3.2 ± 0.1	0.27 ± 0.02	10.5 ± 0.4	5.9 ± 0.3	96.0 ± 1.8
HB3	8	64.8 ± 1.0	3.8 ± 0.2	9.5 ± 0.7	1.84 ± 0.07	0.35 ± 0.08	6.9 ± 0.4	3.9 ± 0.9	91.1 ± 0.9*
HB4	10	60.3 ± 0.9	5.5 ± 0.3	6.9 ± 0.3	3.1 ± 0.1	0.39 ± 0.03	9.2 ± 0.3	4.7 ± 1.0	90.2 ± 0.7*
A05	7	66.7 ± 1.1	13.7 ± 0.7	2.0 ± 0.1	5.9 ± 0.2	1.4 ± 0.1	4.6 ± 0.3	5.4 ± 0.4	99.7 ± 0.6
B14	9	52.4 ± 0.9	15.7 ± 0.2	9.2 ± 0.3	11.5 ± 0.1	0.06 ± 0.03	7.5 ± 0.6	2.2 ± 0.2	98.5 ± 1.0

49 *Low totals may be due to graphite microinclusions in the samples.

50 n_{EPMA} indicates the number of EPMA analyses on each sample.

51 Reported uncertainties are 1 σ standard deviations.

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 53 **Table S2.** Fe and Pt contents of metal alloys determined by EPMA, and their N and C contents
 54 determined by SIMS.

Sample	n_{EPMA}	Fe [wt%]	Pt [wt%]	n_{SIMS}	C [wt%]	N [ppm]
HB01	5	93.7 ± 0.7	0.07 ± 0.08	2	0.110 ± 0.001	28 ± 3
HB05	5	93.6 ± 1.2	0.7 ± 0.4	4	6.06 ± 0.01	1571 ± 1287
HB15	2	89.6 ± 0.1	bdl	3	2.66 ± 0.06	682 ± 267
HB3	5	92.2 ± 3.2	0.2 ± 0.4	4	5.74 ± 0.01	1493 ± 149
HB4	11	97.1 ± 1.5	0.1 ± 0.6	6	5.73 ± 0.02	1488 ± 14
A05	6	93.4 ± 0.2	0.6 ± 0.8	3	2.552 ± 0.001	669 ± 125
B14	7	94.6 ± 1.2	bdl	3	7.42 ± 0.01	1012 ± 20

55 bdl: below detection limit.

56 n_{EPMA} and n_{SIMS} indicate the number of EPMA and SIMS analyses, respectively.

57 Reported uncertainties are 1 σ standard deviations for Fe and Pt contents and 2 σ standard deviations
 58 for C and N contents.

60 Raman spectroscopy

61 For silicate glasses, Raman spectroscopy measurements were carried out using a LabRAM
 62 HR microspectrometer (Horiba Jobin Yvon) at GeoRessources (Nancy, France) using the
 63 457.9 nm radiations of an Ar⁺ laser (Stabilite 2017, Spectra-Physics) with 100–155 mW
 64 output. The laser intensity was reduced with neutral density filters to avoid thermal
 65 degradation of the samples and focused to a ~2 μm spot size with 8–23 mW on sample
 66 through a 50 \times long-working-distance Olympus objective with a 0.5 numerical aperture.
 67 Scattered light was collected through a confocal aperture into a focal length of 800 mm. The
 68 spectrometer was equipped with an 1800 grooves $\cdot\text{mm}^{-1}$ grating. Acquisition time was 10 s,
 69 with 60 acquisitions collected per spectrum. Raman intensities were corrected from the
 70 instrument response curve by calibration of the spectrometer toward a white lamp (5). To
 71 observe molecular N₂ vibrations, spectra were acquired in the 2200–2400 cm^{-1} spectral

72 window. C-H, N-H, and O-H vibrations were observed in the 2800–3700 cm^{-1} spectral
73 window.

74 For metal alloys, we used a LabRAM microspectrometer (Horiba Jobin Yvon) at
75 GeoRessources. Sample excitation was accomplished using the 514.5 nm line of an Ar⁺ laser
76 with 100–155 mW output. To avoid melting the metal, the laser intensity was reduced with
77 neutral density filters to between 9 and 15 mW. Measurements were performed using an 1800
78 grooves·mm⁻¹ grating centered at 950 cm^{-1} . Ten acquisitions of 10 s were collected.

79 Baseline corrections were performed using the IGOR software package (Wavemetrics
80 Inc.). A linear baseline was used for the 2200–2400 cm^{-1} part of the Raman signal of silicate
81 glasses, whereas a spline correction was fitted for the 2800–3700 cm^{-1} baseline of silicate
82 glasses and the 200–900 cm^{-1} part of the Raman signal in metal alloys.

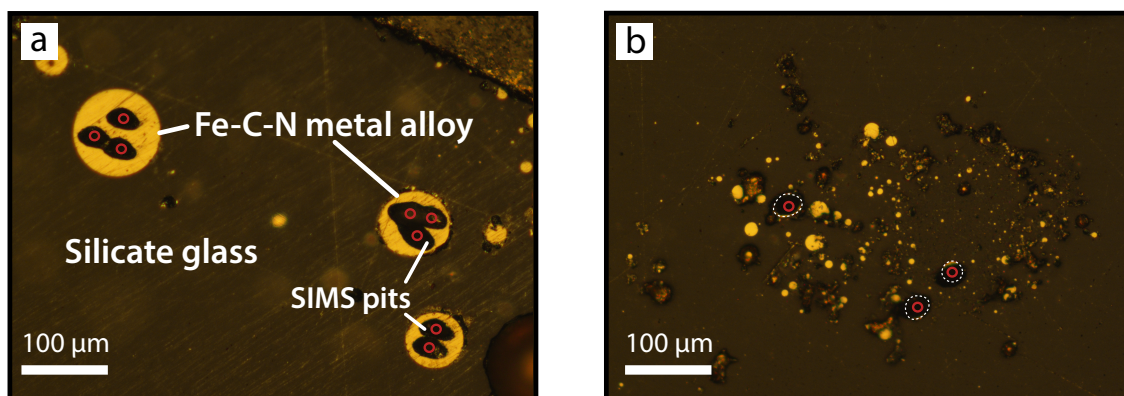
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84 **Secondary ion mass spectrometry (SIMS)**

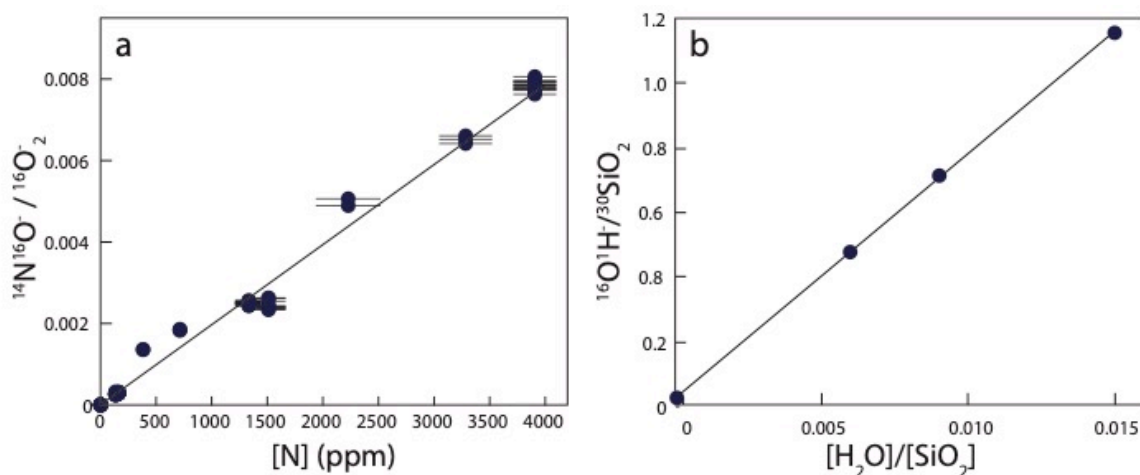
85 *In-situ* measurements of N concentrations and isotopic ratios were performed at the Centre de
86 Recherches Pétrographiques et Géochimiques (CRPG, Nancy, France) using the CAMECA
87 1280 HR2 and 1270 ion microprobes for silicate glasses and metal blobs, respectively.
88 Sample mounts were coated with gold and left in the instrument airlock for at least 24 h to
89 ensure thorough removal of any adsorbed water before introduction into the sample chamber,
90 although any hydride species are well-resolved from the peaks of interest (6). Furthermore, to
91 minimize any surface contamination, the surface of the glasses and metals were pre-sputtered
92 for 180 s over an area of 10 $\mu\text{m} \times 10 \mu\text{m}$ prior to signal acquisition. For all abundance and
93 isotopic analyses, the beam was rastered over an area of 5 $\mu\text{m} \times 5 \mu\text{m}$ (**Fig. S1**), and a
94 dynamical transfer operating system was used to compensate the primary rastering by
95 recentering the beam in the secondary optic of the ion probe. Prior to data acquisition, the
96 secondary ion beam was automatically centered in x and y on the field aperture and the
97 contrast aperture, followed by a mass-centering routine in order to compensate for any
98 magnetic field drift.

99 Nitrogen isotopes in silicate glasses (Table S3) were measured on the CAMECA 1280
100 HR2 ion microprobe by spot analyses of $^{14}\text{N}^{16}\text{O}^-$ and $^{15}\text{N}^{16}\text{O}^-$ molecular ions at masses 30 and
101 31, respectively, at a nominal mass resolution $m/\Delta m = 14,000$ using a 10 kV Cs⁺ primary ion
102 beam, a ~10 nA current, and a normal-incidence electron gun for charge compensation (6).
103 The $^{14}\text{N}^{16}\text{O}^-$ and $^{15}\text{N}^{16}\text{O}^-$ ions were measured for 25 cycles in peak-jumping mode on an
104 electron multiplier for 4 and 20 s, respectively, together with $^{27}\text{Al}^-$ (4 s), $^{30}\text{Si}^-$ (4 s), and $^{16}\text{O}_2^-$
105 (4 s) on a faraday cup. A suite of 12 reference glasses with known ^{14}N contents (6) was used
106 to determine the nitrogen concentration of the samples based on the $^{14}\text{N}^{16}\text{O}^-$ count rate
107 normalized by the $^{16}\text{O}_2^-$ signal (**Fig. S2a**). Based on repeated isotope ratio measurements in 5
108 out of the 12 reference glasses (with N content ≥ 136 ppm) with $\delta^{15}\text{N} = -4 \pm 1\text{‰}$ (6), the
109 instrumental mass fractionation (IMF) for glass analyses was determined to be $\alpha_{\text{inst}} = 1.0259$
110 ± 0.0074 (2σ). Thus, the measured $^{15}\text{N}/^{14}\text{N}$ ratios of the experimental glasses were
111 subsequently corrected for IMF according to $(^{15}\text{N}/^{14}\text{N})_{\text{corr}} = (^{15}\text{N}/^{14}\text{N})_{\text{measured}} / \alpha_{\text{inst}}$.

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 114 **Fig. S1.** Reflected-light microscope images of (a) sample HB3 and (b) sample A05 showing the
 115 variable sizes of metal alloy blobs among different samples. Red circles (~5 μm) indicate the location
 116 of ion probe spots for metal C-N measurements. The surrounding black spots are the area where the
 117 gold coating was removed due to primary ion beam sputtering. The white dotted circles in (b)
 118 represent the initial shapes of the metal blobs.
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 121 **Fig. S2.** Calibration lines for N and OH abundance analyses in silicate glasses. (a) The relationship
 122 between the secondary ion intensity ratio $^{14}\text{N}^{16}\text{O}^- / ^{16}\text{O}_2^-$ and the known ^{14}N content of the reference
 123 glasses ($r^2 = 0.95$). (b) The measured and reference values of H_2O and SiO_2 concentrations in the four
 124 glass reference materials provide excellent consistency ($r^2 = 0.99$).
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126 Nitrogen and carbon concentrations, as well as $^{15}\text{N}/^{14}\text{N}$ and $^{13}\text{C}/^{12}\text{C}$, in the metal blobs
 127 were measured with the CAMECA 1270 ion microprobe using a 10 kV Cs^+ primary ion
 128 beam, a ~2.4 nA current, and a normal-incidence electron gun for charge compensation. The
 129 size of the primary beam was set to ~5 μm to analyze metal blobs 10–65 μm in diameter (Fig.
 130 S1). Nitrogen isotopes (Table S3) were measured as $^{12}\text{C}^{14}\text{N}^-$ and $^{12}\text{C}^{15}\text{N}^-$ at masses 26 and 27,
 131 respectively, with a mass resolution of 8,000. Twelve cycles were collected for each analysis,
 132 following the mass sequence $^{12}\text{C}_2^-$ (8 s), $^{12}\text{C}^{13}\text{C}^-$ (16 s), $^{12}\text{C}^{14}\text{N}^-$ (8 s), $^{13}\text{C}^{14}\text{N}^-$ (8 s), $^{12}\text{C}^{15}\text{N}^-$ (8
 133 s), $^{28}\text{Si}^-$ (8 s), and $^{56}\text{Fe}^-$ (8 s). With the exception of $^{12}\text{C}^{13}\text{C}$, signals were measured on a
 134 faraday cup in most cases. For samples HB3 and HB4, $^{13}\text{C}^{14}\text{N}$ was measured on the electron
 135 multiplier. Because the metal blobs of sample HB01 contained only 28 ppm N, $^{12}\text{C}^{14}\text{N}$,
 136 $^{12}\text{C}^{15}\text{N}$, and $^{13}\text{C}^{14}\text{N}$ were measured on the electron multiplier. Carbon and nitrogen elemental
 137 abundances were determined using the ^{12}C signal and the $^{12}\text{C}^{14}\text{N}/^{12}\text{C}$ ratio, respectively.

138 Carbon concentrations were calibrated using a set of four certified NBS stainless steel
 139 reference materials (NBS661, NBS662, NBS663, and NBS664), containing between 0.16 and
 140 0.87 wt% C (**Fig. S3a**). Nitrogen concentrations were determined using the certified standard
 141 NBS662 ($^{12}\text{C}^{14}\text{N}/^{12}\text{C} \geq 0.03$) and sample B14 (**Fig. S3b**), for which the N content and $\delta^{15}\text{N}$
 142 value were independently measured by noble gas static mass spectrometry (see below).
 143 NBS661, NBS663, and NBS664 were not used for N analyses because the uncertainties on
 144 their $^{12}\text{C}^{14}\text{N}/^{12}\text{C}$ ratios were greater than or equal to the measured values, likely due to a
 145 highly heterogeneous nitrogen distribution in these stainless steel samples. Although only two
 146 metallic calibrants were used to derive the N content in metals, the calibration is reliable since
 147 partition coefficients calculated from these values are consistent with literature data (~150
 148 data points, Fig. 1 in the main text).

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 150 **Table S3.** $^{15}\text{N}/^{14}\text{N}$ ratios (corrected for IMF) determined by SIMS in silicate glasses and metal blobs.

Sample	n_{SIMS} silicate	$^{15}\text{N}/^{14}\text{N}^{\text{silicate}}$	n_{SIMS} metal	$^{15}\text{N}/^{14}\text{N}^{\text{metal}}$
HB01	3	0.091 ± 0.001	2	0.070 ± 0.006
HB05	3	0.685 ± 0.011	4	0.652 ± 0.007
HB15	3	8.197 ± 0.140	3	7.298 ± 0.364
HB3	3	0.828 ± 0.001	4	0.724 ± 0.004
HB4	3	0.864 ± 0.002	6	0.790 ± 0.005
A05	3	0.672 ± 0.001	3	0.656 ± 0.001
Reference material				
B14*	–	nd	3	0.003725 ± 0.000049

151 *B14 served as a calibrant for N analyses in metal; its $^{15}\text{N}/^{14}\text{N}^{\text{silicate}}$ was not determined (nd).

152 The reproducibility on B14 SIMS measurements is 1.3%.

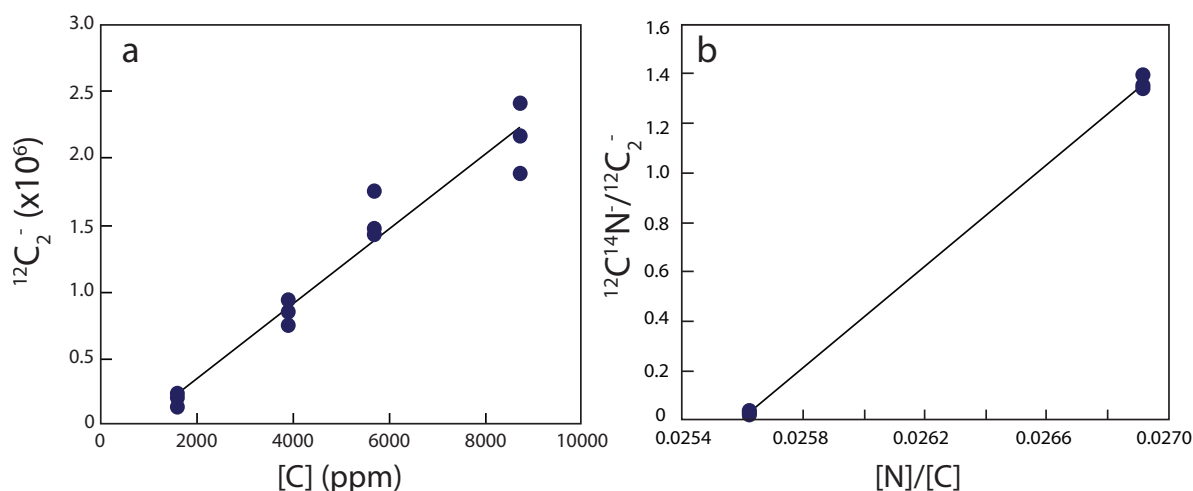
153 n_{SIMS} indicates the number of SIMS analyses.

154 Reported uncertainties are 2σ standard deviations.

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156 Sample B14 was also analyzed by noble gas mass spectrometry. Thus, we were able to
 157 directly measure the N isotopic compositions (relative to the atmosphere) of its metal blobs
 158 ($\delta^{15}\text{N}^{\text{metal}} = -12 \pm 1\%$). Based on these independent isotope ratio measurements of B14, the
 159 IMF of the ion probe during metal analysis was determined to be $\alpha_{\text{inst}} = 1.0251 \pm 0.0859$ (2σ).
 160 Thus, the measured $^{15}\text{N}/^{14}\text{N}$ ratios of all the metal phases in the Fe-rich basalt and andesite
 161 samples were subsequently corrected for IMF according to $(^{15}\text{N}/^{14}\text{N})_{\text{corr}} = (^{15}\text{N}/^{14}\text{N})_{\text{measured}} /$
 162 α_{inst} .

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165 **Fig. S3.** Calibration lines for C and N abundance analyses in metal alloys. (a) The relationship between
 166 the secondary ion intensity ratio $^{12}\text{C}_2^-$ and the known C content of the NBS stainless steel reference
 167 materials ($r^2 = 0.95$). (b) The relationship between the secondary ion intensity ratio $^{12}\text{C}^{14}\text{N}^-/^{12}\text{C}_2^-$ and
 168 the known N/C ratio of NBS662 and sample B14 ($r^2 = 0.99$).

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171 Hydrogen abundances in silicate glasses were measured with the CAMECA 1280 HR2
 172 ion microprobe. A liquid-nitrogen cold trap was used to reduce the H_2O background and
 173 maintain a pressure below 2×10^{-9} Torr in the analytical chamber. A 10 kV Cs^+ primary ion
 174 beam was used for the analyses. Prior to analysis, a 180-s high-current (1 nA) presputtering
 175 was rastered over an area of $20 \mu\text{m} \times 20 \mu\text{m}$ to remove the gold coating and reach the
 176 sputtering steady state. The samples were then sputtered with a current of 350 pA rastered
 177 over an area of $10 \mu\text{m} \times 10 \mu\text{m}$ and a normal-incidence electron gun was used for charge
 178 compensation. A small field aperture (1000 μm) and a high magnification (40 μm maximum
 179 area) were used to restrict the analytical areas to $5 \mu\text{m} \times 5 \mu\text{m}$ and eliminate hydrogen
 180 contamination from the crater edges. The $^{12}\text{C}^-$, $^{16}\text{OH}^-$, and $^{29}\text{Si}^-$ ions were collected
 181 sequentially by changing the magnetic field and counted with a monocollection electron
 182 multiplier. The mass resolution was set to 7,000 to avoid interferences of $^{17}\text{O}^-$ on $^{16}\text{OH}^-$ and
 183 $^{28}\text{SiH}^-$ on $^{29}\text{Si}^-$. The H_2O concentrations of the experimental glasses were determined using
 184 the calibrated relationship between the secondary ion intensity ratios $^{16}\text{OH}^-/^{29}\text{Si}^-$ and the
 185 known H_2O abundances of four glass standards (**Fig. S2b**): KL2-G [0.015 wt% H_2O (7)], VG-
 186 2 [0.28 wt% H_2O (8)], M48 [0.77 wt% H_2O (9)], and MC84-df [0.707 wt% H_2O (10)].

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187 Noble gas mass spectrometry

188 Nitrogen abundances and isotopic ratios in sample B14 were determined by CO_2 laser
 189 extraction static mass spectrometry at the CRPG noble gas analytical facility (11). Samples
 190 were cleaned in an ultrasonic bath filled with acetone, then weighed and loaded into different
 191 pits of the laser chamber. Analyses were carried out on a 36- μg metal alloy blob and on a 21-
 192 μg fragment of silicate glass (free of visible graphite from the capsule or graphite inclusions,
 193 as observed under the microscope). The samples were heated individually with a continuous-
 194 mode infrared CO_2 laser mounted on an x - y stage. Samples were reheated after melting to
 195 verify that their N was completely extracted during the first heating step. After gas

196 purification (11), nitrogen isotopic data were collected on a Noblesse HR noble gas mass
197 spectrometer. The Noblesse HR at CRPG is equipped with three Faraday cups and four ion
198 counter collectors, thus allowing nitrogen isotopes to be measured in multi-collection mode;
199 this method provides more precise and reproducible data than those obtained previously in
200 mono-collection mode on the VG5400 noble gas mass spectrometer by Li et al. (12). The
201 analytical procedure consisted of first measuring the $^{12}\text{C}^{16}\text{O}$ signal, followed by the $^{12}\text{C}^{16}\text{O} +$
202 $^{14}\text{N}^{14}\text{N}$ and $^{13}\text{C}^{16}\text{O} + ^{14}\text{N}^{15}\text{N}$ signals using two Faraday cups ($R = 10^{11} \Omega$). After data
203 acquisition, which consisted of 25 cycles, the $^{14}\text{N}^{14}\text{N}$ and $^{15}\text{N}^{14}\text{N}$ intensities were corrected for
204 the CO contribution. Calibrated air aliquots were used to determine the analytical sensitivity
205 ($1.7 \times 10^{-4} \text{ A/Torr}$) and the reproducibility of abundance ($\pm 1.9\%$, 1σ) and isotope ratio
206 measurements ($\pm 0.06\%$, 1σ).

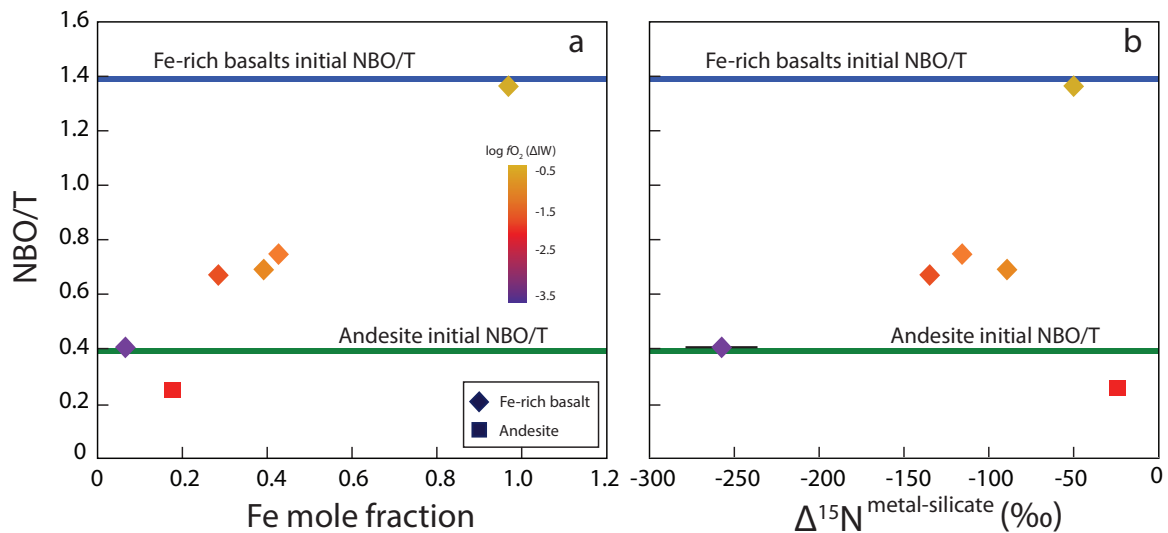
207 **2. Relationship between $f\text{O}_2$, melt structure, and N isotopic fractionation**

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210 The precipitation of Fe metal in various proportions, depending on $f\text{O}_2$, causes a change in
211 melt structure (Figs. S4a and S5). As previously noted by Dalou et al. (1) and Armstrong et al.
212 (2), silicate glasses, for example, become more Si-rich and Fe-poor relative to the starting
213 compositions owing to oxidation of added Si_3N_4 and reduction of FeO in the melt with
214 decreasing $f\text{O}_2$. These changes in the mole fractions of Si and Fe with decreasing $f\text{O}_2$ result in
215 an increase in melt polymerization (i.e., a decrease of NBO/T, the ratio of non-bridging
216 oxygens to tetrahedrally coordinated cations).

217 Melt polymerization does not directly affect N isotopic fractionation. If the increase
218 in melt polymerization was the dominant control, the N isotopic fractionations in samples
219 HB3 and A05, which had a similar Fe fraction and NBO/T after the experiment, should have
220 had similar $\Delta^{15}\text{N}$ or $\Delta^{15}\text{N}^*$ values. However, they show distinct $\Delta^{15}\text{N}$ values of $-135 \pm 1\%$
221 and $-25 \pm 1\%$, respectively. Similarly, as the melts become more polymerized, their $\Delta^{15}\text{N}$ or
222 $\Delta^{15}\text{N}^*$ values should decrease. In both cases, this is not what we observe (Fig. S4b).

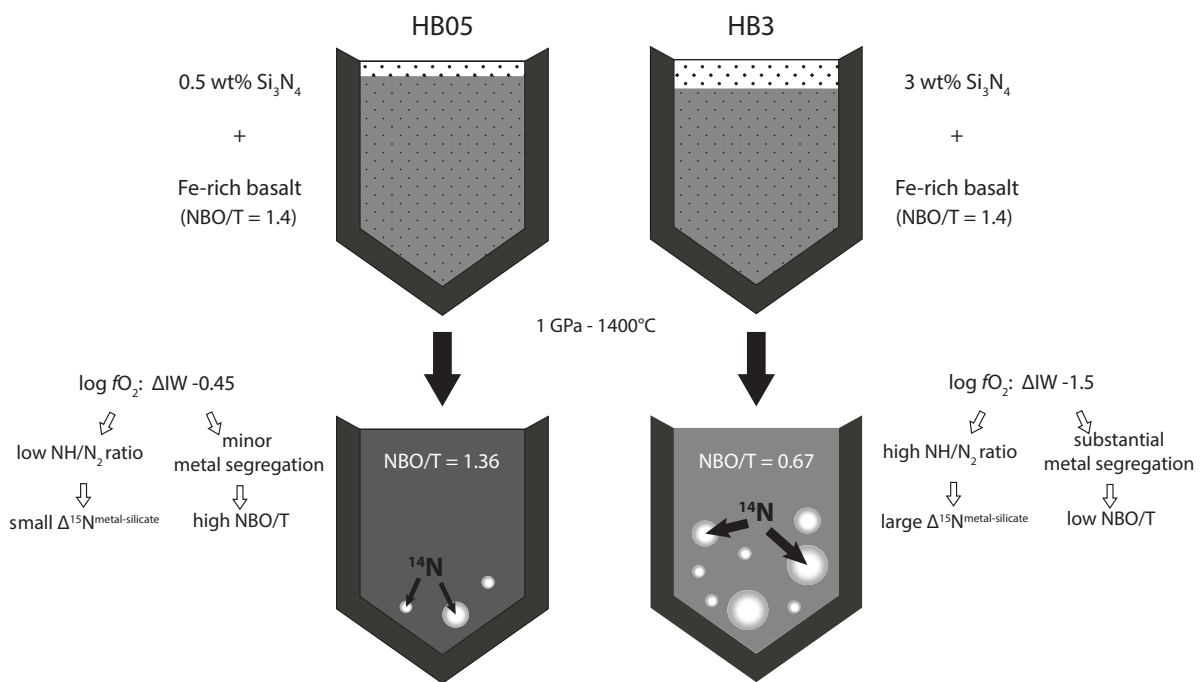
223 In the main text, we argue that the dependence of N isotopic fractionation on $f\text{O}_2$ can
224 be related to variable NH/N₂ ratios in the glasses. The NH/N₂ ratios in the glasses seem to
225 depend on the initial degree of melt polymerization (for reasons that remain to be explored)
226 and on the $f\text{O}_2$ conditions (Fig. S5).

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Fig. S4. NBO/T ratios (lower values being more polymerized) of the glasses as a function of fO_2 (color scale) and (a) Fe mole fraction and (b) $\Delta^{15}N^{\text{metal-silicate}}$.



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Fig. S5. Schematic representation of the experimental procedure and the direct and indirect effects of fO_2 on metal segregation, the NBO/T and NH/N₂ ratios of the silicate glasses, as well as on the N isotope fractionation between the metal and silicate phases.

239 References

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